

Advancing electrochemical jet machining techniques

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Thesis submitted to the University of
Nottingham for the degree of Doctor of
Philosophy

September 2018

Abstract

Electrochemical Jet Processing (EJP) techniques have been traditionally limited in application by the inherent geometric inflexibility and limited process precision in comparison to alternative processes. It has been stated that process resultant geometries are defined by the Gaussian in-jet energy distribution and the hydrodynamic stagnation region formed under a jet on an impinging surface. This thesis reports upon investigations and innovations designed to challenge these assumptions.

EJP is an emergent manufacturing process with a unique capability of subtraction and deposition of metals within a common machine tool. EJP demonstrates advantages beyond traditional electrochemical machining and electrochemical deposition including a high degree of flexibility, simplistic and therefore low-cost plant, requiring no complex, high-cost tooling and no masking requirement to achieve high fidelity geometries. These process traits are attractive to industry but EJP has yet to find significant commercial use.

Electromechanical and electrochemical innovations are presented here demonstrated by electrochemical jet machining (EJM) the subtractive mode of EJP, which allow modulation of the properties of the inter-electrode gap leading to a paradigm shift in the functionality, precision and application of EJP. Electromechanical innovations demonstrate that the Gaussian energy distribution can be modified through the articulation of the jet angle of address and modified jet nozzles to manipulate the in-jet resistance. The outcome being the capability to produce bespoke removal profiles with increased precision and flexibility of form alongside refined surface finishes. Electrochemical innovations demonstrate

an increase in precision through reducing overcut and reducing the feature shoulder radius when using a modified electrolyte. When these electromechanical and electrochemical innovations are coupled together, the overcut traditionally seen to be twice the nozzle diameter is reduced by 99%. Therefore, features can be created at kerfs approaching the nozzle diameter. Alongside this, a bespoke research platform has been built and developed to exploit these findings and incorporate features such as the rotational head for constant profiling and multiplexing of electrolytes to enhance the flexibility of the process.

Process enhancements developed through this thesis have allowed the manipulation of the in-jet energy density profile and dissociation of the dissolution region from hydrodynamic phenomena thus allowing surface structuring by EJP to be developed well beyond the state-of-the-art.

Publications

Included in this thesis

- Clare A. Speidel, A. Bisterov, I. Jackson-Crisp, A. Mitchell-Smith, J. (2018), Precision Enhanced Electrochemical Jet Processing, **CIRP - Annals Manufacturing Technology**
- Mitchell-Smith J., Speidel A., Bisterov I., Clare A. T., (2018). Electrolyte multiplexing in electrochemical jet processing, **Procedia CIRP**
- Mitchell-Smith J., Speidel A., Clare A. T., (2017). Advancing electrochemical jet methods through manipulation of the angle of address, **Journal of Materials Processing Technology**
- Mitchell-Smith, J. Speidel, A. Clare, A.T. (2017), Transitory electrochemical masking for jet processing methods. **Journal of Manufacturing Processes**
- Mitchell-Smith, J., Speidel, A., Gaskill, J., Clare, A.T. (2017), Energy distribution modulation by mechanical design for electrochemical jet processing techniques. **International Journal of Machine Tools and Manufacture**
- Walker, J.C. Kamps, T.J., Lam, J.W., Mitchell-Smith, J., Clare, A. T. (2017) Tribological behaviour of an electrochemical jet machined textured Al-Si automotive cylinder liner material. **Wear**
- Mitchell-Smith, J., and Clare, A. T., (2016). Electrochemical Jet Machining of Titanium: Overcoming Passivation Layers with Ultrasonic Assistance. **Procedia CIRP**

- Mitchell-Smith, J., Murray, J. W., Kunieda, M., Clare, A. T., (2014) Electrolyte jet machining for surface texturing of Inconel 718, ***Proceedings of INSECT 2014***

Not included in this thesis

- Speidel, A. Su, R. Mitchell-Smith, J. Dryburgh, P. Bisterov, I. Pieris, D. Li, W. Patel, R. Clark, M. Clare, A. T. Crystallographic texture can be rapidly determined by electrochemical surface analytics, (2018), ***Acta Materialia***
- Speidel, A. Mitchell-Smith, J. Bisterov, I. Clare, A. T. The importance of microstructure in electrochemical jet processing, (2018), ***Journal of Materials Processing Technology***
- Bisterov, I. Mitchell-Smith, J. Speidel, A. Clare, A.T. Specific and programmable surface structuring by electrochemical jet processing (2018), ***Procedia CIRP***
- Speidel, A. Mitchell-Smith, J. Bisterov, I. Clare. A. T. (2018). The importance of material precondition in electrochemical jet machining, ***Procedia CIRP***
- Clare, A. T., Speidel, A., Mitchell-Smith, J., Patwardhan, S. V., (2017), Electrolyte Design for suspended particulates in Electrolyte Jet Processing ***CIRP Annals – Manufacturing Technology***
- Speidel, A., Walsh, D., Mitchell-Smith, J., Clare, A. T., (2016). Electrolyte Jet Machining of Titanium Alloys Using Novel Electrolyte Solutions. ***Procedia CIRP***
- Speidel, A., Lutey, A. H. A., Mitchell-Smith, J., Rance, G. A., Liverani, E., Ascari, A., Clare, A. T., (2016) Surface modification of mild steel using a

combination of laser and electrochemical processes, ***Surface and Coatings Technology***,

Conferences

- “Electrolyte Jet Machining for Surface Texturing of Inconel 718” 10th International Symposium on Electrochemical Machining Technology (INSECT) November 13th -14th 2014 Saarland University, Saarbrücken, Germany. Paper presented and published DOI: 10.13140/2.1.4832.2242
- Ultrasonic Assistance of Electrochemical Jet Machining: An initial investigation in Inconel 718” Computer-Aided Production Engineering (CAPE) November 3rd -4th, 2015, University of Edinburgh, Edinburgh, UK. Poster presented and published. DOI: 10.13140/RG.2.2.33683.89123
- “Electrolyte multiplexing”, 19th CIRP Conference on electrophysical and chemical machining, April 23rd - 27th 2018, Bizkaia Aretoa Conference centre, Bilbao, Spain, Oral presentation and paper published

Acknowledgements

I would like to thank my primary supervisor Prof. Adam Clare without whom none of the work presented here would have been possible. My continued stubbornness to do things my way was always met with diplomacy and resolve. His confidence in my abilities allowing me to prosper in my research, facilitating and supporting me in every way possible to allow me to academically and personally grow. Thank you also to my secondary supervisor Prof. Phill Dickens for his considered input when it was needed.

I would also like to thank Dr. Emmanuel Brousseau and Prof. Dragos Axinte for their commentary on the thesis and discussion during my Ph.D viva that greatly improved the quality of this thesis.

On this journey I have had the delight of working with some very talented people that have gone on to help shape me as a researcher and my work. None more so than Alistair Speidel whose collaboration has been invaluable to my work in every respect and continued patience with helping me to understand the finer points of chemistry has rewarded us both. I can't thank Alex Jackson-Crisp enough for all his support on a personal level and technical in the laboratory with the continued development of the machine tools alongside technical support from sample preparation to sample scanning. Also, Dr Matthias Hirsch for helping me through these past four years, keeping me in check, pushing me forward and being an excellent soundboard and of course his technical knowledge.

I'd also like to thank all my collaborators in this work. Ivan Bisterov who is fast becoming Integral to this research. Dr Jennifer Gaskell for her knowledge and collaboration on all matters mathematical and Matlab related. Dr James Murray

for his invaluable input, knowledge and willingness to help. Dr John Walker (University of Southampton) for his collaboration across a myriad of tribological studies and Dr Vitali Goriainov (University of Southampton) for his collaboration with the stem cell research. The Manufacturing Metrology Team at the University of Nottingham who have been paramount in the analysis and understanding of the results presented here in their knowledge and continual access to equipment and software.

Finally, I'd like to thank my parents for all their support in times of need and my long-suffering wife Claire and my children Oscar and Jasper for their unwavering and unconditional love, support, devotion and keeping my feet firmly on the ground.

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Nomenclature

J	Current density (A/cm ²)	MRR	Material removal rate (g/s)
v_{noz}	Nozzle translation speed (mm/s)	σ	Standard deviation
v_{jet}	Electrolyte jet speed (m/s)	D	Profile depth or height (μm)
V	Electrical potential (Volts)	K	Dissolution or deposition kerf width
I	Current (mA)	CPA	Area of profile cross-section (μm ²)
R	Resistance (Ω)	P	Feature shoulder precision (μm / μm)
θ	Nozzle angle of incidence with reference to the substrate surface (°)	CWS	Slope of side wall in deposited or removed profile (μm / μm)
d_s	Minimum distance from nozzle tip to surface (μm)	A_A	Annulus area of nozzle tip surface facing the incident surface (mm ²)
d_n	Specific distance of the individual modified nozzle feature from substrate surface (μm)	A_F	Area of current focussing feature facing the incident surface (mm ²)
N	Single point or element on the surface of the nozzle tip facing the substrate surface (S)	A_{exp}	Area of profile expected from calculation (mm ²)
S	Single point or element on the substrate facing the nozzle tip element (N)	E_{eff}	Electrolyte current efficiency (%)
r_{noz}	Radius of the nozzle (mm)	d_{noz}	Diameter of the nozzle
d'	Radial distance from stagnation point (S_p) to the edge of the stagnation region	S_p	Stagnation point of jet flow on impingement

Abbreviations

<i>ECM</i>	Electrochemical Machining	<i>SSC</i>	Skeletal stem cell
<i>EJP</i>	Electrochemical Jet Processing	<i>CNC</i>	Computer Numerical Control
<i>EJM</i>	Electrochemical Jet Machining (subtractive mode of EJP)	<i>MME</i>	Machining mode effect
<i>EJD</i>	Electrochemical Jet Deposition (additive mode of EJP)	<i>ECE</i>	Electrochemical equivalence
<i>PSU</i>	Power supply unit	<i>I.D.</i>	Internal diameter
<i>HMI</i>	Human machine interface	<i>O.D.</i>	Outside diameter
<i>IEG</i>	Inter-electrode gap – nozzle tip to surface stand-off (mm)	<i>CPU</i>	Central processing Unit (machine)
<i>STE</i>	Symmetrical twin element nozzle design	<i>OSPE</i>	Off-centre single point nozzle design
<i>STD</i>	Standard nozzle type	<i>CPE</i>	Centre point nozzle design
<i>WC</i>	Wide castellated nozzle design	<i>NC</i>	Narrow castellated nozzle design
<i>DIF</i>	Design impact factor	<i>SHE</i>	Standard hydrogen electrode

1. Introduction

The requirement for manufacturing technology to cut costs, increase throughput, precision, efficiency and flexibility drives the need for new technologies. This is coupled with a drive to maximise component performance through the use of advanced materials and highly optimised design. This presents a problem within manufacturing to satisfy the needs of the complex component at the same time as maintaining a streamlined process.

Electrochemical Jet Processing (EJP) represents an emergent technique for satisfying this need within a high value, precision, environment. EJP presents the potential to manipulate metals at the microscopic level allowing removal and addition of material within the same process, in successive operations and without the need for re-fixturing. Therefore, improving process fidelity and streamlining the process chain of high value components.

EJP is an umbrella term used to define an unsubmerged, free-air jet process, utilising electrolysis for either removal (subtractive mode) or deposition (additive mode) of material. (Figure 1.1)

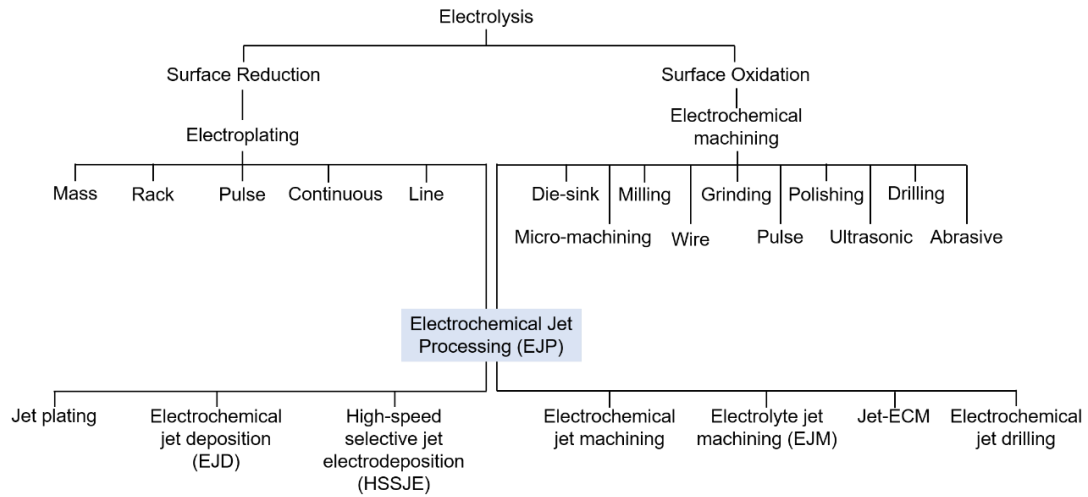


Figure 1.1: Definition of electrochemical jet processing and how it fits in with common electrolytic techniques

The innovations and analysis presented in this work are intended to be applied to EJP as a whole (additive and subtractive). However, advances and innovations are demonstrated in subtractive mode being electrolyte jet machining (EJM). This is intentional for two reasons identified from the literature review (Chapter 2). Firstly, subtractive mode currently presents itself as having a greater scope for development, innovations and applications of the process when compared to jet plating, which the number of patents and process definition is a testament too. Secondly, deposition of metals from a solute form is inherently toxic. Specific chemistry-based advances in this field of widening the spectrum of materials deposited, including co-deposition and enhancing the sustainability of the process are beyond the scope of this thesis. It is intended to demonstrate through the innovations presented here that the precision and flexibility of the features created by EJM can rival competing processes such as laser and electrical discharge machining but at a fraction of the cost and without the material implications of using a thermal based processing technology.

Electrochemical jet machining is a highly localised variant of electrochemical machining (ECM). Both ECM and EJM are anodic dissolution processes based on the electrolysis work of Faraday [1]. Both processes are capable of material removal without affecting a components surface integrity and physical properties such as hardness and toughness have no effect on machinability. However, EJM differs significantly from ECM in that EJM is capable of selective material removal without the need for masking due to hydraulic phenomenon, unlike ECM (discussed in latter chapters). The electrolyte is also delivered as a jet in an unsubmerged manner unlike ECM which is a submerged process. Due to this EJM can deliver far higher mass transport rates due to the electrolyte flow at the point of machining in comparison to ECM. Also, due to the impinging jet size and cooling effect of the high electrolyte flow, much higher current density values are achievable, whilst maintaining an electrochemical removal mechanism.

EJM, in its simplest form, comprises of a nozzle and substrate as electrodes, a free-jet of electrolyte emanating from the nozzle and impinging on a substrate surface. A power source connected between electrodes creates a potential difference thus forming an electrolytic cell. The polarity of the substrate and nozzle denoting the orientation of the redox reaction as to whether material is deposited or removed at the substrate.

Currently EJM is understood to be a two-dimensional planar processing technology, restricted in feature generation by the in-jet Gaussian energy distribution and coupling of feature size to the in-jet hydrodynamic stagnation region formed in an impinging jet scenario. This limits the shape and kerf of the features generated either in subtractive or additive modes, which in-turn limits the application of EJM in comparison to alternative technologies.

This thesis intends to identify an underdeveloped and applicable material to EJM applications and analyse its behaviour in process. The knowledge gained from this enables a suitable demonstration material for further developments. It is intended to develop innovations that seek to dissociate EJM from the current process restrictions thereby presenting itself as a viable micro-machining technology with distinct advantages over competing technology. These innovations can then be applied in appropriate application case studies for demonstration.

1.1. Aims of thesis

The aim of this work is to understand and advance EJM through enhancing the flexibility not only of the process itself but also of the feature profiles alongside increasing the feature precision achievable. Throughout this thesis flexibility of process is defined as the capability of the process to perform different functions such as machining at different scales. Flexibility of feature profile differs in that it can be understood as analogous to using different tools to obtain a different response profile. The response profile being shape of material removed or deposited. Increased precision is defined throughout as minimised kerf, maximised depth, feature side walls approaching vertical and any radius at the feature to surface shoulder being minimised.

An expansive literature review was carried out of additive and subtractive mode EJP which identifies current knowledge gaps in the processing technology. Fulfilment of the identified knowledge gaps through research and development of directed process innovations is intended to fundamentally change the process

capability of EJM. Therefore, demonstrating it as a low-cost, low-impact micro-machining technology.

To reach these aims the following three areas will be explored and form the basis of the results presented here:

- ***Fundamental analysis of complex alloy response.*** The suitability and behaviour of common application high value engineering alloys has yet to be fully explored in EJM. Prior investigation has, for the most part, concentrated on the basic generalised mechanics of dissolution whilst not considering material specifics leading to defined form and finish. Although, considerable research has been carried out in general ECM, as is shown throughout this work ECM material response often does not correspond to EJM. Therefore, the dissolution response and the definition of a process window for relevant materials to form a fundamental understanding has yet to be fully understood and defined in EJM.
- ***Platform and processing innovations for advanced EJM capability.*** Little emphasis has been made within EJM to look at processing from a platform point of view. In general, the use of simple laboratory style machining arrangements or modified ECM die-sink machine tools have been employed in current research with no commercially viable machine available. To carry-out research in EJM, therefore takes a commitment to develop a research platform. The task of development of this machine tool from process fundamentals is intended to be integral to this research, without which this research would not be possible. Through development of the tool and by identifying areas for improvement significant advancement of EJM can be sought.

- **Defining applications.** EJM currently is not used in its entirety in industrial application. Identifying application areas and implementing the process in a highly advantageous manner will define the success of the process. The understanding of the material response and hardware innovations will lead to novel applications fully exploiting the process and leading to a wider contribution to society as a whole.

1.2. Outline of thesis

This body of work is intended to follow a; define, design, characterise, innovate and apply format (Figure 1.2).

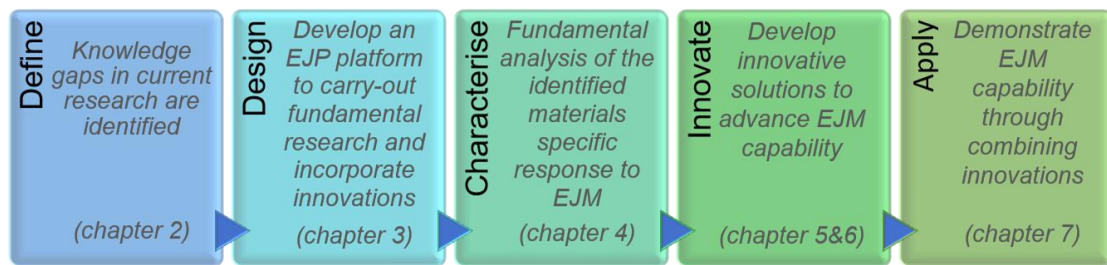


Figure 1.2: Thesis overview showing content of main chapters

A comprehensive review of literature pertaining to this investigation is presented in Chapter 2 covering both additive and subtractive mode EJP. It is necessary to consider both aspects of EJP not just EJM, as significant research has been carried out in this area which will be applicable to EJM, but perhaps not yet demonstrated. Topics of the review include an introduction to EJP as a whole and how it has developed. Identification of the fundamental processing parameters that define the process and its capability, and the research around them. This includes materials used and machine definable parameters such as current density and electrolyte jet speed. The review considers electrochemical and

electromechanical factors and innovations and their influence on the precision and flexibility in EJP. This includes platform and hardware developments and electrolyte considerations. Alternative micro-machining processes are investigated and assessed against the advantages of EJM. This is to help understand how EJM fits with alternative process capabilities and identify technological areas where EJM cannot compete. Finally, a summary is given of the current applications of EJP, again aiming to identify the intended future market and applications where EJP is relevant.

Chapter 3 presents a detailed breakdown of all experimental methods, analysis and characterisation processes used in the work. This also includes an overview of the development of the machine tool from an early generation one platform used for fundamental development of the process, to a more industrially focussed generation 2 platform incorporating some of the innovations developed throughout this project.

In Chapter 4 the dissolution response of Inconel 718 is analysed and compared to that found with titanium grade 5. These two materials identified in Chapter 2 as being of particular interest to high value applications where EJP could develop a niche. The impact of machine controllable parameters on the resultant machined form is experimentally investigated. Using this information, the effect of energy variance on the workpiece regarding form and finish is investigated further, identifying the dissolution mechanism of complex alloys and a comparison of performance and dissolution characteristics of titanium and nickel superalloys.

The results obtained in Chapter 4 are then utilised throughout the following chapters as the base of the innovations presented. Chapter 5 contains research and development of innovations utilising electromechanical design. Investigations are carried out into the changing of the angle of jet address and the impact on the resultant profile. That investigation provided insight that lead to the ability to modulate the energy density profile found in-jet. A model is developed to substantiate the hypothesis that resistance can be modulated in-jet through modifications to the nozzle tip design. This results in the ability to change the shape of the response profile created. The profiled nozzles that are responsible for this are coupled to a further mechanical innovation of rotary articulation of the end effector. This in turn results in the ability to maintain constant bespoke profiles throughout the toolpath or create dynamic changes to the resultant toolpath without changing any hardware as a function of spatial consideration.

Chapter 6 introduces advancements in EJM derived through electrochemical means. Presented here is the use of electrolyte doping to create a transitory masking effect at the target surface to enhance the precision of machined geometry. The electrochemical mechanics of this innovation are developed to describe the causation effect as current filtering and re-fresh rate. The ability to change profile spatial properties through the effects of electrolytes alone are then utilised in a hardware innovation of electrolyte multiplexing whereby the differing characteristics of the electrolytes are manipulated for preferential machining regimes.

Chapter 7 introduces the application of EJM to ultra-precise machining. This demonstrates the compound effect of the electromechanical and electrochemical

advances from chapter 5 and 6 which when combined and shows the effect of overcut commonly associated with EJM can be eradicated. This achieves not only kerf equivalent to the jet diameter but small length scales in line with competing processes. Demonstrating that EJM resultant geometries are no longer restricted by energy distribution and hydrodynamic characteristics.

Finally, Chapter 8 presents the overall conclusions of the research work in this thesis and identifies how this research and innovation development have fulfilled the research gaps alluded to in Chapter 2. Also outlined are the future possibilities for continuation of this work and extend the research findings that have been presented here in order to further advance electrochemical jet processes.

2. Literature review

2.1. Introduction

This chapter provides an overview of EJP from the fundamentals of parameter influence on the deposition and removal of material to mechanical and chemical influences within the process. The review will encompass both additive and subtractive mode electrochemical jet processing and gives consideration of the competing processes and developments of such, along with a review of the current applications of EJP. Through this literature review, design cues are sought to aid the development of the research platform, alongside this current knowledge gaps are identified and in doing so, the scope of the thesis will be defined.

2.2. Definition and Development of electrochemical jet processing

Electrolytic jet processes consist of a nozzle, acting as an electrode, supplying a stream or jet of electrolyte which acts as a carrier and a workpiece with opposite polarity. An electrical potential difference is applied between the two electrodes and forms an electrolytic cell (Figure 2.1). An important distinction of EJP is the description of the jet as an un-submerged, free-air jet process, meaning the jet emerges from the nozzle and moves through a region that is considerably less viscous than the jet fluid, before impingement.

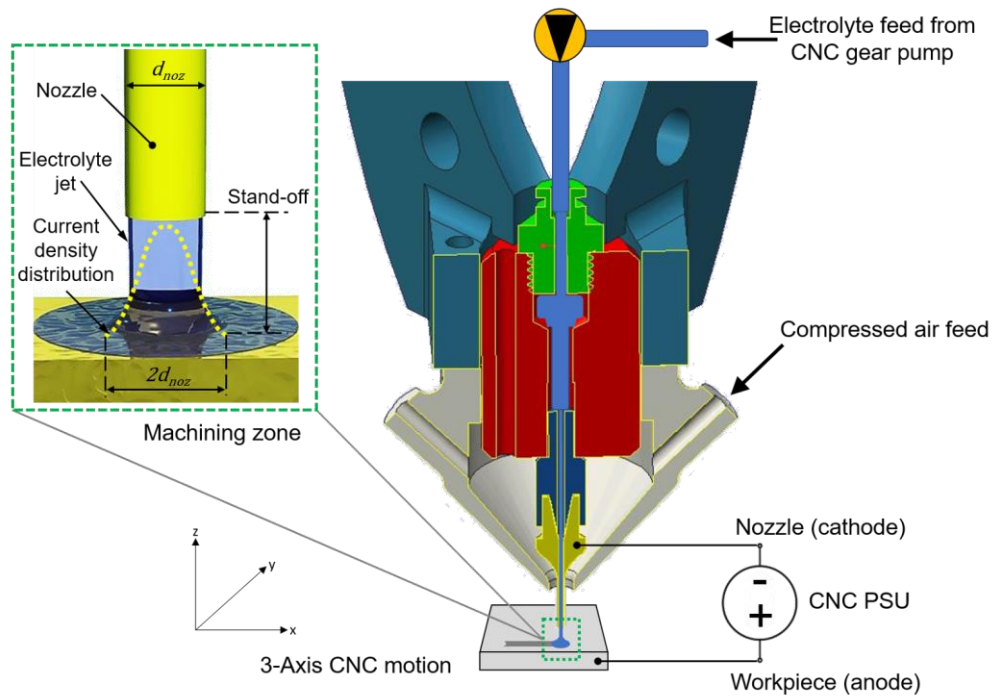


Figure 2.1: Schematic of EJP process in subtractive mode

EJP is the amalgamation of electrochemical jet machining (EJM) [2-5] and electrochemical jet deposition (EJD) [6-9] within a unified machine tool.

This technique can achieve jetted deposition of material with a cathodic workpiece, analogous to electroplating, as well as jetted material removal with an anodic workpiece (Figure 2.2). In EJP the electrolyte is accelerated through the nozzle and expelled at a supercritical speed so that when impinged on the incident surface it forms a thin film radially around the jet. The film then slows as it radiates away from the impingement zone until an hydraulic jump [10] occurs (see section 2.3.5.). This causes a thin, high resistance area adjacent to the impingement zone to be maintained. The energy density therefore is concentrated directly beneath the nozzle in a Gaussian distribution [11] and not in the thin film area surrounding. This phenomenon restricts the development of current flow allowing for mask-less, precision deposition or removal of material.

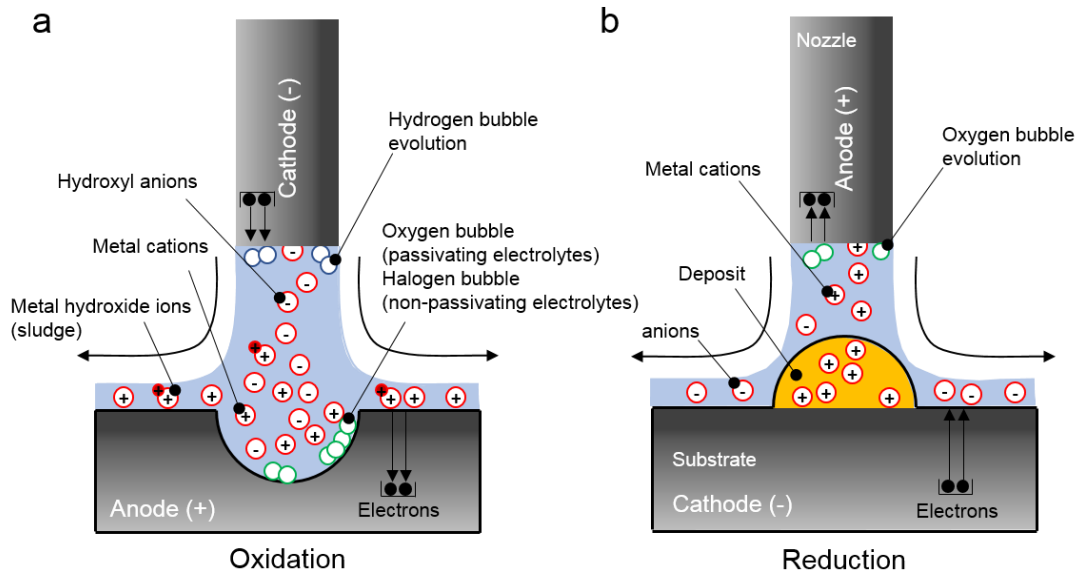


Figure 2.2: Schematic of generalised electrochemical reaction in electrochemical jet processing in (a) subtractive mode (b) additive mode

If the flow rate is not high enough then the hydraulic jump does not occur, and the energy density field cannot be successfully focused and contained hence localised machining is not achieved (discussed in section 2.3.5). This can be further aided by an air shroud co-axial to the nozzle (Figure 2.1) (discussed in section 2.5.5).

EJP achieves many of the same advantages of ECM where by material properties such as hardness and toughness have no bearing on machinability [12, 13]. Machined surface features exhibit no thermal loading thereby avoiding increased residual stress or formation of white layers [5]. Through polarity reversal deposition of metals is achieved without the cost and complexity of alternative methods.

The term electrochemical jet processing (EJP) is used throughout this thesis and is derived from electrochemical machining (ECM) and electroplating (see Figure 1.1). These technologies were developed from the principles defined by Faraday

(1791 - 1867) for anodic dissolution of a metal and Luigi V. Brugnatelli (1761 – 1818) who defined the methodology of electroplating. Electroplating grew quickly in its application due to its ability to turn cheap materials into expensive looking objects. The first major patents being awarded to George and Henry Elkington (British patent numbers 7304; 1837 and 8447; 1840) [14] thanks to the work of John Wright (1808 – 1844) a surgeon from Birmingham. This spawned commercial interests such as Elkington and Mason (1842 – 1861) successfully plating gold and silver objects. It was some time before the first patent related to ECM was filed in 1929 by W. Gusseff [15] (British patent 335,003) recognising the basic architecture and operating features required to exploit the principles of Faraday. This patent identified the significant differences to electrolytic polishing developed by E. Shpitalsky (1911) of far higher electrolyte flow between the electrodes and vastly increased current density (100 A/cm^2 compared to 10 A/cm^2) [16]. ECM then received little attention, with the first notable research paper on the subject being by C.F. Burgess published by the electrochemical society (1941) [17] defining the differences of ECM from the mechanical machining process. However, with the development of advanced alloys during the late 1950's and 1960's displaying high hardness and toughness forming components of increasing design complexity (notable gas turbines and forging dies), therefore making them difficult to machine by traditional shear-based methods, highlighted the advantages of ECM. The first industrial machine tool was introduced by Anocut Engineering company of Chicago, USA (1959) followed by increasing research, development and introduction of new methods and machine tools across the USSR, USA, Western Europe and Japan [18].

Subtractive mode EJP is also referred to as electrochemical jet machining [2, 19], electrolyte jet machining [4, 5, 20] and Jet-ECM [21, 22]. Throughout this thesis the term electrochemical jet machining (EJM) will be used to describe subtractive mode EJP. There are a wide range of similar nozzle based ECM technologies, the earliest found patent of which relating to this was in 1953 and entitled electrolytic shaping (Figure 2.3) [23]. This describes a method of removing metal from a workpiece comprising a jet of electrolyte impinging on an anodic workpiece, the direction of the jet either remaining fixed or in a predetermined path. It further describes an adaption of this process akin to turning whereby the workpiece is rotated and a jet of electrolyte impinges radially on the surface. Nannichi [1961] [24], further demonstrated in publication some of the advantages that could be gained in the use of high-speed collimated jets.

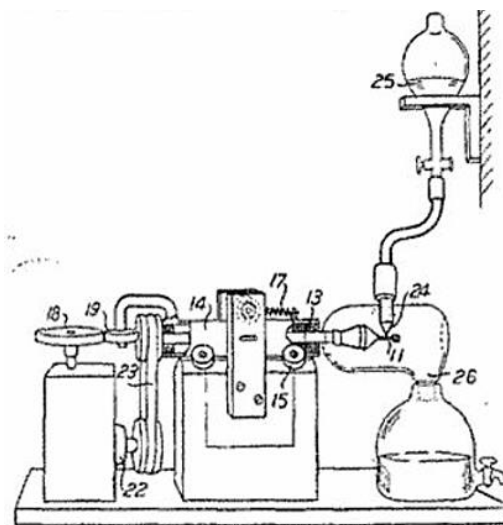


Figure 2.3: Schematic of the earliest found patent related to EJP developed by the National Research Development Corporation (UK) August 24, 1953

However, the application of electrolytic jets was reserved for fine hole drilling [25], sample polishing [26] and etching [27] often using highly acidic electrolytes. Figure 2.4 shows schematic of these drilling processes each with their individual

characteristics [19, 28]. The majority use insulated or glass nozzles which move towards the workpiece in the z direction as dissolution of the substrate occurs. Drilling applications remained the staple industrial application for subtractive mode EJP, for example in creating cooling holes in turbine blades [13, 29]. However, the use of highly toxic acidified solutions meant that this application was to have a limited shelf life due to hazardous waste and handling concerns.

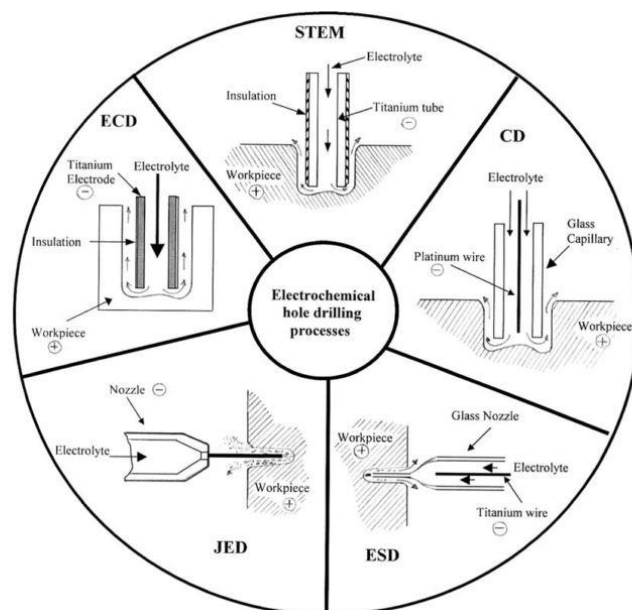


Figure 2.4: Electrochemical hole drilling processes utilising jet architecture [28]

Fletcher et al. [1974] [30], filed a patent entitled “scanning nozzle plating system” which describes a method for selective plating using a high-pressure jet impinging on a substrate surface. The deposition only occurring in locations in which the voltage amplitude is above a minimum known value. The patent describes in detail the machine architecture required of an orthogonal X, Y axis coupled with a controller to create deposition patterns. The deposition patterns are generated using a scanner, copying an already defined pattern and storing it in a recorder

which can be played back to the controller. No more technical detail is given as to how this is achieved only describing the possible methodology. It goes on further to describe how this method can also be used for selective etching by directing a constant flow of etching solution towards the substrate, etching only occurring during periods where the voltage amplitude is above a predetermined level. It must be noted that the electrolyte pressures described in this patent are extremely high by current standards (500 – 700 psi). Few other details regarding material removal is given. Melcher et al. [1981] [31], followed this filling a patent based on the selective removal of material entitled “Method for mask-less chemical and electrochemical machining” in which a method is described as “*To machine, a stream or jet of electrolyte impinges on the workpiece, and the stream is maintained at a lower electrical potential than the workpiece. Since the workpiece is anodic with respect to the stream, metal ions will be transferred to the stream from the workpiece resulting in selective etching*”. The use of a jet however, was not implicit to the patent as the main focus of the patent was selectivity, which could also be achieved in an electrolyte bath using a laser focusing on the workpiece through the bath. von Gutfeld et al. [1983] [32], then expanded on this earlier work, though only focussing on deposition, with the inclusion of a free-air jet defining the characteristics of the jet as being collimated and un-submerged. Presenting the advantages of using this type of process as able to provide a rapid resupply of fresh ions into the region of plating, so enabling higher current densities as the process is not limited by mass transfer rates associated with other plating technologies. This was then followed with a further patent by this group relating directly to laser assistance in 1985 [33] for enhanced removal and deposition using an un-submerged jet.

The first demonstrations of translating electrolytic jets being used for machining simple grooves was by Datta et al. [1989] [34] in the micromachining of nickel and steel. This is the first time the distinct advantages of the jet process over conventional ECM is outlined stating the high current densities that can be created which directly relates to the high material removal rates that can be achieved, and the selective, mask-less nature of the process, alongside the use of non-acidic common salt electrolytes. A further review paper on the subject in the same year [35] reiterates these findings and makes comparison to other chemical and electrochemical processes.

During the early nineties electrochemical jet processing techniques in the form known today, started to become more established as a research avenue. Kunieda [1993] [2], published a paper on the creation of micro indents to improve rolling contact fatigue. The first time a paper had been released using a full CNC operated machine where the nozzle was translated for the application of surface texturing of a component surface. Kunieda and Yoneda in 1995 [11] went on to detail the energy distribution and processing shape simulation within electrolytic solution jet machining. Their findings further supported by Kozak et al. [1996] [19] where a similar model was developed. Both of which form the basis of the current understanding of EJP in-jet energy distribution.

Additive mode EJP also continued to develop during the development of subtractive mode EJP. From the early rudimentary work of Alkire et al. [1982] [36] through developments in the technology and understanding [6, Bocking [1994] [37], 38], [Dover et al. [1996] [39], 40], and Kunieda et al. [1998] [7] were now all able to carry out micro-fabrication of 3D structures, aligned with rapid

prototyping / tooling techniques termed high speed selective jet electrodeposition (HSSJE).

Both processing modes of EJP had now achieved a level of maturity in process development that meant they can be defined in their own right as a stand-alone process with a common architecture.

2.3. Parameter influence on deterministic feature precision and flexibility in EJP

2.3.1. Introduction

Consideration of the variation of process parameters is fundamental to the understanding of any process behaviour. Hence in EJP this is a major research focus. The following section reviews the literature pertaining to this, identifying these underlying concepts being required to underpin any future innovations to improve the flexibility and precision of EJP.

2.3.2. Current density

Energy application in ECM processes is generally quantified by current density (J). This is defined in ECM processes as the ratio of the machining current to the machining area [18] Equation 1 .

$$J = \frac{I}{A} = \frac{k_e V}{h} \quad \text{Equation 1}$$

Where J is the mean current density, I applied current, A the machined surface area, k_e electrolyte conductivity, V the applied potential difference and h the working gap between electrodes (IEG) [16].

The importance of current density in electrochemical processes can be demonstrated by consideration of Faradays first law of electrolysis (1833) [1] defined as:

“The amount of chemical change produced by current at an electrode-electrolyte boundary is proportional to the quantity of electricity used.”

Therefore, the mass of a substance (m) deposited or removed at an electrode is directly proportional to the quantity of charge (Q) passed and is defined by Equation 2:

$$m = zQ \quad \text{Equation 2}$$

Where z is the electrochemical equivalent (ECE) which is defined as the mass of a substance produced at an electrode during the electrolysis reaction by one Coulomb of charge.

Noting that

$$Q = It \quad \text{Equation 3}$$

Where t is time and current is therefore proportional to the amount of material removed or deposited.

In EJP, current density is commonly regarded as the applied mean current density by the cross-sectional area of the electrolyte jet exiting the nozzle [5]. This is ideally demonstrated when Ohms law is applied to the IEG of a typical jet arrangement:

$$V = IR = \pi \frac{d_{noz}^2}{4} JR \quad \text{Equation 4}$$

Where V is voltage, R resistance and d_{noz} nozzle diameter.

However, this is merely an assumption and bears little relationship to the complexities of the current density and its distribution within the IEG. It does allow an easy comparison between parameters and machining modes and as previously stated relates directly, with a linear relationship to material removal. This has been demonstrated in EJM by Datta et al. [1989] [34] and Liu et al. [2016] [41], and by Bocking [1991] [42] in deposition. However, Bocking commented that beyond 10 A/cm^2 the quality of the deposition structure becomes poor with dendritic like structures forming. It should be noted however that time of exposure by the jet plays an integral part (see Equation 3). However, in EJP the material removal or deposition occurs in a specific direction, removal gets deeper and deposition gets higher, not wider, as current density increases so defining the mask-less nature of EJP [43].

Across the majority of studies 100 A/cm^2 was noted to be a commonly applied value and falls in with commonly accepted ECM parameters of 50 to 150 A/cm^2 [16] where anodic dissolution is the only machining mechanism in effect. This is termed ECM conditions, beyond which unstable machining conditions occur, leading to excess gas generation at the electrodes and increased probability of electrical discharge (arc and spark) within the IEG [18]. This definition of values however is unlikely to be relevant to EJP in subtractive mode due to the high flow of electrolyte, relatively high translation speeds, large IEG and small interaction zone (these are fully defined in the following sections). This minimises the heating effect in the IEG caused by current flowing through a resistance (joule heating) and rapidly removing debris in comparison to die-sinking ECM. Schubert et al. [2011] [43], when investigating the electric potential in jet-ECM stated that they could achieve up to 2100 A/cm^2 . This further highlights the deficiency of using

current density as a controllable and defining metric. In that study and successive studies [44-46] where these high J values are quoted, a fixed voltage is used. The high current density is achieved by enlarging the IEG and so increasing resistance. To compensate for this, the current value is required to increase in order to maintain the balance (noting the relationship in ohms law, Equation 4) rather than by what is required in the removal of material. Therefore, current is used in overcoming resistance rather than anodic dissolution, the material liberated would be the same as with a much lower current density but smaller IEG. This is the reason why in the case of some simulations [47] the simulated depth always exceeds the actual depth from experimentation. The energy found at the surface is less than that at the end of the nozzle (set as a boundary condition) having been reduced by the resistance found in the jet due to the electrolyte conductivity, bubble formation and debris and passivation effects of the material, depleting the energy which is available for removal at the surface.

Kozak et al. [1996] [19], developed a more intricate method to calculate current density which determines the current density by considering the electrolyte conductivity changes due to temperature effects of joule heating for given values of voltage and size of IEG. Kozak et al. state that MRR becomes limited by the boiling of electrolyte due to joule heating leading to cavitation and unstable machining conditions. It was found that the calculated level of current density is almost twice that determined when the changes in electrolyte conductivity are disregarded. The model was found to provide good adherence to actual experimental removal rates. This however, still does not accurately depict current density as it only considers a single arbitrary element within the jet rather than at the surface.

The difficulty in describing mathematically what is occurring at the surface is due to the complexity of all the contributory boundary conditions, but also the distribution of the current density or potential gradient beneath the nozzle. Alkire et al. [1982] [36], developed a fundamental mathematical model for the distribution of current along the workpiece surface under an impinging un-submerged jet. The model was then verified using a segmented electrode that could measure the current radially every 3 μm from the jet axis with insulating layers in-between (Figure 2.5a). It should be noted that this model was developed and verified for use with additive mode EJP hence the low current density values used.

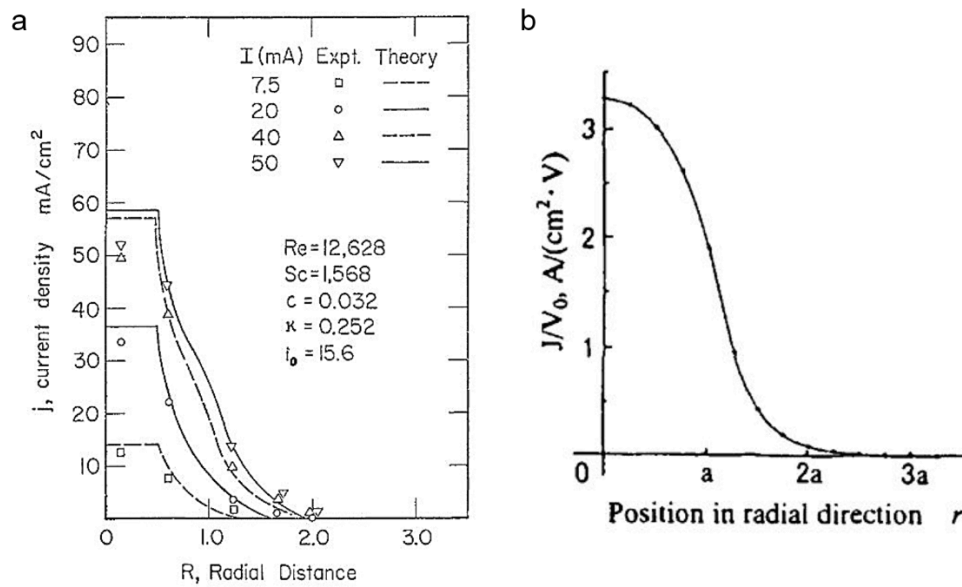


Figure 2.5: Effect of applied current on current distribution in impingement region (a) Alkire et al. [1982] [36], (b) Yoneda et al. [1995] [11]

Yoneda et al. [1995] [11] (Figure 2.5b) and Kozak et al. [1996] [19], in subtractive mode EJP and Rajput et al. [2015] [48] in additive mode, further developed more sophisticated models of the expected distribution of the current density profile based on the potential gradient developed within the jet and according to the

boundaries of the jet stream. These can be deemed to be correct when the typical removal profile is considered. Kozak et al. also considered the current density profile could change as a function of increasing voltage, changing nozzle-tip to surface stand-off, nozzle diameter, electrolyte pressure and jet dwell. This Gaussian type distribution is consistent with the energy distribution found within alternative energy beam processes such as laser [49] , electron [50], focused ion-beam (FIB) [51] and water jet [52, 53] which results in profiles which exhibit tapered sides, a rounded apex and diffused edge definition.

Surface finish on a machined feature is another effect which is strongly dependant on applied current density. Various studies have noted that as current density increases, surface roughness tends to reduce. Natsu et al. [2007] [5] and [Kawanaka et al. [2014] [54], 55] proved this by exploiting the relationship in Equation 3. An inverse relationship was established between current and dwell time. A series of pits was machined and for each pit as current density increased so dwell was reduced to achieve a constant charge. Therefore, the depth of each pit remained constant at 50 μm . It is obvious from Figure 2.6 the reduction in surface roughness is directly attributable to the increase in current density rather than any consideration arising from increasing pit depth (increasing IEG) or change in overall charge as the charge supplied is constant due to the balance of current and time.

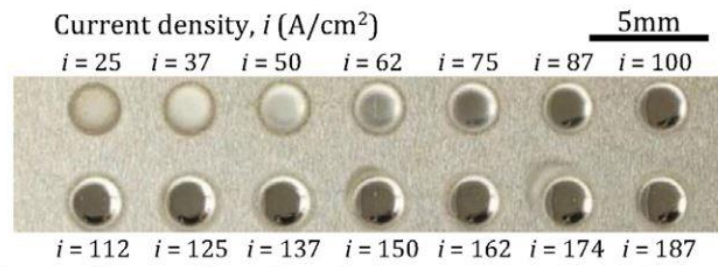


Figure 2.6: Demonstration of decreasing roughness as current density increases in Stainless steel whilst maintaining a constant electrical charge [55]

Kawanaka et al. [2015] [55], explained this phenomenon using the diffusion layer theory (concentration boundary layer). This is described as “a region in the vicinity of an electrode where the concentrations are different from their value in the bulk solution” [56]. Defined by Nernst with the concept of a stagnation diffusion layer across which the solute diffuses from the solid surface into the bulk solution and forms a linear concentration profile [57]. The effect of this is a limiting value of the faradaic current available at the surface. At low current density ($<50 \text{ A/cm}^2$) the diffusion layer is thin; therefore, the dissolution is even across the surface and protrusions are machined at the same rate as valleys on the surface (Figure 2.7a). Hence the roughness remains constant regardless of overall material removal and exacerbated by material considerations of passivation (see section 2.3.6). With increasing current density, the diffusion layer increases. The potential gradient under the jet and concentration of molecules and ions, governing the electrochemical reactions at protrusions above the mean surface being steeper than those in the valleys because the interface between the bulk flow and diffusion layer becomes flat (Figure 2.7b). The protrusions are therefore machined at a higher rate reducing roughness. However, the diffusion layer at current densities $>200 \text{ A/cm}^2$ become so thick (Figure 2.7c) that once again dissolution rates over the surface equalise and so dissolution is unable to

efficiently focus on the protrusions. The surface becoming more randomised leading to a less effective reduction of surface roughness. This hypothesis for the higher current density is however in contradiction of earlier work in the same material [5] where the roughness is seen to be stable and consistent beyond 200 A/cm² showing no indication of increasing roughness. This could simply be due to how the roughness measurements were obtained however requires further investigation to clarify.

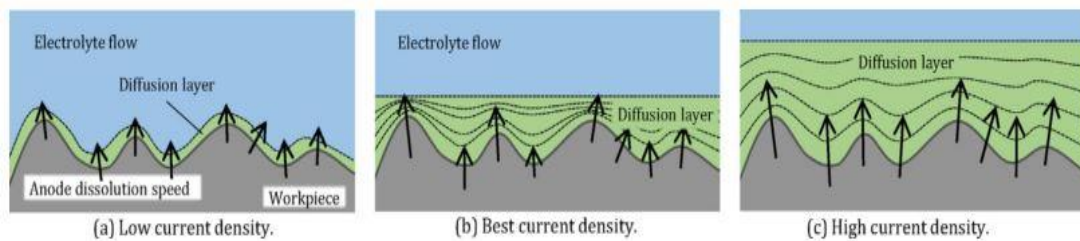


Figure 2.7: Principle of surface finishing through consideration of the diffusion layer [55]

The implication of current density in additive mode EJP has also been investigated. Although due to the inherent nuances required in deposition, where consideration of the material nucleation rate is required due to changes in current density, it is possible to more easily define a rigid current density level. Bocking [1992] [58], determined the maximum current density in gold and copper deposition under a stationary jet, that could still produce quality deposits with high deposition rates up to 3.4 $\mu\text{m/s}$ as 6.5 A/cm². For comparison the deposition rates of similar plating technologies was in the region of 0.5 to 1 $\mu\text{m/s}$ [42]. Beyond this deposition rate, deposits were nodular and dendritic in structure and repeated layers would serve to worsen this [39]. Below this current density, deposition rates were seen to be low and the adhesion and morphology of the structure poor. Investigation into the process beyond this work have sought to use current

densities related to these guideline parameters [7, 9, 38, 40] even when considered with nozzle traverse speed.

2.3.3. Nozzle traverse speed / dwell time

As noted in Equation 2 and Equation 3 exposure time is as relevant as the level of current in the level of material liberation or deposition. Often not considered in mathematical modelling of EJP as found in the work of Kozak et al. [1996] [19] and Yoneda et al. [1995] [11] where the model is assumed to be axisymmetric, static and stable for mathematical simplicity of calculation. In the case of Kozak current density was calculated at $t=0$, when compared to experimental values, machined pit diameters showed a 14% error to the model due to the dwell time. However, these assumptions allow for a two-dimensional model to be extracted. Due to the improvement of computing power, practitioners such as Hackert-Oschätzchen et al. [2015] [47] still using a stationary jet, have factored a dissolution time into the model. This demonstrates the change in shape of the material removed noting an increase in depth with increasing time. When factoring in hydrodynamic influences (again with respect to time) the simulation also showed the lack of increase in diameter of the machined pits which was then demonstrated to be correct in the experimental validation. Natsu et al. [2007] [5] and Kozak et al. [1996] [19] found the same phenomenon when machining pits that a longer dwell time lead to deeper pits, but Natsu et. al. also found when machining grooves into the workpiece the same relationship between traverse speed and groove depth was evident.

The relationship of current and dwell has been further demonstrated [5] in the previous section where an algorithm was created exploiting this relationship to

maintain a consistent machining depth not only in pits but in grooves for a set value of speed and current density. Natsu et al. [2007] [5], found that surface roughness was not affected by machining time. Through machining pits at the same current density but for increasing dwell times, the surface roughness remained almost constant throughout even as the pits became deeper with longer dwell. The nozzle traverse speed (scan speed) was used as the primary function along with tool path by Natsu et al. [2008] [59] in order to create complex 3D geometries by superimposing elemental curved grooves. Good correspondence to the target superimposed feature profile was achieved although errors were found in some cases due to anomalies that are discussed in the following sections.

Kai et al. [2012] [60], also carried out investigations using traverse speed and repeated passes for the purpose of slot and plate cutting. It was found that using the side wall of the jet approaching a plate, thicknesses up to 3 mm were able to be cut by reducing translation speed to 0.3 $\mu\text{m/s}$ in a single pass. In comparison with the jet approach being normal to the substrate surface, with extremely slow translation speeds, perforation was possible through 80 μm thick plate. However, the resultant slots were not symmetrical in the cross-section and with a high degree of profile variance and poor perforation at the slot beginning. They further demonstrated that increasing the number of passes over the same toolpath can be seen as analogous to increased dwell or reduced speed which was also remarked upon by Natsu et al. [2007] [5]. This was demonstrated through cutting thin plates using a faster speed and repeated striations. This achieved a much more uniform and repeatable profile albeit with a higher taper, although the reasons behind this are not fully explained. The methodology of repeating the

number of scans over the same toolpath was also demonstrated [5] to have another advantage of reducing surface roughness, the more scans that are made reduces the level of roughness ($R_z \approx 0.4 \mu\text{m}$ 1 pass to $\approx 0.1 \mu\text{m}$ seventh pass). Although this would seem in contradiction to earlier statements that dwell time had no influence over surface roughness, it is hypothesised that using high nozzle traverse speeds, minimises the time the machine surface is exposed to low current density areas found at the periphery of the jet. Considering that as stated in the previous section, low current densities are responsible for a higher surface roughness. Kawanaka et al. [2015] [55], further expanded on this, finding they could achieve a mirror finish over a large area regardless of current density, although it must be above the decomposition current required for the material (see section 2.3.6.). The number of reciprocating translations was changed in proportion to the translating speed and inversely proportion to current density. Therefore, the lowest surface roughness was achieved with a 100 mm/s translation speed, 94 A/cm² current density and 200 repeated scans. This was found to be comparable to the lowest possible roughness with a stationary jet and with increasing current density the repeating translations method achieves lower surface roughness than a stationary jet.

In additive mode EJP the relationship between current density and traverse speed again is a subject of investigation. It was shown that there is an optimum scan speed for the process due to the finite nucleation time for copper deposition being 1.5 mm/s [6], although this should be taken in consideration of the current density. Above this only the trailing edge of the jet will produce enough time for full nucleation to occur and so the current density is focussed in this area.

Resulting in a low quality deposition structure with undesirable vertical columnar growth occurring [39].

2.3.4. Inter-electrode gap (IEG)

The inter-electrode gap (IEG) in subtractive mode EJP has received little research in comparison to general ECM where the interactions between electrodes, electrolyte, flow, tooling and resultant features has been investigated [12, 17, 18, 61, 62]. In comparison investigation of the IEG in EJP has been restricted in the most part to the effect on kerf by changes to the size of the IEG as part of process kinematic studies. Ikeda et al. [2006] [20] noted during his investigation on the use of multiple nozzle arrays, that as the IEG is reduced from 1.7 mm down to 0.5 mm the pit diameters dropped from ≈ 0.475 mm down to ≈ 0.4 mm from a nozzle I.D. of 0.26 mm. It was however commented that the pits started to become more oval at the reduced standoff. Although this study looked at close packing jet arrays for large area coverage and the effect was thought to be due to the interaction with the other jets in the nozzle array. Kunieda et al. [2011] [63] found the same trend when machining with a newly designed slit nozzle (see section 2.5.5) whereby the width of the groove cut increased from ≈ 75 μm to ≈ 100 μm as the IEG increased from 1 mm to 3 mm. However, at IEG values < 1 mm the width was observed to be larger at 110 μm , roughly two times that of the nozzle width. This relationship of machined kerf approximating to two times the nozzle I.D. is found throughout EJP and is discussed further in section 2.3.5. Schubert et al. [2011] [43] found that with increasing the IEG from 10 μm to 100 μm there was a decrease in groove kerf as the IEG increased. This was due to the inability to define a free jet at smaller distances, so the nozzle is

completely immersed leading to a loss in precision of dissolution. It was also observed that at reduced distances a greater depth is achieved due to a reduction in resistance found in the IEG therefore allowing greater dissolution energy at the surface.

Previously in-jet resistance had been largely ignored as subtractive mode EJP had been described as tolerant to significant changes in the gap width of the IEG [5, 64]. This is however reliant firstly on the power supply to the electrolytic cell being able to compensate for an increase in resistance by increasing the electrical potential in order to maintain a constant current (see Equation 4). Secondly there should be no latency in the power supply unit (PSU) in the reaction to these changes in the resistance. This effect of increasing resistance for changing IEG sizes could help explain the errors found by Natsu et al. [2008] [59] where by a 30 μm difference was found between simulation and actual machined profile at the depth maxima. This was investigated further by machining grooves at an IEG of 0.3 and 0.42 mm, relating to the changes during the prior feature generation. They found the kerf of the groove to be wider with the larger standoff, concluding that generated gap width should be taken into account during precision machining.

The concept of the electrolyte being analogous to an ohmic resistor is common place in the modelling of ECM processes [65]. The resistance in the IEG occurs due to several individual phenomena all of which must be overcome to allow current to flow. These can be seen in the simplified potential profile shown in Figure 2.8. The electrode potential between the substrate and electrolyte being the readiness of ions to discharge and form a barrier to the rate of reaction. Thus, additional energy is required so that ions discharge at the required rate known as

the activation polarisation (or activation over-potential). Films formed on the surface of the electrodes (discussed later in this chapter and throughout this thesis) such as metal hydroxides inhibit the flow of current, this potential loss being known as ohmic overvoltage.

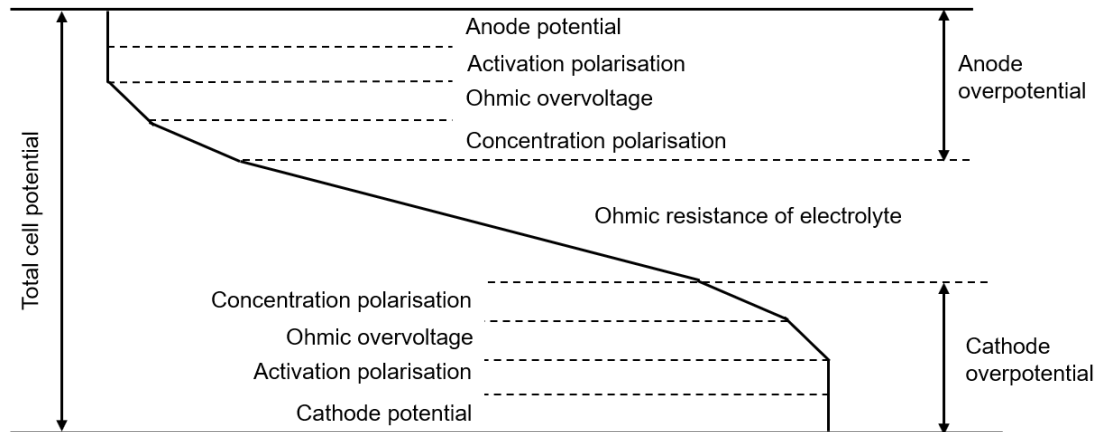


Figure 2.8: Simplified potential profile found in the IEG derived from Wilson [1971] [18]

Inert loose oxide films and metal hydroxide layers allow current to pass through electrolyte pathways through the structure, however more tenacious oxide films will only pass ions through diffusion greatly reducing dissolution rates. The migration of ions to the electrode surface under applied electrical conditions causes concentrations to form (diffusion layer) which ions must pass through inhibiting the ions release of charge at the electrode surface and newly formed ions dissipating into the bulk electrolyte. The energy required to overcome the concentration polarisation being the concentration overvoltage. It should be noted one of the distinct advantages of subtractive mode EJP is the high rate of fluid flow which vastly reduces concentration polarisation allowing much higher current flow than a stagnant or low flow rate scenario.

Further expansion to the description of the IEG is the incorporation of the electrical or electrochemical double layer [66] (DL) (initially based on a model proposed by Helmholtz (1853)) which is compared to an electrical resistor capacitor circuit (RC circuit) [67, 68] (Figure 2.9).

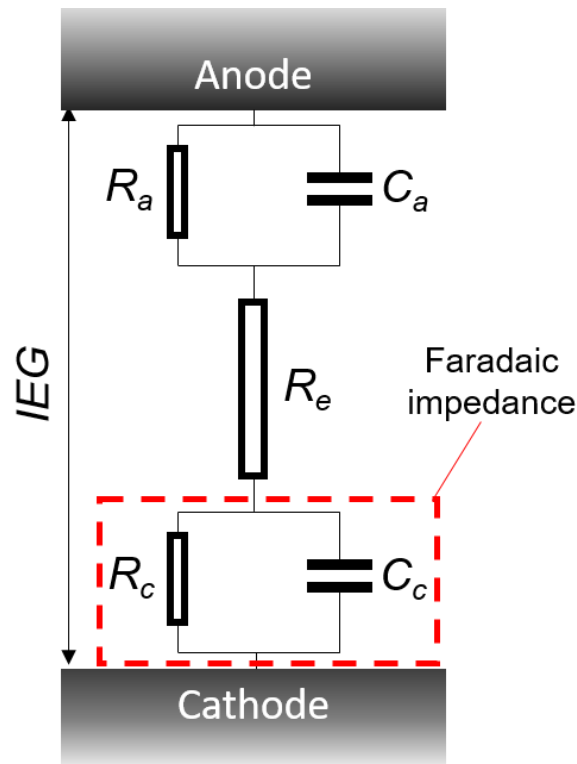


Figure 2.9: Schematic of an electrical representation of the IEG featuring the electrical double layer

Where R_a and R_c is electron transfer resistance at the electrode surface, R_e the electrolyte resistance, and C_a and C_c the double layer capacitance. The combination of the resistor and capacitor at the electrode surface being referred to as the Faradaic impedance. The double layer forms on the surface of any object when exposed to a fluid consisting of two parallel layers of charge. The first layer being the surface charge of ions adsorbed onto the object due to chemical interactions and the second layer being the diffuse layer comprising of free ions attracted to the first layer through electrical attraction and thermal motion. This is the basis for precision improvements by pulsed power supplies

and will be discussed further in section 2.5.4. Hackert-Oschätzchen. et al. [2014] [46], developed a method to combat these changes in the IEG by exploiting this resistance model. This gap control strategy similar to that developed by Bilgi et al. [2004] [13] for deep hole electrochemical drilling with a dynamic cathode feed mechanism. Short circuiting between nozzle and workpiece is sensed by a current sensing comparator circuit and the quill feed retarded. Hackert et. al instead used fluctuations in resistance, the starting point of the geometry to be machined used as a datum to which all other movements of the nozzle are relative. As machining of the desired geometry takes place the electric current within the IEG is continually monitored. If the current decreases by 1 mA, the nozzle is fed towards the surface until the current established at the starting point is resumed. If the current increases by 1 mA the nozzle is fed away from the surface until the datum current is established. Although the method was observed to be successful, some error was found in the resultant geometry due to the way the control strategy was implemented. The latency in the controller to react to changes in the resistance and resolution of the stages meant a delay in the changing of the IEG so leading to deviations in the resultant profile.

Investigation into the IEG on additive mode EJP has again been mainly concerned with the initial setting of the nozzle tip stand-off. Karakus et al. [1994] [69], observed that when the nozzle tip stand-off is reduced, the profile of the metal deposits became more localised under the nozzle side wall giving a more even deposition distribution under the nozzle as opposed to the Gaussian distribution. In this case a ratio between IEG (H in this case) and jet I.D. (d in this case) was developed, the variation was experimentally observed between $H/d = 0.25$ (125 μm IEG) and $H/d = 4$ (2 mm IEG) using a 0.5 mm nozzle (Figure 2.10a).

This can also be compared to Kozak et al. [1996] [19] who hypothesised current distribution for changing nozzle stand-off again as a function of H/d (Figure 2.10b) in subtractive EJP. This has not been proven experimentally in subtractive mode EJP as the vastly reduced IEG required to demonstrate this would have the associated problems of maintaining a free jet to achieve profile precision, but also where a high enough current density is required to form a precision shape there is a high chance of electrical flash-over between the nozzle and workpiece.

Bocking [1994] [37], carried out a detailed analysis of the effects of changing the nozzle stand-off on precision, quality and mass transfer rates. He concluded selectivity (precision) of the depositions was improved for H/d values under 1 due to the current density distribution and definition of the electrolyte flow. At IEG values of $H/d < 1$ the effects of secondary current distribution (found in the radial area on the surface beyond the jet diameter) are vastly reduced.

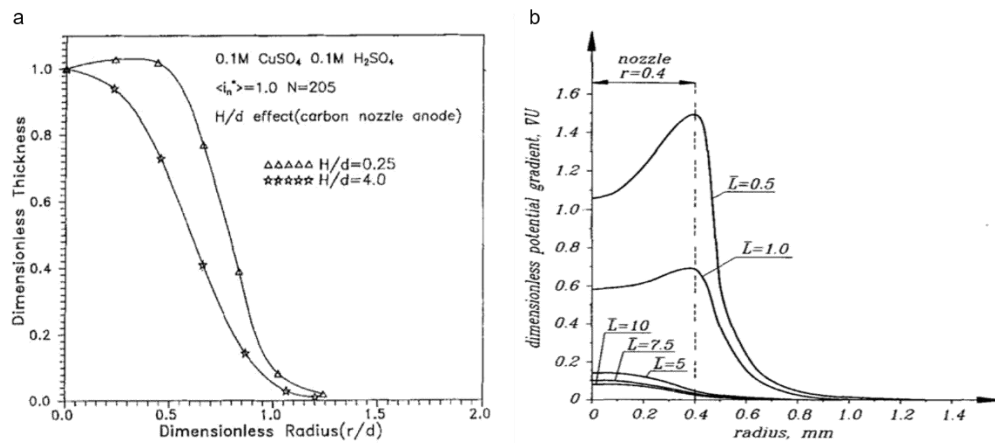


Figure 2.10: Effect of changing IEG width on a) distribution of copper deposition [69] b) change in gradient of electrical potential [19]

This will be pronounced if the IR (voltage) drop between electrodes is less than the total over-potential at the anode and cathode, therefore primary current distribution will dominate. This is based on spatial factors rather temporal factors

as related to charge (Equation 4). Therefore, deposition rates were seen to be increased in the impingement area. Also, at values of $H/d > 1$ jet flow is affected by the surrounding air leading to a reduction in flow at the jet periphery. However, this is noted to only really have an effect at $H/d > 4$ and is dependent on the jet speed.

2.3.5. Electrolyte flow

There is considerable literature surrounding impinging jets both in submerged form and free jet states [70-72] due to the high heat- and mass-transfer rates encountered. Therefore, the understanding and definition of flow regimes and parameter variation impact is well understood regarding a radial jet impacting on a flat surface. Figure 2.11 shows a two-dimensional schematic of the jet flow composed from observations within the literature that relates to the architecture found with EJP. The relationship as defined in the previous section between the size of the IEG (in this case denoted as H) and nozzle internal diameter remains as a boundary condition for discussion of the flow characteristics being relevant for EJP. It has been noted that increases in H/d_{noz} lead to increases in turbulence in the stagnation zone. This is seen to be undesirable both in additive and subtractive mode EJP as this will lead to un-stable machining conditions [73]. The impingement region or stagnation region can be defined as [74]:

$$\frac{d'}{d_{noz}} \leq 1 \quad \text{Equation 5}$$

Where d' is the radial distance from the stagnation point S_p to the edge of the stagnation region upon translating into the wall jet and d_{noz} is the inside diameter of the nozzle (Figure 2.11).

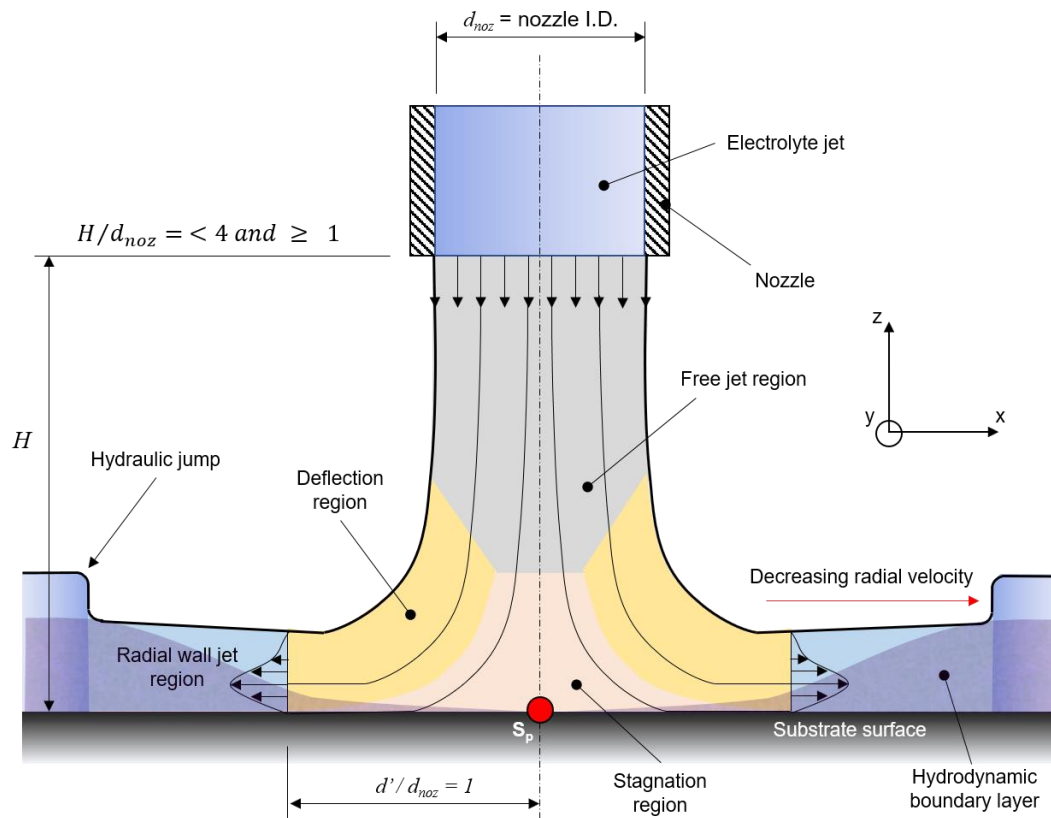


Figure 2.11: Schematic of electrolyte jet with designated fluid flow areas and boundary relationships

This can be correlated with the twice nozzle diameter associated with removal and deposition feature kerfs in EJP [19, 60, 75, 76] the jet being described as the factor that restricts the dissolution area [5, 11, 77]. Beyond this the stagnation region of the impinging jet flow field, transforms into the radial wall jet region and a boundary layer forms at the workpiece surface. This creates a highly resistive thin film layer where dissolution is inhibited. A minimum required jet velocity of 20 m/s [4, 75] has been defined as necessary to create the thin film layer (wall jet). The thin film exits radially away from the impingement zone at a supercritical flow regime decreasing in velocity as the hydrodynamic boundary layer near the surface thickens owing to viscous drag [36] (Figure 2.11). At the point where the boundary layer encompasses the fluid layer, a sudden transition occurs to a

subcritical flow regime in order to conserve momentum and incites a hydraulic jump, identified by a sudden increase in film thickness [78]. Hardware innovations described in section 2.5.5 however, show that this minimum jet speed is not necessarily required.

Kozak et al. [1996] [19], factored in variation in electrolyte supply pressure into the 2D mathematical model that was created to define the anodic dissolution rate. Good agreement was found between predicted rates of dissolution and actual, showing that dissolution slowed marginally as jet velocity increased, even at reduced IEG and high potential (1.4 mm/min to 1.25 mm/min @ 250 V and IEG 2 mm). The diameter of the machined dimple was also observed to be larger at 0.6 MPa than at 1 MPa (1.5 mm to 1.6 mm respectively @ 250V, IEG of 2 mm and 0.8 mm diameter nozzle). Liu et al. [2014] [79], also found that with increasing jet pressure (1.5 MPa to 3 MPa) MRR experienced a marginal decrease from 13 $\mu\text{g}/\text{min}$ to 11.9 $\mu\text{g}/\text{min}$. This was attributed to the effect of joule heating in the electrolyte stream. As jet velocity is lowered so temperature of the jet increases as the effect of the high refresh rate of the electrolyte aiding cooling is restricted. Increased temperature leads to increased conductivity of the electrolyte. Thus, resistance drops allowing a higher charge to be seen at the surface and generate higher material removal. This effect is much more aggressive at higher potentials and smaller IEG's. The generation of hydrogen at the cathode was also seen to be dependent on the electrolyte flow rate with the greatest generation of hydrogen occurring at the lowest electrolyte flow (1.2 cm^3/s) and highest applied current (1 A). These observations are partly re-affirmed by Lipiec et al. [2013] [64] who also found that, in this case groove depth, decreased with increasing pressure and applied voltage. However, in contradiction, the width of the groove was observed

to increase with the increase in pressure. Identified as caused by increasing pressure extending the impact area of the jet stream so de-localising the dissolution process. It is worthy of note that the electrolyte supply pressure was higher than that used by Kozak being varied between 3 MPa and 7 MPa. Typically, most practitioners use 0.5 MPa in subtractive mode EJP which achieves the ≈ 20 m/s jet speed as noted earlier. Lipiec et al. also investigated the influence of electrolyte pressure on MRR. It was found that at 2 MPa, MRR decreases with increasing resistance (increasing electrical potential) which supports Kozak et al. findings, but at 100 MPa MRR increases with increasing electrical potential which is in contradiction. This would imply that there are likely two mechanisms of material removal occurring. The significantly higher electrolyte jet pressures introducing an erosion process mechanic beyond simply corrosion which is expected in subtractive mode EJP. This secondary phase coupled with the dissolution phase resulting in higher MRR. This can also be observed when slurry is introduced into the jet-stream for the purpose of introducing an erosion mechanism to increase MRR [79, 80]. In Liu et al. [2014] [79] the comparison of electrochemical slurry jet machining (ESJM) (introduced in section 2.5.6) and subtractive mode EJP, showed little difference to surface roughness (Ra) with increasing jet pressure. A slight increase was observed from $3.55\text{ }\mu\text{m}$ at 1.5 MPa to $3.91\text{ }\mu\text{m}$ at 3 MPa. It should be noted though that these roughness figures are considerable higher than those typically found in EJP being $< 1\text{ }\mu\text{m}$ [54].

Hackert-Oschätzchen et al. [2015] [47], factored in hydrodynamic effects from the impinging jet into the process model and investigated the secondary machining effects as a result of electrolyte rebound due to ejection during machining.

Utilising a dynamic jet shape (although movement is static in translation) it was demonstrated that as machining progresses, so the flow conditions become increasingly unstable. This is accompanied with the radial wall now detaching from the workpiece surface and ejecting at increasing angles towards the point of jet origin. Although not fully shown in the model due to boundary conditions, but found experimentally, at machining times >2 s the ejected electrolyte contacts the nozzle making a secondary, unstable, current pathway for dissolution. This undesirable effect leads to poor edge and profile definition, and extended kerf of the machined features. This could explain the deleterious effects found by Kai et al. [2012] [60] when attempting to cut plate material at relatively low speeds and suggests a minimum translation speed for precision machining. The hydrodynamic effects are likely to differ when considered with a translating nozzle due to the available electrolyte ejection routes from already machined geometry.

In additive EJP, Bocking [1994] [37] observed that jet velocity had a significant effect on the quality of deposits. However, unlike subtractive mode EJP, increasing jet velocity was seen to have little effect on the selectivity of the depositions. It was hypothesised that selectivity may be improved at higher jet speeds but only at relatively higher current densities, but this would be at the expense of deposition quality as mentioned in section 2.3. This is in contradiction to Fan et al. [2015] [81] who found with increased jet speed from 2 m/s to 10 m/s spot size increased from 5.5 mm to 6.2 mm. It is, however, unclear as to the other parameters used or the quality of the depositions in this study. Bocking also observed that as deposits grow in height, the electrolyte flow is no longer perpendicular to the surface. The flow into the wall jet becomes accelerated so reducing the thickness of the boundary and diffusion layers. Consequently,

allowing a higher current density to develop at the periphery of the deposit in the transition region before formation of the wall jet. This can be observed by preferential deposition under the nozzle initially becoming thicker across the whole region up to the radial wall giving a more domed appearance with a lower side-wall-slope of the deposits. This could explain the findings of Fan et al. [2015] [81] where a slight increase in electroforming rate was seen between 1 m/s and 10 m/s (8 mg/min to 8.25 mg/min). In this case however it was explained that is was due to the reduced time that the copper ions had to travel, this being the equivalent to reducing electrolyte resistance. The increased number of copper ions per unit time will therefore lead to an increase of electroforming current density. Qiao et al. [2005] [9], found that through variation of jet speed from 4 m/s to 9 m/s they were able to vary the content of cobalt when depositing Co-Ni alloys. As with Bocking they acknowledged that increasing the jet speed reduces the diffusion layer thickness therefore the metal ion concentration increases and as cobalt is the lesser noble constituent of the Co-Ni alloy it is preferentially deposited. Although this is not stated by Kawanaka et al. [2015] [55] reviewed in section 2.3. where increases in current density lead to a thickening of the diffusion layer affecting the resultant surface roughness. It has been indicated in additive mode EJP the increasing of jet speed would lead to the reduction of the diffusion layer. Thus, it can be inferred that this would also influence the resultant surface roughness. Perhaps identifying an ideal jet speed for minimal surface roughness, although this is not a result that has been found in this consideration of the literature. Qiao et al. also found that increasing jet speed lead to refinement in grain structure of the deposits for this same reason of increased localised current

density due to reduced diffusion layer thickness which would support Bocking's observations that the quality of depositions improved with increased jet speed.

2.3.6. Influence of material on geometric flexibility and precision in EJP

The ability of a material to dissolve under ECM conditions can be considered as one of the major limiting factors of performance in subtractive mode EJP. Material with respect to additive mode EJP is dealt with under section 2.4 for electrolytes. The material physical properties of hardness, toughness and strength have no bearing on the machinability of a material by ECM and instead is reliant on the materials electrochemical equivalent (ECE) [82]. The electrochemical equivalence as defined in 2.3 is the mass of an element that can be liberated for 1 coulomb of charge. Every material element possesses a differing ECE dependant on the materials atomic weight and valance. It should be noted however that valence can change during electrochemical machining [18]. When the ECE is combined with Faradays laws (section 2.3) (Equation 5) can be used to calculate the theoretical rate of removal:

$$m = \frac{A}{z} \frac{It}{F}$$

Equation 6

Where m is the mass of material removed, I is the current passed for time t . A is the atomic weight of the dissolving ions, z is the valence and F is faradays constant [16]. F is a proportionality constant equal to 96,500 C, being the charge required to liberate the chemical equivalent weight of a single element or molecule. This equation forms the basis of a number of process models [11, 19, 22] for differing materials. During the machining of complex alloys, the difference in ECE between these alloys and their distribution within phases can, in part,

explain the differences found in machinability and surface finish between materials (reference to section 2.3 can provide further information). Natsu et al. [2007] [5], described this process in stainless steel (grade 304) stating that dissolution of a material element will not occur until a decomposition charge is reached that is required for each individual element. This being the ECE defined as A/zF . Therefore, at low current densities, individual elements will dissolve at different rates leaving an uneven surface. Where certain elements are more prevalent in a specific phase, that phase is likely to machine at a different rate and therefore effect the overall form of a machined feature beyond just the surface finish. Natsu et al. goes on further to state that as current density increases, so the decomposition charge required to dissolve all elements is reached and the machining rate becomes equal across all material constituents. When this is considered with the results found in this paper and subsequent publications around the subject [54, 55] this theory in specifically stainless steel holds true for current density values $<100 \text{ A/cm}^2$.

Often materials employed in subtractive EJP studies are used only as example target sample materials rather than any specific considerations of the material response. These tend to be materials that are generally processed by ECM which are difficult or in-efficient to be processed by other means. For example Kozak et al. [1996] [19] used a nickel superalloy Inconel 600 for experimental validation of the process model and Hackert et al. [2007] [4], [83] also used another nickel based superalloy, Nimonic 80A, for demonstration of machine processing capability. However, Ni-superalloys represent significant usage in the high-value-add industries most applicable to EJP (discussed in detail later in this chapter). They are applied in high temperature and hostile environments often in gas and

fluid facing applications. Favoured due to their high yield, fatigue and ultimate tensile strength, and the ability to retain corrosion and oxidation resistance at elevated temperatures with good creep resistance [84].

Although these qualities are favoured in service, it makes In718 difficult to process by shear-based processes (American Iron and Steel Institute (AISI) machinability rating 0.3 compared to B1112 grade Steel machinability rating of 1) due to high material toughness, poor thermal conductivity and abrasive carbide precipitate inclusion. This, in turn, leads to increased high temperatures in the cutting region creating work-hardening of the surface and the requirement for further finishing process steps [85].

Steels have received a great deal of interest within EJP research. Stainless steels (grades 304 and 316) have been used extensively for demonstration of processing techniques [4, 5, 20-22, 59, 75, 86] rather than material response. Datta et al. [1989] [34], compared the response of nickel (Ni 99.6%, C 0.1%) and steel (Fe 98.5%, C 0.6%) in material removal and current efficiency. To assess the effect of stray current effects the volume of material removal was denoted as a ratio to depth (v / d) machined with identical machining parameters. A lower value denoting less stray cutting effects. It was observed that nickel achieved a v / d value of $0.015 \text{ cm}^3 / \text{cm}$ in comparison to steel achieving a peak of $0.03 \text{ cm}^3 / \text{cm}$. Nickel having deeper narrower dimples than steel for the same parameters. It is also of interest to note the nickel achieved virtually the same ratio of volume removed to depth regardless of current density (up to 80 A/cm^2). In comparison steel exhibited a steep rise in ratio up to 40 A/cm^2 where upon it saw a slight decrease up to the maximum current density. Although there is no commentary

to this, it is likely that these effects are a consequence of passivation layers (surface oxidation) forming (also demonstrated in other materials), initially restricting dissolution in the steel which are overcome at 40 A/cm² this phenomenon not occurring in the nickel. It was also observed that at current densities below 50 A/cm² resulted in crystallographic, grain boundary preferential machining giving poor surface quality.

Hackert-Oschätzchen et al. [2011] [87] conducted research into the material response of steels to subtractive mode EJP machined by NaNO₃. Four different types of steel were compared; hardened tool steel (1.2379) characterised by the high amount of carbide inclusions, stainless steels 1.4301 and 1.451 characterised by the corrosion resistance of CrNi content with 1.451 also containing titanium and a non-tempered stainless steel 1.5920 with much lower Cr and Ni content and so high Fe content offering high strength and ductility over the previous stainless steels. Tool steel was found to produce much rougher finish for comparable machining conditions than the other steels. This is due to the carbide inclusions being resistant to dissolution and so standing proud of the machined surface with the martensite in the structure being dissolved preferentially. Steel 1.451 produced a smooth finish although the grain boundaries are visible and poorly machined inclusions are apparent. The inclusions were identified as titanium and oxygen under EDS, a TiO₂ layer formed on the titanium alloying element. It is stated that the TiO₂ layer blocks the anodic current and cannot be electrochemically dissolved with a neutral electrolyte. Finally, the steel 1.5920 demonstrates no visible inclusions however, the perlite and ferrite crystal structure are obvious. When the different steels were machined with varying charge (created by varying traverse speed) the widths of striations

were found to have little variance (as discussed in previous sections). However, steel 1.5920 was found to achieve a greater depth (depth decreasing as traverse rate was increased in-line with the finding in section 2.3.3) across the experimental range. Steel 1.2379 achieving the next largest depth for comparable machining conditions. The corrosion resistant steels 1.4301 and 1.4541, achieving the least, and virtually identical depth across the range. This occurred due to the ECE calculated for each steel, although in this case it is termed the specific dissolution volume as it also factors in the material density. Steel 1.5920 demonstrates the highest specific dissolution ($2.42 \times 10^{-5} \text{ cm}^3/\text{As}$) and 1.4301 and 1.4541 having the lowest (2.15 and 2.17 respectively). This relationship is further outlined in the consideration of the current efficiency for each material. This follows the same pattern with steel 1.5920 achieving the highest efficiency at $\approx 120\%$. This is explained by consideration of the iron content of each steel which follows the same pattern of highest content having the highest efficiency and therefore dissolution volume due to the propensity of iron to electrochemically dissolve in a bivalent manner (Fe^{2+} and Fe^3) [88]. Although there is little investigation of this phenomena at the charge densities experienced in EJP. The findings throughout this work outline the importance of the correlation between the combined ECE of a material and machining performance.

The passivation effect which can be considered as a condition of anode polarisation, whereby inert layers are formed on the target surface as oxides during the process of anodic dissolution are due to the availability of oxidising ions from the electrolyte, dissolved oxygen and air bubbles [89]. These oxides demonstrate a high dielectric constant and high electrical resistance and inhibit machining [18]. Generation of these passive layers during the processing of

titanium [87], demonstrates the difficulty in processing it by EJP. Although some level of de-passivation is achieved hydrodynamically in EJP due to the constant flow of jetted fresh electrolyte between the electrodes. However, this is offset by the high electrolyte flow supplying oxidising ions and dissolved oxygen at the thick film area directly below the nozzle leading to increased passivity at the workpiece surface. The desired use of titanium in aerospace [90] and biomedical applications [91] has meant the more recent research in subtractive mode EJP has started to consider the machining of titanium alloys. Lu et al. [2005] [92] used subtractive mode EJP to machine high-aspect hole arrays in Ti6Al-4V using a NaBr electrolyte to combat the passivation effects [93]. Liu et al. [2016] [41] and [94] conducted a full parametric study into the machining of titanium TB6 comparing both NaCl and NaNO₃ electrolytes. Through the experimental research a value for charge (Q) was determined which would ensure uniform dissolution of the TB6 substrate in a NaCl electrolyte which was stated as 492 C / cm².

Machining of metal matrix composites (MMC) is a more recent material grouping that has provided much interest in EJP research. The inclusion of high hardness often ceramic particles in a metal matrix (binder), creates difficulties in machining by traditional means due to high tooling wear rates [95]. The machining of cemented carbides through subtractive mode EJP was initially proposed by Kunieda et al. [2012] [96] and later expanded by Mizugai et al. [2013] [97]. It was found that tungsten carbides (WC-Co) could be machined with NaNO₃ using a direct current power supply, due to the creation of NaOH at the nozzle (cathodic reduction reaction) enabling machining to take place. The carbides forming an inert passivation layer in the same manner as titanium inhibiting machining.

Hackert-Oschätzchen et al. [2013] [98], also investigated the machining of cemented tungsten carbides utilising a doped electrolyte already containing NaOH, finding that this allowed machining to take place (further discussed in section 2.4). Miyoshi et al. [2016] [99], applied this methodology to electrochemical jet turning (EJT) (discussed further in section 2.5.2) of cemented carbide rods. Using a flat jet, they successfully created micro rods 36 μm in diameter with features of an aspect ratio of 20. The grain size of the tungsten carbide was seen to influence the feature size that was possible to achieve. The finer the grain resulting in higher material removal and smoother surface. Hackert-Oschätzchen et al. [2016] [100], considered the machining of Al-Si MMC's with pH-neutral electrolytes further discussed in section 2.4. They also investigated the effect of the volume of SiC particle inclusion on machining performance. This was assessed between 5% and 10% volume inclusion. However, no significant influence was found on machinability of the material by EJP.

One of the issues identified across all cases is the selective machining of the metal matrix over the carbide inclusions. Hackert-Oschätzchen et al. [2016] [101] developed a Multiphysics simulation of these dissolution effects to inform the process design. The inert nature of SiC inclusions and the effect on current density distribution within the jet for an evolving surface (Figure 2.12) can be seen in the simulation.

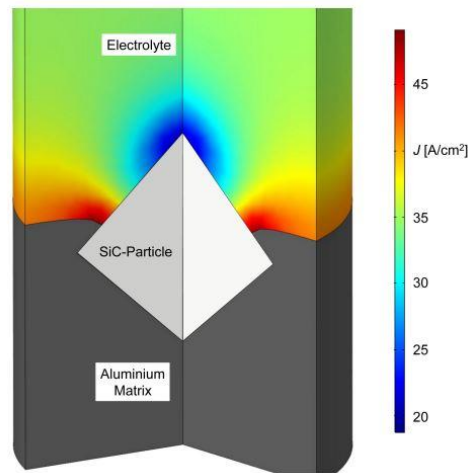


Figure 2.12: Process model developed for carbide inclusion to demonstrate the changing current density at the surface as a function of dissolution time ($t = 0.3 \text{ s}$) [101]

As machining time progresses it can be observed that the area available for dissolution reduces as the surface recedes around the SiC particle. This leads to an increase in localised current density which can be seen to concentrate at the interface between the lower J regions formed over the particle and the matrix, so generating a higher dissolution rate at this point. This means that the dissolution rate will not be constant for this type of non-homogenous material with the dissolution increasing exponentially as more of the particle is revealed and available surface reduced leading to increased J values to the point where the particle is removed. Understanding of this effect is key to the machining strategies required for MMC's.

2.3.7. Summary of identified research gaps associated with parameter influence

Through the review of the literature concerning the influence of parameter selection and choice of substrate on precision and capability the key gaps in current knowledge can be identified:

- Energy and its distribution, seen at the surface, defines the volume of material liberated or deposited. Thus, the geometric form of material removal or deposition is limited by the Gaussian distribution of the energy with the peak at the centre of the jet dissipating towards the peripheral of the jet impingement zone which is considered deleterious. No consideration has been given in EJP to understand the influences on this effect and how it may be manipulated for better effect
- Kawanaka et al. [2015] [55] hypothesis that the diffusion layer is responsible for the surface finish with respect to the level of applied energy is not yet fully validated. This is important to the understanding of the resultant finish and manipulation of the process mechanics across a variety of relevant materials.
- Little consideration has been given to the localised properties within the IEG, so called “in-jet” properties in comparison of global properties i.e. changing the overall IEG. The energy at the surface is influenced by many factors the most important of which are the applied mean current and resistivity within the IEG caused by localised spatial and electrochemical influences. Understanding and manipulation of these may instigate changes in precision and profile shape flexibility.

- The stagnation region under the jet is seen as defining the dissolution or deposition width and within optimum IEG conditions, translating to approximately twice the I.D. of the nozzle. Control or dissociation of this boundary factor would be required to implement changes in precision
- The effect on feature width and precision through increased jet speed is unclear with contradictory results being presented therefore requires further investigation.
- Important materials in the manufacturing area of subjective EJP application have so far been largely un-characterised such as nickel superalloys. Understanding of the parameter influence and intimate dissolution mechanisms of the material are required to demonstrate the viability of EJP.

2.4. The Influence of electrochemical factors on feature geometric flexibility and precision of EJP.

2.4.1. Introduction

The electrolyte in ECM processes is a major factor in determining material removal rate, accuracy, surface texture and surface integrity [18]. Type of electrolyte, and level of concentration shapes the attributes of the IEG, its conductivity denoting the level and distribution of energy available at the target surface. A wide range of electrolyte types, concentrations and additives have been used in ECM and electroplating. However, this is not the case in EJP. In the case of ECM processing of titanium for example, several strategic electrolytes have been developed to deal with passivation effects [18]. Bannard [1976] [102],

developed potassium bromide-based electrolytes to achieve increased precision and performance when machining titanium. Specific types of electrolyte have been investigated [103, 104] alongside concentration [12, 105], which have been shown to improve precision of machined features. Further examples of this can be found with Ryu [2009] [106] who developed a citric acid electrolyte and Yang et al. [2011] [107] who developed an electrolyte from mineral water, in both cases to enhance the sustainability of the process. This diversity of electrolyte type and exploitation of chemical effect within research in subtractive mode EJP has yet to be fully explored.

2.4.2. Subtractive mode

Early electrolytic jet processes, especially drilling operations, were reliant on acidified electrolytes [24, 34, 108] thought to be required to overcome polarisation effects in the IEG due to the impinging jet (breakdown of the metal hydroxyl ions Figure 2.2). This was led by the common use of aggressive electrolytes in ECM to gain high removal rates and accuracy, exemplified by their use in electrochemical etching and polishing by cylindrical jets [109]. However, Datta et al. [1989] [34] found that electrolytic jet processes are capable of delivering far higher current densities than those used in ECM or jet polishing. Meaning the formation of passivation layers by the impinging jet can be overcome without the use of acid electrolytes. The high refresh rates of the electrolyte in EJP enables continual fresh electrolyte at the jet interface with the surface. This allows the removal of heat and debris and allowing increases in current without introducing unstable machining conditions. Datta et al. investigated the use of neutral passivating and non-passivating salt electrolytes Sodium Nitrate (NaNO_3) and

Sodium Chloride (NaCl) respectively, albeit at high concentrations by today's standards (5M). It was found that sodium nitrate minimised stray cutting whilst still maintaining relatively high MRR in comparison to chloride solutions. It was also demonstrated that NaCl maintained a constant current efficiency (Equation 21) ($\approx 90\%$) from 10 A/cm^2 to 80 A/cm^2 unaffected by material or increasing current density. In comparison NaNO_3 displayed an increasing current efficiency as current density increased. This differed between materials, nickel demonstrating a logarithmic type curve still increasing at 75 A/cm^2 (75%) with a sharp increase in efficiency up to 20 A/cm^2 . In comparison steel demonstrating a linear increase in efficiency up to $\approx 80\%$ at 60 A/cm^2 before decreasing. Directly influenced by Datta et al. work Lu et al. [2005] [92] used a 5 M solution of NaBr (sodium bromide) to machine titanium. Although no account is given for this choice or as a comparison to alternative electrolytes, it is likely to have been steered by Bannard [1976] [110] work in the ECM of titanium.

NaNO_3 and NaCl have remained as the common choice for subtractive mode EJP to the present day due to their relative low toxicity, cost and ready availability [111]. The precision created by the use of nitrate solution was further discussed by Natsu et al. [2008] [59], stating that when a passivating electrolyte is used, the generation of oxygen at the anode leads to oxide film formation in low current density areas. Thus, inhibiting machining further at the peripheries of the energy distribution and enhancing precision. Hackert-Oschätzchen et al. [2013] [98], compared both chloride and nitrate solutions for the machining of carbide metals, finding both solutions adequate to machine cobalt. However, the neutral salts had little impact on tungsten carbide (WC-Co), so a doped electrolyte containing alkaline electrolyte of sodium nitrate and sodium hydroxide was developed [112].

The addition of NaOH being required to remove the inert WO₃ oxide layer that forms on the carbide which hinders machining of the substrate. This was capable of good quality material removal albeit the resultant machined geometry was observed to have a peak in the centre creating a “w” profile. The definition of the profile shape of the central peak and overall kerf were able to be varied through electrolyte composition and parameter selection. Kunieda et al. [2012] [96] and Mizugai et al. [2013] [97] however noted that utilising a simple NaNO₃ electrolyte enables machining of tungsten carbide with DC current as NaOH is formed on the inner surface of the cathodic nozzle (cathodic reaction $\text{Na}^+ + \text{OH}^- = \text{NaOH}$ (sodium hydroxide)). This then transfers to the substrate surface directly below the nozzle edges, in-jet. This leads to preferential material removal at the periphery of the pit in comparison to the centre so creating the central peaked feature as found by Hackert et al. However, in their case it was further exacerbated by the addition of the dopant. To create a profile more akin to a traditional profile Kunieda et al. developed a ceramic nozzle which meant the NaOH developed in the nozzle body rather than nozzle edge, and so mixed through the electrolyte achieving a more consistent resultant profile.

Kawanaka et al. [2014] [54], compared the surface texture that was achievable in stainless-steel using both chloride- and nitrate-based electrolytes for selective surface texturing on components. They concluded that larger pores on the surface were generated when a NaCl electrolyte was used compared to NaNO₃, giving a more aggressive and rougher finish. Hackert-Oschätzchen et al. [2016] [100], also compared NaNO₃ and NaCl of equal conductivity (185 mS/cm) for machining of aluminium matrix composites. Both NaNO₃ and NaCl were identified as being capable of machining Al-SiC MMC's. It was observed that NaNO₃

generated a passivation effect on the Al surface which restricted the depth that could be generated. To produce repeatable features using NaNO_3 slightly higher energy was required to machine the material due to the formation of passivation layers. It was also observed that machining with NaCl produced dimple depth twice that, on average, of those produced with NaNO_3 . Although diameter of the machined dimple remained constant regardless of electrolyte used. NaCl is well understood to be a more aggressive electrolyte demonstrating greater throwing power due to increased electrolyte conductivity [113].

Across all literature, since the work of Datta, concentration of both NaCl and NaNO_3 has remained relatively consistent maintaining $\approx 20\%$ wt of salt to solution so achieving $\approx 2\text{M}$ NaNO_3 concentration and $\approx 3\text{M}$ NaCl. Little consideration has been made between the variations of the concentration of solutions within the same experimental investigation. The exception to this is Liu et al. [2016] [41] investigation into the machining of titanium TB6. It was found that high concentrations of NaCl can achieve excellent removal rates and mirror like surface finishing, but at the expense of inferior accuracy and excessive overcut. Therefore, the optimum concentration was 15% wt. which gave a good compromise between finish, performance and accuracy. This corresponds to the concentration levels suggested by Bannard [1974] [114] for NaNO_3 and NaCl that are common-place in ECM.

2.4.3. Additive mode

As the electrolyte forms the deposited material and therefore the end product in additive EJP, there is some diversity in the type of electrolytes in comparison to subtractive mode. Fletcher et al. [1974] [30] patent on jet plating referred to

copper based electrolytes and this has formed the basis of the majority of research into microfabrication by this technique. Dover et al. [1996] [39], used an acidified copper sulphate solution (0.5M sulphuric acid and 0.8M copper sulphate) to manufacture 3D objects. Kunieda et al. [1998] [7], investigated the differences between applying copper sulphate and copper nitrate aqueous solutions. It was concluded that copper nitrate electrolytes increased precision, giving a more concentrated solution under the nozzle as deposition did not occur in low current areas. Bocking [1994] [37], considered the deposition of gold noting its suitability for the process due to it only requiring a small over-potential (see section 2.3.4 for definition) for reduction from the ionic state to a metallic state. Acid citrate gold electrolyte was investigated alongside the deposition of an acid sulphate copper [42]. It was found that both copper and gold reacted similarly to parameter changes. Increased electrolyte temperature, electrolyte velocity and metal ion concentration led to increased plating rates. The concentration however had a ceiling limit in gold of 0.7M and 0.8M for copper. These concentrations were maintained later by Dover et al. [1996] [39] and Rajput et al. [2015] [8] using copper sulphate and sulphuric acid. However Kunieda et al. [1998] [7] used 1.5M concentration ($\approx 20\%$ wt), although citing Bocking's work gave no rationale for this choice. Fan et al. [2015] [81] also used a 1.5M concentration this time of copper sulphate in their parametric study of jet electrodeposition of copper parts, again without rationale.

Qiao et al. [2005] [9], carried out an extensive investigation into the deposition of nano-crystalline Ni-Co alloys. Complex electrolytes were used based on chloride-sulphate solutions of cobalt sulphate (0.2M), Nickel chloride (0.8M) and boric acid (0.4M) and balanced to a pH of 3.1 using sulphuric acid. In some sample sets

saccharin was also added to refine the grain size of the deposited layer. It was noted that with increasing current density, cobalt ions in the feedstock, jet speed and reduction of electrolyte temperature causes the cobalt content in the deposits to increase and the grain size to become finer. It was also shown that the phase content changed from face-centred cubic (fcc) when cobalt content is below 60.39% to a mixture of fcc and hexagonal close-packed (hcp) phase when above. Both Thiemig et al. [2007] [115] and Osborne et al. [2007] [116] researched the capability of an electrolytic jet to co-deposit nano-composite films. In both cases a copper sulphate and sulphuric acid [116] electrolyte was used typically of 1M with a pH of 1.5 and incorporated nickel from a sulphate bath containing boric acid (39% wt.) [115]. Alumina nanoparticles were then held in suspension in the electrolyte feedstock. In both cases a parametric study was carried out and the rate of particle incorporation noted. In both cases the particulate loading in the electrolyte was found to linearly increase the co-deposition of particle volume. It was also found that increasing current density had an opposing effect on particle inclusion in the deposition, dependant on the size of the particles, increasing for 50 nm and reducing for larger 1 μ m particles, although it was unclear as to the reasoning behind this. It was also found that decreasing the acidity of the solution from a pH of 0.8 to 1.5 increased particle incorporation into the deposits.

2.4.4. Summary of identified research gaps associated with the electrochemical influence on EJP

The influence of the electrolyte which defines the chemistry element in EJP was reviewed through the literature. The key findings are presented as:

- Changes in the chemical composition of the electrolyte when combined with a specific material found the resultant machined profile was changed. This requires investigation and exploitation with relation to the aims of this thesis and has not been fully considered beyond changing the pH level in EJP.
- Different base electrolytes display different characteristics regarding the precision and resultant profile geometry in subtractive mode which can be understood by observation of the individual electrolytes current efficiency. It is likely that this in combination with the previous point, may offer insight into addressing the thesis aims and has yet to be explored in EJP.
- All electrolytes for deposition considered through review are acidified, this is problematic in modern sustainable manufacturing processes due to operator handling and disposal. To enhance the methods industry acceptance would require lowering of the toxicity which has yet to be considered.

2.5. The influence of electro-mechanical design on geometric flexibility and feature precision

2.5.1. Introduction

There are several patents that relate to the hardware design and innovations of both additive and subtractive EJP platforms [23, 30, 31, 117-120]. Hardware of a typical EJP platform consists of four constituent parts; nozzle, power supply, electrolyte supply and actuation. These areas will be individually reviewed over

the following sections in view of the aims of this thesis of improvement of precision, resultant profile flexibility, along with design cues for the platform development.

2.5.2. System architecture

Actuation across all planer EJP systems remains typically common in an x,y,z axis configuration. The nozzle, in all cases, is maintained perpendicular to the target surface, with the tip of the nozzle parallel with the surface. Therefore, EJP is considered a two-dimensional planar machining technology. The main difference between platforms is the stacking of the axis and the mounting orientation of the nozzle relative to the axis. Bocking [1991] [42], Datta et al. [1989] [34], Lu et al. [2005] [92], Sen et al. [2005] [121], and Lipiec et al. [2013] [64] all maintained the nozzle orientation horizontally with the workpiece vertical, in all other cases the nozzle is kept vertical and the workpiece horizontal as is the case with most energy beam processes. Although no direct research has taken place into the orientation effects of the nozzle it is inferred that in deep hole drilling [122] the vertical orientation of the workpiece aids evacuation of the debris from the hole although the pressure of the jet should render this unnecessary. The three main stacking arrangements of the axis are; stationary workpiece and nozzle is moved in x, y, z [41], nozzle is mounted to the x and z axis and the workpiece is moved in y [75], and the nozzle is mounted on the z axis and the workpiece moved in x and y [20]. One of the most significant changes that has been introduced in the architecture of EJP is the use of a rotary axis to hold the workpiece. Lu et al. [2005] [92] and Kunieda [1993] [2] used the rotary axis for positioning in order to machine holes around a curved component enabling the

jet to remain perpendicular to the surface it was machining at all times (see Figure 2.27). Hackert et al. [2010] [123] used this arrangement in a different manner named Jet-EC turning (Figure 2.13).

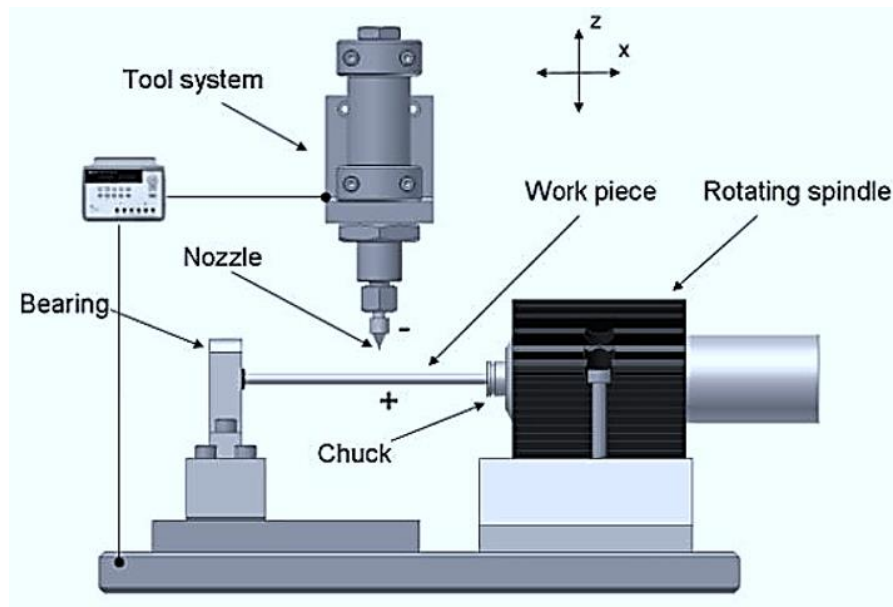


Figure 2.13: Schematic of Jet-EC turning system [123]

The workpiece could be rotated up to 6000 RPM while the jet was applied perpendicular to the workpiece enabling material removal. Profile, cylindrical and contour turning processes were carried out using 50 μm and 100 μm I.D. nozzles. In contour turning, through decreasing the nozzle motion in the x direction from 1000 $\mu\text{m/s}$ to 20 $\mu\text{m/s}$ over a distance of 2 mm it was possible to create a decreasing diameter rod (Figure 2.14a). Miyoshi et al. [2016] [99] employed a flat jet (Figure 2.14b) (discussed in detail later in this section) to produce micro rods of tungsten carbide using this same arrangement. Utilising their earlier work in cemented carbides (discussed in section 2.3.6 and 2.4) they were able to reduce a cemented carbide rod from a diameter of 300 μm down to 36 μm (Figure 2.14c).

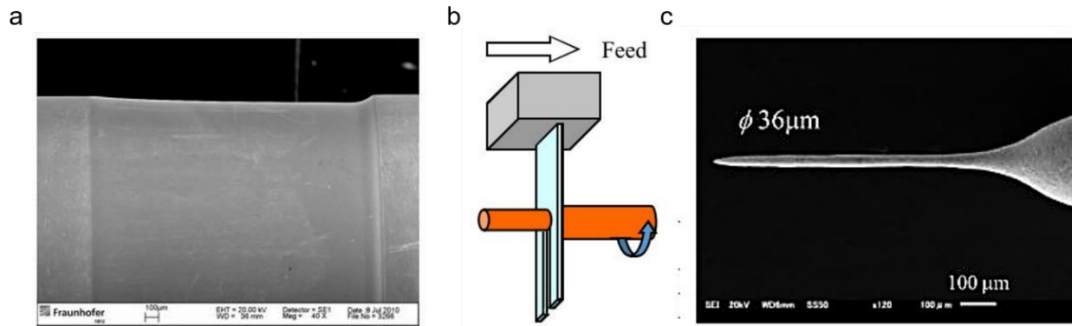


Figure 2.14: Turning operations with EJP (a) variable contour turning on a 3 mm shaft [123] (b) use of a flat jet for greater efficiency in turning process and resultant (c) fabrication of tungsten carbide micro rods [99]

Lipiec et al. [2013] [64] used a variation on this technique whereby the jet was configured facing the end of the bar. This enabled the machining of grooves in the bar-end and face turning operations replicating traditional lathe techniques.

2.5.3. Electrolyte supply

The supply of electrolyte to the nozzle is required to be pulsation free to avoid detrimental surface effects caused by non-uniform flow leading to unstable anodic films whilst machining [18] and capable of producing a 20 m/s jet speed with the appropriate nozzle (see section 2.3.5). Across all reviewed platforms electrolyte delivery is carried out in one of two ways. Either utilisation of a micro-pump using gears to pump the fluid by displacement (Figure 2.15a) or a compressed air system whereby a reservoir of electrolyte is pressurised by compressed air to force it to the nozzle at the required flow rate (Figure 2.15b).

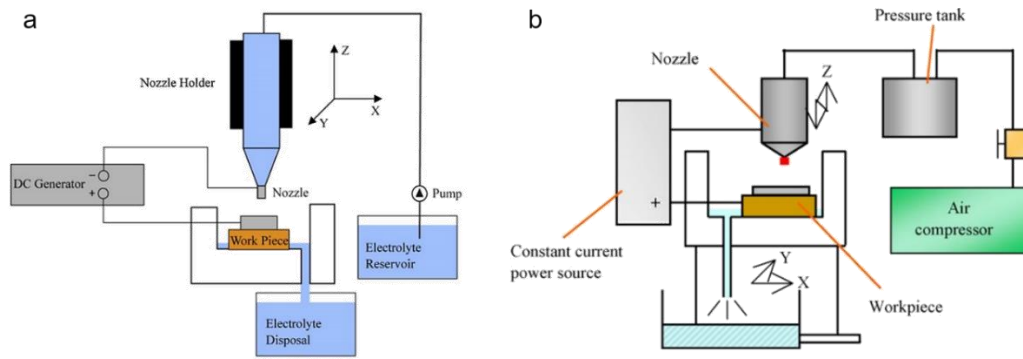


Figure 2.15: EJP architecture configurations demonstrating the alternative methods of electrolyte supply (a) gear pump [75] (b) compressed air [5]

Although no comparison experiments are available in the literature between the two systems, it is likely that the choice between the systems is down to usability and packaging within the machine tool. The gear pump arrangement giving a much more compact and flexible arrangement avoiding health and safety issues associated with pressurised containers.

2.5.4. Power supply unit

The power supply unit (PSU) is critical in EJP applications defining the ability to deposit or remove material. From the literature three main types of PSU are used in EJP; direct current (DC), alternating current (AC) and pulsed DC (Figure 2.16).

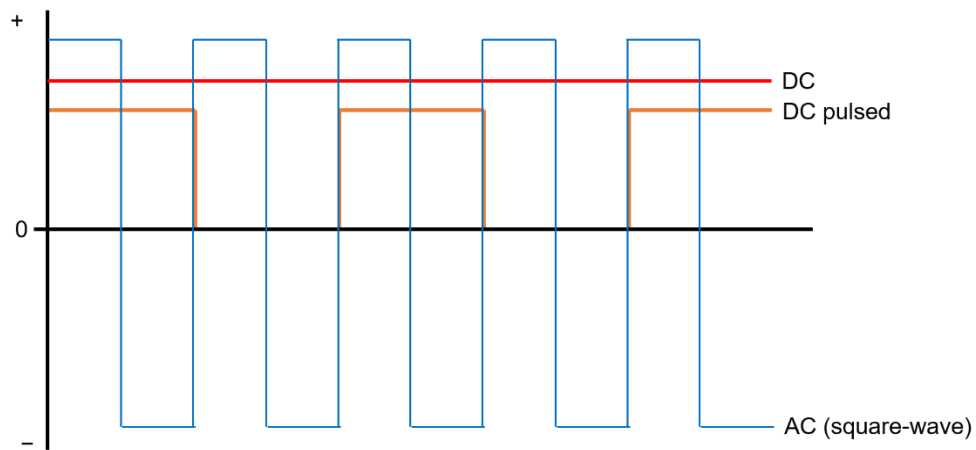


Figure 2.16: Schematic to describe the current output modulation used in EJP

Direct current is the most common power supply type. Produced by a unipolar power supply DC current is unidirectional only flowing in one direction. In the case of EJP this means the electrodes will remain in a fixed polarity while the current flows in a constant direction. In comparison alternating current (AC) periodically reverses direction. In relation to EJP this means the electrodes periodically swap polarity dependent on the frequency required. This has limited use in EJP. Typically, either deposition or removal should be taking place at the workpiece surface, not both in the same process which is the outcome of using an AC supply. The single niche application that has been identified by Mizugai et al. [2013] [97] for machining cemented carbide substrates (outlined further in section 2.3.6 and 2.4). Using a square-wave shaped AC supply so there are discrete changes in polarity rather than a sweeping one as found with a sine-wave profile, they were able to machine tungsten carbide without addition of NaOH required to breakdown the WO_3 passivating films. This is because as the workpiece becomes positive (noting it is usually set to negative for machining) NaOH is generated at the surface. This will then breakdown the films, therefore as the polarity of the electrodes is then reversed back to machining mode material removal can take

place. This enabled an even machining effect across the profile in comparison to DC which tended to have a higher rate machining at the periphery of the pit than the centre. They were also able increase selectivity and generate a dimple with less overcut using a 50% Duty factor (5 Hz frequency) when compared to using a DC supply. This is due to the distribution of NaOH following the current density distribution, therefore higher rates of machining occur towards the centre of the jet footprint. The drawback of using this method is that when the nozzle becomes the anode, material is removed from the nozzle therefore changing the jet shape and hindering selectivity. To combat this a ceramic nozzle was used which was inert to dissolution. Pulse power supplies whereby the DC signal is periodically switched on and off has received considerable research interest in ECM [12, 66, 67, 124, 125]. The application of a pulsed supply is advantageous in three ways. In ECM reductions in the size of the IEG lead directly to increased accuracy of the geometry produced due to localisation of current pathways so restricting stray current [105, 126]. However, a reduction in the gap distance leads to a higher possibility of machining debris build up in the gap causing shorting between the electrodes and possible damage to the workpiece and or tool. During the current off period of the cycle, high flow flushing of the IEG can take place to ensure the gap remains clear for the next power on pulse operation. The effect of this increased clearing ability means higher energy can be used in the pulse on times to generate greater material removal without the decreased IEG becoming fouled leading to shorts and flow restriction. This also helps to offset the increased machining times encountered due to the pulse off period in the cycle where no material is being removed. Secondly with the increased energy and small IEG there is an increased heating of the electrolyte due to joule heating phenomena.

The pulse off period allows the electrolyte and surfaces surrounding it to cool and disperse the heat, minimising build-up which can lead to boiling of the electrolyte causing cavitation and unstable machining conditions. The pulse off period allows a stable and uniform process in the IEG. The final advantage gained comes from the way the double layer in the IEG reacts under pulsed conditions. Referring to Figure 2.9 and section 2.3.4, the IEG is described as consisting of a capacitor at each electrode with a resistor in the electrolyte between. This double layer (DL) works like a parallel plate capacitor requiring charging time before machining can take place, charging occurring at the start of the pulse on period and discharging initialising at the beginning of the pulse off period. Therefore, a reference DC voltage is required to be constantly supplied to inhibit tool erosion and maintain polarity. If we consider the DL at discrete points across the IEG (Figure 2.17), the shorter current path at a protruding feature leads to a smaller resistance at that point ($R_{e2} < R_{e1}$).

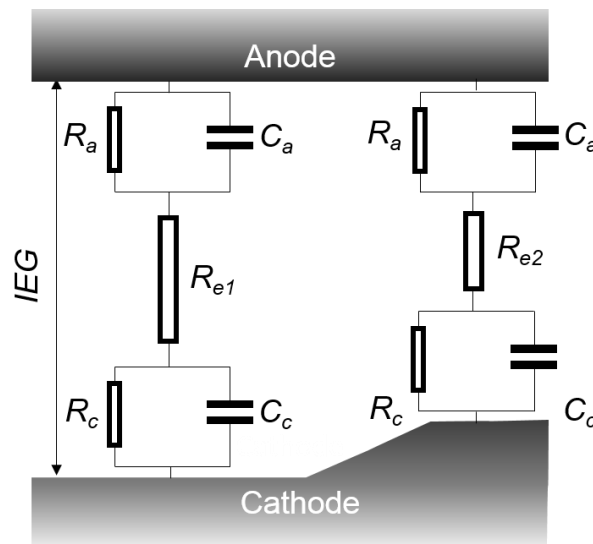


Figure 2.17: Schematic overview of the principles of enhance fidelity in feature generation in pulse ECM by consideration of the DL in the IEG

Therefore, (noting Equation 4) a reduction in resistance allows for an increase in current available to firstly charge the DL, then for dissolution. As less current is available in the longer path, charging of the DL takes longer than at the protrusion which maintains a preferential current path. Therefore, machining will initiate faster at the protrusion than elsewhere. If the pulse on time is shorter than that required for the DL to be overcome (typically ranging from 5 to 5000 ns [127]) at areas with a large IEG then machining will not occur at these points. Hence anodic dissolution is localised, and higher fidelity can be maintained to the design intent of the features.

The introduction of a pulsed power supply in EJP has been demonstrated in both additive and subtractive modes. Bocking [1994] [37] experimented with pulsed power supplies for the deposition of gold. It was observed that at low duty cycle ($< 30\%$) and short pulse on time (< 0.2 ms) smooth deposits can be created. Outside of this, the deposits were found to be nodular in appearance in comparison to those made with DC supply, the smoothest deposits however were also produced with lower deposition rates than with a DC supply. It should be noted that the pulse on time used in this study is quite large in comparison to that found in subtractive mode ECM, so this may account for the lack of improvements.

Application of a pulsed power supply in subtractive mode EJP has been shown to have mixed results. Hackert-Oschätzchen et al. [2012] [75] commented that EJP could achieve higher dissolution rates than pulsed ECM because there was no need for a flushing regime due to the high velocity and supply of electrolyte directly into the impingement area so continual machining is possible. Yu et al. [2010] [3] observed that when drilling micro-holes the use of pulsed power (50%

duty cycle and 0.25 ms pulse duration) minimised the stray cutting area around the entrance to the hole making a cleaner hole with better surface finish, although not noticeably reducing the hole diameter. It was claimed that the flushing in the pulse off period was partly responsible for this disagreeing with Hackert-Oschätzchen et al, however this maybe the case in drilling operations where flow is confined to a single point and ejection of debris from the hole is restricted. Again, the comparatively long pulse on time in comparison to pulse ECM could explain the lack of reduction in diameter in comparison to the DC machined hole. Martin et al. [2016] [128] applied a pulse supply to create a surface with predefined waviness on a WC6Co substrate using a $\text{NaNO}_3 + \text{NaOH}$ hybrid electrolyte (as discussed in section 2.4.2). It was found that a defined surface waviness could be created across an entire surface through rastering a jet across the surface adjusting the step-over to vary the waviness. Removal depth of each rastered pass was found to be controllable by adapting the duty cycle of the pulse on time, larger duty cycles creating a larger depth. It was also suggested that the use of a pulsed power supply would inhibit the formation of passivating layers leading to increased removal depths, although this was not experimentally proven. Kawanaka et al. [2015] [55] employed pulse power for generation of mirror like surfaces and compared to both DC and AC current supplies (see section 2.3). When DC is used a very high nozzle translation is required to generate low roughness surfaces because of low current density developing at the jet peripheral. When a pulsed supply is used, mirror-like finishing cannot be achieved with pulse durations longer than 100 μs . However, it was found using a duty cycle of less than 1 % a mirror-like finish can be achieved with much lower

translation speeds than DC (0.1 mm/s as compared to 100 mm/s) which underpins the concept of pulse application, to filter out low current areas.

2.5.5. Nozzle

Further hardware development found in EJP includes the nozzle and hardware surrounding it. One of the major developments seen in this area is the addition of air assistance around the nozzle which was first seen in the Fletcher et al. [1974] [30] patent. Described as air streams driving the non-plated solution and the droplets off the surface without disturbing the jet stream (Figure 2.19a). The application of air-assistance was not reported in literature until Hackert et al. [2008] [83] where the use of an additional jet of compressed air was introduced directed at the nozzle tip via an external tube. It was demonstrated that the use of an air-assist could restrict stray cutting and enhance feature geometry by allowing a small IEG (100 μm) and maintaining a free jet (Figure 2.18)

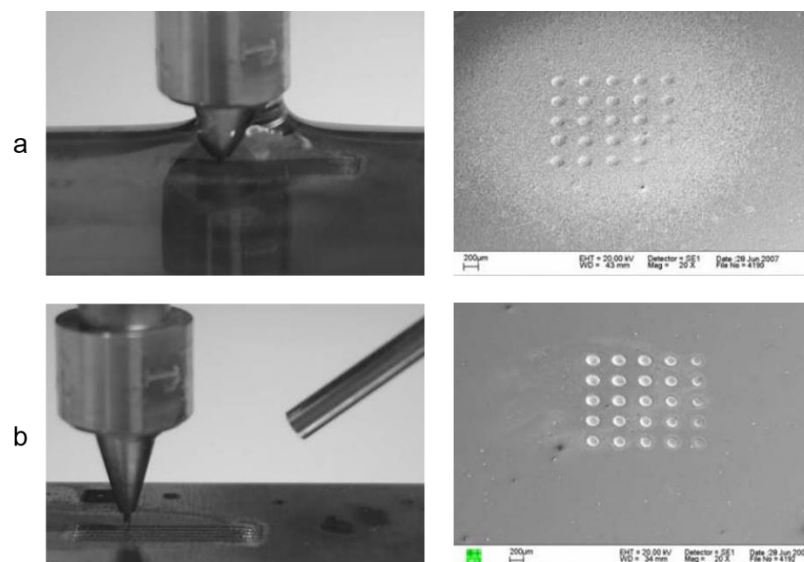


Figure 2.18: Optical images of the nozzle (a) without air assistance and the resulting machining (b) with air-assistance and the resultant machining demonstrating the reduction in stray cutting [83]

This work was then expanded upon by Kai et al. [2012] [60] who applied the airstream coaxially to the jet forming part of a patent for the machine architecture (Figure 2.19c) [129]. It was noted that the airstream gives momentum to the radial electrolyte flow moving the hydraulic jump away from the jet impingement area and reducing the thin film thickness minimising stray current. It was demonstrated that even with very low electrolyte flow rates the thin-film required for selective machining could be created. For comparison, without air assistance supply pressure was maintained at >0.5 MPa (≈ 20 m/s jet speed) to achieve selective machining, with air it could be reduced to 0.05 MPa and still achieve selective machining.

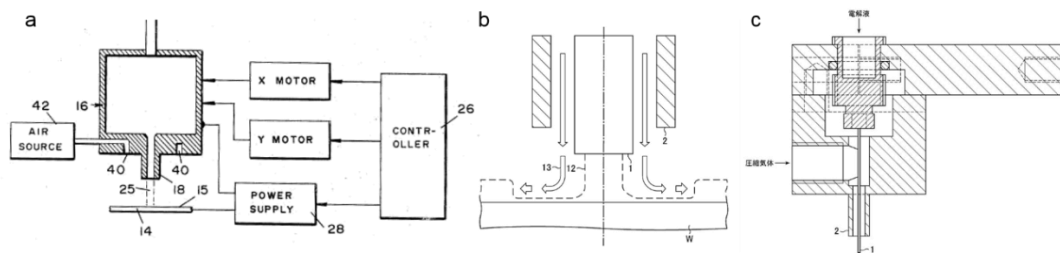


Figure 2.19: Schematics of inclusion of compressed-air assistance to the jet stream (a) showing inclusion within the head but not designed to aid the jet specifically [30] (b) showing how the air-stream aids the clearance of the hydraulic jump when coaxial and (c) showing a patented design of inclusion of a co-axial air-stream into the head to assist the jet [129]

Kai et al. also found the air assistance improved deep hole drilling. It was stated that with deep hole drilling in EJP because the hole is constantly filled with electrolyte, the applied energy dissipates to the side walls widening the hole rather than progressing depth. This meant the maximum depth that could be machined was $125\text{ }\mu\text{m}$ regardless of processing time. However, with air-assistance the depth continued as a function of time up to a maximum of $180\text{ }\mu\text{m}$ at 30 s.

There has also been some development with the type of nozzle used for specific operations. Ikeda et al. [2006] [20] developed the concept of using multiple standard cylindrical nozzles placed in an array to create a large area coverage. The spacing of the nozzles was seen to be critical as the removal profile under the jet has an effect on the neighbouring jets removal profile and machining accuracy deteriorates. Kunieda et al. [2010] [130] further developed the idea of increasing the machining efficiency through large area coverage by using a slit type nozzle. The slit type nozzle was first seen associated with additive mode EJP by Alkire et al. [1987] [131] but was intended only as an analytical tool for the assessment of a two-dimensional fluid jet flow. Kunieda et al. first iteration of this was created by machining a long thin slit into the side of a nozzle tube and then sealing the normal aperture. This was used to machine a thin metal wire and enabled a dimple to be formed around the circumference of the wire facing the jet and maintaining a constant depth all the way round with a single application. This was developed further [63] by developing a bespoke nozzle system producing a flat jet (Figure 2.20a). They found that machining speed could be increased in groove machining as the jet now produced a long but still thin footprint (nozzle aperture $2290\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$). This nozzle was then applied to turning operations (Figure 2.20b, c) which allows impact across a larger area of the circumference of a machined part, reducing cycle times. This further allows the operations of grooving, parting-off and face turning to be quickly and efficiently carried out alongside turning down the outside diameter (O.D.) of micro rods including cemented carbide rods [99]. Kawanaka et al. [2015] [55] also found application for the flat jet in large area mirror-like finishing (Figure 2.20d), as the coverage is increased in comparison to a cylindrical nozzle. Also, as the slits are

very thin the low current area of the jet is minimised due to the increased gradient of the current distribution therefore creating a lower roughness final finish more easily (see section 2.3.2). The slit nozzle to produce the flat jet now comprised of 5 separate parts, a flat Teflon spacer being used to form the nozzle shape which means the nozzle could be used with bipolar supplies without degradation and can be varied easily as per application.

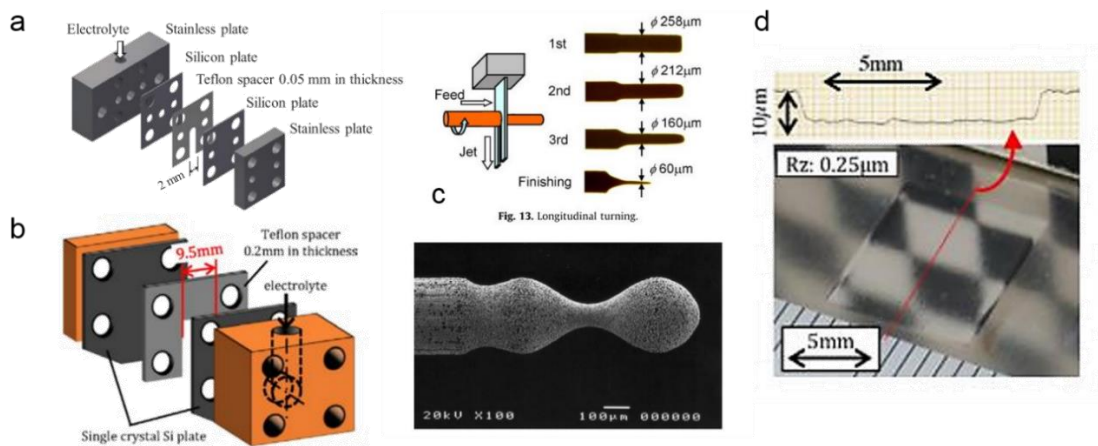


Figure 2.20: Design of the slit nozzle and application of the flat jet produced by it. (a) Design of the slit nozzle for turning [99] (b) large area surface texturing [55] (c) The application of the flat jet in turning to produce micro-rods and (d) in large area surface texturing to a mirror-like finish.

2.5.6. Hybrid processing

Attempts to negate the deleterious effects of the characteristic bell type energy distribution curve found in EJP and therefore improve the dimensional accuracy, aspect ratio and increase material removal and deposition rates, include the innovation of the hybrid EJM processes (Figure 2.21). Hybrid processes integrating EJP have been developed in both subtractive and additive modes. The addition of a laser, coaxially to the jet, using the jet as a beam guide has

found a great deal of interest in the literature. Puippe et al. [1981] [132] and Von Gutfeld et al. [1982] [133] found that very high plating rates could be achieved through the addition of a laser to electroplating in an electrolyte bath building on their patent [31]. Gold was deposited on nickel-plated beryllium-copper substrates depositing 0.5 mm diameter spots at the rate of 10 $\mu\text{m/s}$ utilising cyanide-based chemistry, faster than previously reported rates for gold plating. This was attributed to a localised increase in temperature leading to an increase in the charge transfer rate and micro-stirring of the solution because of localised thermal gradients. The effect of possible boiling was also identified due to high laser powers. The technique was identified as being most useful for selective small area plating. von Gutfeld et al. [1983] [32] then applied this knowledge of laser enhancement to a free-standing jet as a method of high-speed maskless patterning. Wholly concerned with deposition it was considered that the laser was entirely responsible for the selective nature of the deposition and did not consider the jet itself could provide the selectivity through increased jet speeds. Jet speeds of 10 m/s were used in this study which as mentioned previously would not achieve the required hydrodynamic effects for selectivity. The jet was merely an enhanced method for increasing the refresh rate of ions into the impingement area allowing higher mass transport rates due to increased current density. Following work in this area [134, 135] maintained the use of lower speed jets acknowledging the possibility of selectivity contributions of a free standing jet and the thin film area reducing conductivity. No in-depth analysis was given alongside any information on the size of the IEG, however applications within the micro-electronics industry were identified. Datta et al. [1989] [34] carried out an experimental comparison of laser assisted and non-assisted subtractive mode

EJP utilising NaNO_3 and NaCl electrolytes. It was concluded that the addition of laser when used with non-passivating electrolytes (NaCl) significantly reduces overcut during micro-machining in comparison to NaNO_3 . This is due to the localised conductivity increase at the centre of the jet from heating, creating a steeper spatial energy distribution curve, noting from section 2.4 the characteristics of chloride electrolytes. However, when the laser is applied with NaNO_3 it enhances oxygen evolution at the workpiece surface so negating any benefits of the laser, not achieving any reduction in overcut compared to NaNO_3 .

DeSilva et al. [2004] [136] developed a process model for laser enhanced removal to explain the dissolution localisation effects (Figure 2.21b). This was used to demonstrate that the laser energy component supplied to the process has a direct effect on the electrochemical dissolution velocity explaining the localisation effects leading to higher MRR and precision. Although no electrolyte type was mentioned in the article it was demonstrated that the addition of laser can yield up to 54% increased MRR and up to 38% increase in precision. This work was developed [137] further across multiple materials citing an increase in material removal over non-laser assisted jet removal of 20% (Hasteloy), 25% (Titanium), 33% (stainless-steel) and 54% (aluminium alloy) and reduction in taper of 38, 40, 41 and 65% respectively along with a 20% reduction in surface roughness of the holes machined. It was also noted that this was done with 20% wt NaNO_3 which would appear to be in contradiction to Datta et al. earlier findings. Further studies have taken place which instead compare laser hole drilling with addition of an electrolyte jet. This is intended to improve the near surface morphology, minimising the heat effect zone and re-cast layer.

Zhang et al. [2009] [138], [139-141] observed that the addition of an electrochemical jet in high power laser drilling operations effectively removes spatter and recast developed by laser ablation. Although a consequence of this is a slight annular overcut around the entrance of the hole indicative with the removal profile in EJP. Material removal is mainly carried out by the laser ablation, EJP only providing an auxiliary effect mainly due to the large IEG (up to 9 mm). The cooling effect of refreshing electrolyte aids reduction of the HAZ although this is at a sacrifice of process efficiency achieving around 70% of laser ablation on its own.

Electrochemical slurry-jet machining provides a further adaptation of subtractive mode EJP [79, 80] (Figure 2.21a). The anodic dissolution mechanism being complemented by the application of an abrasive slurry in-jet combining the mechanisms of erosion and corrosion. Addition of Al_2O_3 abrasive particles to the jet stream generated material removal rates up to 3 times that of the jet alone when a high fraction of particle inclusion was used. This was found to be especially useful in machining tungsten carbide producing a much higher precision cut in comparison to electrochemical jet methods. This is due to the formation of passivation layers which the abrasive system would remove, keeping the surface clean for anodic dissolution. It was noted that to obtain the best surface finish and MRR, a balance between erosion and corrosion must be obtained by careful consideration of supply pressure and abrasive concentrations.

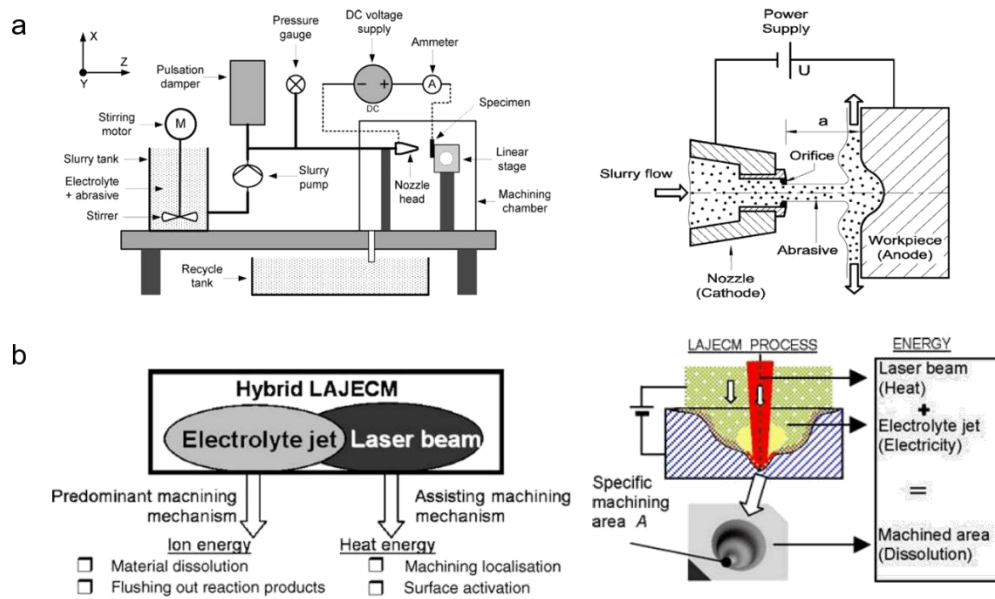


Figure 2.21: Electrochemical jet hybrid processes (a) electrochemical slurry jet machining [79] (b) Laser assisted electrochemical jet machining [136]

A hybrid system was developed in additive EJP to tackle the process issue of uneven deposition layers, meaning parts greater than 0.5 mm in height could not be built [39]. This is because if there is any protrusion from the cathodic surface it provides a preferential current pathway causing intensification of the electric field at that specific point, so generating preferential deposition and allowing further magnification of the protrusion. Katoh et al. [1997] [142] and Kunieda et al. [1998] [7] developed a lapping system whereby an abrasive lapping machine was used across the deposition surface after every deposition layer in order to create a flat smooth surface before the next layer was applied. For the optimised study a 150 μm layer height was deposited, then 100 μm in depth from the top of the deposit would be removed after every layer. Using this method walls over 2 mm were easily created, however the side profile of the walls was still distorted with over-hangs and each layer definition being easily visible.

2.5.7. Summary of the identified research gaps associated with electromechanical influence on EJP

The influence of the electro-mechanical design and innovation on flexibility and precision in EJP was reviewed through the literature. The key findings of knowledge gaps are presented as:

- Currently the machine tool architecture in EJP can be described as a simplistic, two-dimensional processing technique maintaining the nozzle perpendicular to the workpiece. Exploitation of further articulation degrees of freedom and its effect has yet to be understood.
- Modifications to the machine tool complexity have not been undertaken beyond the inclusion of air assistance coaxially to the jet. The same simplistic machine architecture has been maintained. Increased architecture technicity will lead to process enhancements.
- The influences of the hardware in relation to the IEG have not been fully considered. Especially when considering highly localised strategies effecting the surface response to electrochemical and mechanical influences. Improvements have only considered increases in process efficiency i.e. processing larger areas faster.
- Although hybrid processing routes provide some increases in precision, results are often contradictory. However, the increased technical complexity of these systems and difficulty of balancing the competing removal mechanics to produce advantage limit their application. Finding

more simplistic methods of achieving increases in precision and geometrical flexibility would be highly advantageous.

2.6. Competing processes

2.6.1. Introduction

To ascertain if a process is comparable to EJP the key attributes of EJP can be compared to alternative processes, which are identified from the literature. Only processes of the typical generated feature length scales found in EJP of meso- to micro-scale (5 mm to 0.1 μm) [143] are considered. Examples of these technologies can be seen in Figure 2.22 taken from Rajurkar et al. [2006] [144].

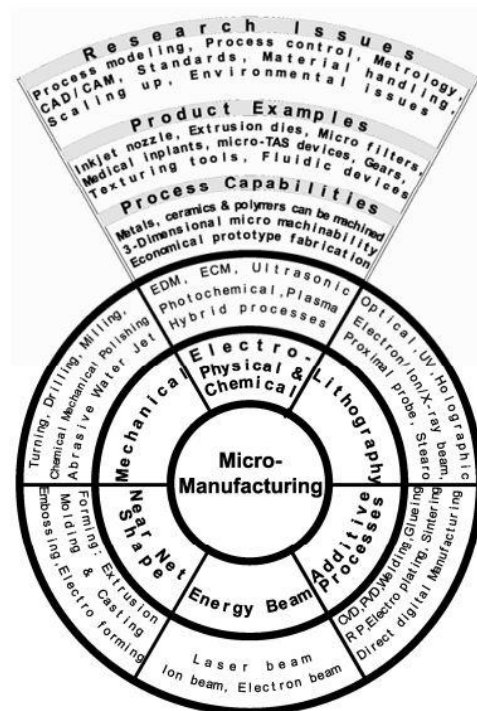


Figure 2.22: General classification of micro-manufacturing processes [144]

EJP does not require heat to affect material unlike laser beam micromachining (LBMM) [145] or electrical discharge machining (EDM) [146]. Removal therefore does not impart thermal loading into the workpiece surface causing a heat affected area or recast layer [92] (Figure 2.23a,b) and can therefore be described as athermal. EJP is non-contact therefore does not impart residual stresses, cracks, burrs or damage to the material structure of the workpiece [5] (Figure 2.23c) like shear or erosion based techniques such as micro-milling [147] or abrasive water jet (AWJ) [148]. EJP is considered to not require specialist tooling as the energy density combined with the electrolyte jet is responsible for material removal and so is analogous to the tooling in the traditional sense. EJP is considered mask-less as it can selectively add or deposit material without the need for prior mask creation. Other electrochemical micro machining (EMM) techniques, by comparison, require a mask to create complex precision features. Material removal is achieved using through mask electrochemical micro machining (THEMM) [149] and deposition using the Lithographic, Galvanoformung and Abformung (LIGA) process of through mask electroplating using electron beam, ion beam or X-ray lithography to create the masking [150]. Both of these technologies however are also considered hybrid technologies therefore requiring multiple and often highly complex manufacturing process steps, in comparison EJP is considered a one step process [92].

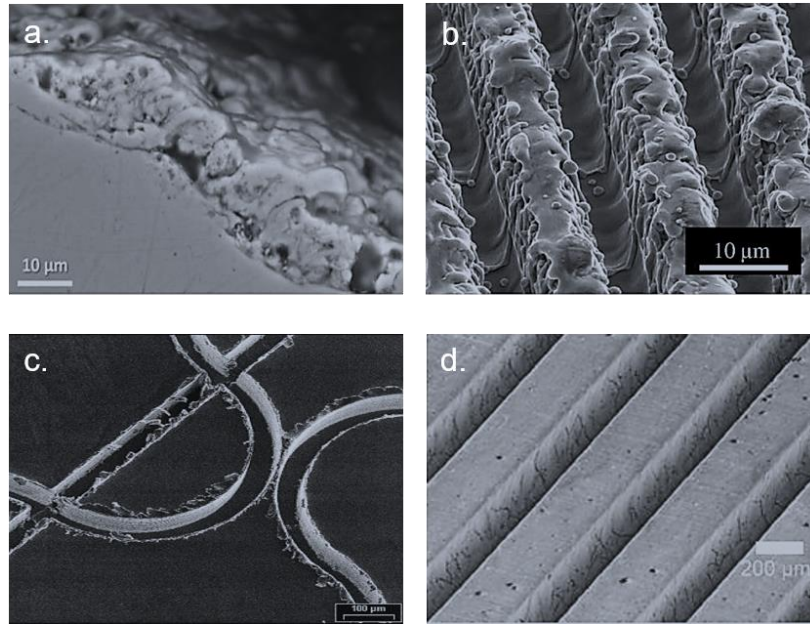


Figure 2.23: Resultant surface effects across varying processing techniques (a) EDM processing showing formation of re-cast layer in stainless steel [151] (b) Micro grooves machined with nano-second excimer UV laser ablation in titanium showing extreme case of heat affected zone and recast layer [152] (c) Micro-milling of stainless steel showing burrs formed at the feature edges and poor surface finish [153] (d) for comparison micro grooves machined by subtractive mode EJP in Nimonic 80A [4]

A further distinct advantage of EJP is the ease of which material can be removed or deposited within the same machine architecture with minimal changes required of reversal of polarity and change of electrolyte feedstock [7]. The final attribute associated with EJP is the low complexity required of the platform. This can be defined by it requiring four main elements (as described in section 2.5). In order to effect material removal or deposition, none of these components are required to be technically sophisticated [92]. This simplicity translates to a relatively low capital expenditure when compared to similar processes with comparable capabilities. Table 2.1 shows these process attributes related to EJP and lists the micro-machining technologies that also possess these attributes.

Table 2.1: Comparison of EJP process attributes with comparable processes

Process Attribute	Comparable process
No tooling	Micro AWJ [154], Laser beam [155], Focussed ion beam (FIB) [156]
Non-contact	Micro-EDM [157], EMM [127], Laser, FIB, Micro-AWJ
Athermal	EMM, Micro-AWJ
Mask-less	Micro-EDM, Micro-AWJ, Pulsed-EMM [104], Conventional micro-milling [158]
Subtractive and additive modes in the same machine architecture	Laser (SLM) [159], FIB, micro- EDM/EDC [160]
Simplistic machine architecture	Conventional micro-milling

Table 2.1 demonstrates there are several processing technologies that are comparable in attributes to EJP. Micro-AWJ, although not capable of deposition, possesses many of the attributes of subtractive mode EJP. It is also capable of higher removal rates than EJP and the ability to machine a wide range of materials including chemically inert substrates [161]. However, surface residual stress, surface damage, burrs and possibility of embedded grit [162] make the technique difficult to employ in applications where the surface integrity of a component must be assured. It is also been reported by Axinte et al. [2014] [163] that cut tolerances of $\pm 10 \mu\text{m}$ with repeatability of $3 \mu\text{m}$ are achievable. In comparison subtractive mode EJP has been reported to achieve cut tolerances of $\pm 5 \mu\text{m}$ [164]. The resultant kerf in micro-AWJ has been reported by Liu [2010]

[165] to be as low as 150 μm , stating that clogging of the nozzle would limit kerf reductions further, although the use of plain water jet micro-machining [166] (without abrasives) may negate this issue. Although kerf in AWJ is comparable to the majority of subtractive mode EJP reported it has been demonstrated that kerfs as low as 70 μm can be created using 50 μm internal diameter nozzles [123, 130].

Micro electrical discharge machining / coating (micro-EDM / EDC) is also comparable to several of the attributes of EJP. Although EDC has yet to be functionally demonstrated in selective precision structuring beyond simply coating, the use of the sacrificial electrode to deposit material [167] will mean the deposition will follow the form of the electrode. However, this could present a process limitation of the available feedstock for micro-structuring. Micro-EDM has been widely demonstrated in research and industry for the machining of high aspect ratio features beyond that currently demonstrated by EJP [168], with notable research dedicated to deep hole drilling [169]. However, the tooling defines the kerf of any features created and therefore manufacturing techniques of the electrodes become the limiting factor. It is a worthwhile observation that both additive and subtractive mode EJP have been used to fabricate micro-EDM electrodes [40, 99]. Kerfs down to 20 μm have been reported for EDM drilling and die-sinking operations with feature tolerances of $\pm 1 \mu\text{m}$, although milling kerf is much larger at $\approx 100 \mu\text{m}$ [170] due to tooling considerations. However as discussed by Hackert-Oschätzchen et al. [2012] [75] the crater-like topographies characterised in the surface finish of EDM along with the heat affected zone creates surface finishes significantly poorer than EJP which achieves R_z values of $\leq 1 \mu\text{m}$.

Other energy beam processes such as FIB are capable of both additive and subtractive machining within the same structure [171] although the length scales found in FIB research are $< 10\ \mu\text{m}$ [156] and often demonstrated down to $< 1\ \mu\text{m}$ [172]. The technical complexity and therefore cost required to do this makes FIB difficult to employ in an industrially robust environment. Laser based micro machining (LBMM) processes however appear to provide an almost comparable process to EJP. Hallmann et al. [2015] [159] for example, demonstrated the combined additive and subtractive modes using selective laser sintering (SLM) and laser ablation for the manufacturing of medical implants with SLM being used for the fabrication of the part and laser ablation used to impart preferential surface textures. LBMM additive and subtractive technologies can now demonstrate a level of process maturity. Such process derivations as direct metal deposition (DMD) [173] have been combined with CNC milling in commercial machining centres [174]. LBMM in specific circumstances can achieve a similar surface finish to EJP and achieve slightly higher aspect ratios with smaller profile kerfs [175]. However, it should be noted that this is often achieved at the expense of near-surface quality (Figure 2.24).

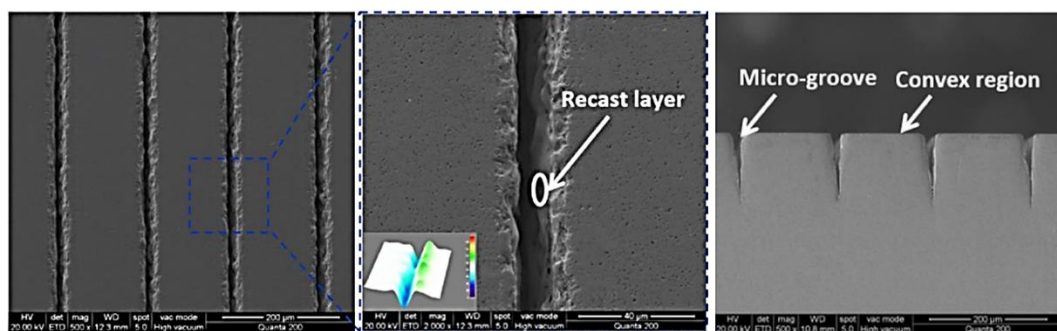


Figure 2.24: Overhead and cross-section SEM images of micro-grooves machined for analysis of wear behaviour [175]

Dimensional accuracy combined with surface quality has somewhat been addressed using high frequency optical pulsing of lasers in the pico- and femto-second ranges. Through use of ultrafast lasers, the heat affected zone is vastly reduced. This is due to the reduction of hydrodynamic expansion as the absorption of laser radiation and ablation occur concurrently allowing precise control of the energy deposition. The absorption length of the laser radiation is greater than the thermal diffusion length, therefore the heat conduction can be neglected as evaporation remains the dominant mechanism, with ablation occurring in the vapour phases [176]. Therefore thermal diffusion is minimal leading to a vastly reduced liquid phase reducing the re-cast layer and heat affected zone (HAZ) [177]. This results in a much finer and more reliable micro-machining technique particularly where the machining of temperature sensitive applications are concerned, with minimal cross section components such as biomedical stents [178]. It should be noted however that these components still require finishing by electrochemical means to remove sharp edges and burs in a commercial setting. The further implication of using ultra-fast lasers is the increased capital investment required and reduced material removal rates. It is not just the laser source, (powerful enough to ablate metals, up to 100W) that is required capable of fast pulsing, but the means by which to control the pulse, diagnostic systems for pulse energy control and validation, optics trains (fibre optics are preferred in manufacturing systems), safety costs associated with high intensity light sources, and typical translation and suitable machine architecture (servo driven smooth system). It is reported that these systems combined can cost upwards of £250k with relatively small working volume, although costs continue to reduce as competition and market factors change [179, 180].

Another process that has benefitted from pulsed generation is electrochemical micro-machining (EMM) [124]. The use of pulsing EMM is the same as EJP as described in section 2.5.4. As EMM is a submerged process and the resultant feature is reliant on the cathodic tooling, often masking is still required to create precision features. The use of a pulsed energy supply means a higher instant current density can be applied during the pulse on time and IEG recovery during pulse off time (debris clearance), therefore the IEG can be vastly reduced to $<50\text{ }\mu\text{m}$ [104]. This means mask-less geometry is possible and vastly enhanced [88] along with improved surface finish. However, as with micro-EDM the resultant geometry is still reliant on the ability to generate the tooling which is not only technically difficult but costly. Consideration must be made within the tooling to allow for adequate electrolyte flow to clear the debris which is often delivered axially to the tool. The machined geometry therefore must allow for a flow path around the tool and ejection. This leads to overcut, although careful parameter selection and use of the pulsed supply can minimise this [181]. Due to the small IEG, flushing procedures are also required to clear the debris from the IEG and avoid shorts between the electrodes which is carried out during the pulse off time [125]. Inherently this adds time to the process cycle and complexity to process planning for the machining of complex shapes [75]. Although these flushing sequences can be used for monitoring of the IEG. This is currently a limiting factor of precision in EMM, the precision of the geometry is inherently linked to the ability to maintain a consistent and small IEG [104]. This is not the case in EJP. Selective deposition is possible through EMM in reverse polarity requiring masking technology, often photoresist [182] or insulating film such as Ta_2O_5

which are machined to create the mask [183]. This induces a great number of process steps, increasing process complexity and reducing process efficiency.

2.6.2. Energy beam-based process development

Most processes that compare well to EJP can be described as energy beam based (EBB) processes, the jet in EJM and micro-AWJ being synonymous to the energy beam. Thus, the development of more mature processes set the benchmark for what EJP needs to be capable of achieving. One of the major influencing factors of EBB processes is the energy distribution within the beam. As outlined by Yoneda et al. [1995] [11] and Kozak et al. [1996] [19] the energy distribution in EJP is considered to be of a Gaussian nature producing a bell curve which is reflected in the resultant profile geometry. This has also been found to be the case across other EBB processes (see section 2.3). The resulting profiles exhibit tapered sides, a rounded apex and diffused edge definition. This type of profile is unfavourable across applications such as microelectromechanical systems (MEMS), microoptoelectro-mechanical systems and microfluidic systems [184] which have previously been dominated by fabrication in polymers and glasses. However, with the increased desire for repetitive use, higher temperatures, higher pressures and aggressive environments the use of metal components has become desirable [185]. Alongside this the cost and time reduction, and flexibility of non-lithographic methods are advantageous. Generally squarer uniform profiles or specific constant profiles are required such as equal flow channels in heatsinks [186, 187] or micro-channel design for enhanced mixing [188]. The EBB tapered profiles also present difficulty in

integrating the profile into computer-aided manufacturing (CAM) systems to predict required removal for complex feature generation.

Significant work has been undertaken in the field of laser processing to modify the defined energy distributions away from the Gaussian distribution to create a more even distribution of energy across the machined surface. This is coupled with a more flexible and desirable deposited or machined profile. Beam shaping can be carried out in a number of ways [189-192]. Holographs generated by custom optics have been used to define the incident energy distribution across a number of applications including laser welding, wire-based deposition and ablation [193-195] (Figure 2.25). This represents a step forward in the flexibility and capability of laser processing.

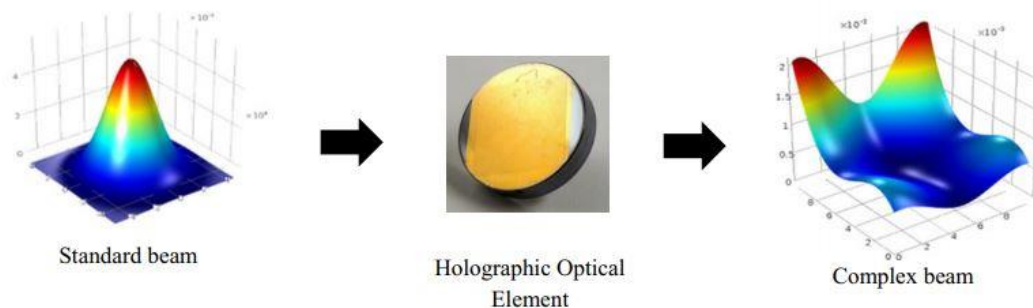


Figure 2.25: Schematic of the principles of holographic control of laser beam profile [195]

Another area of energy beam processes that has received considerable research interest is how the energy distribution within beam, therefore the resultant geometry, is affected by changes to the beam approach angle. This is potentially an important research area as consideration of approach angle is a key concern in industrial usage of all energy beam processes.

Examples of this type of investigation can be found across many energy beam processes. In abrasive water jet (AWJ) it was initially investigated by Venkatesh [1984] [196] to find the optimum angle for increased depth of cut and later as part of a complete empirical study for overall volume removal [197]. Hashish [1993] [198] also considered changing the angle of approach for the effect on volume removal, and more recently an assessment of AWJ for 3D milling through changing the jet impingement angle was carried out by Srinivasu et al. [2009] [53]. In focussed ion-beam micro-milling, Xu et al. [1992] [199] considered the influence on deposition rates and milling quality as a function of beam incidence angle. For laser based processes, such as ablation, Tokarev et al. [1995] [200] developed a self-limiting method for polishing of diamond films utilising changes in the beam angle of incidence. George et al. [2004] [201] investigated the angular dependence of focused laser ablation with nanosecond pulses and the resultant geometry in polymers for the development of simulations for direct-write applications. In comparison Palmer et al. [2004] [202] and Yang et al. [2004] [203] investigated the effect of changing the angle of incidence in femtosecond laser processing through varying the substrate angle to understand the influence of a changing topography on the resultant profiles. Groenendijk et al. [2006] [204] carried out similar experiments to study the effect on the formation of periodic microstructures for large area surface texturing and the parameter influence on their formation linking the liquid phase of ablation with the formation of ripples. Guo et al. [2007] [205] found they could use a changing angle of incidence for laser writing across a large area without the use of projection masks by manipulation of the resultant features due to the changing incident angle alongside parameter changes.

Throughout these investigations it was found that the energy density maxima are maintained in line of sight of the approaching beam regardless of surface considerations and the angle of address. This was demonstrated by George et al. [201] who found that ablation depth along the direction of the incident laser beam is independent of the angle of incidence in laser ablation and Srinivasu et al. [53] found the same phenomena in AWJ, whereby the slope of the kerf trailing edge decreases with the lowering of the approach angle alongside the maximum kerf depth which remains in line with the jet axis (Figure 2.26). It was also noted by Srinivasu et al. that the kerf width increased as the angle of incidence with respect to the surface decreased, due to the increased width of the jet foot print as the jet plume becomes divergent or defocussed at larger nozzle stand-offs.

Significant progress has also been made in process modelling of typical energy beam process which may enable a more intuitive process model for EJP than those described in section 2.3. EJP also being a time-dependant process reliant on energy constraints to affect material removal. This would enable the generation of freeform surfaces and allow the process model to deliver complete control parameters to generate a defined surface thus solving the inverse problem. Across a number of EB process such as laser [206] and abrasive water jet [207, 208] alongside EJM [11] the use of finite element analysis (FEA) has been considered either considering the high velocity particles [209] or energy density considered across the elemental mesh [210] or even multiphysics approaches coupling multiple physical phenomenon [45, 211]. However, these methods are computational expensive and so difficult to apply when larger surface area is considered and too timely to employ on-line [212]. A further approach has been developed to define the footprint of a particular energy-beam

process that has intended not to consider material constraints as these are often considered a variable, especially in advanced alloys which are inhomogeneous when considered at the microscale. It has also been demonstrated some machining methods alter the near surface microstructure of material during processing thus effecting boundary conditions of the simulation [213]. This more mathematically efficient process model utilises partial differential equations to govern process footprint evolution, considering the surface, toolpath vector and erosion or etching rate function which is dependent on energy distribution and considering the dependence of the MRR on the gradient of the evolving surface. This has developed from initial simpler solutions for example in the etching of glass by powder blasting [214-216] to much more advanced methodologies considering more complex toolpaths and machine dynamics [217, 218]. More recent evolutions of the surface evolution equation are intended to be applicable for multiple energy beam processes. A solution to the linear inverse problem was first considered suitable for constant angle of jet address to the surface thus shallow removal [219]. This was further developed where non-linear effects are considered achieving a surface evolution equation whereby the machining footprint can be defined for deep removal and greater complexity of toolpath and thus resolved to identify machining parameters required for a large area freeform surface [220]. This methodology requires defining the etching rate function to define the cross-sectional profile of the footprint. It has been shown to be possible to generate this from a minimised empirical data set gained from a specific calibration machining routine [221] gaining an average kerf profile thus, energy distribution and as such the etching rate function. This step can be avoided when the energy distribution is already known for example in FIB [51] or AWJ [212]

when a simplified Gaussian distribution can be applied, thus the calibration step is not required, producing a highly efficient surface evolution modelling process.

A further area of process development that has been exploited by energy beam machining is the creation of large area micro-surface texturing. There is a strive within manufacturing to optimise component potential through the application of next-generation, high-integrity surfaces [222-224] which presents a significant manufacturing challenge. Advantages have been demonstrated for anti-fouling, drag-reduction, enhanced adhesion [225, 226] and enhanced osseointegration [91, 227] in applications where complex surface structuring has been previously employed. Previously creation of these complex surface structures have required contrived process chains involving polymer deposition [228, 229]. However, energy beam processes can provide a one-step fabrication method to create these surfaces on metal components. Processes such as FIB and micro laser milling have been used to create micro and nano-scale deterministic repeatable surface structures reliant on biomimetic design cues [230]. Lasers have also been employed in non-deterministic surface texturing, whereby the parameters and attributes of process and material interaction have been manipulated to efficiently create a sub-micron scale texture across a component surface.

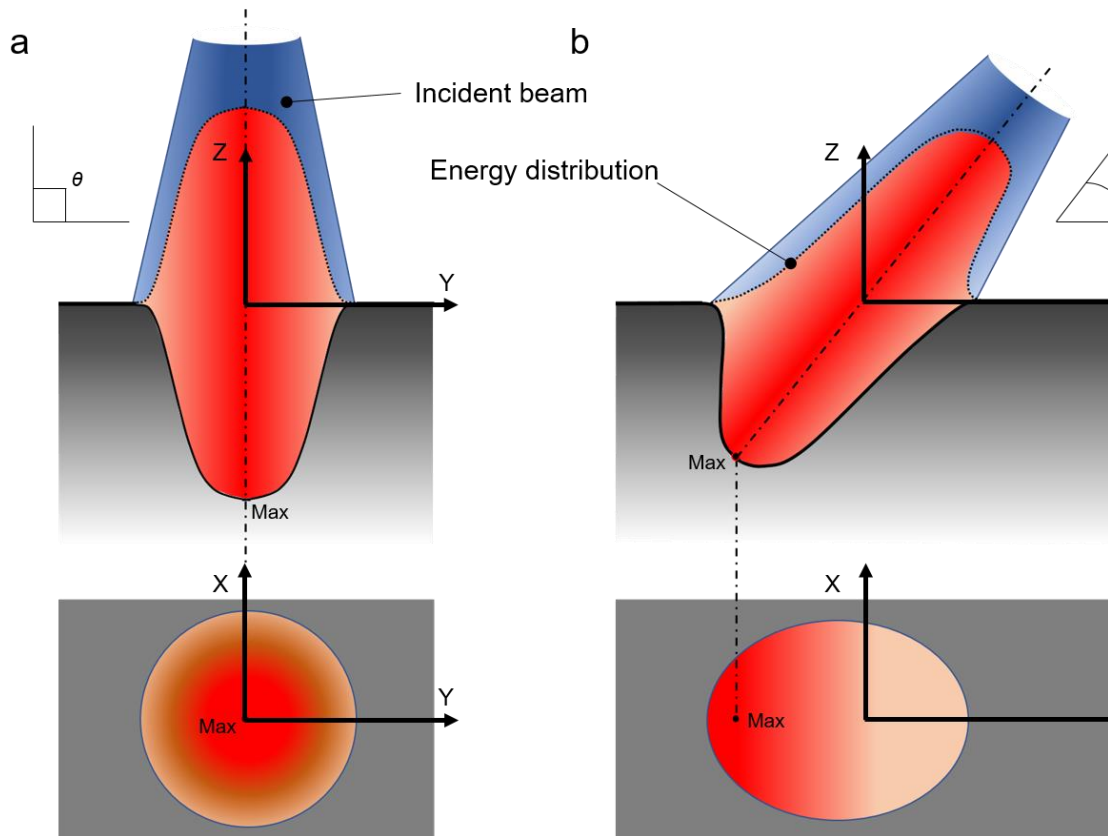


Figure 2.26: Schematic of removal profile effect based on abrasive waterjet derived from Srinivasu et al. [2009] [53], whereby the maximum energy density is maintained in line of sight of the beam address regardless of the approach angle a) angle of address normal to the workpiece surface, b) reduced angle of address

Example application areas where this technique has been used include; enhanced adhesion surfaces [231], biomedical applications [232, 233] often specifically to promote a cell response in implants [234, 235], increased stiction in interference fit applications [236] and creating superhydrophobic surfaces [237-239]. In biomedical applications the use of textured surfaces in skeletal implants has received a great deal of interest for enhanced bone to tissue anchorage [240-242], lubrication in metal-on-metal implants [243] and enhanced osseointegration [227, 244]. Traditionally surface topography changes had been carried out using acid etching techniques [245] whereby the component would be immersed in a strong acid solution (HCL, HF, HNO₃) heated above 100°C in order

to produce micro pits on the surface, length of immersion and solute concentration imparting the required roughness to the surface. Although a relatively straightforward method it requires multiple process steps of pre- and post-treatment and the cost and sustainability of the process due to its hazardous nature in comparison to laser processing makes it difficult to employ in industry.

2.6.3. Summary of the identified research gaps relating to competing processes

Consideration of comparable processes to EJP and the development thereof was reviewed through the literature. The key findings are:

- Although several technologies share distinct attribute similarities to EJP none can match all. However, several technologies demonstrate advantages over EJP that could make them currently more viable of increased precision and flexibility. Therefore, EJP is required to address this in order to enhance its viability.
- Several electromechanical innovations have been presented in these technologies to enhance precision and manufacturing flexibility. Laser beam processing for example, has demonstrated it can be used not only for deterministic micro structured feature manufacture but also for large area non-deterministic texturing of surfaces. EJP has yet to exploit this capability in a meaningful manner.
- It also been demonstrated in laser beam manufacture that the resultant energy density curve affecting the removal profile can be manipulated in

an advantageous manner. It would be necessary for EJP to demonstrate this type of innovation to make the process more viable in micro manufacturing.

- Changing of the angle of incidence in comparable technologies has been intently researched allowing process innovation. This is not an area that has been investigated in EJP.
- When compared to laser processing EJP still lacks the precision and flexibility to be competitive although the low cost and zero thermal impact could make it preferential.

2.7. Applications of EJP

2.7.1. Introduction

EJP in both additive and subtractive modes have so far found limited application in industry. However, a wide number of applications for EJP have been demonstrated through research. All of these are centred on the length scales appropriate to EJP, demonstrated throughout this review, of meso- to micro-scale manufacturing. To understand if EJP is industrially relevant and identify the requirements needed in EJP, the following section reviews the research and industrial applications where EJP has been employed.

2.7.2. Additive mode

In additive mode EJP the majority of applications have centred around the electronics industry such as; the direct writing of microwave integrated circuit

substrate (MICS) [182], reel-to-reel fabrication of components and conductors and the direct writing of etch resist for printed circuit boards (PCB) [37]. Fletcher et al. [1974] [30] developed the scanning nozzle plating system as part of NASA. It was developed specifically for the deposition of copper on bespoke circuit boards. Bocking et al. [1994] [38] also found industrial application in the electronics industry for the deposition of gold for electrical connectors.

Although both Bocking et al. [1995] [246] and Kunieda et al. [1998] [7] were both able to microfabricate small components they both alluded to the inherent problem of high walled structures in EJP (discussed in section 2.5.6).

Dover et al. [1996] [39] investigated the use of additive EJP for rapid tooling including successful generation of moulding tools for micro-injection moulding and tooling for EDM alongside assessing the wear rates for the EJP created EDM tools [40].

2.7.3. Subtractive mode

In subtractive mode EJP the main industrial application was the drilling of micro-holes in gas turbine blades [15, 28]. Although it must be noted that the machine architecture and process parameters differed considerably to the current definition of EJP (see section 2.2 for further discussion). However the use of acid based electrolytes (see section 2.4 for further discussion) meant that these operations were phased out of production by the late 1990's to be replaced by laser and more recently micro-EDM [29]. Subtractive mode EJP has been employed by the Fujii Manufacturing Company Ltd. (Japan) integrated with stamping processes for the selective removal of burrs caused by fine grooving in

stainless steel for the creation of orthopaedic stainless steel accessories [247]. It is noted that the use of EJP reduces manufacturing costs by 20% and reduces delivery time by 50% when compared to post-process finishing by hand.

Subtractive mode EJP has seen a much greater diversification of applications demonstrated in research than additive mode. Kunieda [1993] [2] demonstrated that rolling bearing contact fatigue life could be improved by the machining of micro indents in the bearing surface (Figure 2.27a) so creating an improved lubrication regime and prolonging fatigue life, noting that the machining technique does not induce stresses into the surface so is ideally suited for this type of application. Lu et al. [2005] [92] demonstrated EJP for the machining of bio-medical applications. Specifically creating blind holes hundreds of microns in diameter with an aspect ratio just over 1.3, across the curved surface of an implant where extensive bone-in-growth is required, therefore being beneficial for osseointegration (Figure 2.27b).

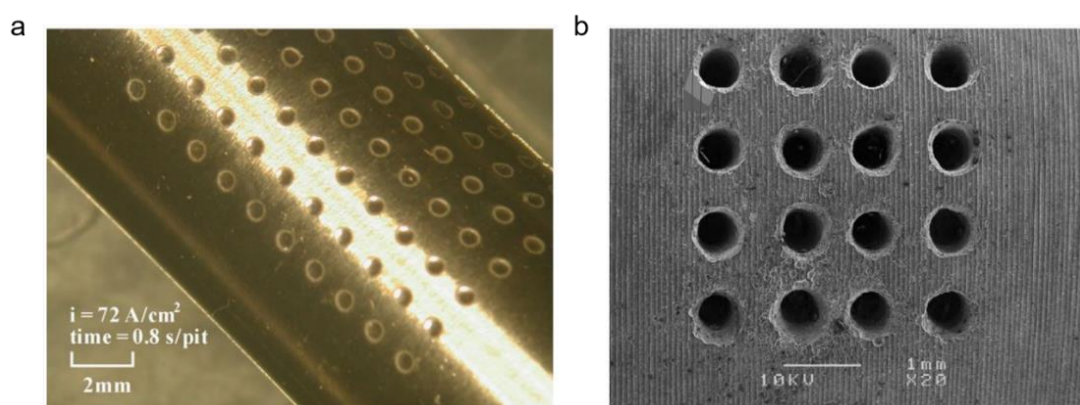


Figure 2.27: Micro-machined features in (a) stainless steel for improved contact fatigue life of a rolling bearing [2] (b) Ti6Al-4V for enhanced bone in-growth on implant surfaces [92]

Kunieda et al. [2010] [130] again used the machining of micro geometries into a component for an enhanced effect, in this case dimples into a saw wire to carry abrasives more efficiently to improve efficiency and accuracy in the slicing of hard and brittle materials. Schubert et al. [2011] [248] used EJP for the realisation of micro-structured surfaces for thermodynamic applications, identifying and designing specific micro-geometries to achieve enhanced heat transfer. EJP was used alongside laser for a direct comparison of the two processing routes in creating identical surfaces with high potential for convection and nucleate boiling processes. EJP was found to deliver a high exactness to the feature design with excellent surface qualities. Laser machined surfaces were found to have a rougher finish which could offer additional positive effects on heat transfer phenomena (Figure 2.28).

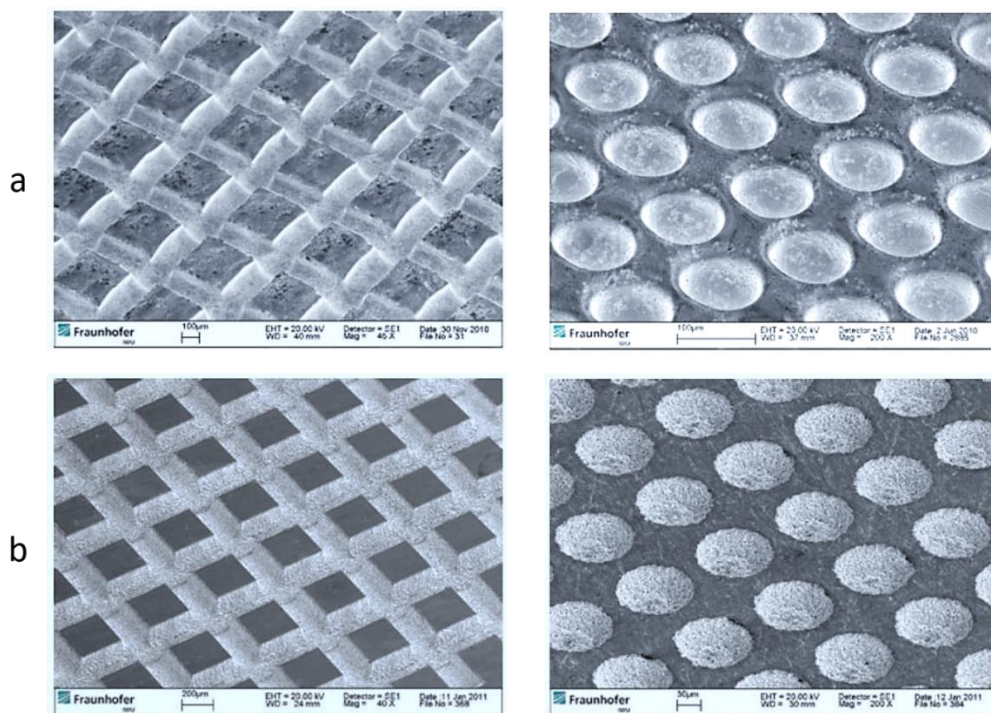


Figure 2.28: Surface structuring for enhanced heat transfer capability carried out by (a) subtractive mode EJP (b) Laser ablation [248]

Schubert et al. [2011] [249] employed micro-structuring with EJP for improved tribological efficiency of powertrain components and forming tools. A repeated dimple pattern was developed and tested for hydrodynamic effect across the lubrication regimes. The aim was to reduce the friction coefficient along the three regimes and shift the Stribeck curve to overcome the boundary and mixed lubrication regimes at lower operating velocities. It was found that patterned surfaces of spherical-segment cavities (dimples) yielded a friction coefficient reduction of up to 27 % dependent on loading parameters. Reducing wear on hot-forging tools using thermal-spray coatings was also considered. It was intended that the cyclic properties and adhesion of these coatings could be improved by the application of deterministic surface structures by EJP on the substrate to be coated. However, no experimental evidence was provided for this application. Kato et al. [2013] [250] investigated the application of surface texturing of moulds used in polymer injection moulding. Through varying the process parameters used to create dimple structures on the surface they were able to create differing textural qualities on the mould surface. These textures were then tested for reproducibility and durability in process. It was found that at high mould temperatures the surface textures transferred well to the moulded components. It was also noted that little wear of the surface structures occurred during use, even at low temperatures.

Yang et al. [2016] [251] combined subtractive mode EJP to control and regulate the adhesion of water droplets for implementation in water harvesting and trace analysis of aqueous solutions. They first electrochemically etched the entire surface of Al alloy plates creating a superhydrophobic surface. EJP was then used to machine dimples into the surface at varying dwell times and varying

voltage. It should be noted that the voltage used in some of the experiments was very high which would introduce further material removal mechanisms beyond purely electrochemical dissolution. These include discharge machining, where a glow discharge is produced at the nozzle tip due to hydrogen evolution [252] and electrolyte heating [181]. It was observed that by varying the processing time and voltage of the individual dimples would change the roughness and structure of the dimple surface and therefore the hydrophobicity experienced across the surface. There results mimicking the findings of Natsu et al. [2007] [5] that a higher energy experienced by the surface (in this case increased voltage and dwell) leads to a smoother surface. Adhesion force of the droplets was found to increase with increasing processing time and increased applied voltage. This effect was manipulated, and they were able to design surfaces that would shed droplets at pre-determined angles and resist movement until the chosen angle was selected, so allowing a selection mechanism (Figure 2.29)

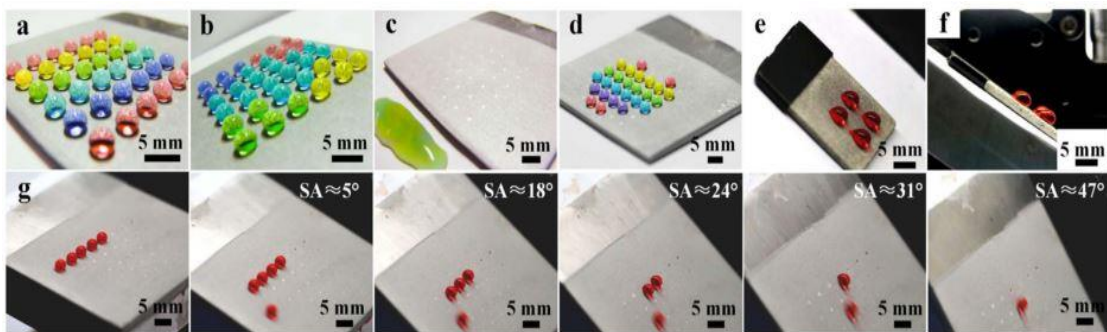


Figure 2.29: Examples of adhesion-controlling patterns on superhydrophobic surface. (a) Water droplets of 20 μL stayed firmly on the surface patterned by the 6×6 dimples, which were processed for 5 s each at 300 V with a 520 μm inner diameter nozzle. (b) Water droplets pinned on a tilted patterned surface. (c) Water droplets all slid off the surface at a tilted angle of about 41° . (d) Heart-shaped patterned water droplets on the surface. (e) 20 μL water droplets were pinned by the 2×2 dimples on a superhydrophobic surface. (f) Side view of (e). (g) Droplets slid at designed angles at appointed positions [251]

To create more complex surface features allowing higher complexity in application requires a more advanced approach to energy delivery or parameter control in EJP. Minimal research has been conducted in this area to create repeatably and efficient 3D surface structures when in comparison to alternative processing methods (see section 2.6). Natsu et al. [2007] [5] used an approach of superimposing simple patterns to create grooves with alternative cross-sectional profiles to that created by the standard bell type removal profile. This was achieved by controlling the position and scanning speed of the nozzle to create features of different depths. Grooves were then overlaid over each other to form a single groove with the required profile shape. Natsu et al. [2008] [59] further expanded this through superimposing elemental curved grooves further adding to the shapes that could be created. Through maintaining a constant current density, as defined by Natsu's earlier work a constant surface finish, repeated curved grooves at differing speeds, and toolpaths could be combined to create a single 3D structure. This is some way analogous as a traditional computer aided manufacturing (CAM) software would vary speeds and feeds on a milling operation for generation of a part. Natsu applied this methodology over several machined features achieving consistency with the expected profile. Hackert-Oschätzchen et al. [2012] [75] utilised variation of the parameter set of EJP along with toolpath to create complex surface structures informed by an FEM process model. Through varying speed, energy and scan repetition numbers over discrete areas, a complex surface pattern could be created with changing depth of features and pocketing areas of the surface. It should be noted that the bell-type removal profile was maintained throughout. Schubert et al. [2016] [86] used a combination of the two previous techniques of superimposition and discrete

parameter control, again based on a mathematical model to inform the final machining process. Using overlaid toolpaths that varied in direction, line spacing (step-over), speed and energy, a V-shaped target profile geometry was achieved with a kerf of ≈ 3 mm and depth 0.4 mm involving hundreds of superimposed single lines.

2.7.4. Summary of identified research gaps relating to the application of EJP

Reviewing the available literature on applications of additive and subtractive EJP the key findings are presented as:

- Additive EJP has found industrial application in the micro-electronics sector where the ability to create bespoke and conducting features is highly desirable. It has demonstrated only limited application in micro-scale fabrication
- The application of subtractive EJP has been limited industrially but shown by research has scope for implication. The surface texture patterns however have been very simplistic, deterministic geometry on a meso-scale in well understood materials often with limited industrial relevance.
- A limited number of approaches in generating complex surface structures have been proposed in subtractive EJP. These demonstrate complex, protracted approaches to the generation of surface structures. A simpler mechanism for this would be advantageous.

2.8. Overall summary of identified research gaps within the literature

This chapter has introduced EJP from its fundamental parameters and electrochemical and electromechanical developments, to comparison with competing processes along with applications.

Considering the literature reviewed it is clear that additive mode EJP has received considerable interest from understanding of the fundamental mechanism to implementation of this knowledge in application. Furthering of this knowledge beyond adaptations and enhancements which serve both modes of EJP are within the realms of advanced chemistry, including greener deposition chemistries and enhanced material selection, which is beyond the scope of this thesis. Although much of this fundamental knowledge is also applicable to subtractive mode EJP and as such has been demonstrated, the specific research gaps are more apparent in subtractive mode.

To advance the EJP process by tackling the current knowledge gaps, the issues identified through the literature review are summarised below:

- **Fundamental understanding of key material response** - The fundamental understanding and definition of the influencing factors on an electrolytic unsubmerged jet is theoretically well defined. However, in EJM these are only generalised and not specific to materials and often theories are not fully validated with conflicting evidence provided. The understanding of the dissolution mechanism of advanced and robust engineering alloys is limited. Such materials as nickel superalloys and titanium are industrially relevant for the high-value-add market sectors

[253, 254]. It is intended to test the theories of Kunieda [1993] [2], Kozak et al. [1996] [19] and Datta et al. [1989] [34] of the effect on material removal by changing process parameters and ascertain if they still apply in titanium and nickel superalloys. Information on the effect on feature geometrics would be valuable to ascertain a bench mark for future innovations through chapters 5, 6 and 7. The consideration of Kawanaka et al. [2014] [54], [55] theories on the mechanisms relating to the response of the workpiece surface to parameter variation and the contributing factors to the resultant surface finish will also be investigated, identified as key in understanding overall process mechanisms. Investigations presented in chapter 4 are intended to fulfil this identified knowledge gap.

- **Adaption of the energy distribution** - The Gaussian energy distribution is identified as being responsible for the resultant profile in EJP. Alongside this the stagnation region below the nozzle is responsible for the kerf in EJP. Both are considered boundary conditions in EJP. To provide greater flexibility to the process and increase precision by reducing kerf these would need to change. Addressing the mechanical (chapter 5) and electrochemical influences (chapter 6) on the IEG, such as spatial and chemical changes influencing in-jet properties thus allowing manipulation of the process energy at surface, may provide insight into possible routes to increasing flexibility and precision of resultant features and allow a new approach to EJP (chapter 7).
- **Architecture development** - Processing platforms in EJP have remained simplistic laboratory orientated hardware. Development of this to a more industrially focussed platform would allow EJP to demonstrate a higher

level of technical and application complexity in line with comparable processes. Development of the base research platform is intended to be dealt with through the methodology section demonstrating the progress through 2 generations of machine. However significant architecture development will accompany both mechanical and electrochemical innovations in chapters 5 and 6.

- **Application development** - Demonstrated applications in EJP have been generally simplistic in nature and often not fully validated. Through this review EJM would appear to offer the potential of flexibility in control both of deterministic and non-deterministic features (form and finish). With enhancements highlighted of increased precision and form flexibility it would be possible to create these complex features in a one-step process, reproducible across large areas and at a low cost. This has yet to be delivered. However, application and demonstration work of this nature, although likely to require innovations developed throughout this thesis, would require extensive external collaboration for analysis therefore would be beyond the scope of this thesis and as such will be dealt with in the accompanying appendixes.

3. Methodology

3.1. Introduction

The following chapter describes not only the methods, techniques and metrics of analysis used throughout this investigation but, also a brief overview of the design and manufacture of the EJP machine over three generations of development from initial laboratory proof of concept at the beginning of the project to a transferable research platform (Figure 3.1) carried out as an integral part of this work.



Figure 3.1: Platform development timeline (Gen. 1) 2014 start of project (Gen 1.5) 2015 / 2016 development of capabilities for enhanced functionality (Gen. 2) 2017 re-model for enhanced capability, precision and operator ease

3.2. Generation 1 research platform

The first-generation platform was based on literature review of Kunieda [1993] [2], Hackert et al. [2007] [4] and Bocking et al. [1994] [38] research (outlined in section 2) which demonstrated the basic architecture required for electrochemical jet machining and deposition shown in Figure 3.2.

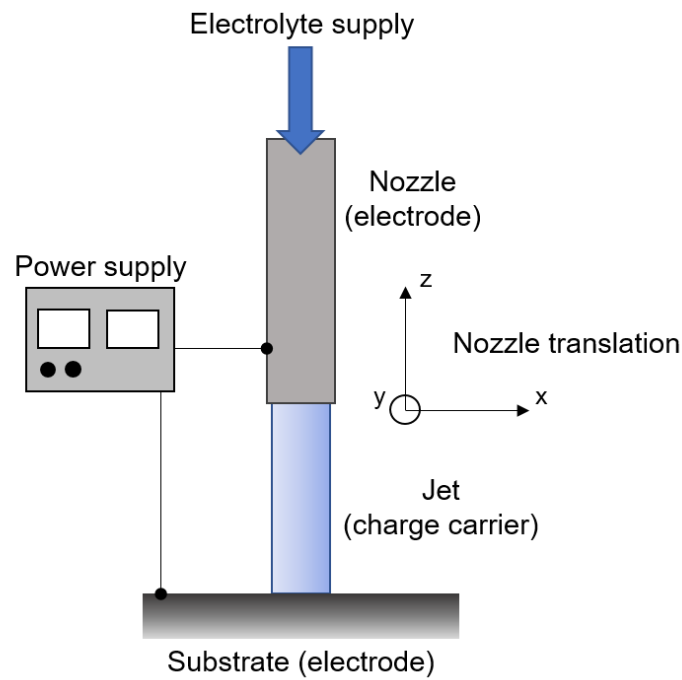


Figure 3.2: Schematic overview of a generic EJP architecture highlighting essential features included in most reported apparatus.

A top down design approach was used as there was no prior design knowledge (Figure 3.3). Therefore, it was required to re-engineer the platform from a concept based on research. From review an overall vision for the architecture could be conceptualised. The sub-systems required could then be identified to meet the chosen concept (Table 3.1). Through careful consideration of these sub-systems options, individual components were evaluated through traditional decision matrix analysis, design morphology analysis and design rationale diagrams (DRD). This enabled progression toward the optimisation of the final machine design.

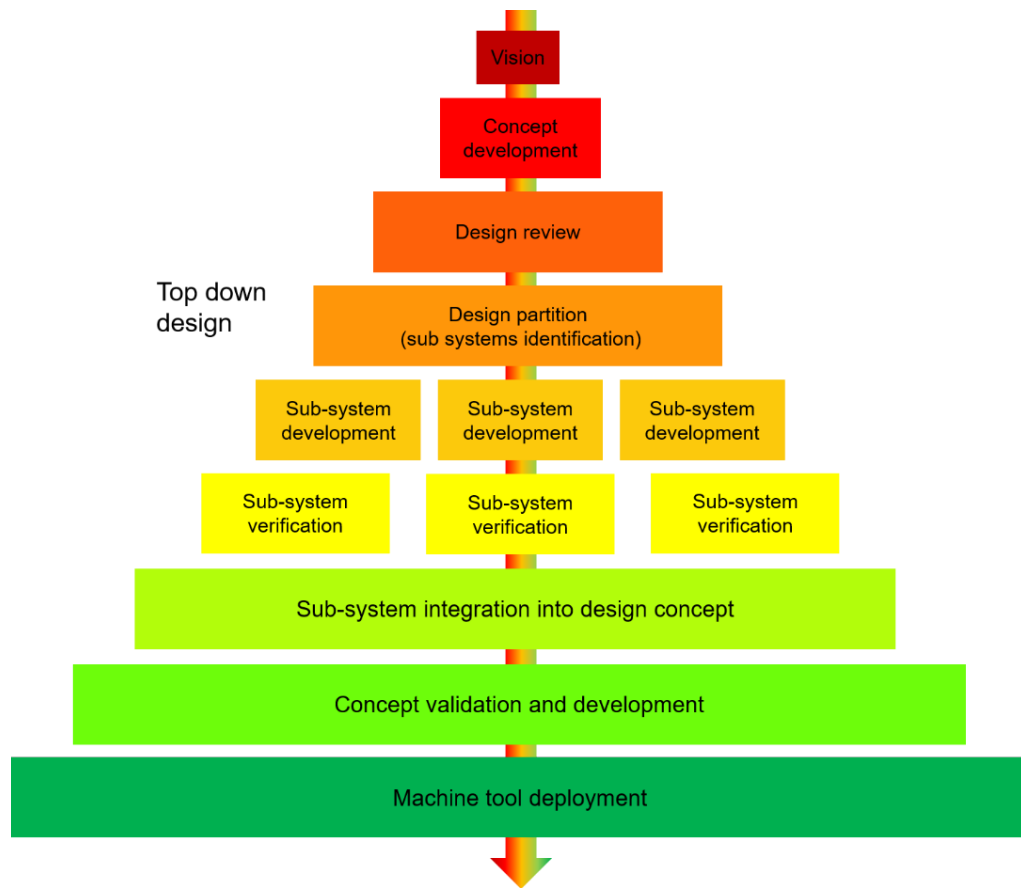


Figure 3.3: Top down design methodology employed in design and realisation of generation 1 machine tool

A statement of requirements (SoR) was set out to incorporate all these findings and include rudimental machine and safety design concerns (Appendix 1). With incorporation of these requirements a simplistic machine tool was manufactured (Figure 3.4) capable of producing material removal following simplistic toolpaths (Figure 3.5).

Table 3.1: Machine sub-systems and associated component systems

	Sub-system	Components
1	Machine structure	Frame, translation axis, machine table, Mounts (axis, head, table)
2	Fluid management	Air supply, Electrolyte supply, electrolyte feedstock storage, filtration, recirculation, waste scavenging, waste storage
3	Workpiece interaction	Head Assemble (encompassing the complete unit from the interface with the actuator (head bracket) to the interaction with the workpiece (end-effector)), end-effector (responsible for jet creation and electrification (electrode)), co-axial air shroud, workpiece holding (including workpiece electrification), power supply to the end effector (PSU)
4	Control	Axis movement, feedback and output, PSU variation, electrolyte supply variation, compressed air variation, safety system

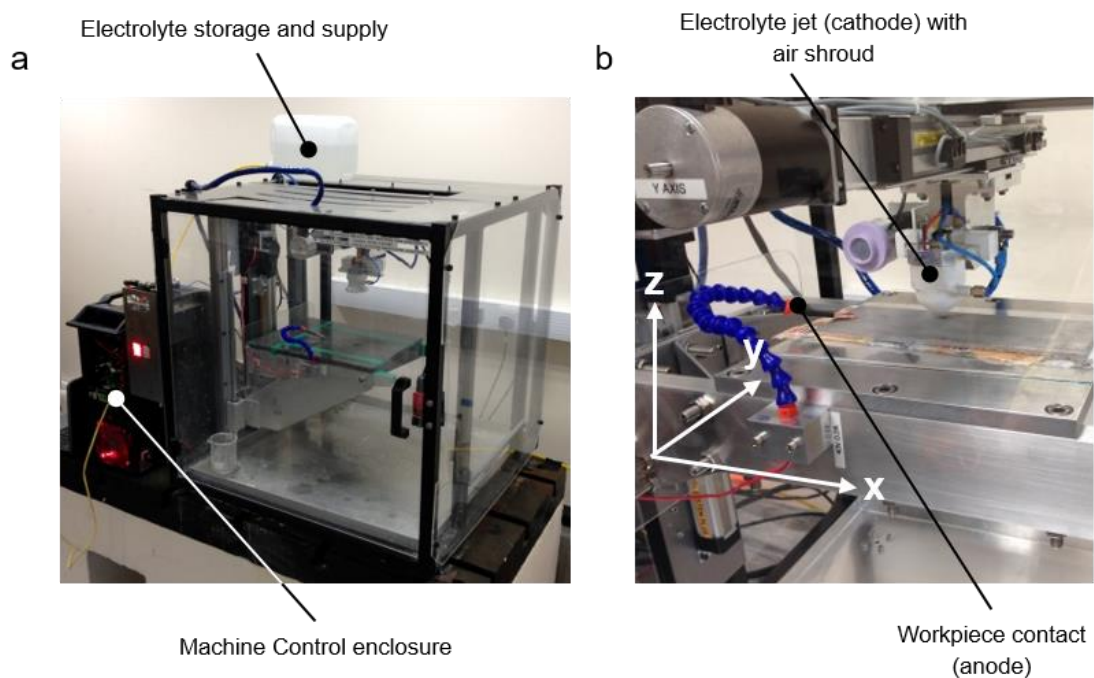


Figure 3.4: Images of the generation 1 platform (a) showing updates to the z-axis and platform (b) in original configuration showing the work area

In its initial form the platform was deemed unreliable demonstrating inadequate precision, poor performance and repeatability generated in the most part by sub-system sub-optimisation and errors generated through operator difficulties.

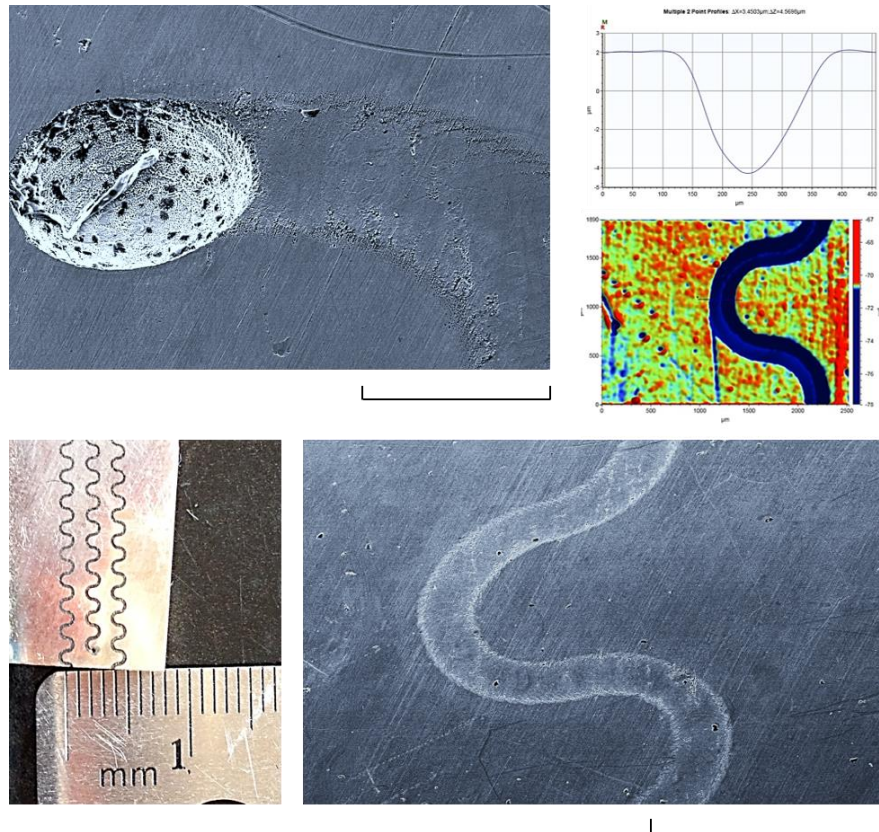


Figure 3.5: Early examples of machining utilising simplistic toolpaths affecting material removal including keyholing at the beginning of feature striations, low material removal due to poor power supply and control, unsymmetrical machining profile due to manufacturing issues and flow lines due to poor electrolyte supply and pump control. scale bars top left 250 μm and bottom right 1 mm

3.3. Generation 1.5 – Platform development

Issues were identified of the original platform of poor operation of the z axis, unstable machining table, poor parameter control, inefficiency of process (current leak down), insufficient power supply, unworkable datum setting method, poor safety systems, no machine or parameter characterisation, ineffective electrolyte

containment and capture, coating forming on nozzle during machining and ineffective air shroud.

The first two years of the project were then concerned with development of the machine tool to an interim stage, Gen. 1.5. Through addressing the identified concerns by redesign of the sub-systems (an example of this process is shown in Appendix 2) and developing platform hardware innovations flexibility, precision and repeatability were greatly improved.

Updates to the Gen. 1 platform to evolve into Gen. 1.5 are detailed fully in Appendix 3 but consist of:

- development of a nozzle touch sense system for ease of datum setting in x, y, and z directions,
- multiple electrolyte control,
- head development for increased precision, longevity, ease of operation and electrical isolation (Figure 3.6)
- Component upgrades including the PSU and electrolyte supply
- Machine architecture to incorporate higher safety standards and new innovations in hardware

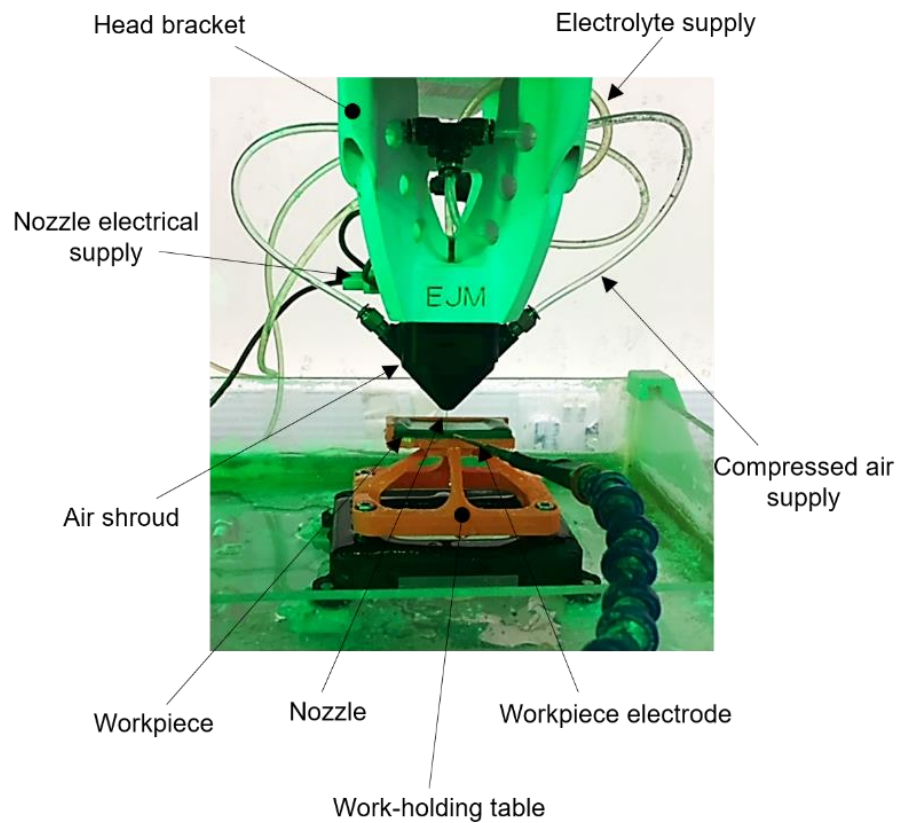


Figure 3.6: The machine head went through considerable development as part of Generation 1 platform development. Seen here machining surface textures for reduced wear the updated head bracket, shroud and work holding making extensive use of 3D printing techniques.

Through these improvements the final machine capabilities (Table 3.2) were improved enough to make a reliable research platform, although requiring an expert user, and form the basis for further research developments.

Work Envelope 200 x
200 x 150 mm, 3
Precision Micro-
stepping axis 1.25 μ m
resolution

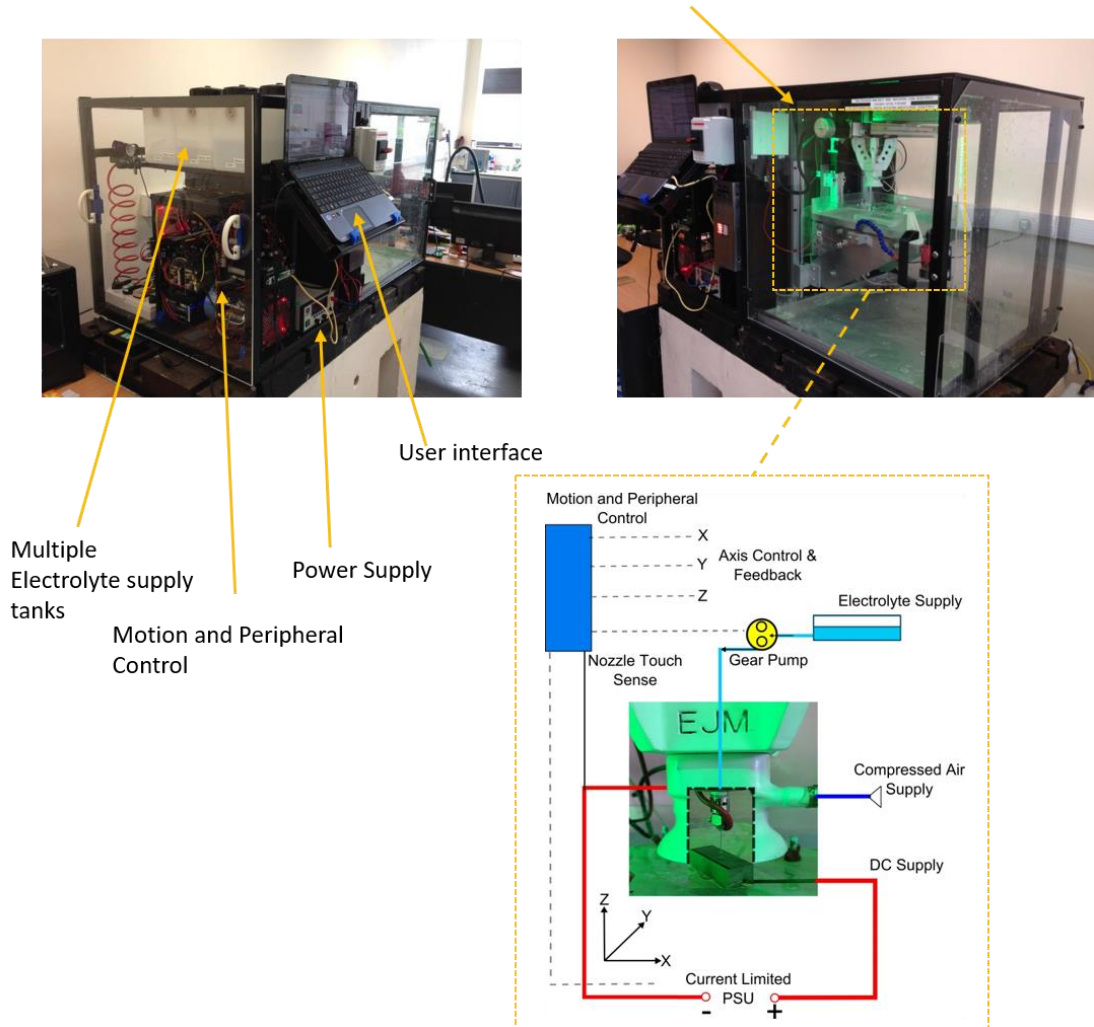


Figure 3.7: Generation 1.5 machine tool with upgrades 2015 /16

Table 3.2: Current capabilities as of 2016 for Generation 1.5 platform

Work envelope	200x200x100 mm (x, y, z)
Available pump flow	0.07 – 0.768 l/m (1 mm I.D. nozzle)
Available power	W (750 V, Amps)
Power increment resolution	10 mA
Nozzle traverse speed	0.01 – 100 mm/s
Nozzle positional resolution	1.25 μ m (x, y, z)
Nozzle positional accuracy	Poor (no feedback)
Nozzle positional Repeatability	Poor (no feedback)
Electrolyte Storage capability	2 x 12 Litres
Electrolyte waste capability	40 litres
Flush capability	12 litres manual / automatic
Electrode polarity	Interchangeable, manual switch
IEG setting capability	Programmable with manual isolation required
Axis capability	X and Y on overhead gantry, Z independent and required to move machining table leading to poor stability. 4 th axis available to drive orientation of A or C.
Operator Usability	Expert knowledge required, all systems required to be programmed, difficult housekeeping including fill and empty of electrolytes and several manual operations required.

3.4. Generation 2 machine tool

The generation 2 platform was designed to address the architecture, operational, and safety issues found as the Gen 1.5 platform was developed. It was also intended to incorporate into the machine design innovations developed on the Gen. 1.5 platform (Figure 3.8).

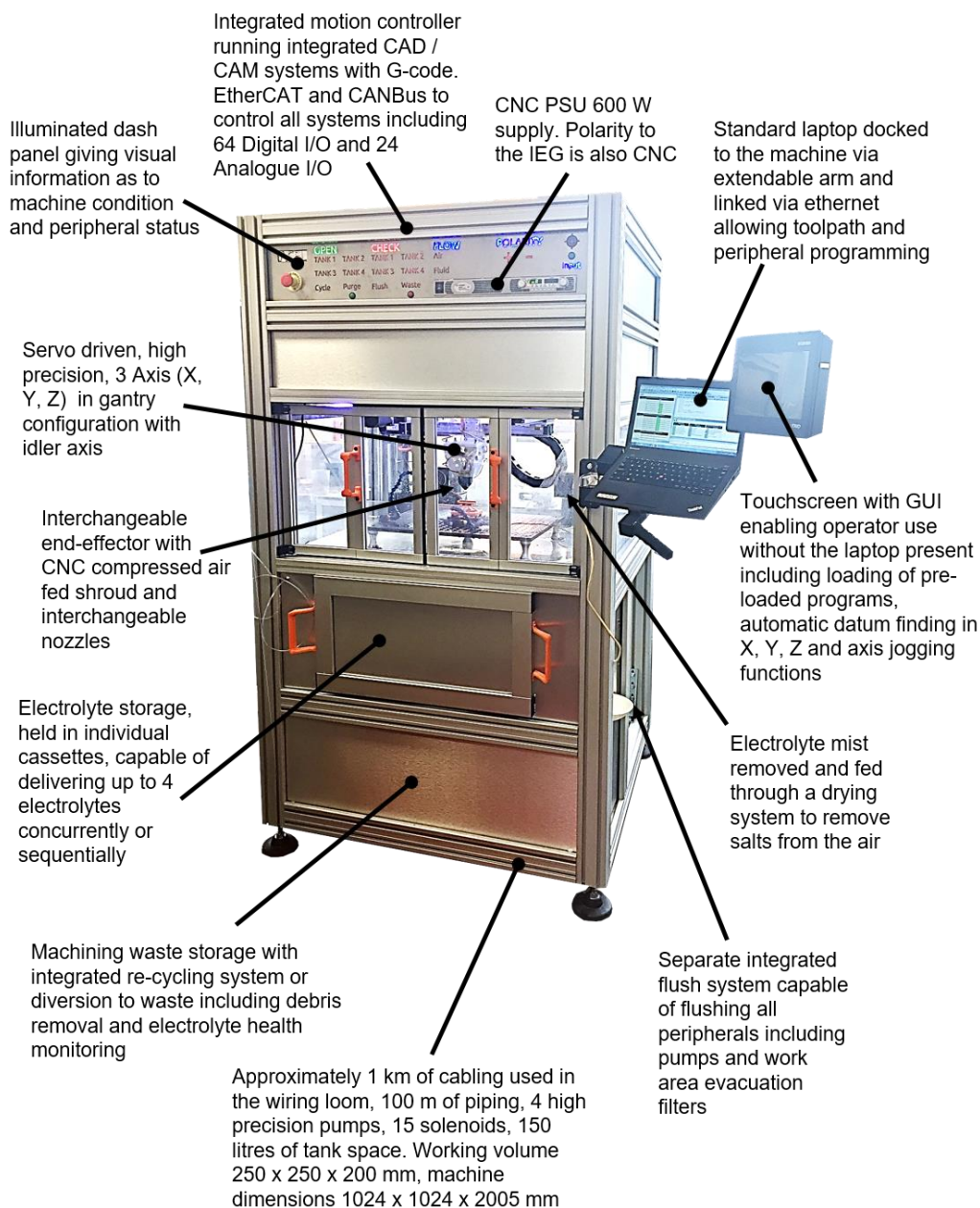


Figure 3.8: Generation 2 machine tool with some of the major developments highlighted (2017)

The generation 2 machine was intended to be more industrially focussed in its design approach and in fact incorporated a bottom-up design methodology (Figure 3.9). This allowed for a more iterative approach and optimisation of sub-systems that had already been defined on the previous generations thereby allowing integration into a single more complex system, function of the sub-systems and their integration defining form. Components that were already proven such as supply pumps and the configurations of sub-systems can be easily integrated.

This re-design of the machine tool was implemented to increase precision, reliability and repeatability of the process. To achieve this, each influencing factor of the process is monitored and controlled, including electrolyte supply and health, energy supply, jet characteristics and machine kinematics. In depth details of which are given in Appendix 4.

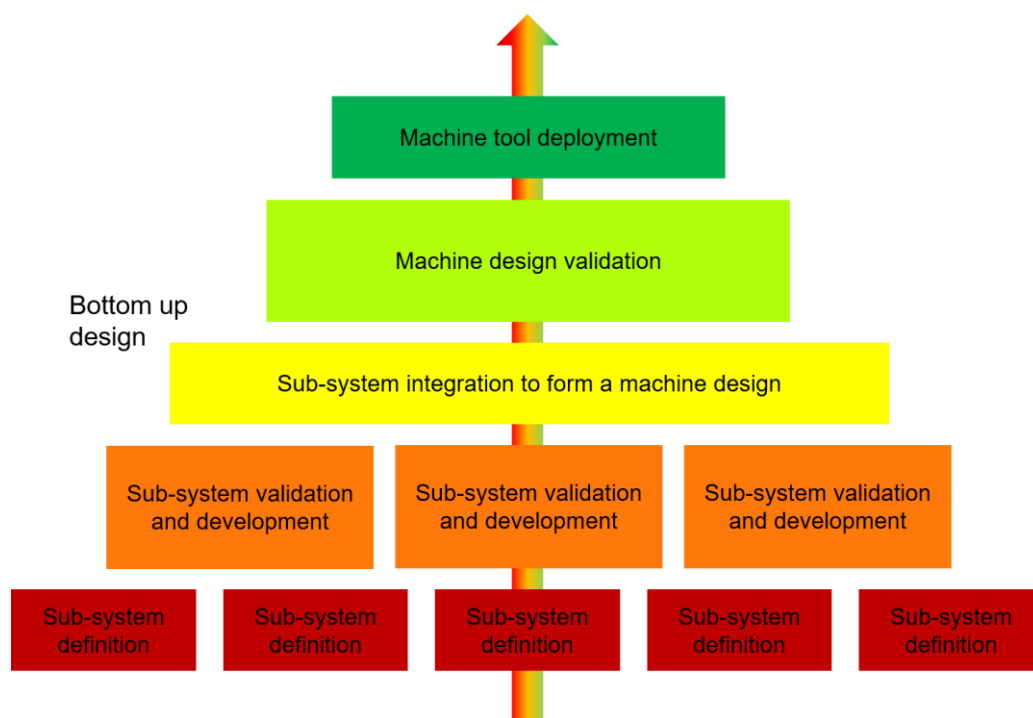


Figure 3.9: Bottom up design methodology employed in the design and realisation of the generation 2 platform

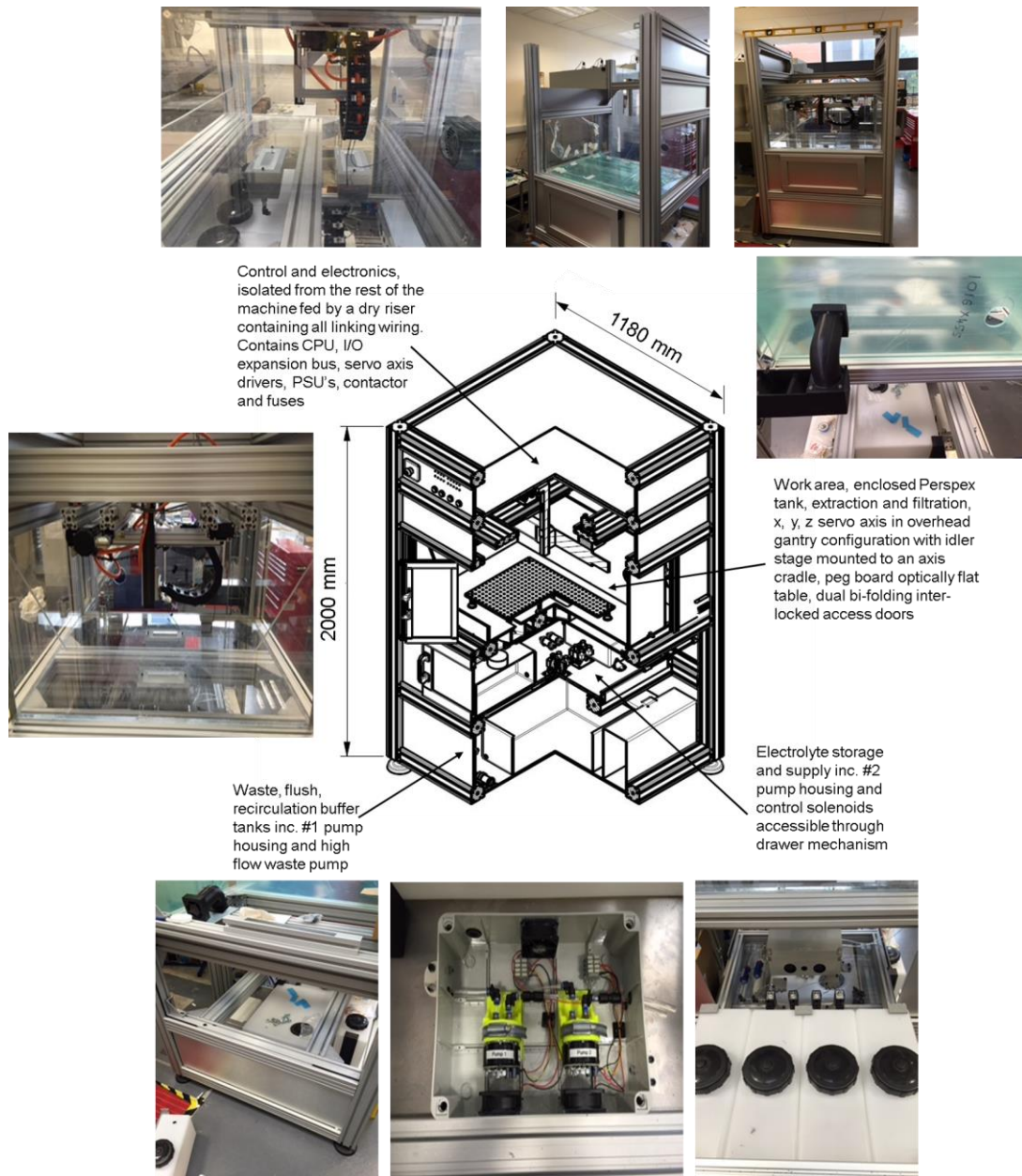


Figure 3.10: Sectioned general assembly drawing from the final generation 2 drawing pack, surrounded by images taken during the construction of the machine tool

With these overall improvements to the machine architecture (Sectioned final GA and images taken during manufacture shown in Figure 3.10) and systems control the generation 2 machine has now stepped away from a purely research platform.

Aimed as much at platform development as process development, to now a more user-friendly machine tool capable of high throughput, increased precision, and enhanced safety purely focussed on process and applications development.

3.5. Microscopy

3.5.1. Scanning Electron Microscope

Characterisation of the surface topographies created by EJM requires characterisation at the millimetre through to sub-micron scale often at an angle and with a need for a large depth of focus. Therefore, electron microscopy techniques are prevalent throughout this work as the depth of field exhibited by electron microscopy is much greater than that of optical microscopy. This allows a better view of the deterministic surface structuring alongside complex non-deterministic surface finishes. This is due to the depth of field becoming greater when the distance to the object is much larger than the diameter of the limiting aperture of the lens. Hence, for optical microscopes to achieve higher resolutions, larger lenses must be used and so the depth of field is typically poor. In electron microscopy, the limiting aperture lens must be made relatively small, and therefore the depth of field is relatively large. [255]

SEM uses electron energies typically between 10-40 kV to produce and detect two main types of electrons by a fine electron beam being rastered across the substrate surface. Secondary electrons (SE) originate from the surface / near-surface regions of the workpiece. They are the result of inelastic interactions between the primary electron beam generated from the standard tungsten filament of field emission gun (FEG) which when impinged on the surface causes

excitation of atoms of the surface and ejection of electrons from the atoms valence shell with some kinetic energy, the intensity of which is dependent on the surface morphology, chemistry and physical state. These electrons, termed secondary electrons are then detected by an Everhart-Thornley detector and through a photomultiplier displayed as a two-dimensional intensity distribution forming an image of the surface. Back-scattered electrons (BSE) are caused by reflection of the incident electrons generated from the electron gun, with atoms which are normal to their path, resulting in 180° scattering back of the electrons and form a contribution to the secondary image. Dedicated backscattered electron detectors are positioned are required above the sample in a ring type arrangement, concentric with the electron beam. BSE imaging is dependent on atomic number (heavy elements = high atomic number) which is characteristic of the elements in the imaged surface resulting in higher contrast for heavier elements. This provides greater contrast to topographic images than secondary electrons alone.

In this thesis SEM was performed using a FEI Quanta 650 ESEM (High vacuum mode), Philips XL30 SEM and Hitachi S-2000N equipped with back-scattered detector for qualitative compositional analysis all located at the University of Nottingham.

3.5.2. Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS) uses the X-ray spectrum emitted from a substrate when a focussed electron beam (in the same fashion as SEM) bombards the substrate surface with sufficient energy to generate X-rays enabling localised information about the substrate chemical composition. X-ray

detectors are often coupled to SEM due to sharing the same requirement of an electron beam. Through comparison with a software-based library (In this case Oxford instruments AztecEnergy and INCA on the FEI Quanta 650 and Philips XL30 SEM respectively) of the reflected line intensities in the x-ray spectrum to known composition calibration sample intensities. Elemental spectra can be developed as a point on a surface, line or through rastering the electron beam to create complete surface maps. This technique is used during this thesis in the characterisation of stock materials and identifying the dissolution mechanisms through tracking the changing elemental compositions of substrate surfaces under differing machining conditions.

3.6. Metrology

3.6.1. Focus variation

For assessments of surface topography generated during this thesis, focus variation microscopy (FVM) was used extensively to investigate the features generated allowing data to be extracted describing geometry of form and finish for analysis and surface reconstructions.

FVM is an optical technique with digital processing. A stack of images is acquired through a pre-defined Z direction range exceeding the scale limits of the feature to be measured with regards to the objective lens. For each pixel in an image from the stack a focus value, being the contrast of a pixel in relation to the neighbouring pixels, is defined. Thus, the more in focus the image is the higher the focus value. For each pixel a mathematical fitting procedure is applied to the focus values at each z-level and the detected z-coordinate of a pixel is

determined corresponding to the z-level with the highest focus value. Therefore, a complete image of the feature with all elements in focus can be assembled, through the feature z range using pixels from different z-levels corresponding to the z-level with the highest focus value of neighbouring pixels (Figure 3.11) [256, 257].

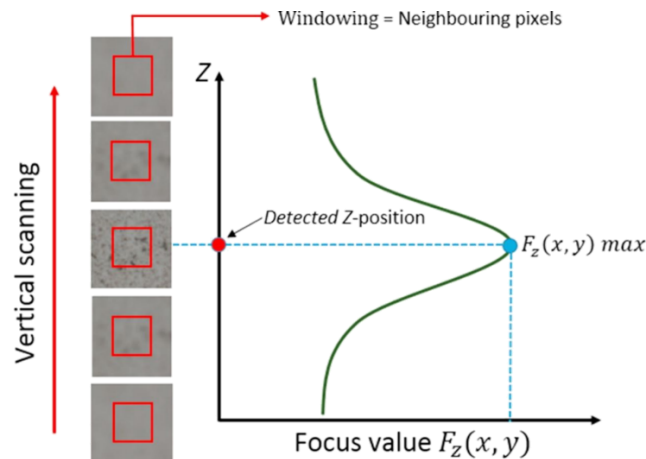


Figure 3.11: Working principle of focus variation microscopy [256]

Thus, FVM can exploit a small depth of field for enhanced detail and large vertical scanning paths to cover large features. Alongside this illumination is not limited to being coaxial therefore the measurement of steep surface flanks is possible beyond that of other measurement techniques [258]. This is especially useful in this thesis due to the multiple scale of features that are controllable by EJM and allows analysis of both form geometry and specific precision of features whilst considering surface finish which is the key thrust of this thesis. Throughout this thesis FVM analysis was carried out exclusively on an Alicona G5 infinite focus FVM with a vertical resolution of 10 nm and lateral resolution of 400 nm.

3.7. Analysis tools

3.7.1. ImageJ

ImageJ is a Java based imaging software originally developed for medical and biological applications [259]. Also referred to as Fiji (Fiji is Just ImageJ) which is the imageJ software with additional processing plugins [260]. It is an open source image manipulation software capable of reading and writing common image data and carrying out operations on individual pixels, image regions, whole images or stacks of images creating a volume. It is capable of carrying out convolution, edge detection, Fourier transforms, histograms and statistical particle analysis, sophisticated editing and colour manipulation including dilation and erosion. In this body of work the main use were visualisation operations. Through using SEM images and thresholding the hue saturation value (HSV) [261] found between different features on a surface the surface area coverage or size of these individual features can be calculated by the program once an appropriate scale has been configured.

3.7.2. DigitalSurf MountainsMap

MountainsMap is a surface analysis software used in conjunction with both SEM (section 3.5.1) and FVM (section 3.6.1) outputs. It is used extensively throughout this thesis for analysis of data produced in order to measure features in surface topography of large scale form and small surface finish to generate quantitative data. The software was also used to generate qualitative data via real-time imaging of surface topography and allow colour overlays to highlight surface features and geometrics. Alongside this 3D reconstructions of surface

topography of multi-focus stacking images can be created. The software allows analysis of surface texture and roughness in accordance to ISO and national standards allowing the correct filtering to be applied (see section 3.8) such as cut-off values for surface roughness.

3.8. Validation Metrics

To ascertain if the key process indicators (KPI) of increased precision and process flexibility are met it is necessary to use a set of metrics to evaluate the measurable effects of innovations made within this body of work. These effects can be assessed across two separate length scales, form and finish. There are any number of standardised metrics (the ones used throughout this study are defined here) which can be used to evaluate the changes in surface finish typical at length scales less than 5 μm . However, with the larger length scale of form it requires the definition of new spatial metrics beyond simply depth and width that address the KPI that are to be achieved. These metrics should allow for repeatable comparison between resulting features. Thus, are proposed as a useful method around which evaluation of independent geometrical features of the resultant feature can be made therefore easily identifying enhancements made through innovation.

3.8.1. Metrics to describe macro-scale features (form)

To be able to assess the impact of variations process parameters and hardware developments several metrics to define the geometrical shape and surface finish of any machined features can be applied. When considering the response profile, geometrical analysis of the profile data through the DigitalSurf Mountains

software (see previous section) can be carried out to obtain basic information about the response profile (Figure 3.12).

- Depth of cut or height of deposition (D), defined as the distance from the substrate surface to the peak maxima of the material removed or deposited in the z direction.
- Dissolution or deposition kerf (K), defined as the maximum width of the dissolution effected region at the substrate surface. Recognised by deviation in the Z coordinate when translating in the X coordinate either in the positive Z direction in deposition mode or negative in subtractive mode from the mean substrate surface level facing the jet. This is easily recognisable in optical images due to the change in surface texture from the substrate surface (Figure 3.12b), but can be difficult with small removal volumes in profile analysis so care must be taken to identify the correct areas through 3D reconstructions and ensuring the sample is prepared to a level of flatness before machining.

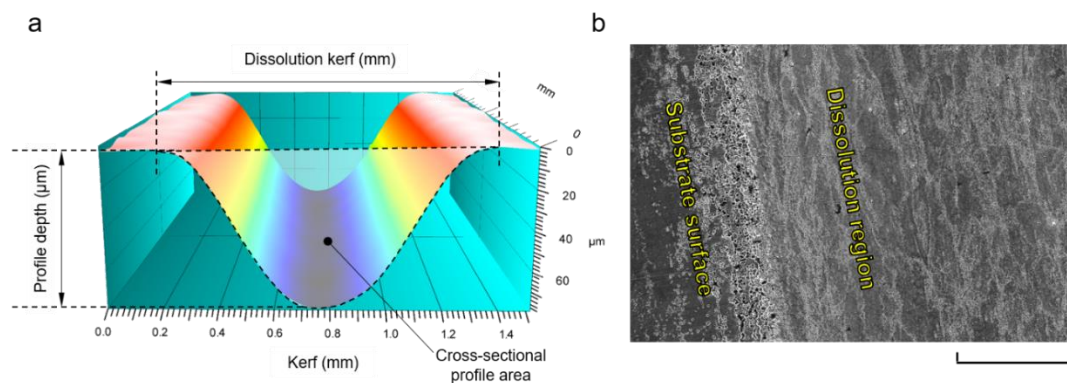


Figure 3.12: (a) Definition of basic geometrical metrics of depth, dissolution kerf and cross-sectional area (b) SEM image showing the transition from un-machined substrate surface into the dissolution region easily identifiable in microscopy. Scale bar 500 μm

As this process is essentially carried out manually in the software this can also introduce a level of human error into the measurement. Random error does not affect the mean value only the variability around the mean value, therefore a large sample set should be used across each striation to enable averaging reducing deviation due random error.

- Cross-sectional profile area (*CPA*) defined as the area of material removed or deposited when taken as a cross-section perpendicular through the feature. This is an automated process carried out through the analysis software. Through selection of the correct method the software calculates the area based on a theoretical filling of the profile to a water line at the top or base of the feature. In subtractive mode this corresponds to the dissolution kerf.

More complex metrics are used to describe specific features of a resultant profile geometry. These are used when identifying process improvements pertaining to increases in taper, precision and undercut.

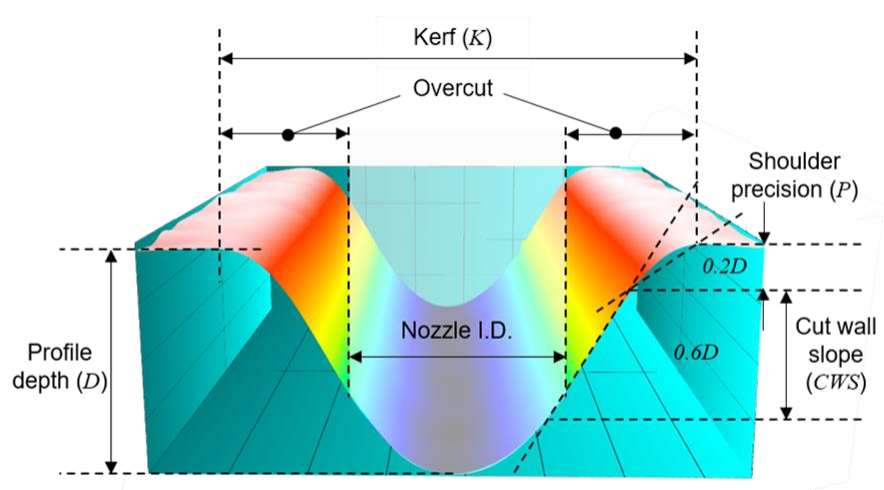


Figure 3.13: Schematic to show the definition of more specific metrics used in this study (a) the definition of undercut (b) definition of sidewall slope across the middle 60% of total depth and (c) the definition of precision using the top 20% of the total depth.

- Total overcut (Figure 3.13) is defined as the remaining area of the removed profile on both sides of the resultant feature. This is achieved by removing the idealised profile, being the area removed directly below the nozzle, the width corresponding to the nozzle I.D., for the full depth or height of the resultant feature. Minimising overcut is also seen as advantageous within the process as not only does this demonstrate an increase in fidelity of the response profile to that expected, but also makes the process more easily implemented into component design for manufacture.
- Cut wall slope (CWS), (Figure 3.13) is defined in this case as the gradient of the side wall in rise over run format. Side wall slope was extracted from the bulk of the edge ignoring both the radius at the top (top 20% of the total depth) and bottom of the wall (bottom 20% of the total depth) pertaining to the 60% about the middle of the maxima depth of the profile. This is analogous to the taper defined in machining processes and allows comparison between the profiles that are created, greater slope giving a more uniform squarer cross section and a lower slope value giving a more triangulated profile.
- Feature shoulder precision (P) (Figure 3.13) is defined as the slope of the side wall taken to a depth of 20% of the total depth from the top substrate surface. This allows comparison of the individual innovations ability to influence low current areas. The greater the slope, the greater the precision, as the un-wanted rounding effects on the shoulder of the cut are minimised and this therefore reflects on the overall kerf dissolution in comparison to the nozzle I.D.

3.8.2. Metrics to describe micro-scale features (finish)

Alongside geometrical information about the surface features created through EJM it is also necessary to consider the finish that can be achieved. Not only on the features themselves as a by-product of the machining process but, as will be demonstrated later, the creation of non-deterministic microscale surface textures that can be regarded as a surface finish and cannot be easily quantified through the aforementioned metrics due to their complexity. The type of measurement metrics used in this thesis can be divided into 2D profile measurements and 3D areal measurements. 2D Profile measurements are used in the assessing the topography inside cut machine channels and deposited features where extracting surface information can be difficult to acquire and analyse with confidence due to the restriction caused by the feature geometry. Where possible 3D areal parameters were used especially when assessing large area surface texturing due to their ability to more accurately describe not only the complete topography but the functionality of the surface [262]. In the first instance the simplest quantification of a surface textural quality is the definition of the roughness of the surface. Considering a 2D profile approach the standard used throughout this thesis is the roughness arithmetical mean deviation (Ra) (Equation 7):

$$Ra = \frac{1}{l} \int_0^l |z(x)| dx$$

Equation 7

Described as the arithmetical mean of the absolute ordinate values in z co-ordinate at discrete points (x) within a sampling length, l , by taking the mean amplitude [263].

Throughout all analysis, filtration and evaluation is carried out in line with ISO 4288:1996. In comparison roughness calculated using arithmetic mean height within a defined sampling patch (S_a) generates a less subjective roughness value by definition of a much greater sample size accounting for a much greater amount of the topography. S_a is used wherever possible for a general descriptor of surface finish quality, low S_a equalling a smoother surface (Equation 8) [264].

$$S_a = \frac{1}{A} \iint_A |z(x, y)| dx dy \quad \text{Equation 8}$$

Described as the arithmetical mean of a surface by taking the absolute ordinate values in z co-ordinate at discrete points (x, y) within a sample patch, A , by taking the mean amplitude.

However, roughness parameters do not describe anything about the spatial frequency of the irregularities, patterns or shape of the surface topography. Further quantitative information can be attained to help characterise the type of surface that had been created. A number of parameters to define the surfaces created were chosen from those defined in ISO 25178 3D [265] including height parameters of Skewness (S_{sk}) Kurtosis (S_{ku}) (Figure 3.14) used to describe the geometry, symmetry and randomness of the surface and volume parameters relating to the areal material ratio curve (bearing area curve) which is established by evaluating material ratio (mr) (Figure 3.15) at various levels between 0% being the highest point on the surface to 100% which represents the lowest point on the surface within the evaluated area.

The most commonly used parameters throughout the analysis in this thesis are defined as [266].

- Skewness (S_{sk}) – This demonstrates the profile symmetry about the mean value of the heights within the sample (mean plane). For a surface with a random (or Gaussian) height distribution that is symmetrical about the mean, the Skewness is zero, if the bulk is above the mean it will be indicates the predominance of peaks or below the predominance of valley structures.
- Kurtosis (S_{ku}) – Demonstrates the spread of the height distribution of the texture. An ideal or Gaussian distribution has a value of 3. Below 3 shows a bumpy surface whereas above shows a spiky surface with high peaks. Further away from the ideal value shows a greater localisation or grouping of features rather than a uniform distribution.

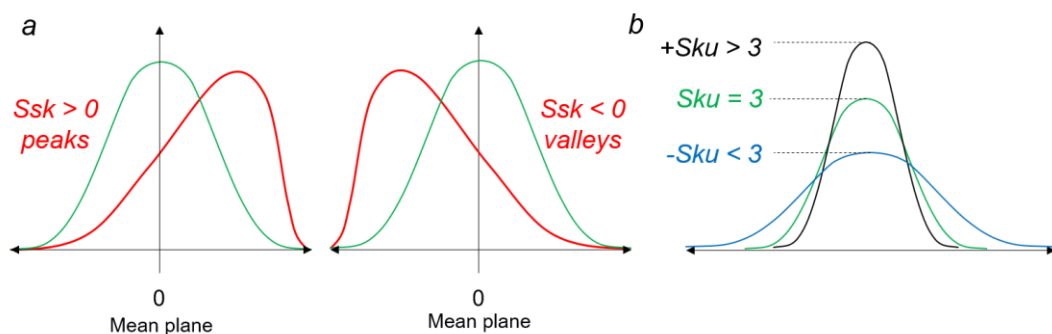


Figure 3.14: Schematic representation of topography distributions relating to (a) skewness and (b) Kurtosis

- Peak Material Volume (V_{mp}) – Volume of material calculated within the peak set at 10%
- Dales Void Volume (V_{vv}) – Volume of fluid retention in the deepest valleys of the surface set at 80%
- Core void volume (V_{vc}) / Core Material Volume (V_{mc}) - These describe the void volume and material volume respectively at the bulk of the

material avoiding the highest peaks and deepest voids between mr1 and mr2 set as 10% and 80% respectively

These metrics along with the roughness values allow the level of definition of surfaces required for this work in for the comparison of different surfaces created by parameter and process variation. Although there are a great many other parameters available to describe surface topography, this is not the main thrust of this work. The parameters selected are intended to give the reader an overview of the changes in surface texture and a descriptive value of possible functionality using bearing areal ratio curve diagrams. Further reading on 2D and 3D texture parameter definition and derivation can be found in the works of Leach [2013] [262], Blateyron [2013] [264] and Waterworth [2006] [267], alongside the “good practice guides” produced by the National Physical Laboratory. All of which have been fundamental in the authors understanding of this area.

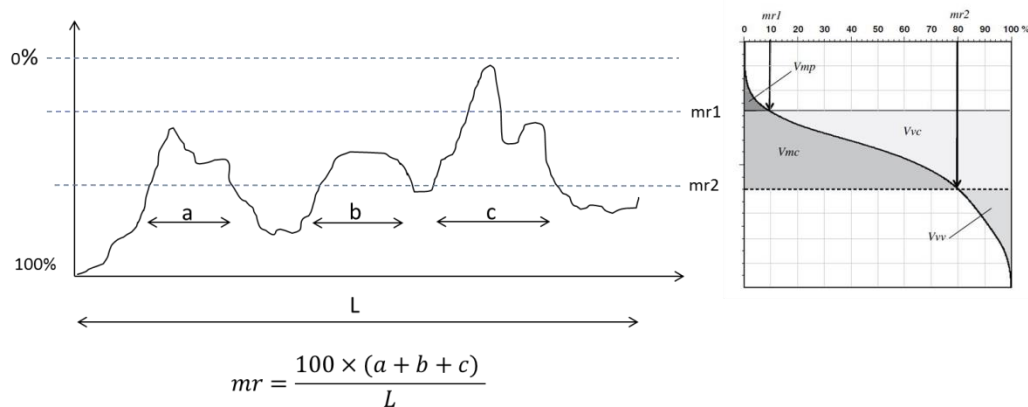


Figure 3.15: Surface defined by Material ratio (mr) and Bearing curve relating to the v-parameters

3.8.3. Standard deviation

When numerical data from a metric is presented this is accompanied with the standard deviation presented as either a percentage or numerical value dependant on which is more relevant in that case. Standard deviation (σ) throughout this thesis represents the standard deviation of the population about the mean value represented by Equation 9:

$$\sigma = \sqrt{\frac{\sum(x-\mu)^2}{N}}$$

Equation 9

Where x is the sample measurement, μ is the mean and N the population. This informs the reader as to the expected variation of the process in generating that feature. Thus, assumptions can be made especially when considering performance improvements, whether the improvement is repeatable and if it is even an improvement at all over the baseline presented. When errors bars are presented in graphs this also uses the same method. If error bars overlap between two separate measured points, it is indeterminate whether there is any difference in the two measurements in X number of repeats. When the standard deviation is presented as a percentage this is calculated as per Equation 10:

$$\sigma\% = \frac{\sigma}{\mu} \times 100$$

Equation 10

When the standard deviation is less than 1% of the mean this considered to be within the error of measurement so specific values are not reported.

4. Parameter influence on the machining of high value alloys

4.1. Introduction

From the review of the available literature (see section 2.3.6) it was clear that although some investigations had been carried out into specific materials, namely steels (including stainless), cemented carbides and MMC's, and to a degree Titanium (Ti-10V-2Fe-3Al), materials appropriate to the applications where EJM would find natural applications in low-volume, high-value industries (aerospace, biomedical, automotive and tooling) have yet to be thoroughly researched as being appropriate for EJM.

Nickel superalloys were identified in Chapter 2 as being valuable to the intended high-value-add markets that the process traits of EJM are suited to. Currently the understanding of material response of Ni-superalloy is underdeveloped having only been used as a process demonstration. Inconel 718 (In718) is a commonly used Ni-superalloy favoured in high value industries of aerospace, power generation (nuclear and gas turbines) and the automotive industry [268]. However, it is known to be inefficient to process by shear based and thermal based processes due to the material properties as outlined in the review of the literature (section 2.3.6).

In718 is considered a complex alloy consisting of 16 separate elements (see Table 4.1 for full material composition) and therefore a high degree of variation in the ECE throughout the alloy. In718 is described as a precipitate hardened nickel-based alloy consisting of dual phases alloy γ and γ' . Designed to be strengthened

by the γ' phase including Al, Ti, Nb and Ta elements, the γ phase forming the nickel matrix. The large Niobium carbide precipitates at the grain boundaries (δ phase) obvious in the centre of Figure 4.1a and identified through EDS (Figure 4.1d), are used to control grain size during heat treatment and thermomechanical processing and also serve to enhance some of the mechanical properties.

As discussed in section 2.7, material physical properties do not influence machinability by EJM. Thus, In718 provides an excellent demonstration of the advantages of EJM over conventional techniques when creating micro-machined surface geometry (outlined as one of the primary application areas for EJP in subtractive mode in section 2.7.). It is necessary for a thorough material response analysis to be carried out to form a benchmark by which other developments throughout this thesis can be assessed. This will identify ideal processing parameters along with difficulties and allow characterisation of material response allowing appropriate solutions to be formed and improvements to be quantified in the following chapters.

Alongside In718, to compare and contrast the dissolution mechanisms and machining performance of In718 and to demonstrate a wider capability of EJM, a further relevant material was used for comparison. This would usually be achieved through literature review however, in the case of EJM there is little published data of EJM on application relevant materials. Thus, to understand the capability of electrolytic jet methods in processing In718 requires the processing of a further comparison material.

Titanium, in this case grade 5 or Ti-6Al-4V (see Table 4.2 for composition), is another important material, due to its high strength to weight ratios, excellent

biocompatibility and high corrosion resistance [269] making it ideal for high value applications in aerospace and for biomedical application, specifically skeletal implants [270, 271]. Titanium grade 5 is a two-phase material, described as an alpha-beta alloy containing both an alpha stabiliser and beta stabiliser, in this case aluminium and vanadium respectively. Table 4.2 demonstrates it as a simpler alloy in comparison to In718, containing eight elements. The majority alloy being pure titanium ($\approx 90\%$). Therefore, reaction to dissolution will be more likely to be defined by the properties of the pure base element when compared to In718 (nickel content $\approx 50\%$). Titanium demonstrates an ECE of 0.4468 g/Ah when compared to nickel of 1.09 g/Ah. When the ECE is calculated across all elements (taking note of Equation 3) using Equation 11,

$$ECE = \sum \%_1 \cdot \frac{A_1}{z_1 \cdot F} + \%_2 \cdot \frac{A_2}{z_2 \cdot F} \dots\dots\dots + \%_n \cdot \frac{A_n}{z_n \cdot F} \quad \text{Equation 11}$$

the ECE only reduces to 1.067 g/Ah. Therefore, In718 should demonstrate a much higher MRR in process than Ti-6Al-4V, identified in section 2.3.6 as having received some prior research interest. The dissolution mechanisms of titanium are understood and the difficulties in processing this material with passivating electrolytes have been identified. However there has been minimal directed research as to its overall machining performance in relation to EJM parameters and comparison to other materials.

The material machining capability of EJM is reliant on several basic process parameters each with its own influence on the processability of materials as defined in section 2.3:

- Electrolyte composition
- Material composition and pre-condition

- Current Density
- Nozzle traverse speed
- Stand-off of the nozzle tip to workpiece - IEG
- Electrolyte flow rate / jet speed

However, as outlined in section 2.3 the primary factor is the energy density developed at the workpiece surface of which current density (J), nozzle traverse speed (v_{noz}), Nozzle tip stand-off (IEG) and electrolyte jet speed (v_{jet}) (calculated by flow rate with a specific nozzle I.D.) all have an influence over the available dissolution energy. These are all machine tool relevant and defined as a requirement in section 3.1 to be fully flexible and controllable as part of the machine control architecture. Material composition is not varied as this body of work is concerned with the fundamental dynamic processing conditions whereby the material can be set as a benchmark condition to assess parameter changes. However, pre-condition is considered pertaining to the passivation effect in titanium and the general effect of surface oxides on machining performance. These two areas are however under further investigation within the immediate research team utilising the same research platform designed for this work [272, 273].

In the first instance preliminary machining trials are carried out utilising parameter ranges found in the literature to establish the effect of the four-main machine controllable parameters on the depth and width of the striations. From this the main contributing parameter/s can be used to carry-out an in-depth analysis of the dissolution effect of EJM on In718 and Ti grade 5.

4.2. Methodology

20 x 20 mm samples of In718 and Ti grade 5 were water-jet cut from rolled plate, composition shown in Table 4.1 and Table 4.2 respectively. Unless stated otherwise, these samples were ground and polished to 1 μ m surface finish (R_a). The In718 structure and distribution of the elements can be seen in Figure 4.1. A characterisation by EDS and SEM of the base metal was carried out to ascertain a control not only for the elements but also the un-machined microstructure to allow comparison to experimental findings.

Table 4.1: Nominal material composition of nickel -super-alloy Inconel 718

In 718	A	B	C	Cr	Co	Cu	Fe	Mn	Mo	Ni	Nb	P	Si	S	Ta	Ti
Weight %	0.2 - 0.8	0.006	0.08	17 - 21	1	0.3	17	0.35	2.8 - 3.3	50 - 55	4.75 - 5.5	0.015	0.35	0.015	0.05	0.65 - 1.15

All test samples were machined with simple striations across a workpiece with a pre-determined NC program repeated in every case with five repeats of any parameter change proposed. Electrolyte composition in this chapter is confined to the two commonly used electrolytes of NaNO_3 and NaCl as identified in section 2.4 with a constant concentration of 2.3 M in both cases.

Results were then analysed for geometric and surface information as described in section 3.

Table 4.2: Nominal material composition of titanium grade 5

Ti 6Al-4V	Al	C	Fe	H	N	O	Ti	V
Wt. %	5.5 – 6.75	0.08	0.4	0.015	0.05	0.2	87.73 - 91	3.5 – 4.5

4.3. Preliminary investigation – Identifying parameter effect

A simplistic initial investigation was carried out to determine the trends pertaining to the level of influence of these parameters on the depth and width of the machined striation (Figure 4.2). Using a 0.25 mm I.D. nozzle the four parameters were varied across the generation 1.5 machine parameters (see section 3.1) machined into In718. Where a parameter was varied the others remained constant: supplied current = 0.15 A, $IEG = 0.5$ mm $v_{noz} = 1$ mm/s and $v_{jet} = 20$ m/s. These parameters being established from review of the literature.

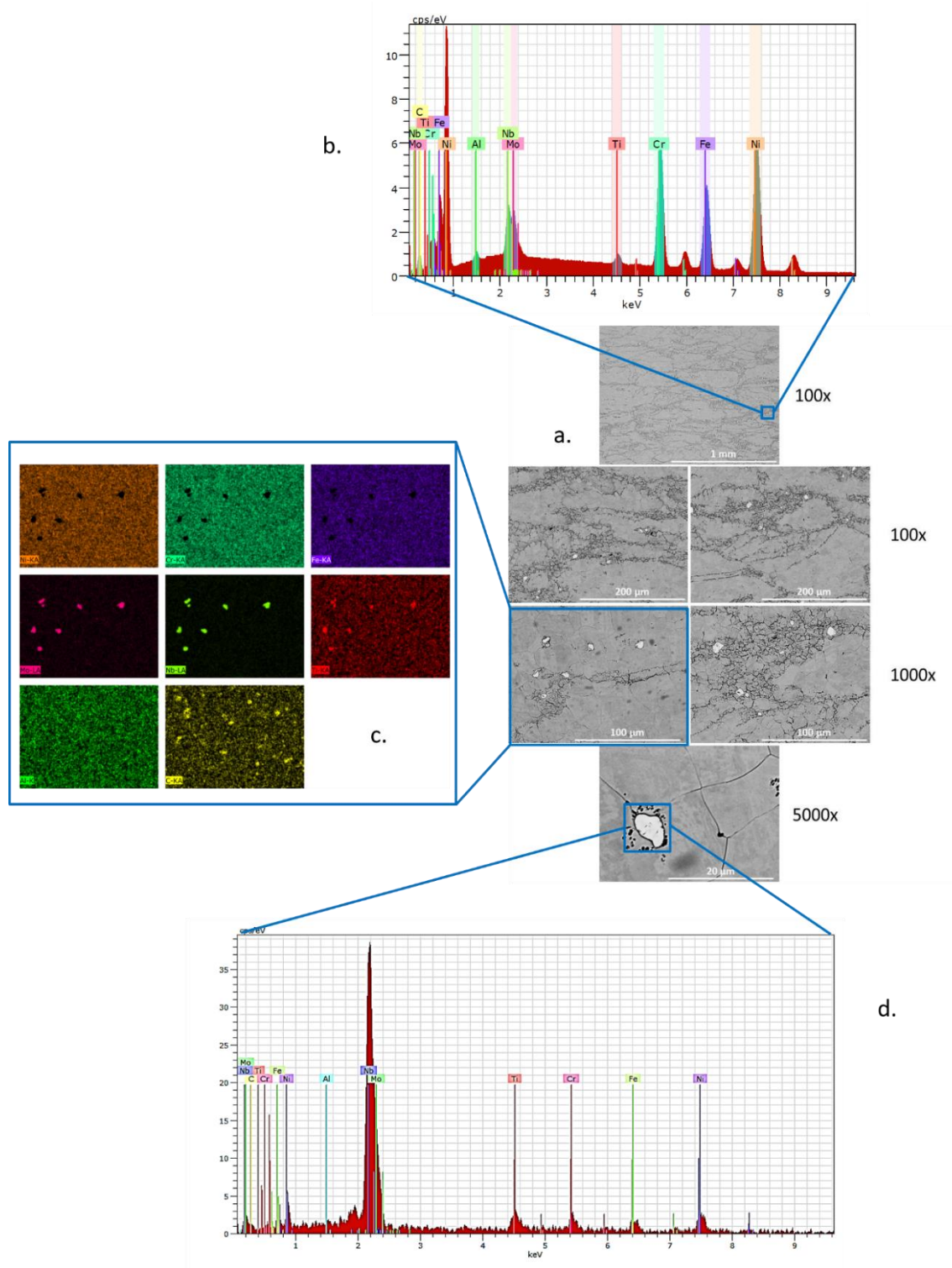


Figure 4.1: Composition of Inconel 718 (a) SEM images of etched Inconel substrate at varying magnifications, the niobium precipitates can clearly be seen at the grain boundaries (b) EDS surface scan of the Inconel substrate showing the chemical composition prior to any machining (c) EDS elemental map of the un-machined surface showing the distribution of the constitute elements (d) EDS point analysis confirming the presence of a Niobium precipitate phase.

Observed in Figure 4.2, nozzle traverse speed and *IEG* supply current have opposing effects as they increase in-line with what has been reported in other energy beam processes. As the traverse speed of the nozzle is decreased, with a constant supplied current, the greater the depth and width (increased material removal) occurs due to the increasing interaction time at a discrete point (dwell). At these slow speeds excessive machining of the side-walls occurs showing the same pattern found when a spot is continually machined without movement over increased time [70]. At slow speeds, poor edge definition occurred accompanied by arcing outside the *IEG* possibly due to high material removal and limited flushing causing debris to collect in the *IEG*. In comparison, as supplied current is increased so material removal increases. Again, as supplied current increases the width also increases as the distance to the base of the cut becomes large therefore preferential machining starts to take place at the side walls, demonstrating the self-limiting nature of EJP. Considering Figure 4.2c and d in variation of the size of the *IEG* and flow-rate little difference is seen over the capabilities of the generation 1.5 platform, which is different to those found in alternative energy beam processes. In the case of variance of the *IEG*, this directly relates to the variation of resistance (as noted in section 2.3.4). Therefore, because the electrode potential is allowed to float this will overcome any changes relating to increased *IEG* by simply allowing the potential to increase, thus compensating for the increased resistance to maintain the ratio defined by Equation 4. This will continue to the limit of the PSU. Increasing flow-rate to the nozzle also appears to have a limited effect within this range, and in these circumstances, on the geometry of the striation. This is because the dominant

mechanism of material removal in EJM is controlled corrosion not erosion. These findings are supported by review of the literature in Chapter 2.

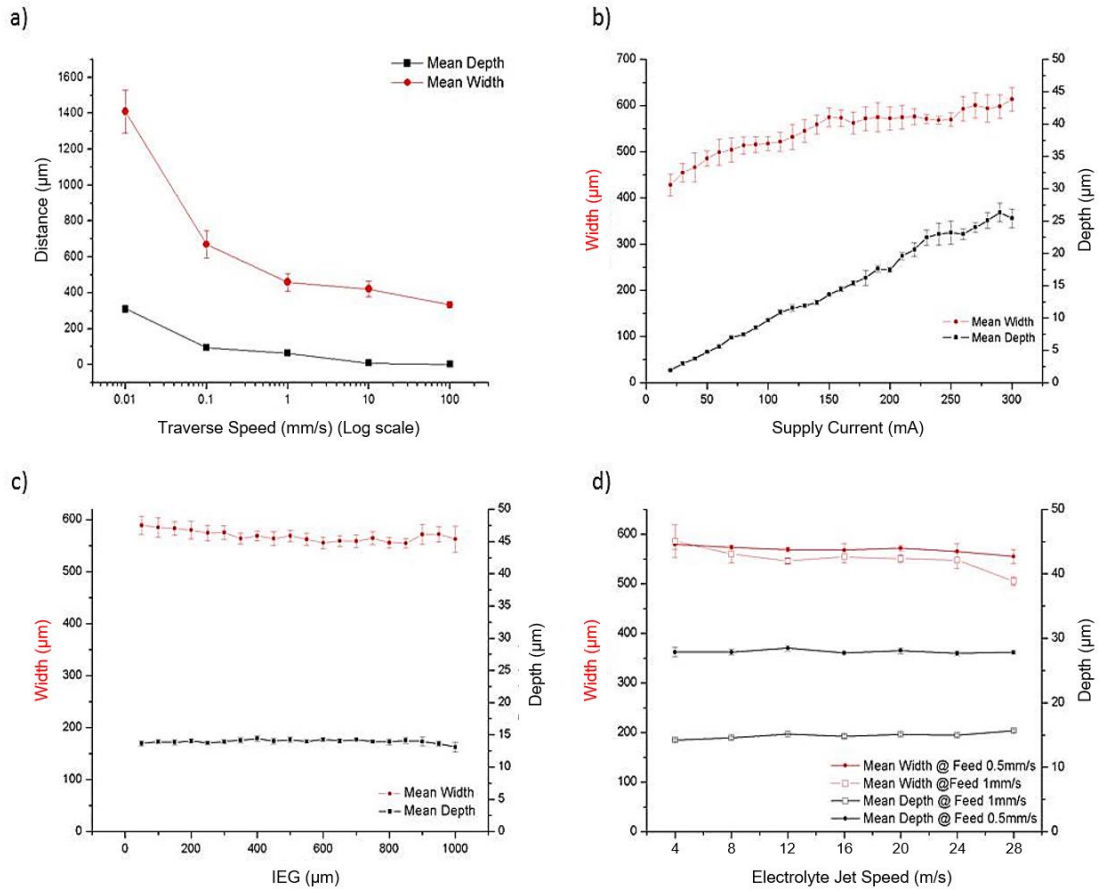


Figure 4.2: Preliminary investigation into the geometric influence of parameter variation when machining Inconel 718 across the capability of the generation 1 platform (a) nozzle traverse speed (b) supplied current to the IEG (c) nozzle tip stand-off from the workpiece surface and (d) electrolyte jet speed as measured at the nozzle tip

In order to study the dissolution effect of changing energy in the chosen material and carry out a comparison to an alternative material, it was decided to limit the variation to the main influencing factor to the “as supplied mean current density” (J):

$$J = \frac{I}{A} = \frac{k_e V}{h}$$

(Fully described in Equation 1) and keep all other parameters as a constant.

Utilising the findings from the preliminary investigation, the effects of the J variation are investigated and discussed. This is carried out by variation of the supplied current (whilst the electrical potential is allowed to float) within the limits of machine capability (see section 3.1). This allows for an identification of an appropriate process window, as changes in traverse speed and IEG can be substituted for changes in applied current. Further to this it serves to identify additional issues concerning the processing of materials and where improvements can be made in methodology to improve material response.

All parameters were maintained as a constant of: V_{noz} (0.5 mm/s), V_{jet} (16 m/s), and IEG (0.5 mm), but with varying current for individual lines (Figure 4.3) between 1 A/cm² and 700 A/cm². Although the platform has the capability to go beyond this, because of the instability of machining with arcs and flash-over it was deemed unnecessary to continue beyond this value.

4.4. Material response to energy variation

Initial investigations were carried out to ascertain the influence of varying current density on surface finish and therefore define the dissolution mechanism. Due to the complex nature and distribution (Figure 4.1) of the alloying elements, each displaying varying ECE, this leads to an increased sensitivity to the energy seen at the surface. Therefore Inconel 718 processed by EJM exhibits a high variation in surface finish.

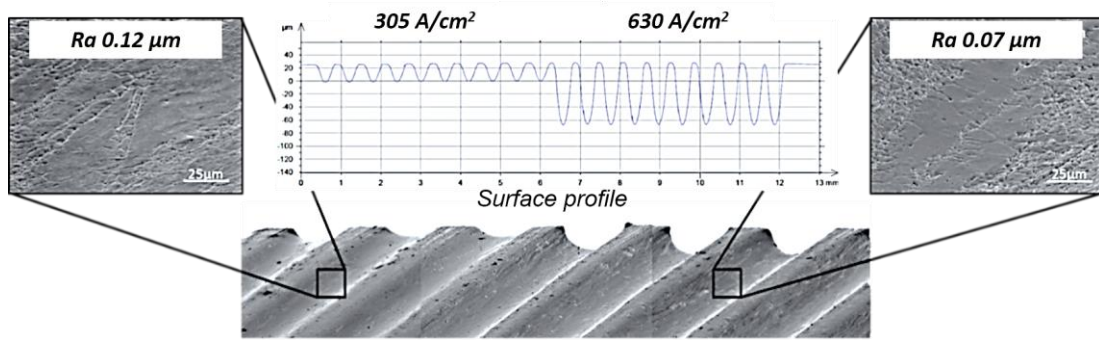


Figure 4.3: sample striations machined in Inconel 718 created to assess geometry and surface finish at varying current densities

It can be observed in Figure 4.3 and Figure 4.4 that the resultant machined profile mimics that of the expected Gaussian current density profile. This profile is consistent throughout features machined by EJP. As noted in the literature review this can be seen as a limiting factor in EJP when compared to competing processes which have gone some way to address this.

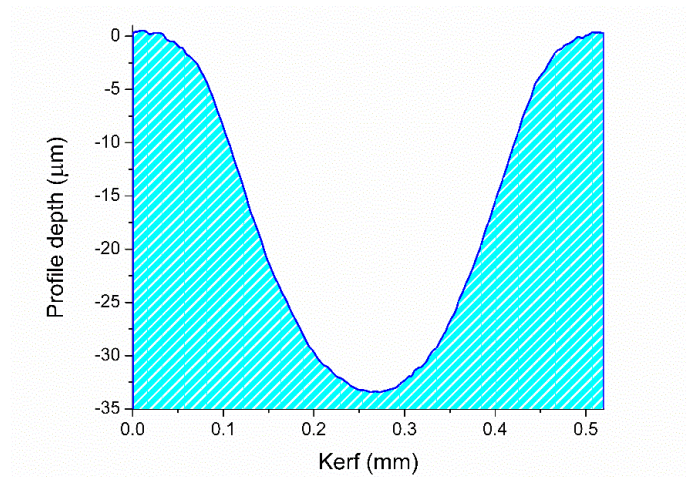


Figure 4.4: Resultant machined profile using a 0.25 mm I.D. nozzle with 2.3 M NaNO_3

Analysis of the cut face reveals that by varying the applied current, a variance in the surface finish can be achieved. This gives a measurable difference in the surface topography due to the changing influence on the material elements.

Through varying J , the resultant surface topography can be seen to be non-deterministic, however there are obvious dissolution state changes that allow the surfaces to be grouped quantitatively and qualitatively.

From Figure 4.5 the changes in surface topography as current density increases can be visualised. Considering *regime 1* as the lowest current density range, the machining mechanism has less reliance on the material composition and more on the processes ability to breakdown the anodic film allowing dissolution to begin [18]. Comparing regime 1 to Figure 4.1 and images in *regime 4* that fully reveal the grain structure, the dissolution pattern bears little resemblance, this has also been observed in other materials [54]. Surface dissolution is highly localised, only occurring at certain points where the potential gradient is peaking, allowing breakdown of the anodic film. Demonstrating, at this low J , dissolution is not equal across the area of jet impingement. From the 1 A/cm^2 image the work-piece surface is still visible as the flat grey areas. These low J striations are observed to be shallow and demonstrate a non-continuous kerf until $>10 \text{ A/cm}^2$.

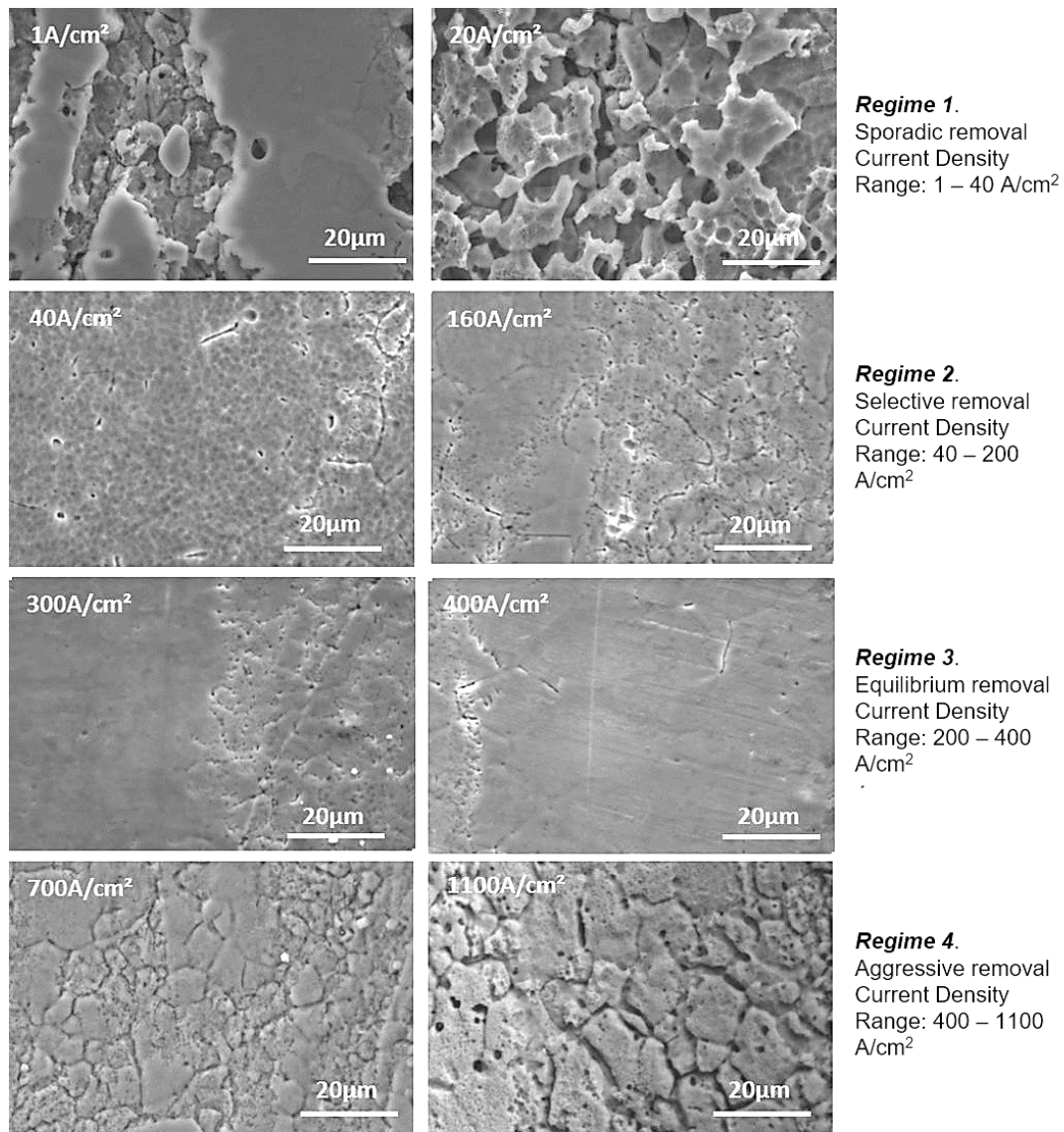


Figure 4.5: Identified regimes of Anodic dissolution as a function of J for Inconel 718 producing a variance in surface texture that can be grouped into 4 dissolution regimes

In comparison *regime 2* shows the start of surface texture dependent on material characteristics. The difference in anode potential of the different alloying elements and grain orientation [274] achieves different etching rates leading to an un-even surface texture, pitting and the grain boundary definition becoming visible showing the same grain structure as the etched sample in Figure 4.1. This can be further related to the EDS surface analysis in Figure 4.6.

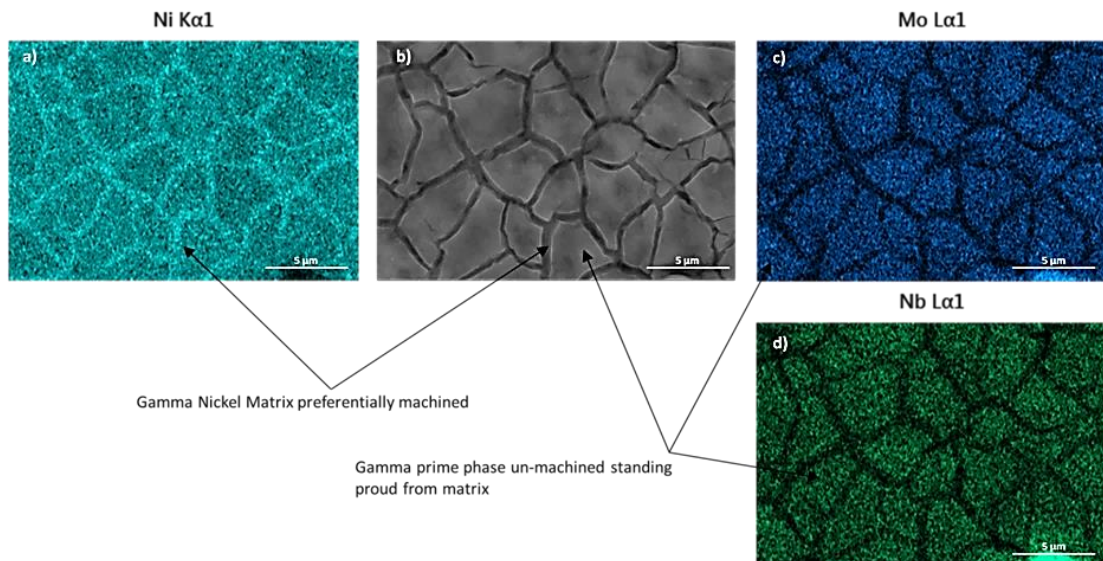


Figure 4.6: EDS surface maps of machined surface of Inconel 718 demonstrating the preferential machining of the nickel matrix leaving the γ' phase containing Molybdenum and Niobium less affected.

At this point in the current density evolution, an undulating surface is starting to form where the γ' phase fails to dissolve at the same rate as the nickel matrix, due to the high Nb and Mo content having a much lower ECE than nickel at 0.69 g/Ah and 0.89 g/Ah respectively. This dissolution behaviour has also been demonstrated in EJM of Stainless steel which also contains a high variation of similar metallic elements [17].

As the matrix is removed, in some cases, the γ' phase is no longer held allowing them to be “washed out” by the electrolyte flow leaving a void behind (Figure 4.7). This is especially prevalent with the undissolved, large, Niobium carbide precipitates leaving large craters behind found at the grain boundaries (seen in Figure 4.7 b and c). This phenomenon appears through all dissolution regimes often sporadic until high J in regime 4 (Figure 4.5) where it is consistent on the machined surface giving a highly porous surface. This phenomenon is completely material dependent due to the precipitate structure of Inconel 718.

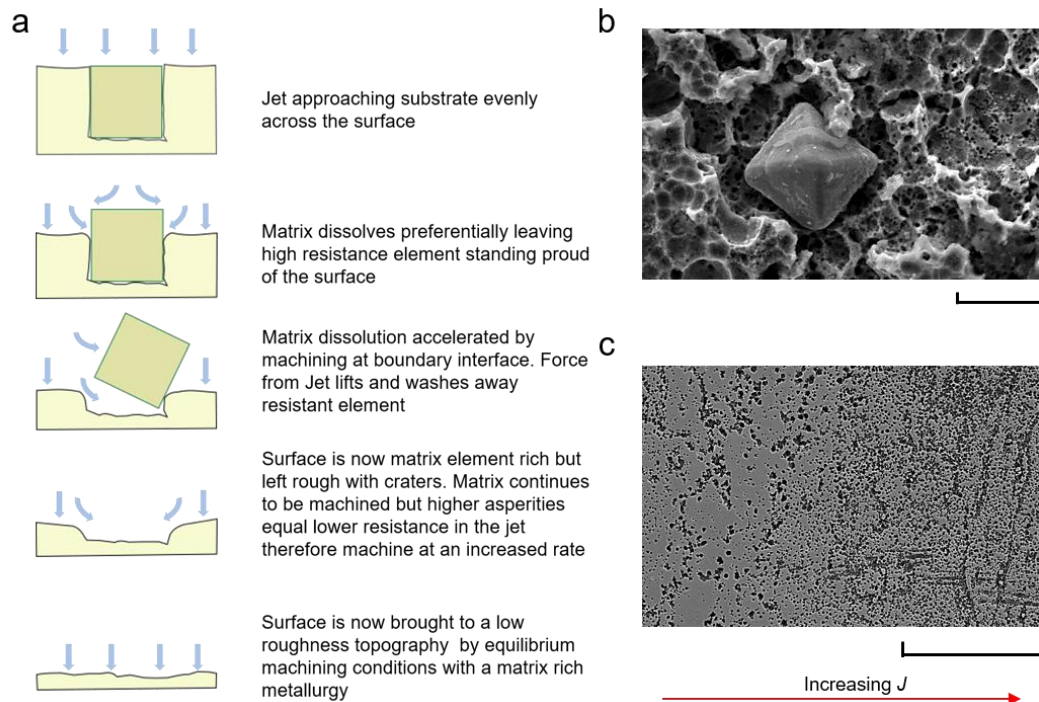


Figure 4.7: "wash-out" leading to crater like topography (a) mechanism of evolving surface under preferential machining regime (b) SEM of large Nb carbide precipitate with dissolution occurring around the boundary just before "wash-out" occurs. Scale bar 10 μm . (c) SEM image of surface with increasing current density from 400 A/cm^2 (left) to 800 A/cm^2 (right) showing the increasing craters left behind as the nickel matrix is eroded away from only the grain boundaries to being consistent across the surface. Scale bar 250 μm

Regime 3 demonstrates a common dissolution rate between elements and phases as J is higher than required to overcome the dissolution potential of all material components. This can be observed from the elemental analysis of the first 3 regimes in Figure 4.8, whereby the elemental balance is much more akin to that found in the control surface. It must be noted that it was found to be difficult to create *regime 4* over a large area that could be analysed due to the very high current densities involved and the resultant deep cut features. It is likely these high J values would be reserved for deep micro machining. Although the pitting and general poor quality of the finish may cause problems in service so an alternative method such as repeated scans as alluded to in the literature review (section 2.3.3), would be required for deep features. Similarly, it has been

discussed in ECM [275] that at *regime 3* *J* level current used for the dissolution of metal is constant and in balance to that used for gas evolution.

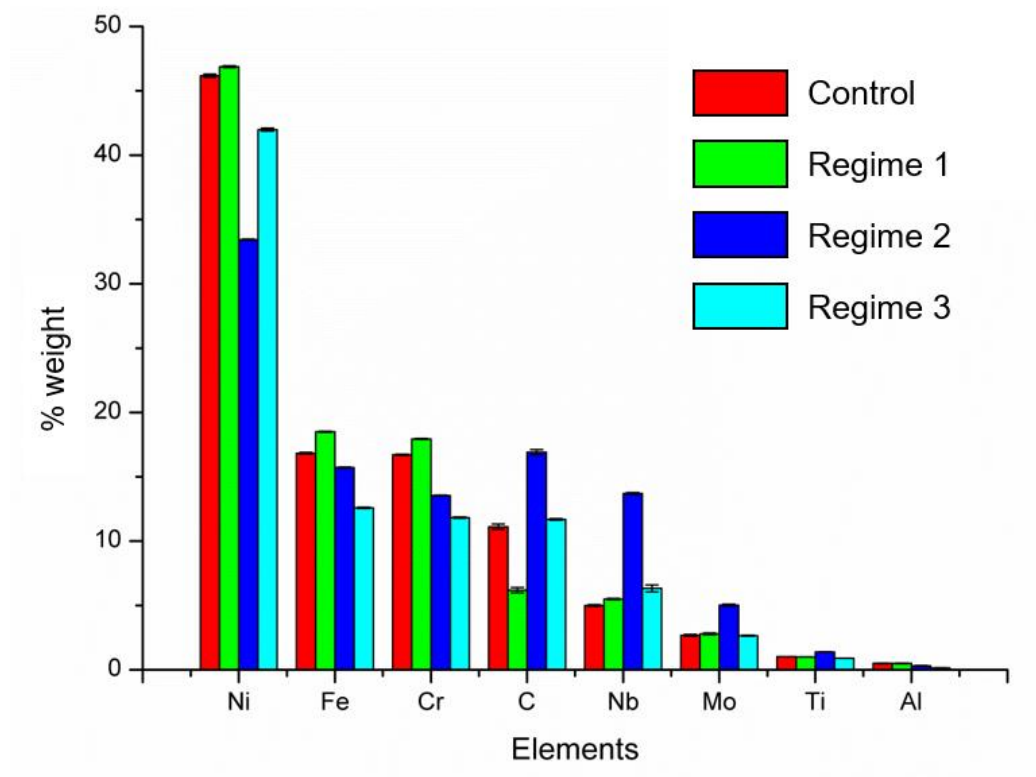


Figure 4.8: Inconel 718 Elemental composition at the surface as a function of the dissolution regime

This would typically demonstrate the ideal process window with the lowest surface roughness finish and a much less defined surface texture (see Figure 4.9). Noting here the increase in surface roughness beyond this point that confirms Kawanaka et al. [2015] [55] hypothesis in a different material discussed in section 2.3.2.

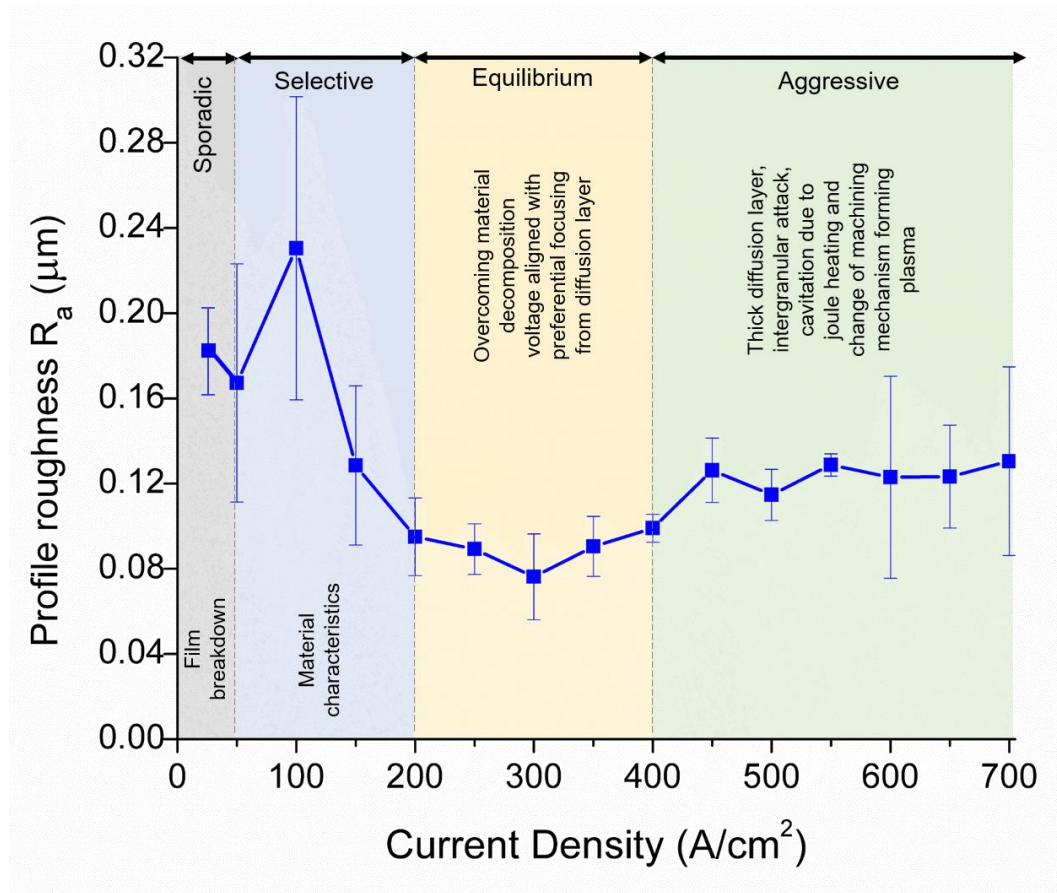


Figure 4.9: profile roughness (R_a) as a function of increasing current density for Inconel 718 when machined with 2.3 M NaNO_3 (error bars are the standard deviation of the sample from the mean) with corresponding dissolution regime and process mechanics responsible for surface finish

This confirms that the role of the diffusion layer found in electrolysis [276] is applicable in EJM, which ensures current concentration at asperities found on the surface [18]. Still some preferential machining of the voids left behind by the larger Niobium precipitates and grain boundaries occurs, but they are much less prevalent and highly localised. It does appear from the example images in *regime* 3 that the texturing is not consistent across the trench with sporadic areas that demonstrate out of regime texture. This is likely due to variation in the dissolution process from the effects of passivation, debris build up, inhomogeneity in the material or fluctuation in process parameters. This effects the distribution and

intensity of the current density field demonstrating the somewhat stochastic nature of EJM.

Regime 4 at high J values shows a much more aggressive pitting effect having similarities to the electro-chemically etched control sample in Figure 4.1. This is due to preferential attack at grain boundaries and surface features. The surface texture is defined purely by the material morphology as aggressive inter-granular corrosion occurs and the porosity of the surface increases. Cavitation occurs due to gas evolution, hydrogen saturation at the cathode leading to bubbles in the electrolyte stream and oxygen evolution at the work-piece surface. This bubble formation within the surface pockets causing unstable machining conditions and possible localised boiling of the electrolyte from Joule heating effect [16, 19]. This contributes to the severity of the texture and leads to sparking and arcing showing a possible current limit to the process within this machine architecture. Surface texture visually becomes rougher and formation of deep voids from extreme preferential machining occurring in these pockets allowing pooling more than the plateau surface above increasing the variation in topography of the surface.

Titanium also presents obvious dissolution regimes (Figure 4.10) over an increasing current density range. The alpha phase is seen to preferentially machine over the beta phase as J increases. In Figure 4.10a, the initial microstructure is revealed leaving the alpha structure to stand proud of the beta matrix. The reasons behind this are not as obvious as that found in In718. In this case the ECE of alpha stabiliser aluminium and beta stabiliser Vanadium (the main constituent differences between the phases) are very close at 0.09 mg/C (Al) and 0.1 mg/C. However, aluminium makes up a higher weight % of the mass. This in turn means that on initial exposure to the jet the alpha phase, due to its

higher presence at the fluid facing surface, will preferentially machine along with the titanium surrounding it.

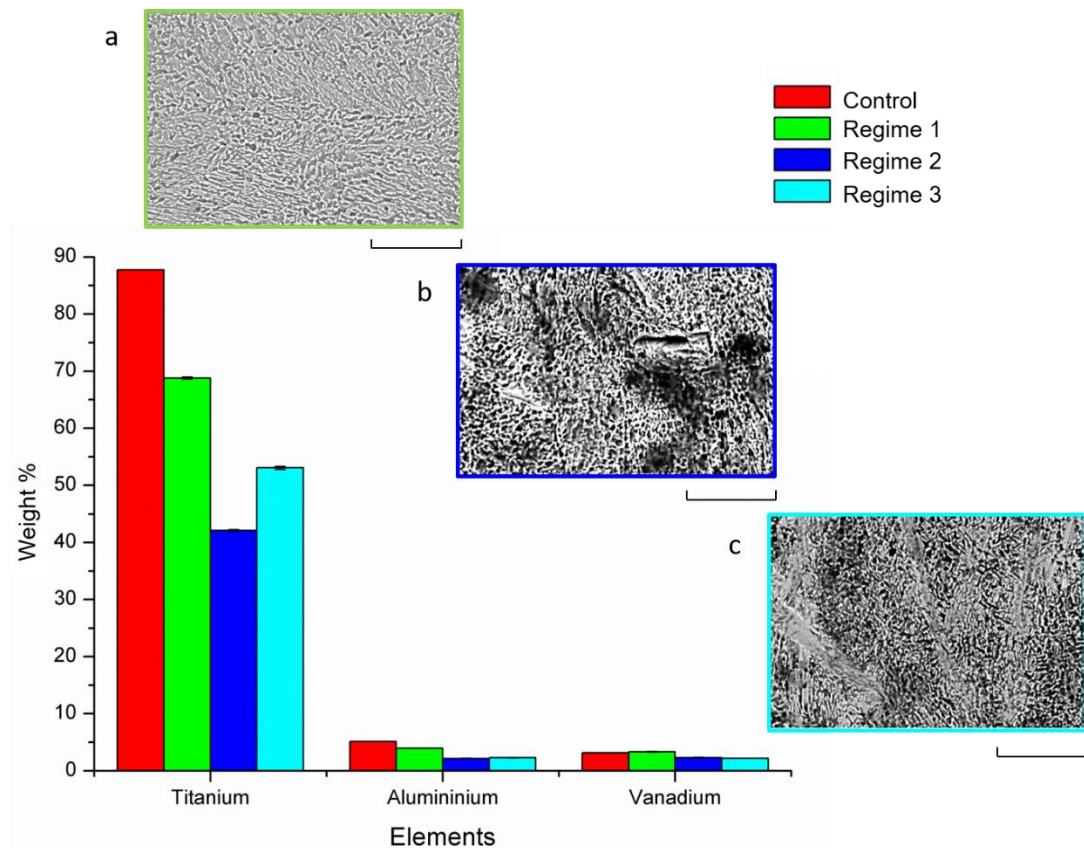


Figure 4.10: EDX surface analysis of Titanium grade 5 machined within the first 3 machining regimes considering the main material elements that lead to changes in topography (a) machined at 35 A/cm², (b) 112 A/cm², (c) 300 A/cm² All machined with NaCl. All scale bars 50 μm

Alongside this aluminium demonstrates a much higher electrical conductivity than vanadium ($\text{Al} = 3.5 \times 10^7 \text{ S/m}$ compared to $\text{V} = 5 \times 10^6 \text{ S/m}$) which means it will form preferential pathways through the material allowing higher anodic dissolution rates at discrete points on the surface where aluminium concentration is the highest. This leads to a highly textured surface effect during the selective machining regime (Figure 4.10b). However, as J increases, a more equilibrium phase occurs where by mass transport-controlled dissolution creates a levelling

effect due to an increased diffusion layer thickness. This means that as protrusions created by the material differences, as described previously, are preferentially machined by concentrations in energy seen at the surface [55] which also overrides charge transfer kinetics due to grain orientation, boundaries, dislocations and inclusions [277] also seen in Inconel 718. This can also be noted from the surface roughness plot in Figure 4.11 which follows the same trend as Figure 4.9 decreasing to minimum roughness at 300 A/cm^2 which is within the equilibrium phase, beyond this the roughness increases dramatically. This dramatic increase may be due to the increased resistance because of the passivating nature of the material causing joule heating and cavitation as discussed in section 2.3.2. It should also be noted that the roughness values are higher here than for In718 partly because this is surface roughness as opposed to profile roughness. When surface roughness is extracted, it incorporates the complete surface area of the striation including areas affected by lower current density at the edge of the features which tend towards being rougher (Equation 8) as opposed to R_a which is extracted as a profile in the high J areas in the centre of the cut which tend towards being smoother so omitting the rougher areas (Equation 7). This was done deliberately to demonstrate that Kawanaka et al. [2015] [55] hypothesis still holds true, even when the entire machined surface is considered and in a significantly different material.

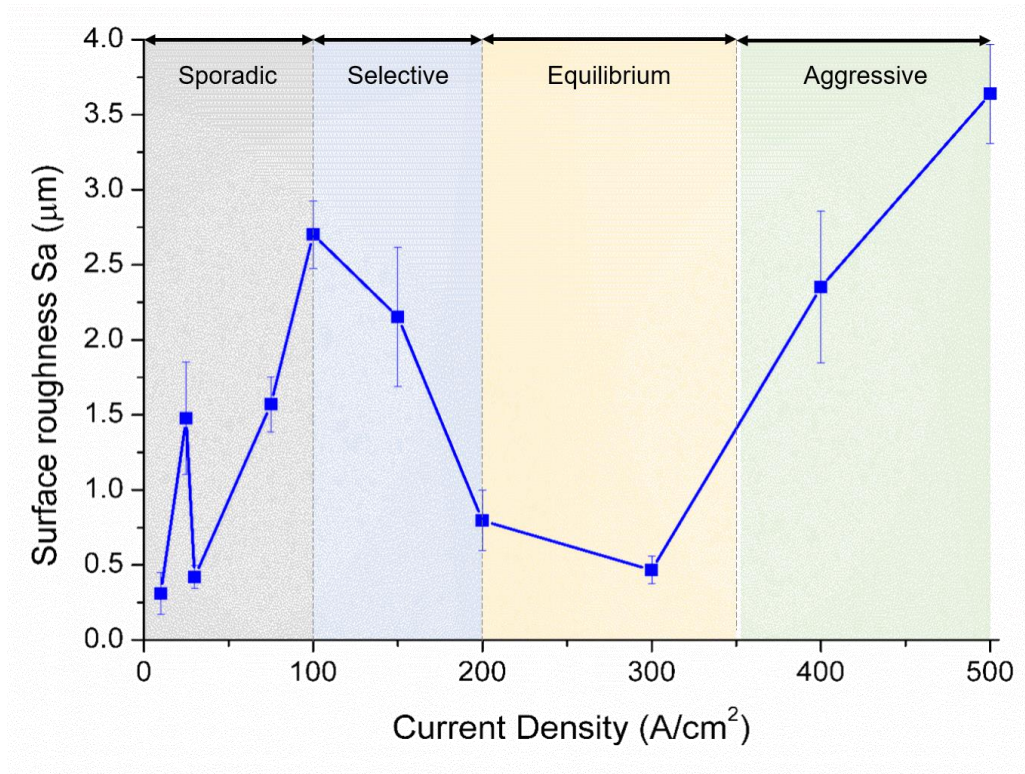


Figure 4.11: Surface roughness (S_a) as a function of increasing current density for titanium grade 5 when machined with 2.3 M NaCl with corresponding dissolution regimes outlined

These changes in the dissolution mechanism noted in both In718 and Ti grade 5 also directly relate to the machining performance. Denoted in section 3.8.1 as kerf, depth and profile area. Observed in Figure 4.12, as J increases so the cut depth increases in a linear fashion.

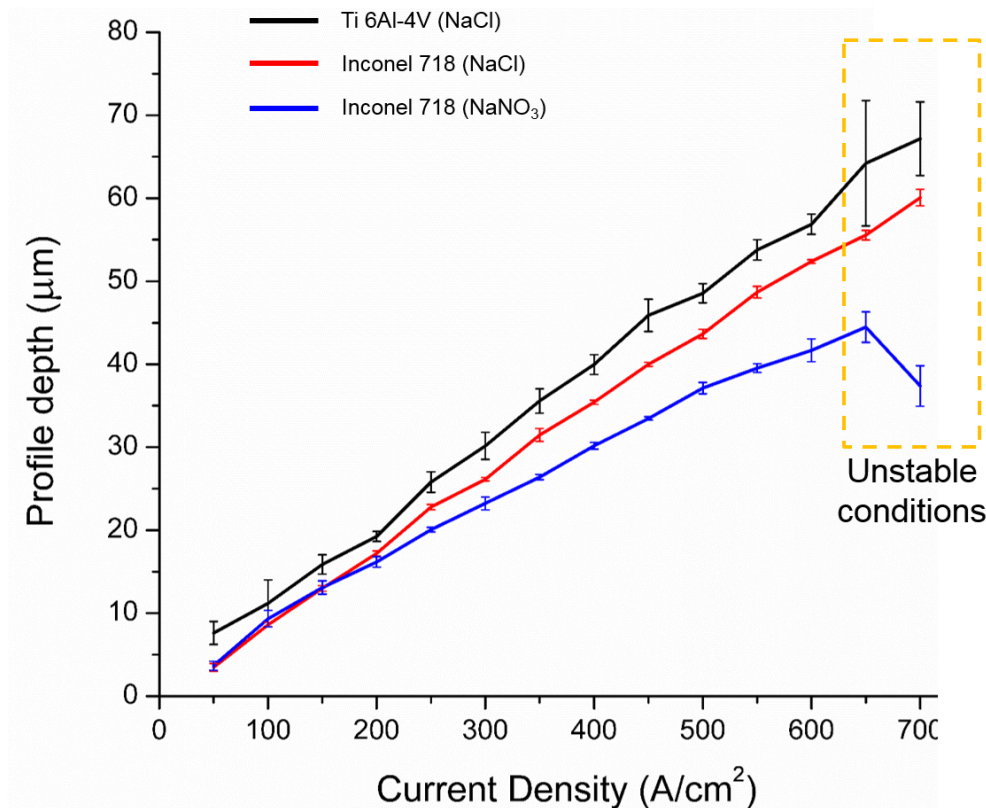


Figure 4.12: Profile depth with respect to applied mean current density across titanium, nickel super-alloy and magnesium utilising sodium chloride and sodium nitrate electrolytes

In consideration of Figure 4.12 and Figure 4.14 it can be seen Titanium exceeds Inconel 718 material removal at comparable J values and electrolyte. This is the opposite of what is expected from consideration of the ECE values. This is likely due to two reasons. Firstly, In718 is designed specifically for high corrosion resistance. This is largely due to the passivation film that forms on the surface resisting corrosion [278], thus resisting machining by EJM. Secondly, the dissolution of Titanium is complex with multiple possible oxidation states (+2, 3, 4). Even considering the same oxidation state for both Ti and Ni when the standard electrode potential of Ti (how readily the electrode material goes into an oxidised state in solution and the potential required to pull the ions back to a reduced form in comparison to that of a standard hydrogen electrode (SHE)) is

compared to nickel ($E^0 \text{Ti}_{(s)} \rightarrow \text{Ti}^{2+}_{(aq)} + 2e^{-} = 1.63 \text{ V vs. SHE}$ compared to $\text{Ni}_{(s)} \rightarrow \text{Ni}^{2+}_{(aq)} + 2e^{-} = 0.25 \text{ V vs. SHE}$) [279] the Ti demonstrates a far higher willingness to be in an oxidised state. However, as previously mentioned the dissolution of Ti is complex and competing anode reactions hinder this removal. One example is considering a higher oxidation state ($\text{Ti} \rightarrow \text{Ti}^{3+} + 3e^{-}$), under dissolution, insoluble hydroxides are formed in the electrolyte (Figure 2.2) ($\text{Ti}^{3+} + 3\text{OH}^{-} \rightarrow \text{Ti}(\text{OH})_3$) this is then oxidised by the influx of oxygen ($2\text{Ti}(\text{OH})_3 + 1/2\text{O}_2 \rightarrow 2\text{H}_2\text{TiO}_3 + \text{H}_2$) to form titanium oxide (TiO_3) which is insoluble in water and easily adheres to the surface. This passivation film then inhibits further dissolution of the surface until it can be overcome and will be discussed later in this chapter. It must be noted that this is only one of many reactions that form oxide layers on the surface during dissolution and there is a direct relationship between increasing J leading to joule heating leading to a stronger oxidation reaction. Thus, elevating the amount of insoluble species at the surface leading to an increase in surface roughness demonstrated by Chen et al. [2016] [280] and evident in Figure 4.11.

Above 600 A/cm^2 the process can be seen to become unstable with increased deviation in the measured depth. This is likely to occur due to a combination of factors. It is possible at this point material removal is large enough to cause metal particulates (sludge) to remain within the IEG leading to micro-sparking and inconsistent surface finish [181]. This is especially prevalent in EJM as within the impingement zone directly below the nozzle a stagnation point forms on the surface where fluid flow is brought to rest which is also the point of the current density maxima. Excessive gas evolution at the electrodes which hampers material removal is known to occur at high current densities [281]. This can be

observed by the fall off in depth of the Inconel 718 at 700 A/cm² whereby excessive hydrogen evolution at the nozzle has restricted the current flow in the IEG. The excessive gas evolution can also be ignited by sparking leading to formation of an arc plasma accompanied with a loud popping sound. This enables stray current to transfer outside of the jet and leading to damage of the workpiece surface (Figure 4.13).

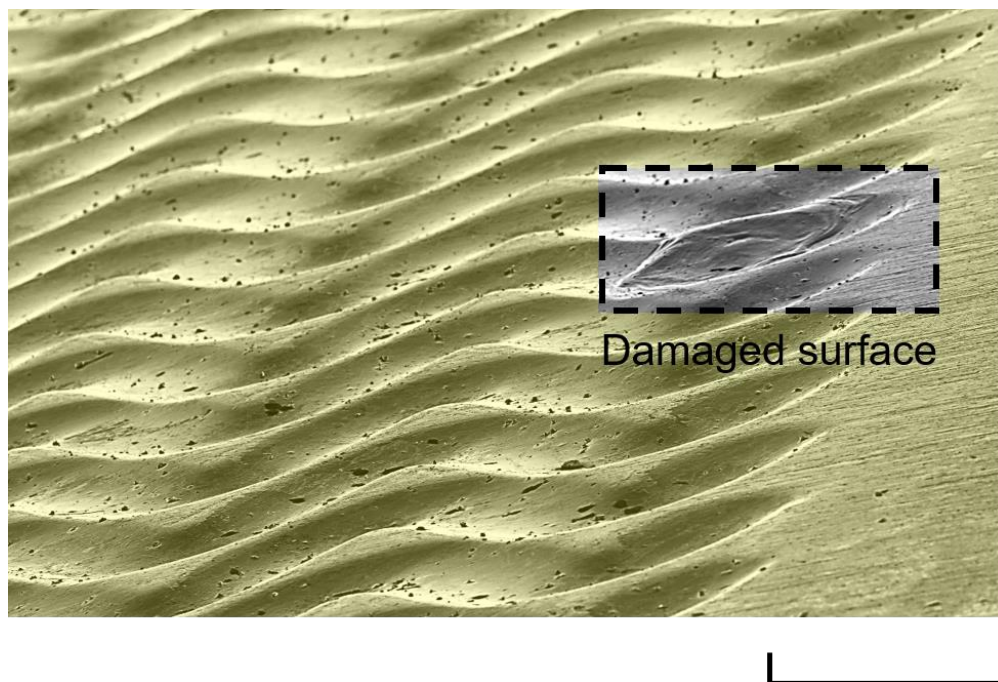


Figure 4.13: Damaged machined Inconel 718 surface due to arcing during processing leaving a re-cast layer on the surface. Scale bar is 500 μm .

Due to the low *ECE* of the inclusions in the γ' phase and the propensity to form a passive anodic film, In718 shows the lowest mean depth of the resultant profile regardless of the electrolyte used. Considering Figure 4.14 it is clear however that although depth increases as current density increases so does the aspect ratio, in this case calculated as depth over width. This supports research outlined

in the literature review that the width of the cuts remains a constant regardless of the increases in J at approximately twice the I.D. of the nozzle.

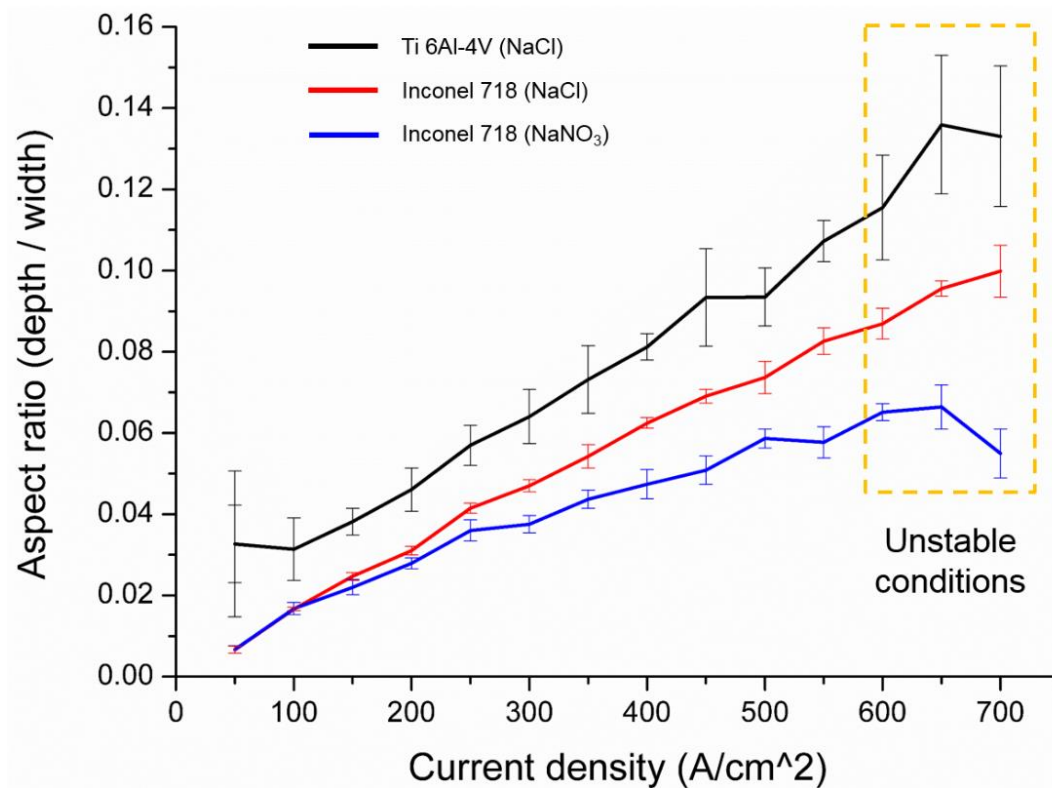


Figure 4.14: Aspect ratio with respect to applied mean current density across titanium, nickel super-alloy and magnesium utilising sodium chloride and sodium nitrate electrolytes

However, as J increases and so according to Faradays law, the material liberated must also increase but, as observed, this is only in the singular direction into the workpiece. This is due to the hydrodynamic effect of the thin film developed upon jet impingement of the workpiece surface and is not dependent on energy control at the surface and as such remains a constant. Therefore, parameter control of the energy displays little influence over the kerf. It follows that to increase precision of the technique and reduce kerf would require further manipulation of the electromechanical factors within the IEG which is addressed in the following chapters.

As previously alluded to when considering the performance, the largest effect on the dissolution and precision of titanium is the propensity to form passivation layers on the surface during machining (Figure 4.15). This is especially prevalent when using passivating electrolytes such as NaNO_3 which is why in Figure 4.12 the only results for titanium are those machined with NaCl . This does not display, to such a large extent, the same willingness to generate passivation effects, but at the expense of feature precision (Figure 4.17c).

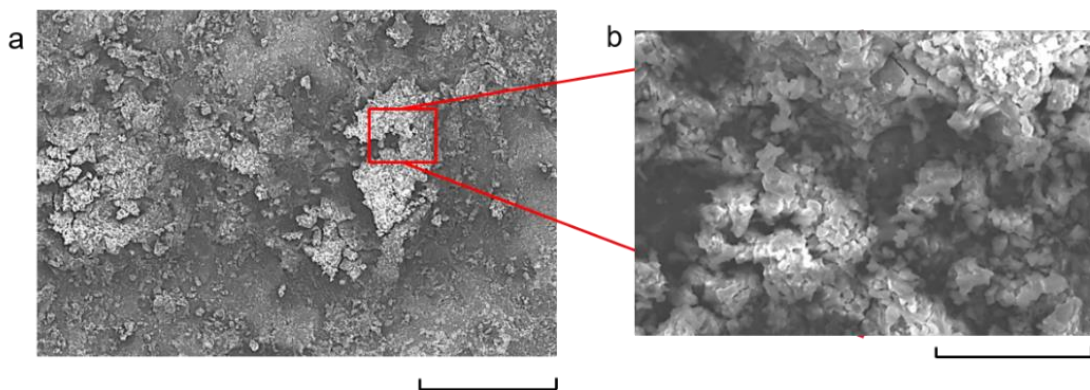


Figure 4.15: Formation of passivating layers (TiO) on titanium substrate during machining with NaNO_3 electrolytes. (a) large scale layer formation over the machined surface. Scale bar $500\ \mu\text{m}$ (b) close-up of passivation build up scale bar $50\ \mu\text{m}$

Considering Figure 4.16, the effect of the passivating layers can be seen when two samples are machined with different pre-conditions, with increasing current density. One surface is “as received” and the other was prepared with a mechanical polish to $1\ \mu\text{m}$ (R_a) immediately before being processed to minimise the chance of oxide formation. There is a distinct difference in the material removal achieved between the un-machined and polished precondition of the material below $300\text{A}/\text{cm}^2$. At lower J values the polished sample achieves up to three times the depth of the un-polished sample and in a more consistent fashion with minimal deviation. At $300\text{ A}/\text{cm}^2$ the un-polished sample starts to overcome

the ohmic overvoltage required to overcome passivation and depth starts to increase rapidly. At 400 A/cm² both samples appear to achieve complete decomposition voltage [59] and material removal increases. Although the polished sample obtains a greater depth, perhaps due to residual passive layers continuing to inhibit performance of the un-polished sample. It is also seen that the deviation from the mean depth is high across all samples showing an increasingly unstable process as passivation breakdown and return occurs throughout the striation length which can be seen in Figure 4.17d.

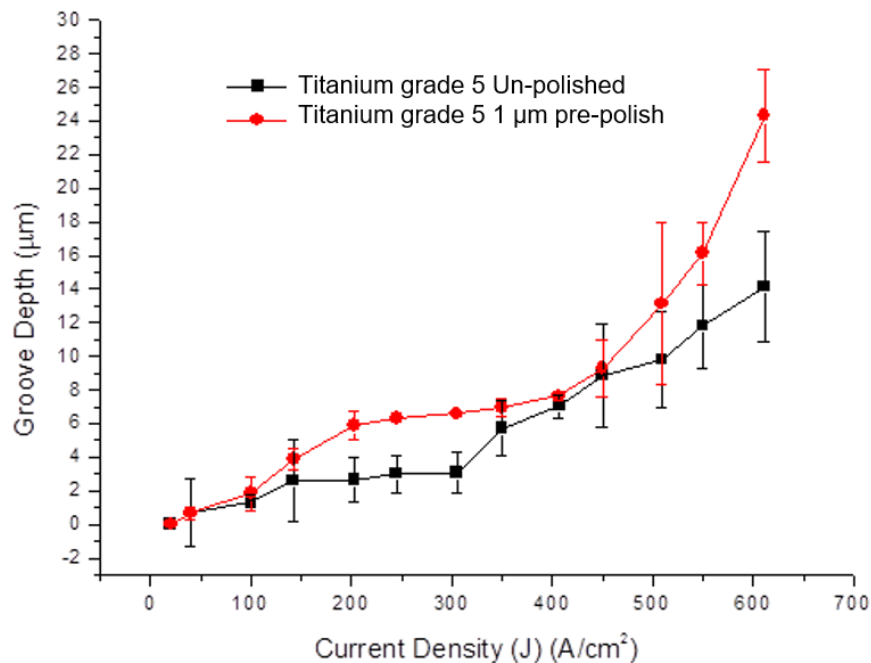


Figure 4.16: Machining performance of titanium grade 5 as a function of increasing current density on samples with an as-received surface and with oxide layers removed prior to machining

The effect of passivation layers on kerf and depth can be explained by consideration of the schematic in Figure 4.17. In Figure 4.17a under normal machining condition the majority of machining energy is concentrated at the base of the resultant profile restricted at the sides by the thin film area at the surface. However, as shown in Figure 4.17b when passivation layers form in the major

machining direction preferential machining moves to the side walls so widening the kerf. This can be seen in Figure 4.17c where NaCl has been used to machine an as-received surface. The undulating surface of the resultant machined geometry and poor edge definition are immediately obvious. This is exacerbated still further in Figure 4.17d when a pattern is machined into titanium using high current densities and a repeating toolpath. As passivating layers build at the base of the cut, so the kerf widens, then as potential exceeds the polarising effect of the oxide machining resumes at the base, giving an inconsistent kerf edge and demonstrates the inherent instability of the process in these conditions.

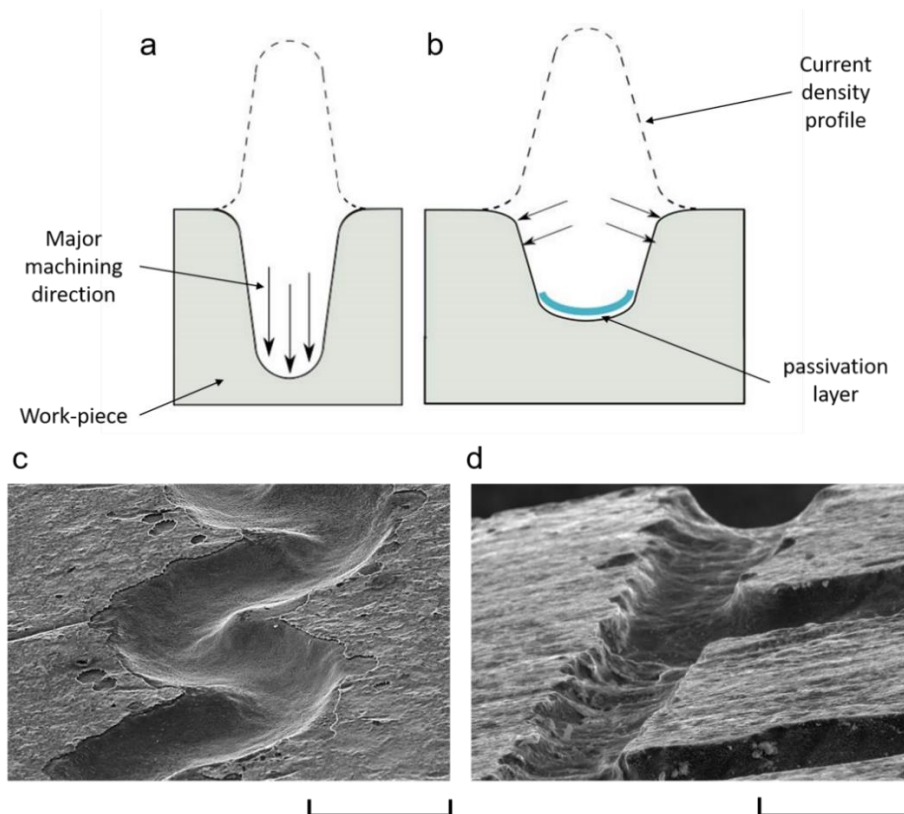


Figure 4.17: Schematic of passivation layers leading to poor precision (a) normal machining mode whereby material dissolution is concentrated at the bottom of the resultant profile (b) when a passivation layer is formed preferential machining is diverted to the side walls of the cut (c) Example of features cut using NaCl where passivation can still occur at lower J values leading to instability in the process so poor geometrical definition added to the poor geometrical control occurring due to the use of NaCl. Scale bar is 500 μm (d) features created using NaNO_3 at a high current density with a repeating toolpath extremely poor edge definition and surface finish is noticeable Scale bar is 250 μm

The knowledge gained through this chapter is demonstrated in Figure 4.18 where examples of meso- and micro-scale features have been created in In718. In comparison to alternative processing techniques described in section 2.6 the control and flexibility of the process is evident not only in the creation of deterministic features, but also the ability to control the surface finish and generation of micro textures in deterministic patterns.

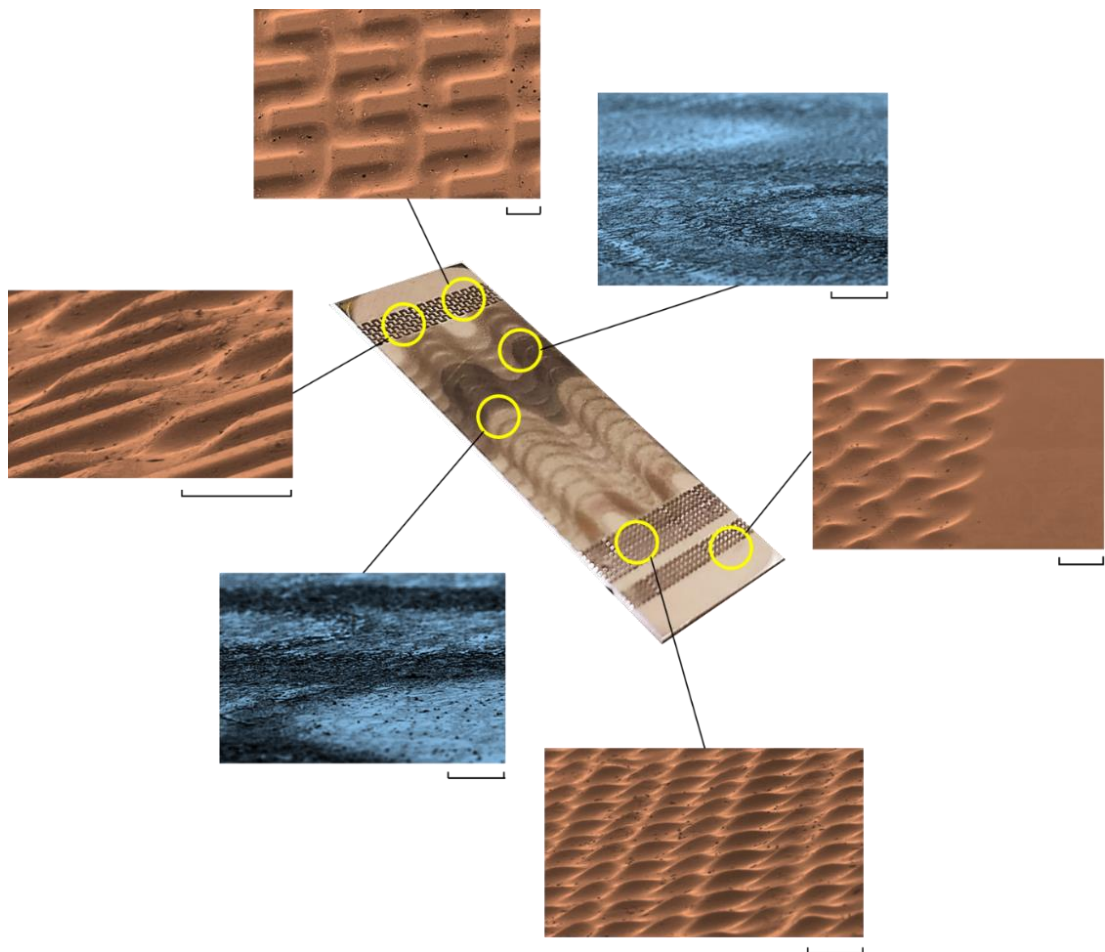


Figure 4.18: Demonstration of Meso- and Micro-scale surface feature generation in Inconel 718. Tinted SEM images of varying features using 0.15 mm I.D. nozzles for deterministic surface structuring (orange tint) and 1 mm I.D. nozzles (blue tint) creating differing surface finishes due to changes in current density. All scale bars are 250 μm

4.3. Chapter summary

Ni-superalloy Inconel 718 and titanium grade 5 were analysed for their response to EJM, both materials demonstrating distinct characteristics. A process window was defined supporting the findings of the literature review for alternative materials. Applied energy is demonstrated as the greatest influence on performance and the variation of which can accurately represent changes to material performance and surface finish.

The key findings of this chapter are:

- IEG and electrolyte flow rate are seen to have minimal influence on performance across values tested.
- The diffusion layer, as hypothesised by Kawanaka et al. [2015] [55] is demonstrated to be responsible for the surface finish.
- The lowest surface roughness in both materials is achieved at 300 A/cm² beyond which roughness increases.
- Both materials go through obvious dissolution state changes as J values increase
- Kerf is not greatly influenced by material and parameter choice and equates to ≈ 2 times nozzle I.D. Polarising effects in the IEG can lead to a high level of deviation.
- Consideration of the electrode redox potential of both materials is required alongside the electrochemical equivalence to understand MRR.
- An erosion material removal mechanism is identified alongside the expected corrosion mechanism due to “wash-out” of precipitates.

- The passivation layer generated during processing of titanium presents a significant barrier to processing. Correct choice of electrolyte and process parameters will overcome the problem to a degree but precision, especially regarding edge definition and performance may still suffer as a result.
- EJM is able to comprehensively change the surface topography and material composition as a function of changing processing energy at the fluid facing surface.

The complexities of the electrochemical reactions in the IEG make it difficult to accurately predict material response without empirical knowledge, hence the importance of such studies as this. Inconel 718 is demonstrated as an excellent substrate for processing by electrochemical jet techniques, especially when comparing the ease and efficiency it is processed in comparison to shear based techniques. Coupled with In718's sensitivity to changes in energy and the importance of the material outlined in the literature review to the expected markets for EJM, In718 and the knowledge gained throughout this chapter form the basis for innovations demonstrated throughout this thesis.

5. Enhanced geometrical flexibility and precision by electro-mechanical innovation

5.1. Introduction

Outlined in section 1.1, one of the primary objectives of this body of work is to investigate process developments that can be employed in EJM to satisfy the key research areas identified in Chapter 2. From the literature review, it is clear, that electro-mechanical developments to system and processing architecture have yet to be exploited. A multitude of approaches in generating complex surface structures have been previously employed in subtractive EJM. Superimposition of toolpaths [5, 59], variation of process parameters [75] and combinations of machining strategies [86] to effect profile changes have all been investigated. These demonstrate complex protracted approaches to the generation of complex surface structures that need to be created repeatably and efficiently. Simpler, more fundamental mechanisms for this would be advantageous. Much of the prior research emphasis has been concentrated on using simplistic laboratory-based apparatus without modification, understanding or exploitation of the inter-electrode gap. In comparison to general ECM and alternative energy beam processes where this is well understood and exploited. However, it is not true to say that innovations found elsewhere are in anyway transferable to electrochemical jet processing techniques as is demonstrated over the following section. EJM exhibits opportunities for exploitation and flexibility that are not available in other techniques.

The following chapter details investigations to understand the process mechanics and innovations concerned with manipulation of electro-mechanical properties within the IEG supported by hardware developments for the enhanced feature flexibility, precision and process function.

5.2. Manipulation of the angle of jet address

5.2.1. Introduction

As outlined in the literature review prior work has considered EJP as a two-dimensional machining technique where the nozzle is maintained normal to the work-piece at all times (section 2.5.). In comparison extensive research in alternative energy beam micro-machining techniques has considered the changing of the angle of approach to enhance process flexibility and for specific response (see section 2.6.2).

EJP is distinct from other energy beam processes, in that the energy distribution is governed by electrical field effects with respect to spatial considerations of the surface. It is therefore proposed that resultant profiles from EJM would not follow the same findings identified with other processes.

A common simplification for EJP modelling dictates that the energy distribution remains as a constant Gaussian distribution (see section 2.3.2) regardless of the spatial influence of standoff, workpiece geometry and traverse speed. Therefore, erroneous or indeed purposeful changes to the jet address have not yet been considered by researchers.

It is well recognised that the IEG in ECM can be considered partially as a simplified resistor (section 2.3.4). If current is constant and voltage allowed to

float, regardless of changing resistance (resulting from variation of the IEG) constant applied current density will be maintained and as such material removal will remain constant. This is true when considering the IEG as a whole (Equation 4).

It is proposed here, that as the nozzle is rotated away from the normal to the workpiece (standard EJP practice) the resulting tip contour is no longer parallel. Since resistance is dependent on spatial considerations of discrete areas between electrodes (Equation 12), localised in-jet resistance across the impingement area becomes dependant on the current pathway at a specific point defined by the localised resistance.

$$R = \frac{l}{A} \rho_E \quad \text{Equation 12}$$

Where ρ_E is the specific resistivity of the electrolyte. This in turn is hypothesised to lead to a change in the shape of the resultant machined profile as the maxima of the energy distribution is shifted.

As noted in the literature review (section 2.7.3), prior work in generating 3D structures in EJM has involved complex approaches to the generation of surface structures. Articulation of the jet in two further axis would negate some of the need for this complexity.

The purpose of this work is to explore the profiles which occur as a result of variation in the incident jet angle. Furthermore, this work intends to identify the fundamental mechanisms which effect material removal mechanics and to enable further implementation of this methodology.

5.2.2. Methodology

To enable this experimentation a new end effector was designed and manufactured (Figure 5.1) using fused filament fabrication (FFF). The standardised stainless-steel insert, Luer lock adaptor and nozzle were incorporated (as detailed in the Chapter 3) into a head that can be set at varying indexed angles to alter the impingement angle of the jet against the workpiece ($\theta = 22.5^\circ, 45^\circ, 67.5^\circ, 90^\circ, 112.5^\circ, 135^\circ, 157.5^\circ$). The axial air shroud was also incorporated although modified to allow for clearance to the workpiece and the air inlets at lower angles.

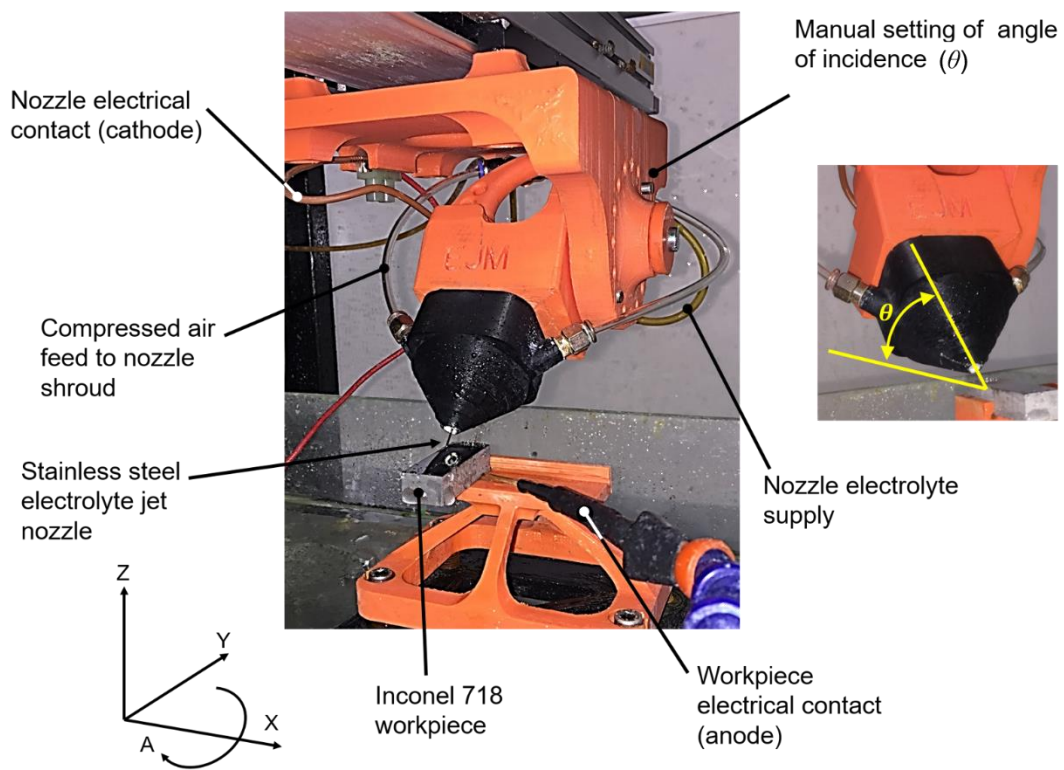


Figure 5.1: Apparatus used to create the varying incident jet angles noting the global co-ordinates system used throughout

5.2.2.1. Influence of angle of address

During experiments some process parameters remained constant. The electrolyte (NaNO_3 , 2.3 M) was maintained at 22°C , and supplied using a $500\text{ }\mu\text{m}$ internal diameter (I.D.) stainless-steel nozzle. The IEG was set at $250\text{ }\mu\text{m}$ from the nearest nozzle edge to the workpiece. Current was maintained at 410 mA ($J = 200\text{ A/cm}^2$) and electrolyte flow rate at 0.27 l/min ($V_{jet} = 23\text{ m/s}$) with a traverse feed of 0.5 mm/min throughout. Compressed air was fed to the air shroud at 4 bar. Single pass striations were repeated across a nickel superalloy (Inconel 718) workpiece (the expected response now defined in Chapter 3.8.3) at each θ value.

The striations were machined in both directions across the workpiece with what is referred to in this instance as the “normal” convention (Figure 5.2a). This is defined as the nozzle being maintained perpendicular to the traverse direction of the head, with the head being articulated in the Y direction through each θ angle. Secondly, repeated striations were machined with the nozzle being translated axially to the traverse direction of the head (Figure 5.2b) again through all θ angles giving rise to a “push / pull” convention where the nozzle tip can be seen to push or pull the electrolyte jet.

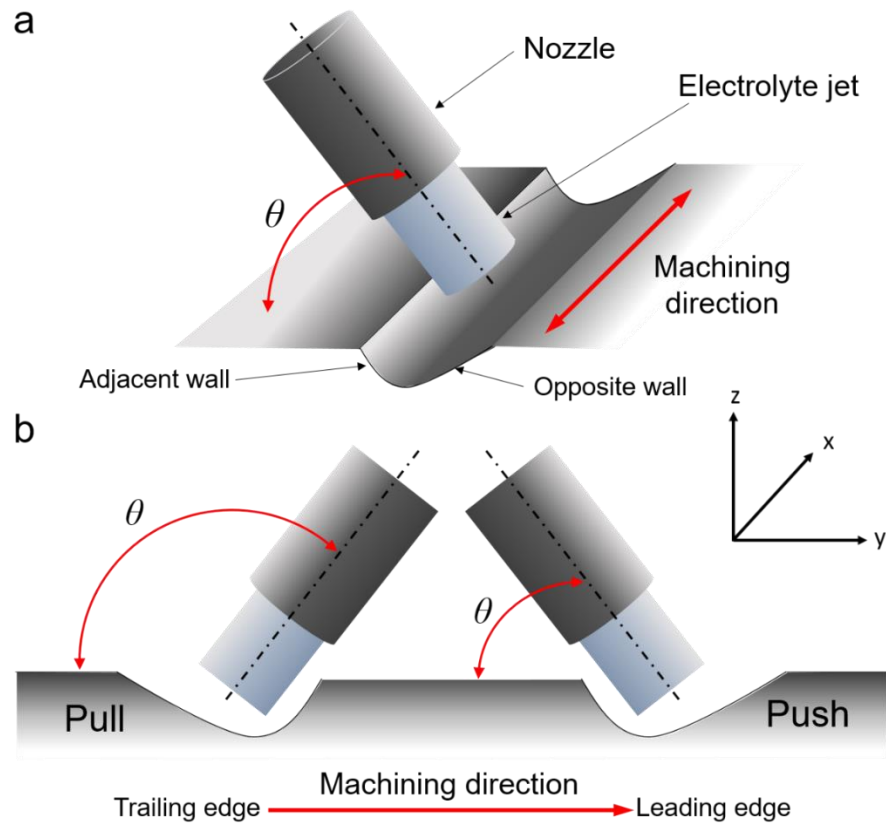


Figure 5.2: schematic of machining approach convention (a) being of normal convention and (b) being push / pull convention.

The resulting machined striations were then analysed using the defined experimental method (see section 3.8) to quantitatively assess the slopes of the cut wall, area of the material removed and depth / width of the resultant profile. The resultant surface textures from the machining push / pull machining convention were analysed under SEM as these are seen to be similar to the ‘climbing’ phenomena observed in conventional milling operations. In this case, it can be described as push mode (climb) and pull mode (conventional).

Profile roughness (R_a) was also extracted in accordance with the methods detailed in section 3.8. This was carried out to ascertain if there is any advantage to adopting a particular machining strategy.

5.2.2.2. Influence of jet speed variation

To ascertain the influence of jet ejection on the response profile, a secondary set of experiments was devised. Repeated striations were carried out using the head indexed at 22.5° and 67.5° using the pre-defined normal machining convention. For each angle, the jet speed of the impinging electrolyte was varied through 3 steps, 4 m/s, 14 m/s and 29 m/s covering the complete capability of the generation 2 machine tool. The resultant profiles from this were then compared to those previously obtained to geometrically assess any variation in the resultant profile attributable to variation in jet speed.

5.2.3. Results and discussion

5.2.3.1. Normal convention

Considering the resultant profiles of the initial experimentation (examples of which can be seen in Figure 5.3) the profile is shown to be dependent primarily upon approach angle and as dissimilar to that found in any other beam type process as denoted in the literature review (Figure 2.26).

It can be considered as opposite to that found in comparable processes whereby the peak in energy is maintained in line of sight of the axial centre line of the beam regardless of approach. Therefore, the slope of the adjacent edge would be of a shallower slope as the angle of incidence lessens and the opposite wall would become steeper and, in some processes, even create an under-cut. This is the reverse of the findings reported here.

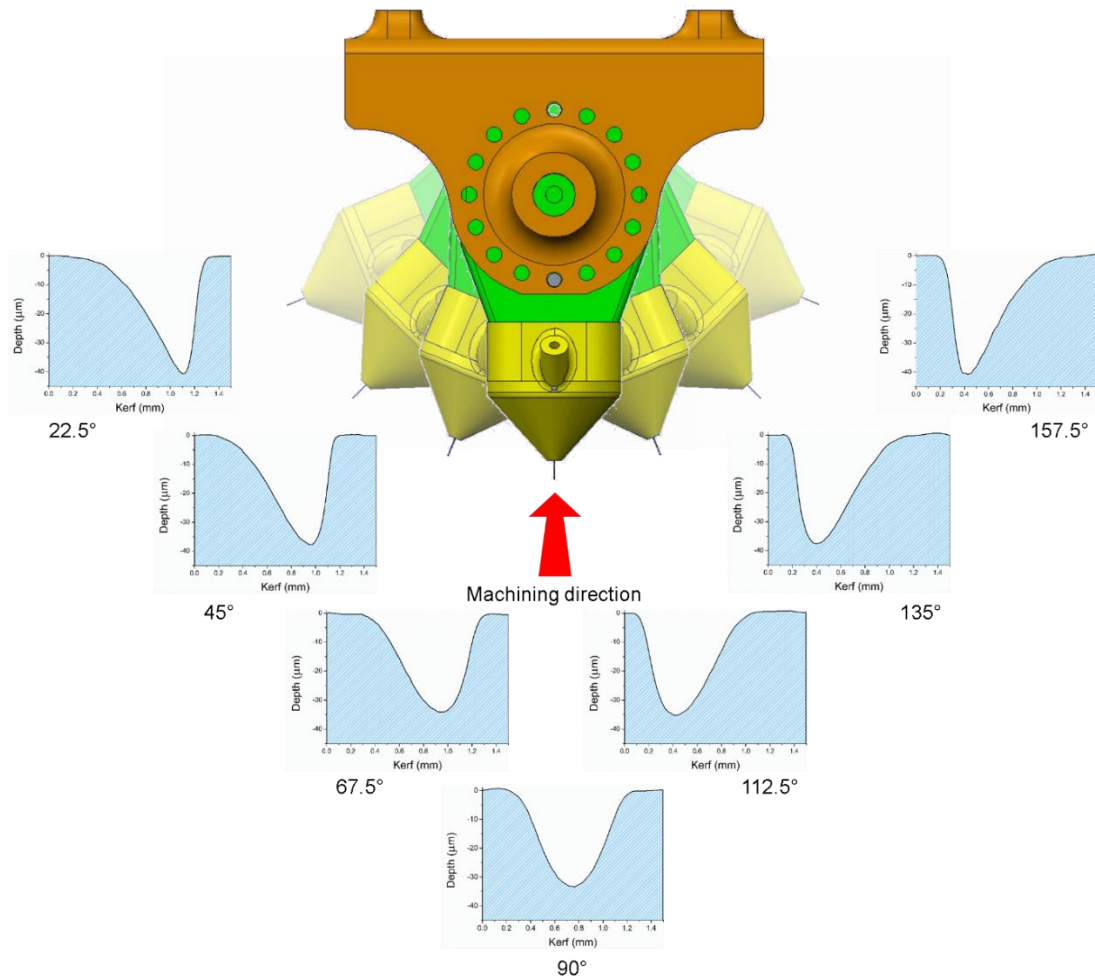


Figure 5.3: Example profiles taken from striations created with the angled head using the normal convention

The cross-sectional area of the profiles shows little variation across all angles of address achieving a mean area of $18323 \mu\text{m}^2$ with a maximum deviation of 3.5% across all angles of address. The depth and width of the striations show variation throughout the different approach angles. The width being the mean taken from 22° sample profiles and 157.5° profiles is $1219 \mu\text{m}$ (σ 2.4%) compared to the width at 90° being $1031 \mu\text{m}$ (σ 1.4%). The maximum depth also shows a reduction from $41 \mu\text{m}$ (σ <1%) measured as the mean depth of 22° sample profiles and 157.5° profiles to $33 \mu\text{m}$ (σ <1%) for the jet normal to the surface. This demonstrates that there is no change in the dissolution mechanism as the area

removed is unaffected so in agreement with Faraday's law thus, the applied energy per unit volume material removed remaining constant. However, the profile geometry is unequivocally affected by the approach angle with the profile displaying an asymmetrical appearance.

Considering Figure 5.4, it is demonstrated that the resultant profiles achieve a high degree of symmetry about the 90° position. The adjacent walls at 22.5° and 157.5° having a variation of 2.2% (368 µm/mm to 360 µm/mm) between the mean slope values and 5.6% variation between the opposite walls (68 µm/mm to 73 µm/mm). The total deviation of the adjacent walls being 7% between opposing angle pairs and 2.3% for the opposite wall of opposing angle pairs. The profile created at 90° shows a 3% variation between the slopes of the cut walls.

The variation in symmetry is attributed to assembly tolerances leading to reduced precision when indexing the head as allied work reported by the author with Walker et al. [2017] [282], where angle of address is not varied, the deviation seen here is not present.

The overall trend can be clearly seen in Figure 5.4. The adjacent slope decreasing as the jet angle approaches 90° whilst the opposite angle increases. The reverse occurring beyond 90°.

Taking the mean of the cut walls for the pair 22.5° and 157.5° the adjacent wall has a ratio of 5:1 times steeper than the opposite wall. This ratio then reduces to 4.5:1 for the 45° / 135° pair and 2.2:1 for the slope of adjacent to opposite ratio for the 67.5° / 112.5° pair. The 90° angle having a ≈1:1 ratio.

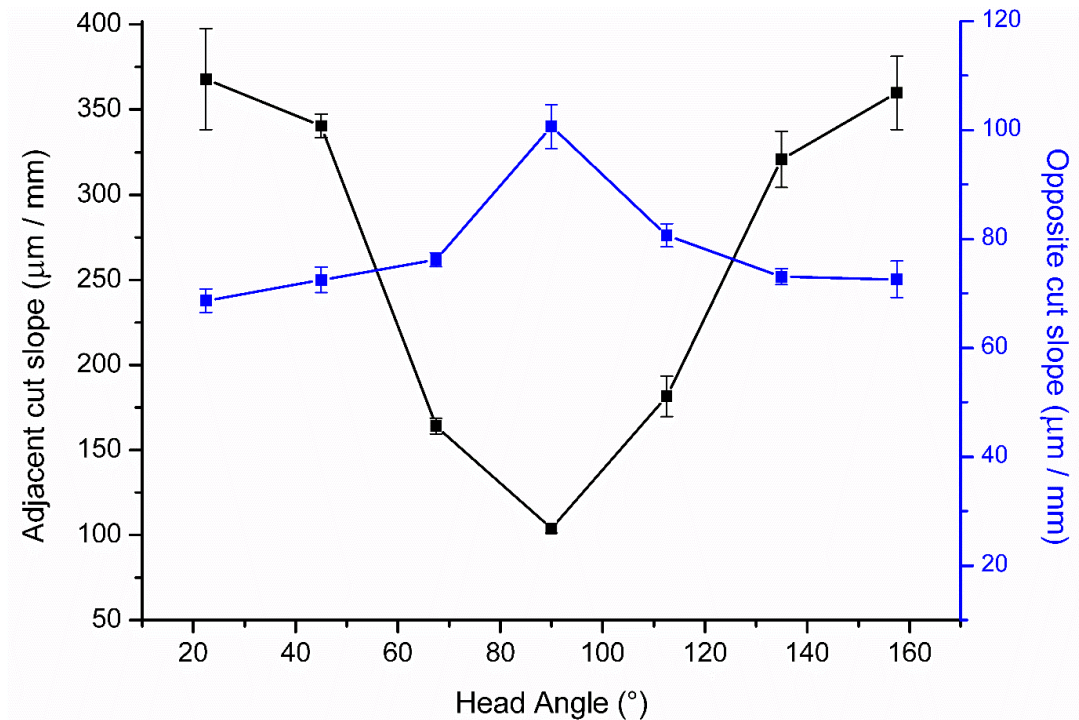


Figure 5.4: Comparison of the adjacent and opposite striation wall slopes through the rotation of the jet

The reason for this trend being different to that found in other jetting techniques can be understood by consideration of Figure 5.5. The 2D schematic describes the two main influencing factors; changing localised resistance in the IEG due to the changing nozzle angle, therefore the distance to the surface at discrete points and secondly the spatial changes due to the nature of the electrolyte jet itself causing a confluence of current pathways. The air around the jet acting as a dielectric to confine the current paths within the jet. With the nozzle perpendicular to the surface, the current density distribution is understood to be Gaussian [11] with equal resistance across the nozzle tip. Using discrete, arbitrary points A, B and C on the workpiece surface, Figure 5.5 highlights the mechanics attributed to the creation of the asymmetrical profiles. Figure 5.5a, shows the nozzle addressed at 67.5° with no jet present. Point C on the nozzle tip is now closer to the surface so will provide the lowest resistance point and therefore a preferential

current pathway and so leading to enhanced material removal at this point. However, the spacing of the primary current paths, which are the most direct path from surface to nozzle tip remain constant.

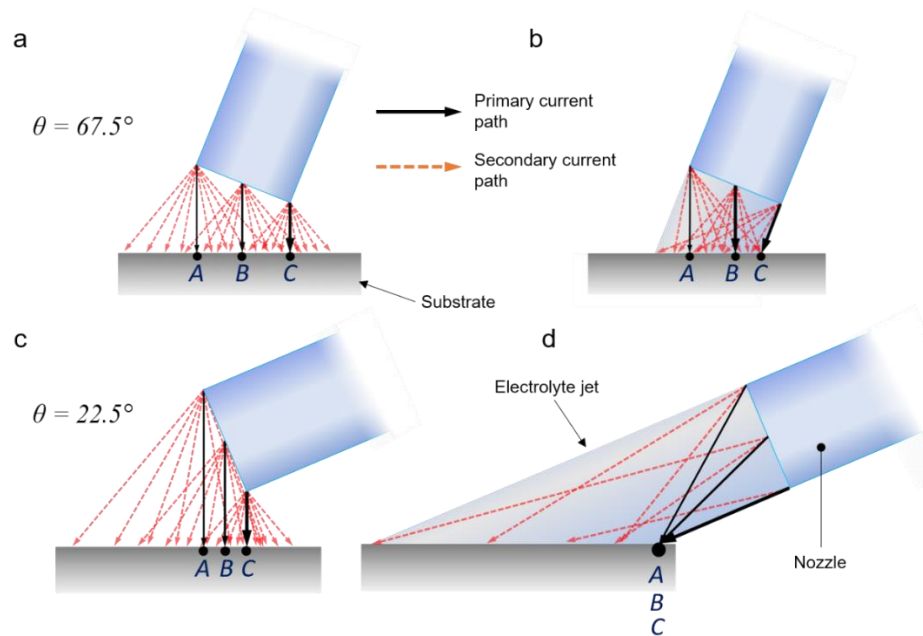


Figure 5.5: Schematic of varying current pathways as a function of nozzle and jet angle. Points A, B and C are discrete arbitrary points located on the surface under the nozzle. (a) and (c) showing the preferential pathways of the primary and secondary current paths with an inclined nozzle. (b) and (d) showing the further influence the electrolyte jet has at redirecting and converging these pathways leading to an asymmetrical machined profile.

In Figure 5.5b the electrolyte jet is superimposed to the electrostatic scenario. Here we can see the spacing between the primary current paths has changed due to the jet bringing point C closer to point B. This is at the expense of the current pathway becoming longer so less preferential at point A. The secondary current paths with less influence on the overall machined shape can also now be seen to be more confined and centred about the B / C zone. Considering the example profile in Figure 5.3 for 67.5°, the slight shift to the right for the deepest point, therefore maximum current density corresponding to this, can clearly be seen. Figure 5.5c, shown without the jet, continues to show the exaggerated

trend. The resistance at point C is now significantly reduced in comparison to any other point on the surface. As the nozzle tip face is now rotated away further points A and B are significantly further away than previously allowing point C to be the preferential pathway and the spacing between the primary current pathways is reduced making the energy density more confined. However, the points maintain an even spacing thus the impact on the dissolution shape is reduced in comparison to when the jet is incorporated. Noting that the secondary current paths are spread away from the nozzle. Considering Figure 5.5d, with the jet incorporated, all primary current paths across the nozzle now converge at a single point, that being the path of least resistance. Only secondary current pathways spread across the jet. Observing the resultant profile from Figure 5.3 for 22.5° the maximum depth that is achieved corresponding to the peak in applied energy is seen at the extreme right of the profile. At this angle, it is also possible that electrolyte ejection effects from the cut could affect the slope of the opposite wall elongating the intersection with the un-machined surface where little current is expected to flow.

At this point it can be proposed that the distribution of the current density field takes on a skewed Gaussian distribution where the peak of the current density is shifted from the centre of the cut in line with the rotation of the nozzle.

5.2.3.2. Push / pull convention

The resultant profiles using the push / pull convention (examples of which can be seen in Figure 5.6) do not demonstrate the same changes in symmetry as seen with the normal convention with profiles remaining symmetrical throughout. The mean variation across all the sample striations from the left-hand slope to the right-hand slope being 1.1%. The resultant profile area again shows little variation

with a mean area across all sampled profiles of $18608 \mu\text{m}^2$ (1.5% difference to the mean area from the normal convention) with a maximum deviation of 1.5%.

There are however changes to the profile geometry. The same trend in depth change from the normal convention is seen in the push / pull convention. Taking the mean depths from the samples of 22° and 157.5° giving $37.7 \mu\text{m}$ depth (σ 1%) compares to the depth at 90° approach of $28 \mu\text{m}$ (σ 1.6%). The side walls show a reduction in slope from the steepest side walls at 22.5° / 157.5° being $123 \mu\text{m}/\text{mm}$ (σ 4%) to $104 \mu\text{m}/\text{mm}$ (σ 2.6%) at 45° / 135° and $95 \mu\text{m}/\text{mm}$ (σ 3.5%) for the angle pair 67.5° / 112.5° .

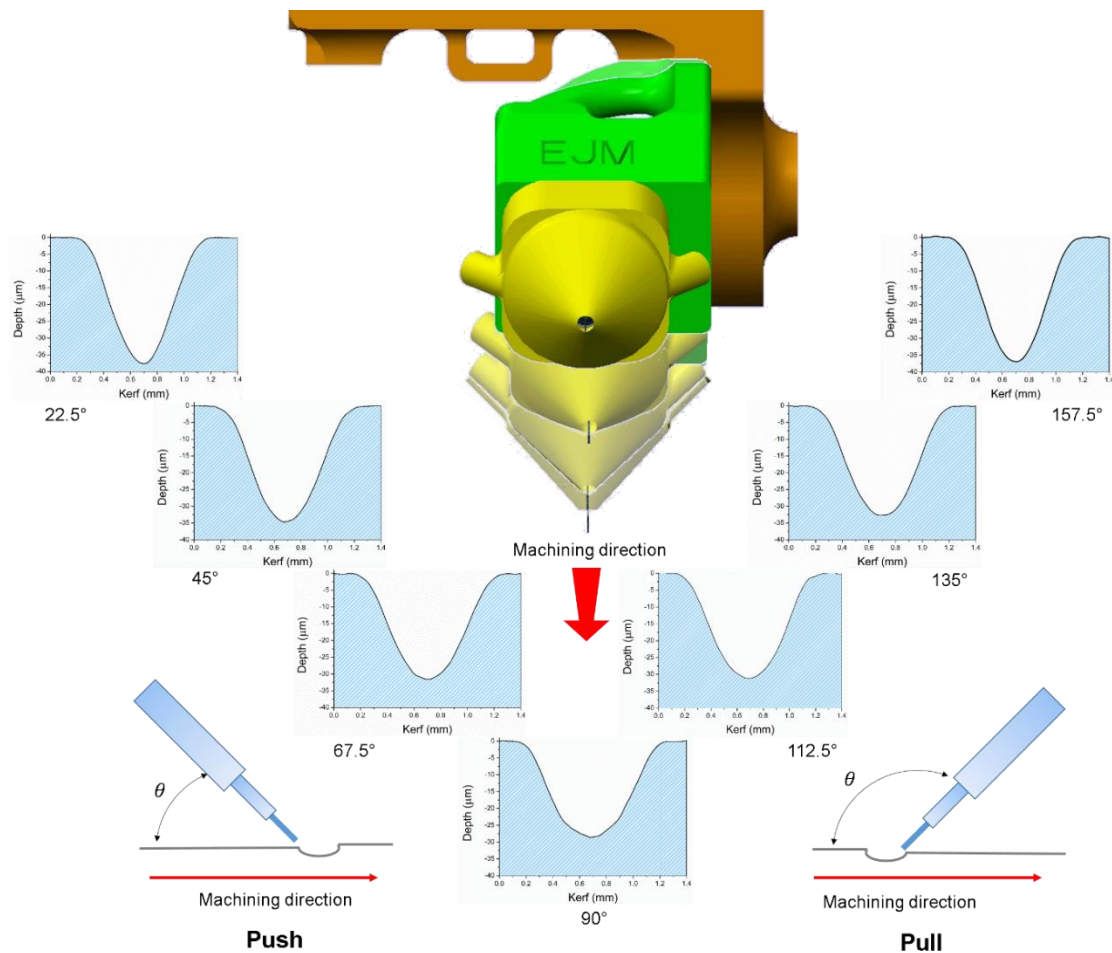


Figure 5.6: Examples of profiles taken using the push / pull convention

The differences can be observed in Figure 5.7 where all the profiles are overlaid on the same axis. The reduction in kerf is obvious as the nozzle rotates, from 1.17 mm ($\sigma = 2.2\%$) with the nozzle perpendicular to the surface to 0.948 mm ($\sigma = 1.5\%$) for the $22.5^\circ / 157.5^\circ$ approaches achieving $\approx 20\%$ reduction in kerf. The conflux effect seen in the normal convention profile is mimicked in the push / pull profiles. Higher angles of address having a deeper, narrower profile with a sharper apex compared to the profile with the jet being perpendicular, causing a wider, shallower more rounded distribution of energy. This is due to the equilibrium distance of all points around the nozzle contour and less confluence nature of the jet as previously noted in the normal convention.

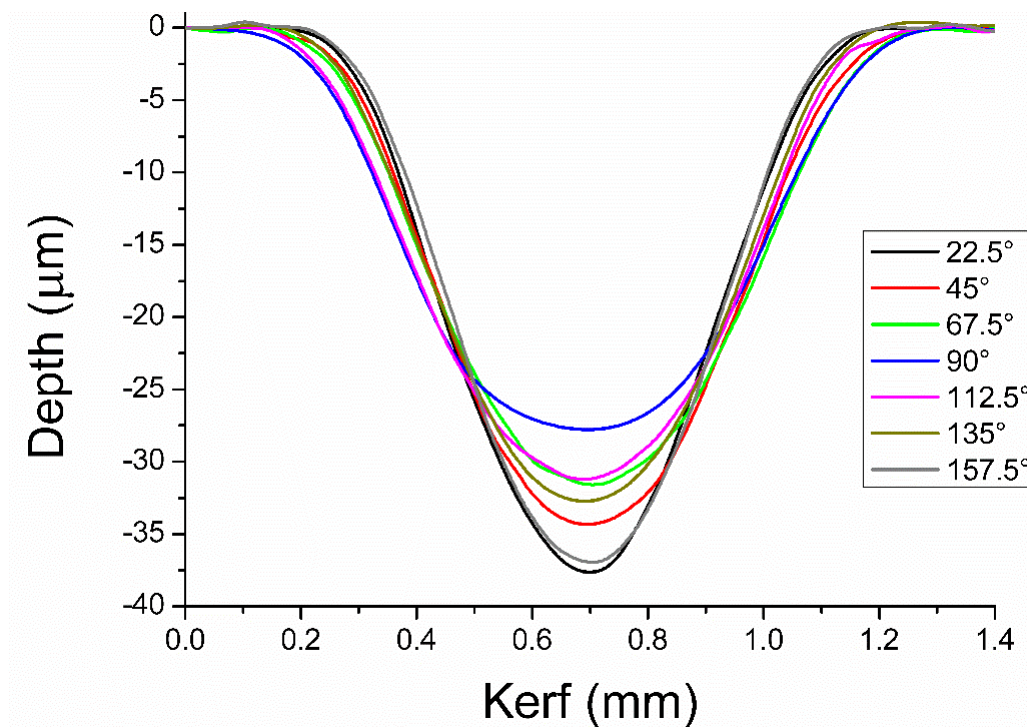


Figure 5.7: Profiles from push / pull convention overlaid to demonstrate changing energy distribution through different approach angles

The change in current density distribution is due directly to the angle of approach. This is further supported when the resultant finish is considered from the push / pull experiments seen in Figure 5.8.

In the push mode of Figure 5.8a, ($\theta = 22.5^\circ$) surface roughness is shown to be significantly lower when compared to the pull mode of operation. This is obvious not only in the surface scans but in the accompanying SEM micrograph (Figure 5.8). This results in a mean R_a across all samples of $0.04 \mu\text{m}$ ($\sigma 0.004 \mu\text{m}$) achieving a high lustre, reflective, appearance corresponding with a near mirror finish as defined by Prakash et al. [1981] [283] and in EJM by Kawanaka et al. [2015] [55]. When the nozzle is at 90° associated with the traditional approach (Figure 5.8b) the resultant finish is markedly different with preferential etching of grain boundaries and the largely nickel matrix, leading to a high degree of precipitate “wash out” (see Chapter 4). This “preferential” machining regime results in a much higher roughness leading to an R_a of $0.14 \mu\text{m}$ ($\sigma 0.006 \mu\text{m}$). Figure 5.8c demonstrates the resultant finish obtained from the pull mode ($\theta = 157.5^\circ$). The form of the profile mirrors that found at 22.5° meaning the workpiece has been subjected to the same applied energy so affecting the same overall dissolution noting the same colour scale for maximum depth. However, the surface can be seen to have undergone a more “sporadic” dissolution effect whereby the breakdown of oxide layers and debris removal is unequal across the surface. Thus, leading to uneven dissolution regimes and a higher roughness in comparison to the two previous modes with an R_a of $0.2 \mu\text{m}$ ($\sigma 0.02 \mu\text{m}$).

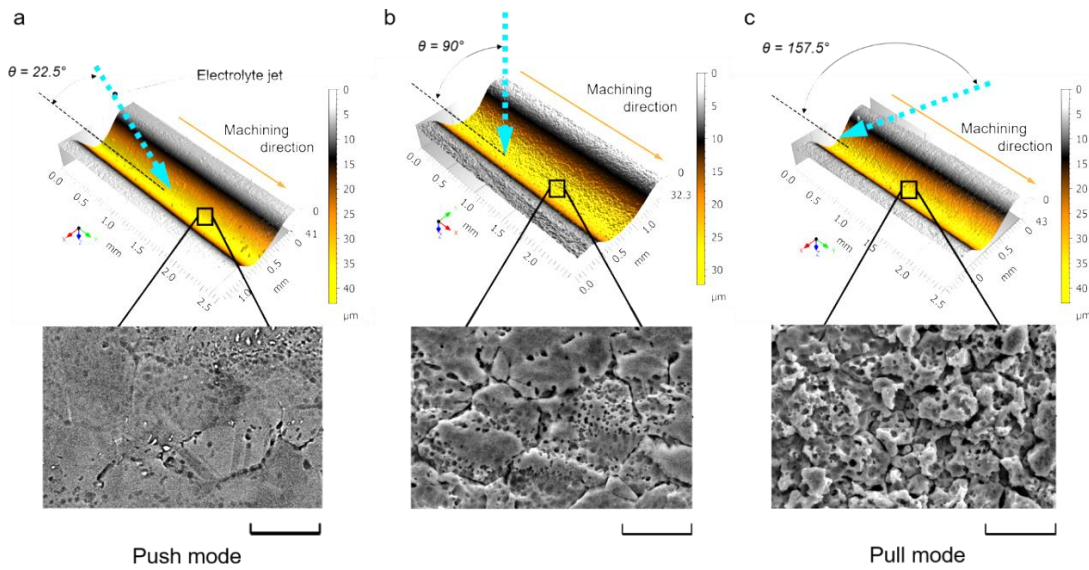


Figure 5.8: Extracted example surfaces and SEM micrographs of resultant surface (7.5k x Magnification, all scale bars are 10 μm) from cuts at 22.5° (a), 90° (b) and 157.5° (c).

These surface texturing effects are commonly associated with the level of current density as observed at the surface, in line with observations by Kawanaka et al. [2014] [54] (section 2.3.2). Consideration of Figure 5.9 highlights that the trailing edge of the jet dominates the final surface finish. In push mode (Figure 5.9a) the energy density at the trailing edge is seen to be at the maximum therefore leading to the smoothest resultant finish. In comparison at the other extreme in pull mode (Figure 5.9c), the IEG is at its largest at the trailing edge, therefore, the energy level is at the lowest leading to a low energy dissolution regime. The normal mode (Figure 5.9b) although having the trailing edge in the lowest area of current density, the IEG is considerable smaller than that at the trailing edge of the pull mode. Therefore, as resistance is directly related to the gap between the electrodes and resistance is inversely proportional to current so, the smaller IEG at that point in the normal mode means a higher current transfer is possible. This

is demonstrated by the lower surface roughness of the normal mode than the pull mode.

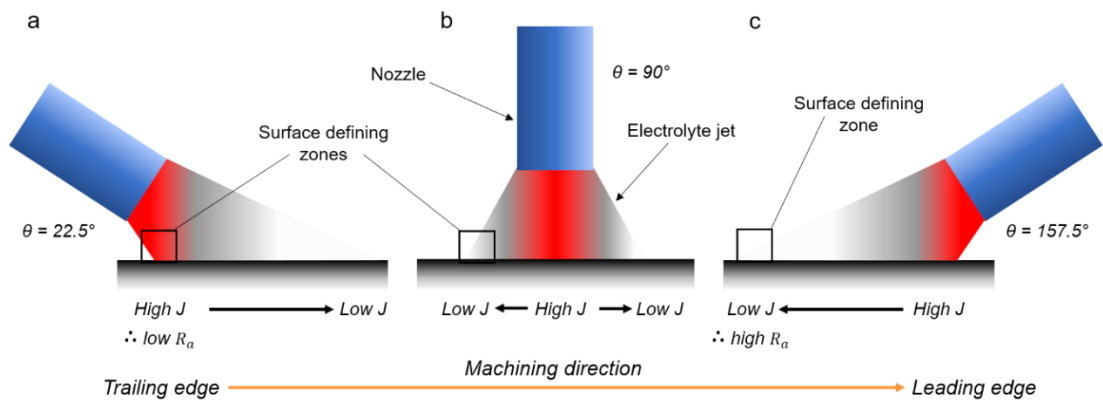


Figure 5.9: Schematic of energy distribution affecting surface finish (a) push mode (b) normal mode (c) pull mode

5.2.3.3. The effect of jet velocity on the resultant profile

Figure 5.10 shows the resultant profiles created when the nozzle is angled at 22.5° , 67.5° and 90° to the workpiece surface and the jet-speed varied through 4 m/s, 14 m/s and 29 m/s covering the range possible with pump used in this apparatus.

It should be noted that achieving precision machining at the lowest jet speeds demonstrated here is only possible due to the use of the nozzle air shroud which creates a thin film area reported with higher jet velocities, where a hydraulic jump is observed at the periphery of a thin film (see section 2.3.5).

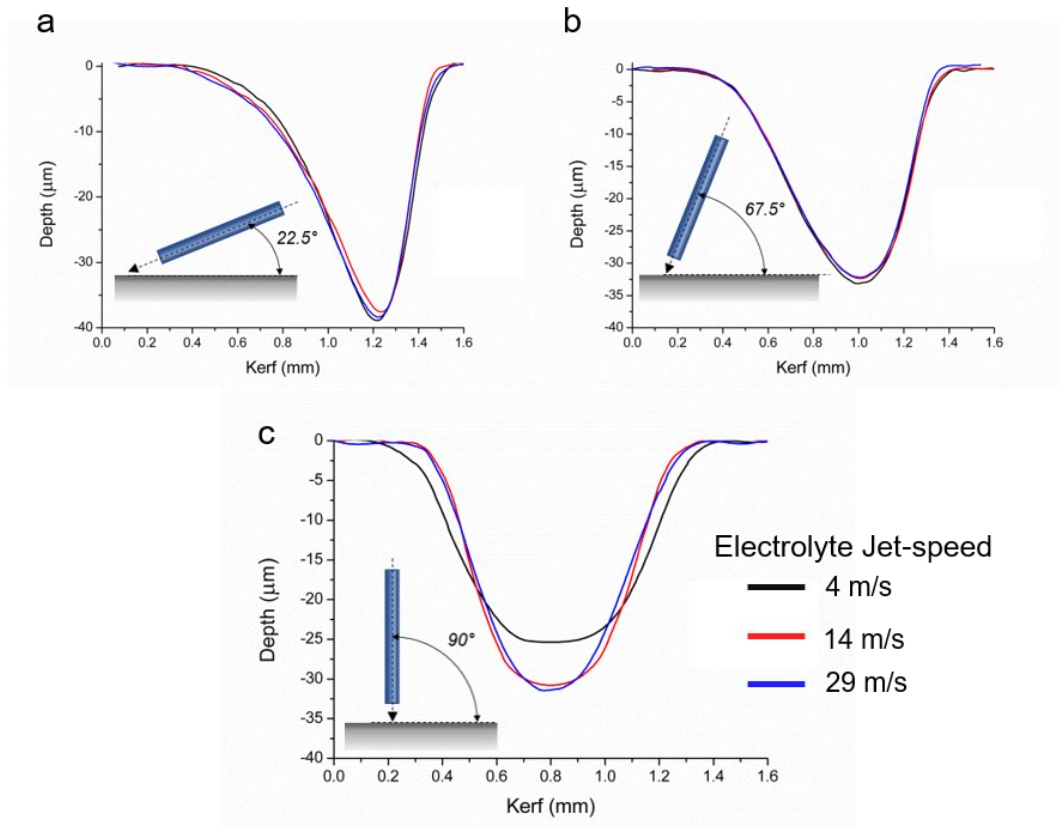


Figure 5.10: Impact of varying electrolyte jet speed on resultant profile. a) with the nozzle inclined at 22.5°, b) 67.5° and c) 90° to the workpiece surface noting the invariance of depth at tilted regimes

Observed in Figure 5.10a and b, there is little impact on the resultant profile within the range tested here. The created profile also mimics those profiles found previously with the lower angles achieving greater depth due to the higher localised current density. Both sets of striations demonstrate a mean profile area of $18493 \mu\text{m}^2$ and a standard deviation of 1.7% across all samples which is less than 1% difference from the profiles created earlier, showing there is no noticeable impact of varying jet speed. This further demonstrates the mechanisms of current transfer dominating the resultant profile, rather than any ejection effects in contradiction to findings in the literature review (section 2.3.5). The variation seen in Figure 5.10c of the depth reduction of 19% ($\sigma < 1\%$) at the lowest jet speed compared to the highest speed and increase in kerf width. This

is explained by the increasing jet speed enabling clearing of debris and localised oxidisation within the cut, leading to a reduction in current flow to the surface directly below the jet. Interestingly, this phenomenon is not encountered when the nozzle is inclined. This may be due to the ejection of debris and other polarising artefacts from the IEG having a facilitated exit route. While in the normal mode a stagnation point will occur in the jet centre and inhibit debris ejection.

5.3. Modulation of in-jet properties

5.3.1. Introduction

Prior work on the angle of address (Section 5.2) found that the angle of jet approach directly affected the resultant kerf profile that was created. It was shown that this was due to altering the resistance in-jet and so both precision and geometrical changes to the profile could be adapted through modulation of the resistance between jet and target surface.

As noted in the literature review (section 2.6), energy beam processes are currently limited by a characteristic energy profile (Figure 2.1) which is the principle factor in determining the dissolution profile. However, some techniques such as laser beam processing have gone some way to addressing this by adapting this energy distribution through various beam shaping strategies (section 2.6.2) and are capable of creating distinct meso- and micro-surface geometries.

The ability to create non-uniform kerf profiles has not been seen before in electrochemical jet processes, either in deposition or dissolution. This type of

flexibility would enable the process to create a higher level of replicating surface patterning or allow the process to be more analogous to other micro-machining techniques where a different tool shape is used to create different feature geometries.

An initial experiment was carried out to establish the change in resistance that can be expected by changing the size of the IEG of a standard 1 mm I.D. nozzle. The voltage required to achieve 750 mA was recorded for each 0.2 mm step height up to 2.75 mm stand-off. Using Ohms law (Equation 4) the resistance could then be calculated. The results of this can be seen in Figure 5.11a, showing that when using a standard profile nozzle, resistance increases from 15 Ω at a nozzle stand-off of 200 μm through to 200 Ω at 2.75 mm stand-off when used with a 2.3 M NaNO_3 electrolyte. As expected a linear trend is seen between resistance and nozzle tip to surface distance. Further demonstrating the electrolyte column can therefore be regarded analogous to a resistor in an electrical circuit.

Considering Figure 5.11b, if the nozzle is considered in single geometric plane it can be hypothesised that by discretely changing the stand-off distance across the nozzle tip would lead too localised changes in resistance, therefore current distribution, and so localised changes in material deposition or removal. It is proposed that the accepted definition of 'stand-off' (inter-electrode gap) is no longer sufficient. Instead, a new parameter is required which defines the spacing between nozzle rim contour and the work. This must accommodate spatial- and temporal-variation as the work piece shape evolves during machining. The result being the creation of preferential current pathways and therefore material removal can be modulated across the area of jet impingement.

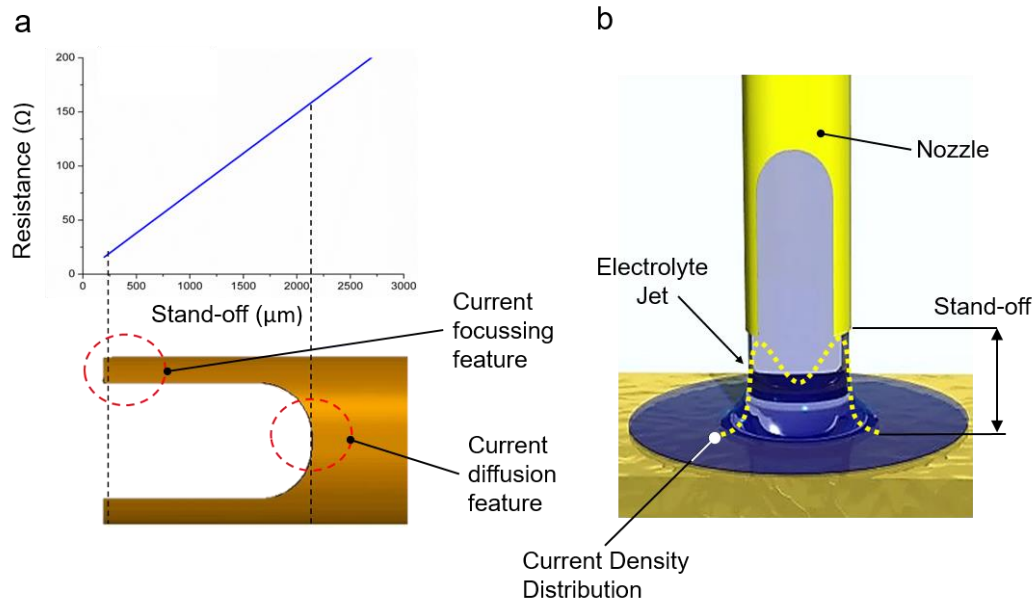


Figure 5.11: (a) resistance is seen to increase as the distance between the nozzle tip and workpiece surface increases. By redesigning the geometry of the nozzle tip, localised resistance can be modulated in-jet (b) thus allowing current distribution to be manipulated in-jet.

A preliminary study was undertaken here to investigate the hypothesis that localised variation of in-jet resistance can be induced and so affect the resultant profile created. A simplistic computationally efficient 2D model is used in the first instance to test the hypothesis and understand the physical process mechanics by applying a modulated current density profile beyond that of a typical single point Gaussian distribution. Based on the results of the simulation, basic nozzle designs were implemented and experimentally tested. The resultant profiles are then compared to the simulation results to understand if this approach is valid. A design equation is developed to incorporate the two major effects of material transfer in an electrochemical cell; variance of distance between electrodes and area of facing electrodes at any single point. This is then utilised to understand the effects of nozzle geometry against response profile and demonstrating the validity of the equation.

5.3.2. Simulation of in-jet resistance modulation

Several process models have been proposed both in EJM and alternative energy beam processes. (see sections 2.3.2 and 2.6.2). In order to form the cross-sectional profile these simulations often rely on a typical Gaussian energy distribution taking into account process specifics such as calculation of the electrical potential across a uniform IEG [210] or empirical knowledge such as particle distribution [208]. Alternatively, they require a calibration profile to ascertain the removal shape [217, 219] as an input to the model which can then be used to simulate process changes, even to the extent of predicting the required inputs to form a surface shape [220]. However from the observations in section 5.2 EJM does not behave in the same manner as other energy beam processes as the removal profile can be manipulated and instead spatial considerations in relation to Ohm's law have the greatest influence along with material considerations denoted in chapter 4. As prediction of the cross-sectional profile shape caused by changing spatial qualities within the IEG was the focus of this work rather than development of a process footprint allowing formation of an overall freeform surface, other more complex surface evolution models were not considered that require empirical calibration data of the dissolution shape so define the etching rate function. It was therefore felt that a simplistic model could be devised using faradays law to predict profile removal area and understanding the impact of spatial changes on the current available for dissolution, i.e. resistance, at any single point across the profile, could be used to understand the impact of a variable IEG. However, to simulate more complex feature surface would require adaption and implementation of the aforementioned surface evolution models. Thus, to assess the hypothesis a simplistic 2D simulation was

created using MATLAB based on the following boundary conditions. Utilising the measured resistance data from Figure 5.11a, it is possible to approximate the shape of the removal profile by considering the percentage of total current that will be available for dissolution with relation to resistance at any single point across the nozzle contour. For example, the resistance on the CPE nozzle at the centre (point 0) with a 0.5 mm IEG will be $\approx 40 \Omega$ in comparison at the edge of the nozzle (point 1 or -1) the resistance will be $\approx 110 \Omega$ with an IEG of 1.5 mm at that point. Thus, there will be 2.7 times less current available for dissolution at the edge in comparison to the centre. Using the minimum and maximum points of current created by the nozzle features and the boundary condition of kerf being double that of the nozzle I.D. a normal distribution is then assigned around these giving an approximation of the current distribution. The area under the curve being equal to the total current density. This is proportional to the total material removed across the 2D section (Figure 5.12).

Novel nozzle designs were created to establish the greatest contrast to what would be expected from a standard Gaussian energy distribution found with standard tip (Figure 5.12a). Termed as the central point element (CPE) design (Figure 5.12b), symmetrical twin element (STE) design (Figure 5.12c) and the off-centre single point (OSPE) design (Figure 5.12d).

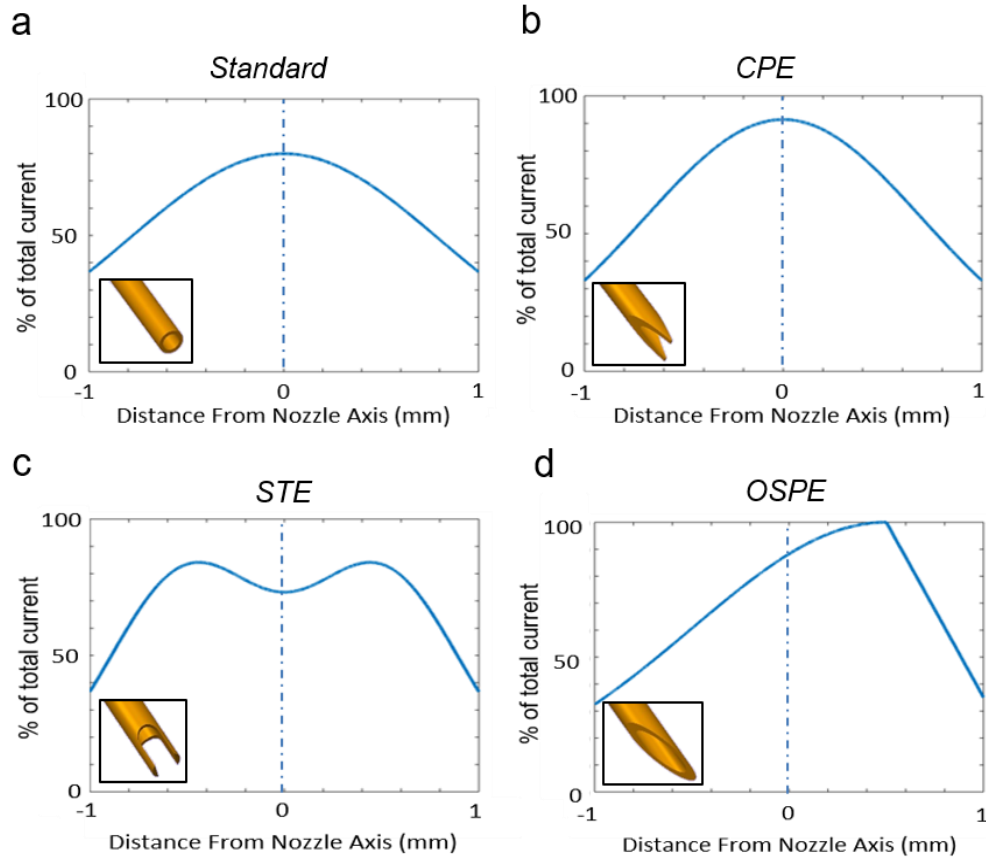


Figure 5.12: Graphical representations of the current distribution expected from the CAD designs in the bottom left corner of the graph creating preferential current paths by lowered localised resistance at discrete points. This achieves a higher weighting of the total current supplied at highly localised points across the nozzle profile expressed as a percentage of the total current supplied (a) standard nozzle tip (b) central point element (c) symmetrical twin element (d) off-side single point element

Figure 5.12 clearly demonstrates that the current distribution across the profile is altered by that found in the standard nozzle tip due to the changing resistance at discrete points. To further understand the modulation of in-jet resistance from the two-dimensional nozzle tip designs, the MATLAB model was further developed in conjunction with Dr. Jennifer Gaskell (Centre for mathematical medicine and Biology, University of Nottingham) to simulate the jet interaction environment between tool and target surface. Variance can be seen in experimental work, even across the length of the sample. This arises due to the natural fluctuations from valence variation, hydrodynamic effects, including wash away of large

undissolved precipitates, and grain boundary effects (as noted in chapter 3.8.3). The model captures this stochastic nature of EJM through inclusion of probabilistic dissolution.

In this model, all machine parameters are assumed to remain constant. Joule heating and erosion effects due to hydrodynamic effects are not considered. Physical properties of the electrolyte are not investigated apart from the electrolyte current efficiency, which is taken to be constant. The material is considered to be homogenous taking the electrochemical equivalence (ECE) as a weighted average from the constituent elements defined for In718 in Chapter 3.8.3.

The current density distribution for each nozzle is calculated from the resistance generated as a function of distance from nozzle tip to contour. Using these 2D representations, the current distribution can be applied to the progressing dissolution.

The electrolysis model was constructed from Faraday's First Law of Electrolysis (Equation 6), adapted for progressing dissolution, which gives the expected value for mass removed (in grams) to be:

$$m = \int_0^{t_m} \frac{I(\tau)M}{Fz} d\tau \quad \text{Equation 13}$$

where t_m is the total machining time, $I(\tau)$ is the current integrated over time step τ , M is the molar mass, F is Faradays constant and z is the material valence.

The total cross-sectional area expected to be removed is thus:

$$A_{exp} = \int \frac{m(x)}{\rho L} E_{eff} dx, \quad \text{Equation 14}$$

where x is the distance across the cross-sectional area in the x co-ordinate (Figure 5.14), ρ is the material density of a single 2D section within the profile (m^2), and E_{eff} is the electrolyte current efficiency (%) calculated from prior experimental work in chapter 4 and compared to theoretical mass removal m .

The model removes elements of the substrate stochastically with respect to a probability of removal (p_R) which is governed by supplied current density weighted by the percentage available for dissolution from the initial simulation, electrolyte, electrochemical equivalent (ECE) of the material elements and condition of neighbouring elements (Equation 15).

$$p_R = \frac{ECE \cdot I(x) dt}{\rho L} \times \frac{1}{A_{exp}} \quad \text{Equation 15}$$

The code for the stochastic simulation was commissioned using the previously defined boundary conditions and generated by Dr Gaskell based on the program architecture shown in Figure 5.13

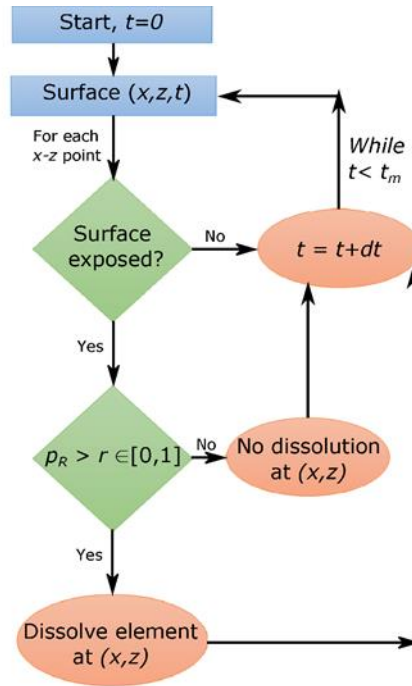


Figure 5.13: A flow chart of the stochastic simulation process as described in the text. If a surface element is exposed and the probability of removal is greater than a random number, $r \in [0,1]$, then the element will be dissolved.

For each time step, each exposed element of the surface will have a respective probability of removal compared to a random number, $r \in [0,1]$. If $p_R < r$, the element is not dissolved. This process continues until the total machining time (t_m) has been applied (with p_R scaled accordingly), or alternatively, until the total area removed across the 3D surface approximates the area expected, A_{exp} . The model provides a predicted surface profile for any nozzle geometry, nozzle distance, and current density combination.

Using these simulated profiles, the process can be reiterated stacking the profiles to create a three-dimensional simulation of the expected profile along a striation length (L) (Figure 5.14). The stochastic nature of the simulation can be seen by the variation in the repeated profiles.

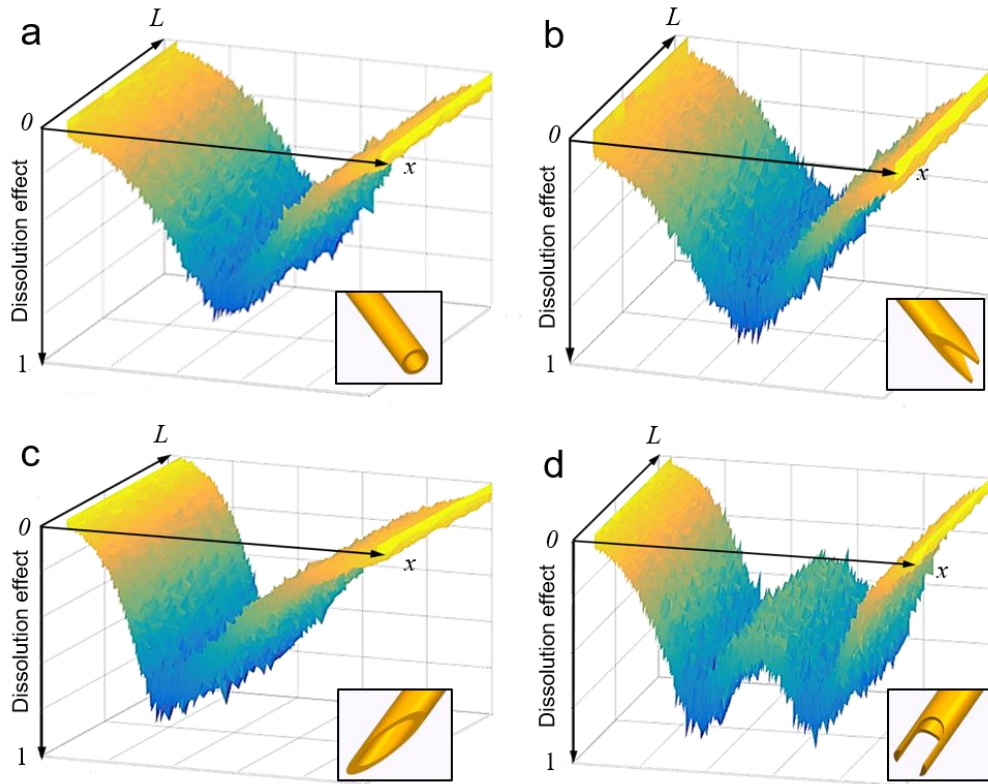


Figure 5.14: Normalised 3D simulations of the expected striation profile created by stacking re-iterated sim profiles along a striation length (L), considering the dissolution effect caused by the current distribution at each discrete point across the kerf (x) for (a) standard nozzle, (b) centre point element (CPE), (c) off-centre single point element (OSPE) and (d) symmetrical twin element (STE)

5.3.3. Nozzle design definition

To further explore the influence of nozzle tip design on the modulation of current distribution two approaches were taken to the design of the nozzle tips. Firstly, a planar approach to design was taken (as demonstrated in the initial model) to establish the influence of changing the distance between the nozzle rim contour and the interaction surface. Secondly, a free-form approach was taken to assess the influence of the area of each nozzle contour feature facing the interaction surface.

These complex nozzle tip geometries require a new metric other than the simple nozzle stand-off distance to understand the impact of the nozzle design on the resultant profile created. This is termed the nozzle design impact factor (*DIF*). This takes into consideration not only the distance of the parallel surface of the nozzle to the workpiece surface but also the area of the nozzle surface. This is expressed in Equation 16.

$$DIF = \frac{A_F}{A_A} \cdot \frac{d_S}{d_N}$$

Equation 16

Where A_F is the area of the specific feature facing the surface and A_A is the annulus area of the nozzle tip, d_S is the minimum distance of the nozzle tip from the surface and d_N being the distance of the individual nozzle feature from the surface (Figure 5.15).

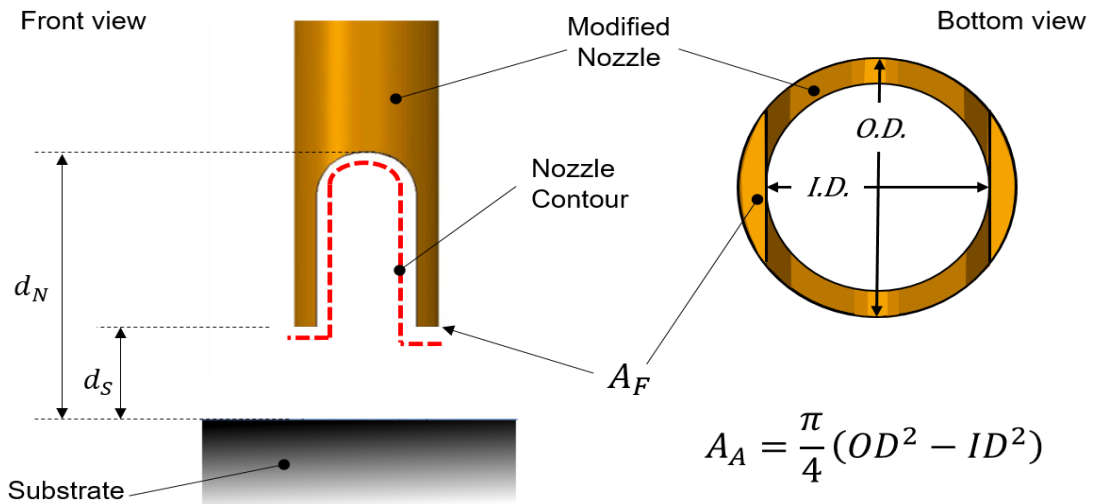


Figure 5.15: Schematic of the modified nozzle tip showing the definition of terms for the DIF

Higher *DIF* values will therefore lead to higher localised material removal due to lower localised resistance. This in turn means a lower voltage is required to generate the determined current density within the jet. Using the *DIF* value allows the performance of nozzle features to be evaluated and their weighted effect on the resultant profile to be predicted.

The relationship seen in Equation 16, although useful in assessing design elements of a simple nozzle design feature, is required to be expanded to address more complex designs (Equation 17, Figure 5.16).

$$\mathbf{DIF}_{surface}(x, y) = \int_{-\pi}^{\pi} \frac{d_s}{d_{NS}(x, y, \theta)} d\theta \quad \text{Equation 17}$$

Where d_{NS} is the Euclidean distance between a nozzle element (N) and substrate surface element (S), located at (x_N, y_N, z_N) and (x_S, y_S, z_S) ,

$$\begin{aligned} d_{NS}(x, y, \theta) &= \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2} \\ &= \sqrt{(x_S - x_N)^2 + (y_S - y_N)^2 + d_N^2} \end{aligned} \quad \text{Equation 18}$$

As the height of the surface is taken as $z_s = 0$.

Equation 17 gives the impact of the nozzle any point on the surface in x and y. To ascertain the influence on cross-sectional profile during translation it is necessary to integrate along the direction of motion which is assumed to be y thus the equation becomes Equation 19:

$$DIF(x) = \int_{-\pi}^{\pi} \int_{-1}^1 \frac{d_s}{d_{NS}(x,y,\theta)} dy d\theta$$

Equation 19

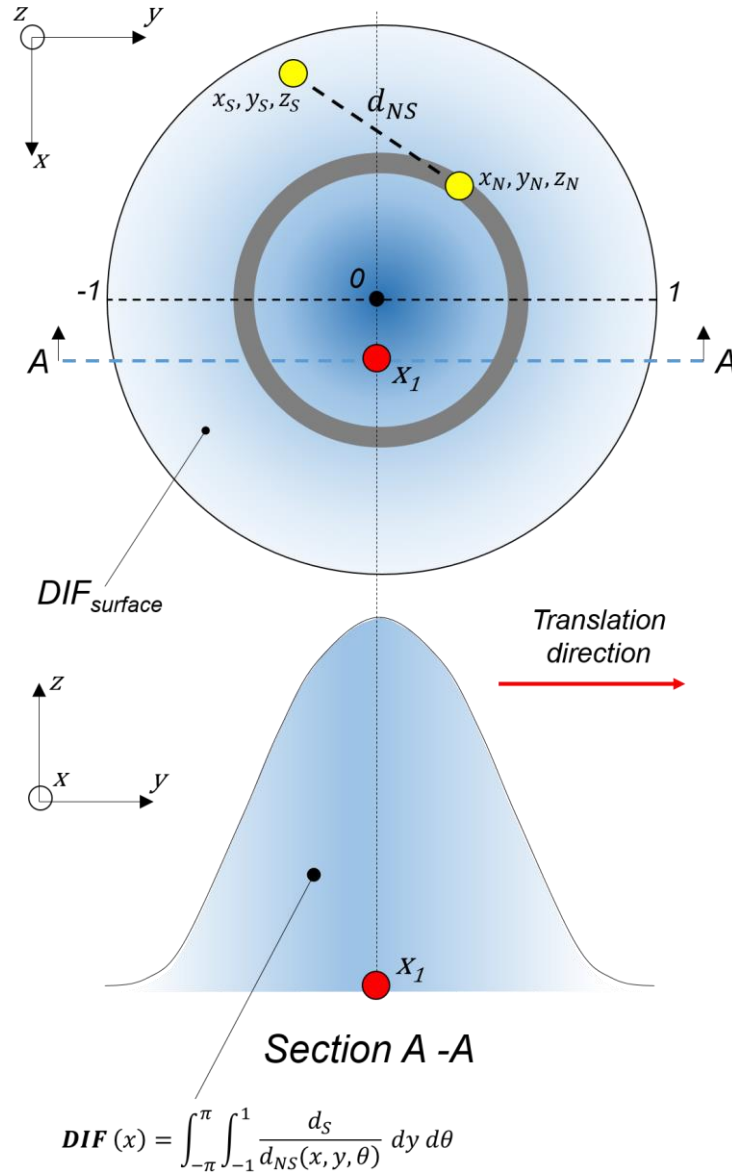


Figure 5.16: Coordinates system and derivation for calculation of the DIF

It is possible to assess the impact of the nozzle as a whole or any individual feature by quantifying the area under the contour of the nozzle. Effectively the

larger the area, the larger the resistance and so the lower the impact (Figure 5.17).

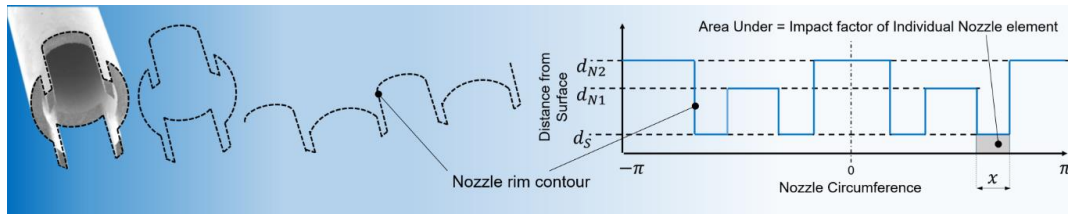


Figure 5.17: Graphical representation of the extended DIF equation for evaluation of a single element of the NC nozzle

The contour of the nozzle is removed from the design intent and unwrapped into a two-dimensional profile, the abscissa being the circumference of the nozzle and the ordinate being the distance from the interaction surface. The total area under the curve between $-\pi$ and π giving the impact of the nozzle as previously described. The impact of any design feature can also be evaluated, seen as x in Figure 5.17 and compared to any other feature in the design.

5.3.4. Experimental validation of energy modulation, and scalability

The generation 1.5 EJP CNC platform (Section 3.3) was used throughout the experimentation. As with the prior work Inconel 718 was again used as the target demonstrator material reliant on the findings of chapter 4.

Machining samples were created by carrying out striations across the workpiece surface with the nozzle orientation set by fixture to create the desired profile as denoted in the simulation. Repeated passes were carried out in separate striations passing over the same toolpath consecutively, increasing passes by one per striation (up to four).

Geometrical analysis of the profile data was carried out in-line with the experimental procedure (section 3) to obtain depth, width, area, overcut and side wall slope (defined in section 3.6) of each of the resultant profiles. Standard deviation (σ) is consistent across all results as the deviation from the mean taken over 30 individual samples.

During experimentation, the electrolyte jet velocity for the 1 mm I.D. nozzle was set at 13 m/s for the initial experimental validation and 16 m/s in all other cases. For the 0.5 mm I.D. nozzle 16 m/s was used except for the form variation due to jet speed experiments where it was varied from 3 m/s to 25 m/s. For the 0.25 mm I.D. nozzle 16 m/s was used in all cases. The electrolyte used throughout was a 2.3 M solution of NaNO_3 . Analytical grade reagents and deionised water were used. Electrolytes were maintained at 22°C during all experiments. Nozzle tip stand-off from the workpiece, in all cases, was initially set at 0.25 mm. A constant applied current was set at 900 mA ($J = 100 \text{ A/cm}^2$) for 1 mm nozzle, 210 mA ($J = 100 \text{ A/cm}^2$) for the 0.5 mm nozzle, except during parameter variation where it ranged from 80 A/cm^2 to 200 A/cm^2 and 100 mA ($J = 200 \text{ A/cm}^2$) for the 0.25 mm nozzle. Voltage was left to float as this was seen to vary dependant on the nozzle geometry and subsequent resistance. Each pass was carried out at 0.5 mm/s translation speed for all work except where specified the translation speed was reduced to 0.1 mm/s.

Standardised stainless steel, cylindrical, straight walled nozzles were used as the control and the base for the modified nozzle tip geometries. The patterns were generated in CAD and toolpaths generated in CAM. Using wire electrical discharge machining (WEDM), the modified geometry was cut into the standard nozzle tips (Figure 5.18, Figure 5.19 and Figure 5.20).

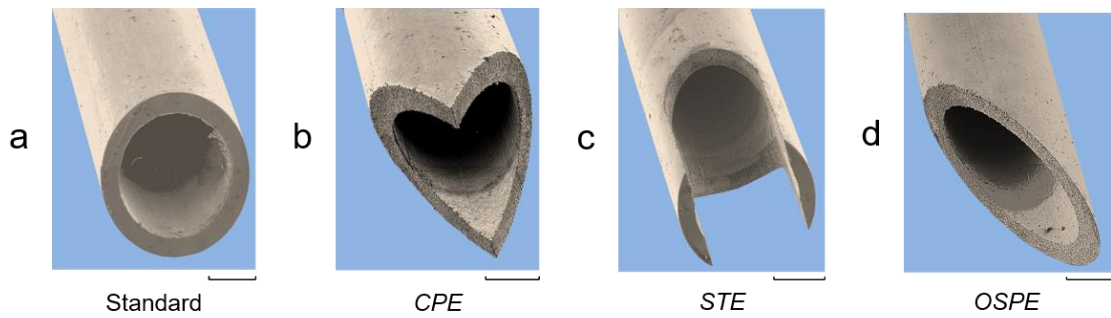


Figure 5.18: Tinted SEM images showing the standard and modified nozzles using a simple planar approach prepared by wire EDM. (a) Standard nozzle, (b) centre point element (CPE), (c) symmetrical twin element (STE) and (d) off-centre single point element (OSPE). All scale bars are 500

The initial planar design nozzle contours were designed to be counter-intuitive to the known current density distribution found with a cylindrical nozzle. Using 1 mm I.D. nozzles, these were tested to demonstrate the resultant profile could be modified by simply moving the focal point of the current density distribution. These rudimentary designs are referred to as (Figure 5.18b) centre point element (CPE), (Figure 5.18c) symmetrical twin element (STE) and (Figure 5.18d) off-centre single point element (OSPE).

Free form nozzles (Figure 5.19) were designed and tested again using 1 mm I.D. nozzles. This was carried out with consideration to the area of the elements of the nozzle tip contour and their position. The resultant profiles were analysed to assess the influence of the changing area of each nozzle tip element, the nozzle as a whole and the resistance characteristics of the nozzle. These are referred to as the wide castellated nozzle (WC) (Figure 5.19a) and the narrow castellated nozzle (NC) (Figure 5.19b).

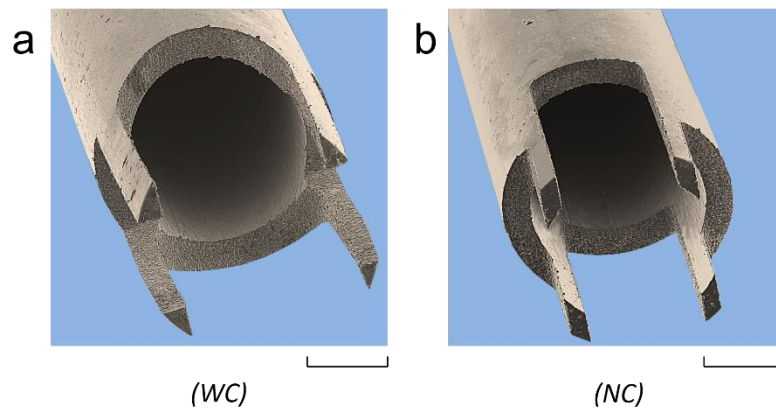


Figure 5.19: Freeform nozzles designs focussing on the area of each individual nozzle element (a) Wide castellated nozzle design (WC) (b) Narrow Castellated nozzle design (NC). All scale bars are 500 μm

The nozzles in Figure 5.20 were machined to experimentally assess the fidelity achievable between nozzle shape and resultant profile with respect to the *DIF* of the individual nozzle features and the scalability of the process. Figure 5.20a shows not only individual steps machined into the section to give three different resistance points but also the side wall of the nozzle is thinned therefore reducing the circumference and area at a localised section. Figure 5.20b copies the *STE* design from previous design except scaled and cut into a 500 μm I.D. nozzle and Figure 5.20c uses a scaled version of the *OSPE* design on a 250 μm I.D. nozzle. Using these smaller nozzles will show experimentally if the energy modulation translates to a smaller scale when reducing distances between nozzle features and the hydrodynamic effects found in a more constrained nozzle.

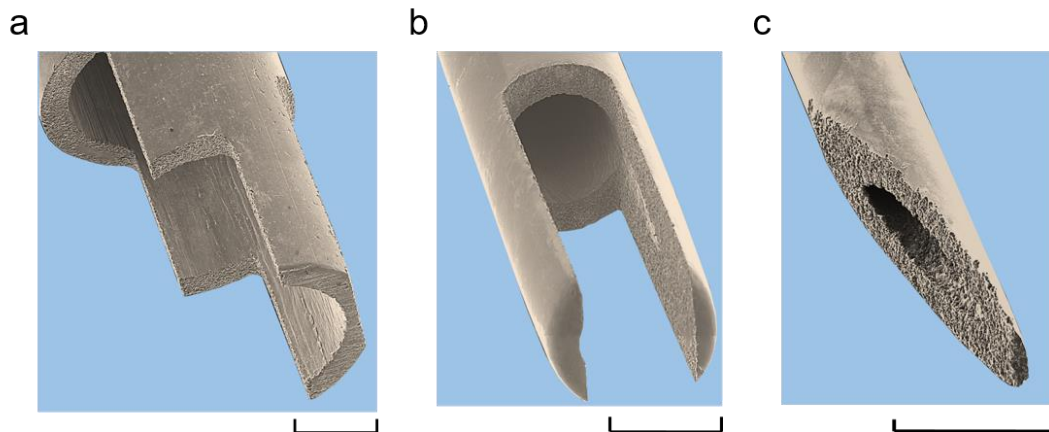


Figure 5.20: Nozzle designs realised to evaluate the effectiveness of the DIF and scalability of the process (a) steps with a 1mm I.D. nozzle, (b) STE design with a 0.5mm I.D. nozzle and (c) OSPE design with a 0.25mm I.D. nozzle. All scale bars 0.5 mm

5.3.5. Validation of nozzle design and simulation

The total current delivered is similar in all nozzle types, but the distribution is modified as a result of the nozzle geometry. This is demonstrated by the area of material removed in the resultant profiles, seen in Figure 5.21 being within a 3.5% deviation of the mean resultant profile area of $39000 \mu\text{m}^2$ the variation coming from the varying *DIF* of each nozzle.

The *OSPE* nozzle exhibits the deepest cut at $50 \mu\text{m}$ ($\sigma < 1\%$) compared to the standard nozzle generating only a $35 \mu\text{m}$ ($\sigma < 1\%$) deep cut. The *STE* design shows a cut depth just over half that of the *OSPE* nozzle at $28 \mu\text{m}$ ($\sigma < 1\%$) at the tip location of each feature. Along with the obvious form changes in the resultant profile (Figure 5.21b), there are also more subtle changes. The overcut area of the *STE* nozzle beyond the ideal column below the nozzle is increased from $9300 \mu\text{m}^2$ ($\sigma 7\%$) in the standard resultant profile to $10100 \mu\text{m}^2$ ($\sigma 7\%$) for the *STE* resultant profile. However, the side walls demonstrate an increase of 19% in

slope, ($83.6 \mu\text{m}/\text{mm}$ ($\sigma < 1\%$) as compared to $70.4 \mu\text{m}/\text{mm}$ ($\sigma 4\%$) of the standard profile. This is due to the floor of the profile being wider as the current focuses under the twin elements at the edge of the jet. In comparison, the *CPE* resultant profile displays a side wall slope of $53.8 \mu\text{m}/\text{mm}$ ($\sigma 3\%$) as the current profile is concentrated to the centre of the jet.

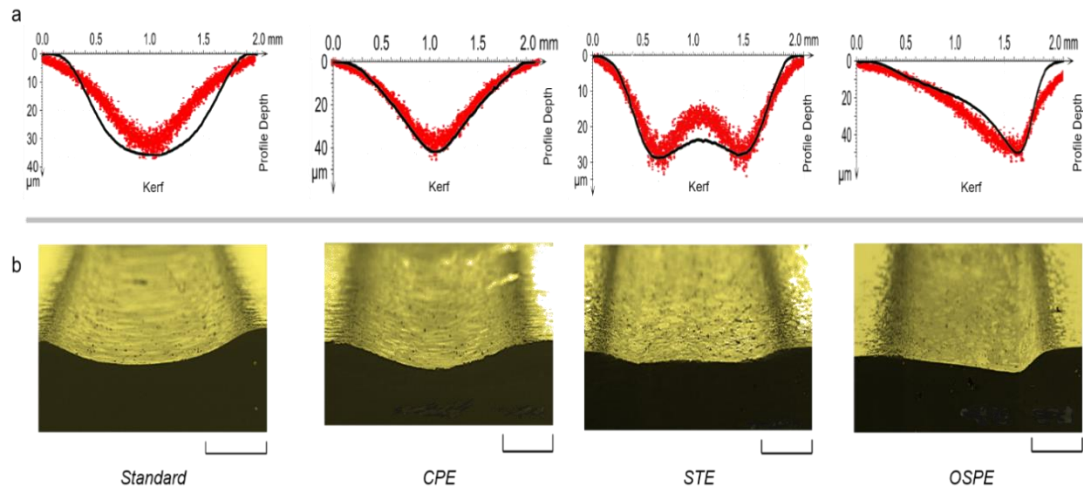


Figure 5.21: (a) Example resultant machined profiles from a single pass (black line) and compared to the simulation derived profiles (red point cloud) (b) Tinted SEM images of the sectioned resultant varied profile channels with 4 passes over the striation showing full geometrical evolution. All scale bars are $500 \mu\text{m}$.

From Figure 5.21a discrete surface point simulation results (shown in red) exhibit good agreement in the cases of the standard, *CPE* and *OSPE* resultant profiles (shown in black) achieved after a single pass. The two-dimensional profile simulations were generated using the probability of dissolution of each element under the jet. This considers the applied current at that point (Figure 5.12b), the electrolyte current efficiency, known material constants and jet interaction availability for each element at the surface. For the standard nozzle profile, the simulation shows an area removal of $39200 \mu\text{m}^2$. This can be compared to the actual response profile of $39100 \mu\text{m}^2$ ($\sigma < 1\%$) removed by the standard nozzle

showing a variance of 0.2% simulation to actual. However, the standard response profile is marked by an increased removal observed at the bottom corners of the cut. This is likely due to hydrodynamic effects and a modified ejection path as dissolution advances. This ejection profile phenomena has been previously noted to occur during machining [47] utilising a cylindrical nozzle. For the *CPE*, *STE* and *OSPE* nozzles it demonstrates a mean variation of 4.8 % from simulation to actual. In the case of the *CPE*, electrolyte ejection from the cut is facilitated by the nozzle geometry and the cut profile, contrasting effects seen in the other nozzles. This permits a more accurate simulation. Jet ejection at the nozzle is not observed to change significantly but interaction and ejection from the machined feature does. Jet-rebounding effects causing re-machining [47] have been reported, however, given the edge effect upon the fluid flow regime, this phenomenon is proposed not to contribute significantly here.

The *CPE* nozzle shows a maintained focus of the energy density to the centre of the feature due to the design of the nozzle. This achieves a high resistance at the periphery of the jet is maintained regardless of the evolving surface profile in the same manner as the standard nozzle (Figure 5.22).

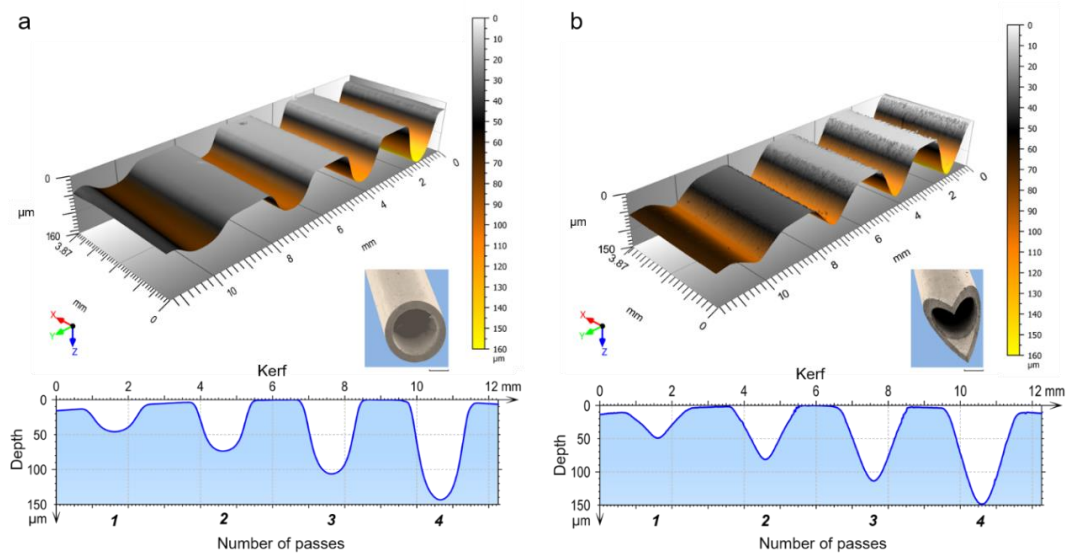


Figure 5.22: Extracted surface and profile from areal scans showing comparison of evolving response profile over four passes of (a) standard nozzle and (b) CPE nozzle demonstrating little change to the profile shape regardless of repeating striations due to the nozzle design type. Scale bars for nozzles 500 μm

The STE nozzle response profile differs whereby the simulation shows a variation in form with a higher peak in the centre of the cut. The actual cross-sectional area removed being 36700 μm^2 ($\sigma < 1\%$) giving an 8 % variation from the theoretical value. This variation can be emulated to a degree by simulation of the electrical field effect occurring during machining and highlights the evolution of the cut profile. However, in this case the nozzle design is detrimental to the fidelity of the response profile to nozzle geometry. In Figure 5.23a, surface scans of striations cut with an STE nozzle over 4 passes demonstrate how the geometry develops for a typical surface feature. The depth increases from 28.6 μm ($\sigma < 1\%$) in a single pass to 112 μm ($\sigma < 1\%$) after four passes. While the depth increases the bottom of the profile flattens and taper decreases with a slope of 83.6 $\mu\text{m} / \text{mm}$ ($\sigma < 1\%$) after 1 pass to 274 $\mu\text{m} / \text{mm}$ ($\sigma 2.4\%$) after 4 passes.

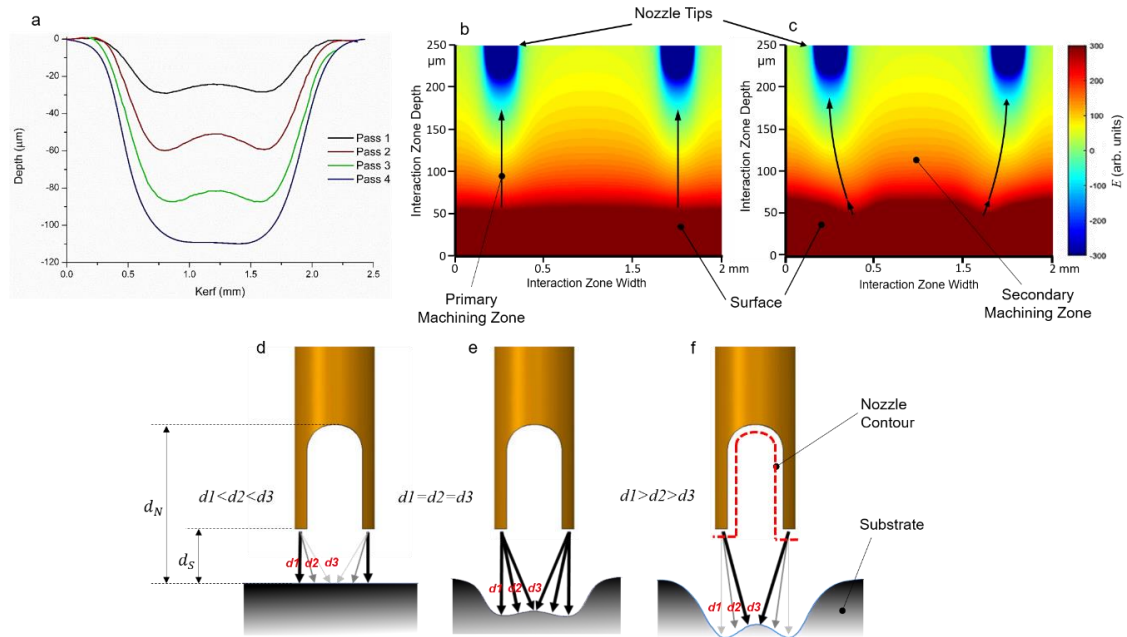


Figure 5.23: Utilising an STE nozzle (a) consecutive passes were made over the same striation equal to a 16 second dwell time after four passes. (b) Electrical field strength map shown for the jet zone when approaching a flat surface. (c) EFSM for interaction zone when approaching a pre-machined surface and the influence this has upon field distribution. Note that arbitrary units are applied for electric field strength. (d) Schematic of an STE nozzle showing the distance (d_s) of the main element tip to the work surface becoming greater towards the centre of the jet. (e) showing the distance of the main element tips to a variable surface having become equal across the entire jet (f) With increasing passes the shorter path length is now to the central feature so shifts machining focus

Considering Figure 5.23b, the electrical field effect is simulated in MATLAB for the initial pass against the flat surface by applying the generalised Equation 20 from Coulomb's law for continuous charge distribution (units: N/C).

$$E(r) = \frac{1}{4\pi\epsilon_0\epsilon_r} \int dA\rho_Q(r') \frac{r-r'}{|r-r'|^3} \quad \text{Equation 20}$$

Where $\epsilon_0\epsilon_r$ is the electrolyte permittivity, $\rho_Q(r')$ is charge density r is the position of the point at which the electric field is calculated, r' is the location of the charge and dA is an infinitesimal element of area.

High field strength areas can be clearly seen below the nozzle tips (primary machining zone) where regions of least resistance i.e. where the path from rim contour to workpiece is the shortest giving the largest removal rates. While areas having a lower field strength surround these and give rise to a secondary lower-rate machining zone. With machining time, the form of the surface being machined changes. The effect of this can be seen in Figure 5.23c where the electrical field simulation is now acting on a non-parallel surface. This is consistent with machining of a pre-existing feature. Here the field strength is shown to be larger in the primary machining zone extending into the central area. As such a shift occurs in the rate of machining of the central feature. Unlike conventional ECM, the form of the response profile does not come directly from the nozzle rather from the interaction the nozzle has with the electrolyte jet. As nozzle tip stand-off is constant throughout from the initial setting, so the subsequent profiles produced may differ as a function of jet dwell or repeat striations. The reasoning behind this changing profile can be seen in Figure 5.23 d,e,f. As the jet impinges on a flat surface, the distance between the nozzle tip and the workpiece surface is at its shortest so achieving the most direct path. As the distance becomes greater towards the centre of the jet so electrical influence is decreased resulting in attenuated removal creating the initial profile. In comparison (Figure 5.23e) where machining of a feature created by a previous pass the distance between the nozzle tips and the interaction surface is now equal across the jet so maintaining the profile. It can be postulated that at this point hydrodynamic effects now start to affect the profile. Due to the rising centre feature, the stagnation point at the centre of the jet is now exacerbated (as defined in section 2.3.5). The impinging jet is forced either side of the central

feature into the base of the valley where effectively a longer interaction is seen at the surface. Therefore, removal at the valley floor is increased and subtle deepening of the valleys occurs taking the distance to the nozzle tips out of equilibrium at discrete points. On a successive pass (Figure 5.23f), the distance to the interaction surface directly under the nozzle tips is now longer than that to the central feature giving a more favourable point for initial current attachment. Therefore, preferential machining takes place with a further shift in the primary machining zone to remove the central feature leaving a flat base to the profile. This effect was observed in Chapter 4 when machining titanium albeit in that case due to polarisation effects masking areas of the profile which do not occur in this material. This aims to not only demonstrate the flexibility achievable with these modified nozzles but also that EJM can be self-limiting with appropriate nozzle and dynamic removal considerations.

Freeform modification of nozzles in multiple planes was then undertaken. Wide castellation (*WC*) and narrow castellation (*NC*) nozzles are shown in Figure 5.24. The machined profiles were compared to the resultant *STE* profile in Figure 5.24a over a single pass. Marked changes to the profile can be seen from the profile scans, the *WC* profile showing a wider profile with a more pronounced double apex than the *STE* profile (exhibiting a side wall slope of $62.3 \mu\text{m} / \text{mm}$ (σ 2%) compared to $83.6 \mu\text{m} / \text{mm}$ (σ <1%)). The *NC* nozzle demonstrates superior geometric enhancement with a height increase of the central feature of 168% (σ 22%, the high deviation likely due to varying hydrodynamic effects) over the *STE* created profile and a reduction of 65% in the side wall taper with a slope of $187 \mu\text{m} / \text{mm}$ (σ 4.4%).

Figure 5.24b shows the comparison of in-jet resistance to the standard nozzle. As expected the majority of nozzle designs had an increase in resistance when compared to the standard nozzle (increasing from 25 Ω for the standard up to 45 Ω for the *OSPE*). The exception to this is the *NC* nozzle which shows a reduction of jet electrical resistance to 23 Ω .

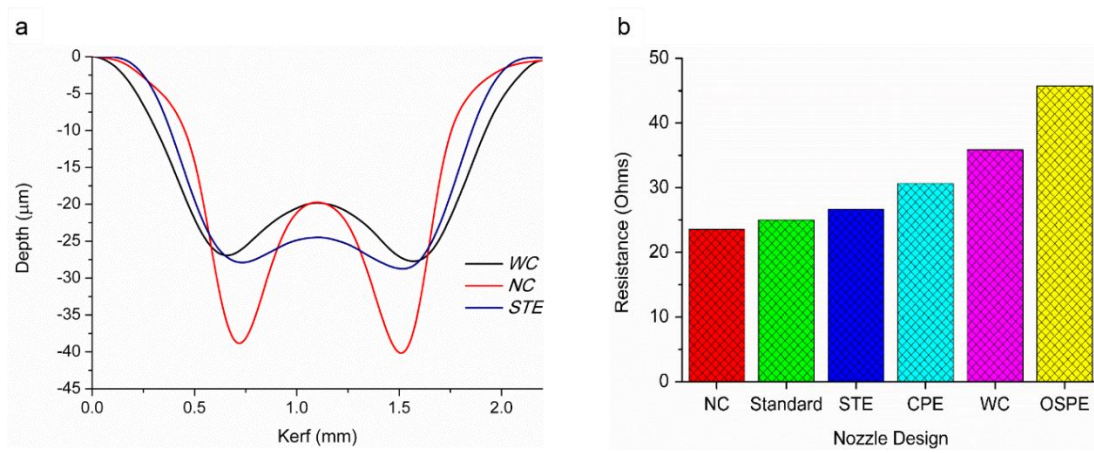


Figure 5.24: More complex 3D designs can be used to enhance the resultant geometry but making changes to the area of elements at specific distances from the work-piece influencing the geometry of the resultant profile. (a) Shows the profiles created by nozzles with varying area the castellated and narrow castellated when compared to the STE nozzle on which they are based but with further material removed (b) demonstrating the differing resistance created by the nozzles the castellated and narrow castellated demonstrates the ability of the nozzle design to affect the machining process and careful consideration of area and distance enables a lower than standard resistance increasing process efficiency.

This is apparent when considering the resultant profiles from the *NC* and *WC* nozzles. The area of the four element tips in the *NC* nozzle being 125000 μm^2 when compared to the *WC* design having an element tip area of 64000 μm^2 . This gives a *DIF* for the *NC* nozzle elements of 0.13 compared to the *WC* nozzle which has a *DIF* of 0.06. When considering the complete tip contour of all facing surfaces at the varying distances from the surface the *DIF* for the *WC* nozzle is 0.14 compared to the *DIF* of the *NC* nozzle being 0.42.

When considering Figure 5.25 showing the profile of the *NC* nozzle over increasing passes the geometry can be seen to again evolve in a similar fashion to that of the *STE* nozzle (Figure 5.25 a) and in contrast to that of the standard or *CPE* nozzle resultant profiles (Figure 5.22). This type of internal geometry can be considered as not being consistent across the range of surface energy delivered and so are prone to a high degree of variation dependant on process parameters and therefore consideration of this must be taken into account when developing the desired geometry. In the case of the *NC* nozzle the central feature is still noticeable after four passes due to its greater prominence in the initial passes from the marked current density profile.

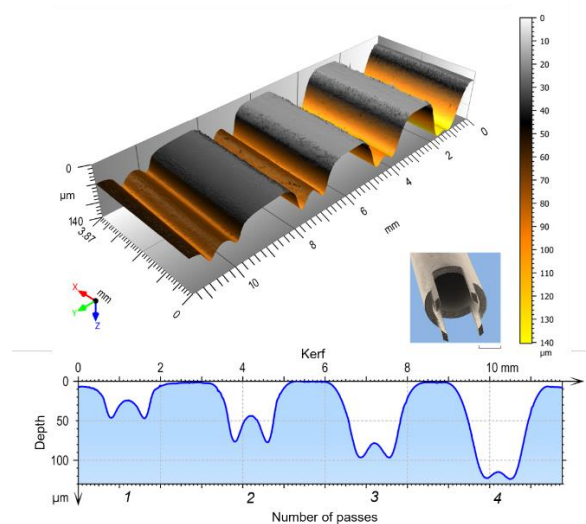


Figure 5.25: Surface and profile extracted from an areal scan of the *NC* nozzle with increasing number of passes. Scale bar for nozzle is 500 μm

Figure 5.26 demonstrates the capability of these nozzles to achieve patterns with complex profiles and interactions which are simplistically and efficiently created with a one step process in a difficult material to competitively machine by other means over large areas. The array of features demonstrated also exhibits the flexibility of this process. *STE* and *OSPE* nozzles were used in combination.

OSPE nozzles were first used at 0.1 mm/s feed, cutting the block in the Y direction over a single pass (Figure 5.26 e,f). Using the *STE* nozzle cuts were then made in the X direction to intersect the first two cuts (Figure 5.26 f, g) being single passes at 0.1 mm/s, the third cut being four passes over the same direction with constant parameters resulting in a much deeper cut ($\approx 600 \mu\text{m}$). It can be observed, the loss of the distinctive 'W' shape with multiple passes generating a flatter valley bottom as noted previously (Figure 5.26b) and the ramping in of the features created in the NC program to avoid key-holing and unstable processing conditions. The shallower features created in the x direction are formed by a bouncing type tool path (further defined in Appendix 6) with alternating start points at 0.5 mm/s (Figure 5.26 b, c, d). Shallower features are observed where the substrate has changed thickness and the stand-off distance has become drastically reduced.

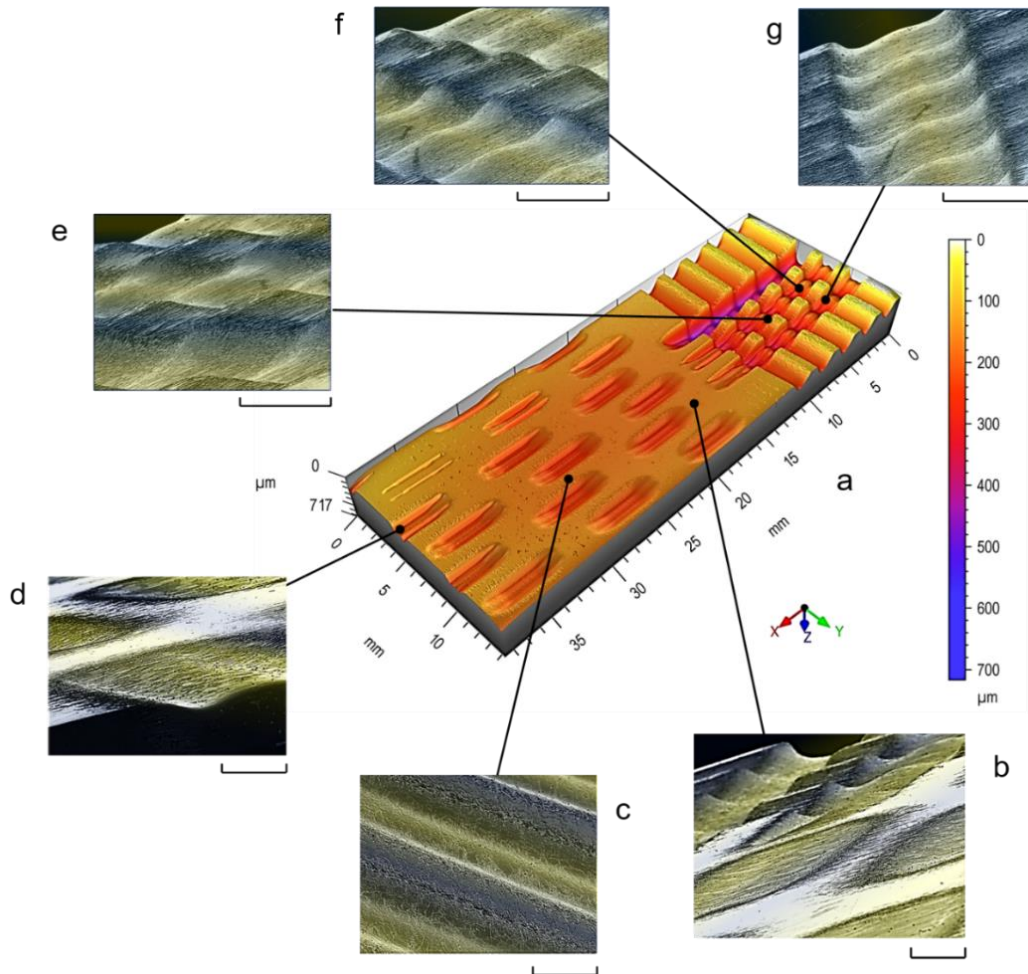


Figure 5.26: Inconel 718 machined by a selection of nozzles. (a) 3D surface generated from areal scan. (b,c,d,e,f,g) Tinted SEM images extracts of the machined piece demonstrating the range of surfaces that these nozzle designs can create. All scale bars are 500 μm

Through parameter variation not only can meso-scale surface structures be created but the microscale finish can be altered across the features as defined by the energy density variation demonstrated by Figure 4.5 in Chapter 4. By lowering jet velocity, low current density areas can be controllably created at the periphery of the features as the jet is no longer as tightly masked. This is observed in Figure 5.26. A rougher finish is achieved here than at the centre of the features where energy density is higher. In contrast, Figure 5.27, alternative finishes are achieved by the use of a higher jet speed, current density and slower traverse

speed leading to greater edge definition, greater variation in surface texture and deeper cuts due to the changing dissolution mechanisms.

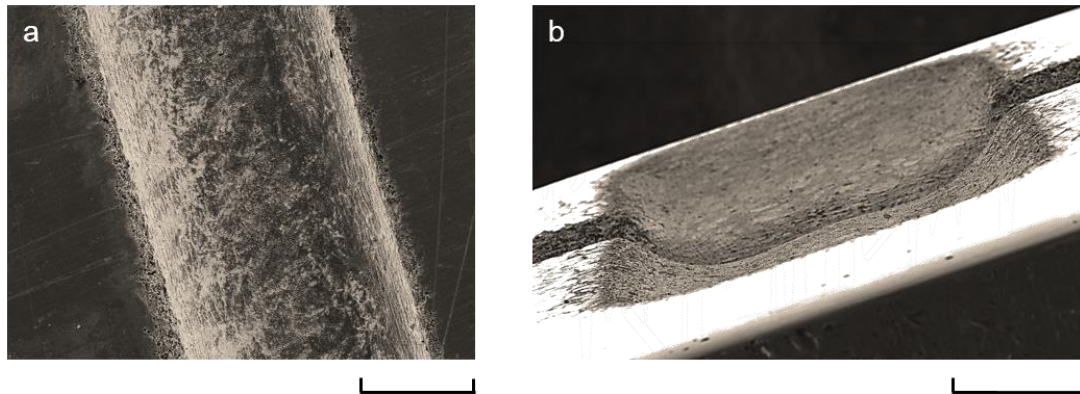


Figure 5.27: SEM images of machine features with an STE nozzle with a modified parameter set to produce different micro-texturing finishes (a) straight cut striation with increased current density and increased jet velocity (b) pocket intersecting a straight cut striation with increased jet velocity but lower traverse speed giving a rougher surface finish. All scale bars are 500 μm

5.3.6. Process fidelity and scalability

Figure 5.28 shows resultant profiles extracted from the striations of the steps nozzle (Figure 5.28a), 500 μm STE 9 (Figure 5.28b) and 250 μm OSPE (Figure 5.28c), after a single pass. The resultant profile of the stepped nozzle (Figure 5.28c and Figure 5.29) shows a limit to the fidelity which can be achieved in comparison to the nozzle shape. The influence of the steps can be observed as distinctly different rates of dissolution occurring under the various features. The influence of the jet exiting the cavity has, to a degree, merged these areas. With the extending distance to the surface of the steps the *DIF* reduces from 0.3 for the nearest step to the surface through 0.07 of the second step to 0.05 for the third step. Even though the third step has by far the largest area the influence of steps two and three is minimal. This can be seen in Figure 5.29 where the

increasing number of steps makes this area of dissolution more prominent with every pass. The extreme version of this being the deepest cut where the influence of the highest step has been minimised. The area of the first step would need to be greatly reduced for greater distinction between the steps in the resultant profile.

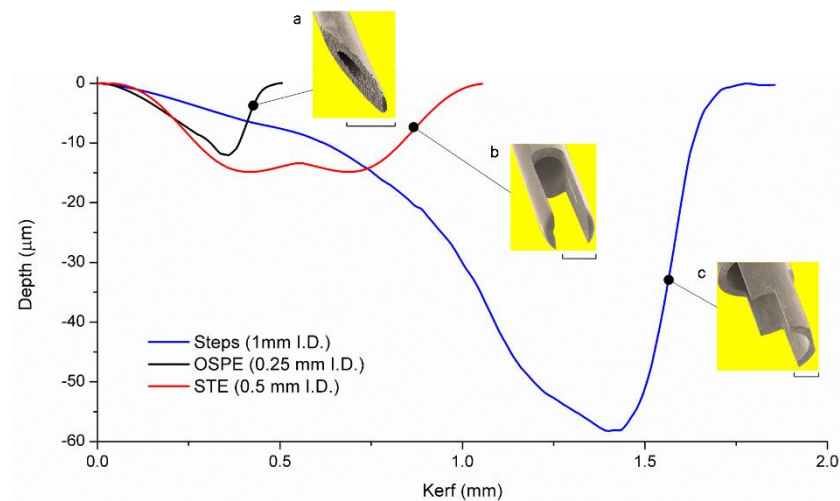


Figure 5.28: Comparison of extracted machined resultant profiles compared to the simulated profile from the DIF equation (a) 0.25 mm I.D. OSPE nozzle. (b) 0.5 mm STE nozzle and (c) 1 mm Steps nozzle. All scale bars 500 μm

When compared to the *OSPE* nozzle design from section 5.3.5 which has a simple design with graduation of decreasing *DIF* across the nozzle, so reflected in a linear graduation of the response profile away from the longest nozzle edge. Alternatively, when this is compared to the response profile of the steps nozzle this gives a curved effect away from the deepest part of the profile due to the sudden and stepped changes in the *DIF*.

It is worthy of note that the reduced kerf, being under the expected minimum of twice the nozzle *I.D.* thought to be defined by the stagnation region noted in

section 2.3.5 (1.64 mm, σ 3.5%). This is also found with the similar designed 1 mm I.D. *OSPE* nozzle (2 mm σ <1%) and again demonstrates alongside the changing of the angle of address that the kerf should no longer be thought to be defined by hydrodynamic effects. Also observed is the sharper intersection with the un-machined surface to the right of the profile. When comparing the distance from the deepest part of the valley to the dissolution interface with the unchanged surface, the steps nozzle measures a mean of 292 μm (σ 6%), compared to the *OSPE* nozzle measuring 507 μm (σ 3%) resulting in a 152% increase in side-wall steepness (219 $\mu\text{m} / \text{mm}$ σ 6% to 551 $\mu\text{m} / \text{mm}$ σ 6%). This is due to the thinning of the outside wall at this point on the nozzle giving a sudden increase in resistance aiding ejection through limiting rebound effects (described in section 2.3.5) therefore minimising the spread of dissolution. The 500 μm *STE* nozzle (Figure 5.28b) shows the characteristic “W” shape usually associated with this design of nozzle. Even though the horizontal distance between the nozzle tip is reduced the twin valleys of the resultant profile remain, albeit at a much closer proximity, giving a sharper apex to the central feature.

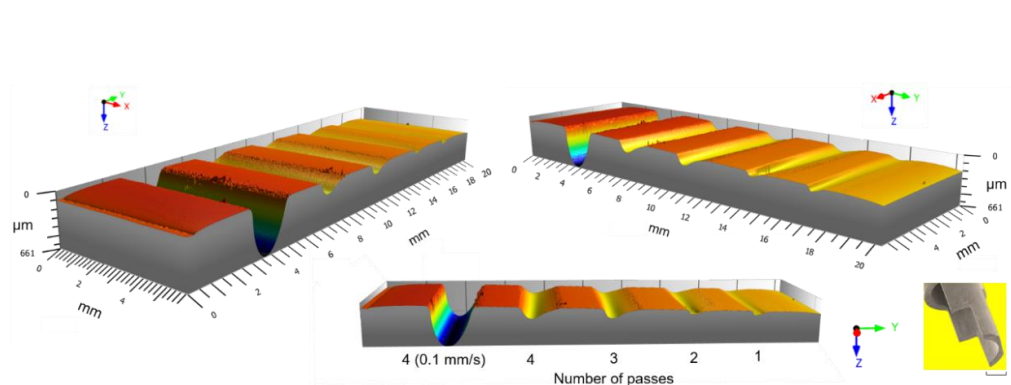


Figure 5.29: Example images samples features machined using the steps nozzles generated from areal surface scans showing single pass (shallowest cut) through 2, 3 and 4 passes with the final deepest groove being created with four passes at 0.1 mm/s traverse speed. Scale bar for nozzle is 500 μm

Similarly, for the 250 μm OSPE nozzle (Figure 5.28a) the resultant profile also remains consistent with that that observed with the 1 mm I.D. OSPE nozzle demonstrating accurate scalability traits across both 500 μm I.D. and 250 μm nozzles with the designs tested throughout the range of the sizes.

As the 500 μm STE nozzle was shown to maintain the expected profile further tests were carried out across multiple samples. Due to the reduced diameter of the nozzle, a higher degree of variation could be obtained within the apparatus for current density and electrolyte jet speed (Figure 5.30) therefore the impact of parameter variation on the profile geometry could be assessed.

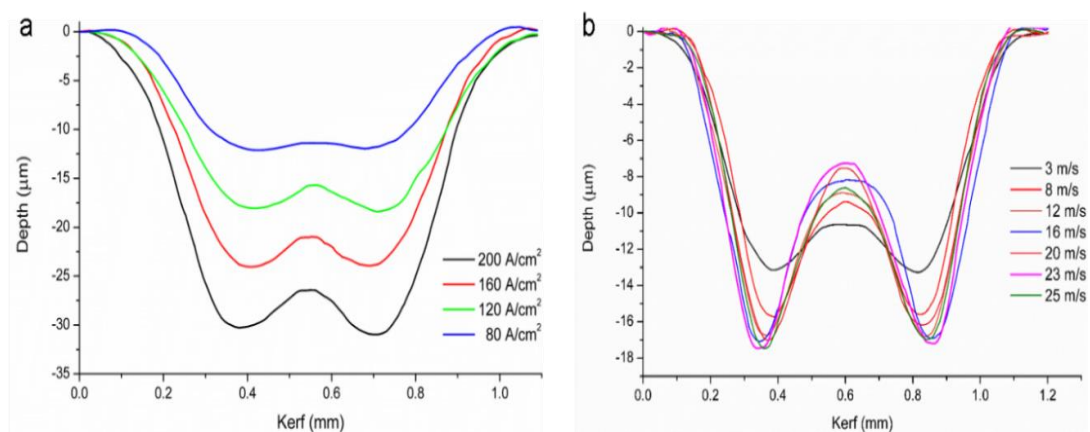


Figure 5.30: Variation of machining parameters with a 0.5 mm I.D. nozzle (a) variation of current density (b) variation of Jet speed

Figure 5.30a, shows the multiple striations machined in single passes with increasing current density. As expected, in line with prior work, as current density increases so the material removal and therefore depth increases. However, the 'W' shape is maintained throughout only increasing in definition due to the localised peaks in current density increasing and overcoming any polarisation effects. This is contrast to the repeating passes due to the jet being impinged on

an un-machined surface, so the focal point of the current density profile is unchanged. Figure 5.30b shows the effect of increasing electrolyte jet speed. Only at 3 m/s and 8 m/s is there a noticeable difference in volume removal due to polarisation effects such as removal of oxide films formed and possible increase in the diffusion boundary thickness which inhibits the current density peaks and effectively evens out the current density curve. Machined at 100 A/cm² the expected profile is generated in all cases with little variation in the side walls slope. However, there is noticeable variation to the profile shape of the central feature between the jet speeds and supports earlier findings where the central feature shows high dimension deviation due to variable hydrodynamic effects directly under the jet.

5.4. Dynamic tooling for electrochemical jet profiling

5.4.1. Introduction

It is preferable to use a number of advanced manufacturing techniques for profiling in low machinability alloys for repeating surface feature generation. However, such techniques as EJM, Micro-ECM and Micro-EDM are currently only able to create 2D single direction linear profiles due to the contouring of the tool being unidirectional, hence the current use of cylindrical tooling which can vector independent of x-y direction and utilise complex tool path procedures. This is not efficient or effective for this type of application.

To maximise the potential of the ability to modify the resultant profile geometry in EJM shown in the prior section a method must be devised to allow the profile to remain constant across a varying toolpath direction (Figure 5.31).

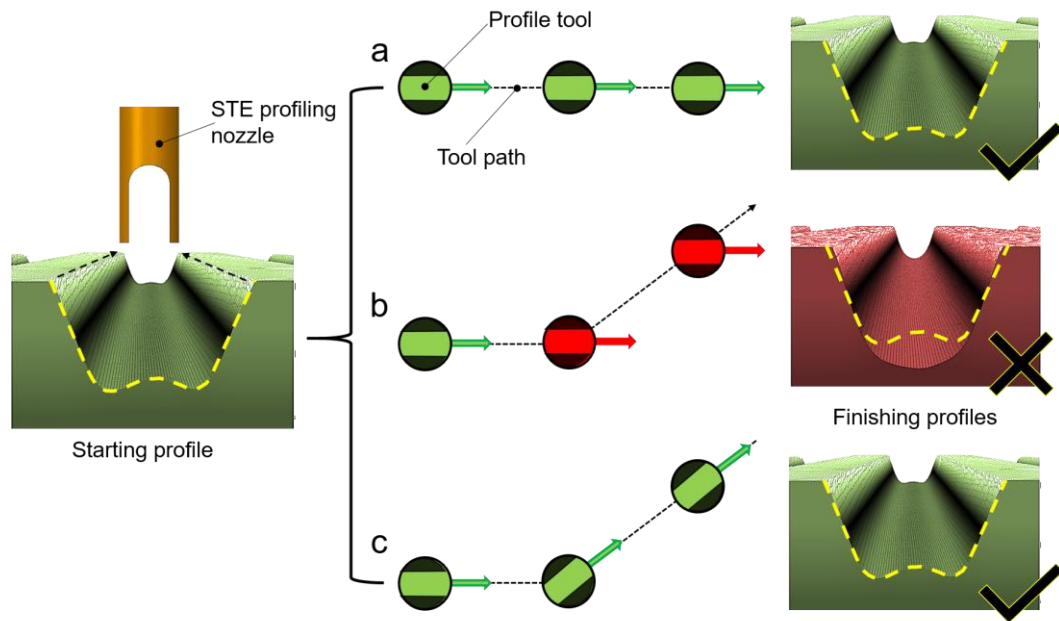


Figure 5.31: (a) currently response profile is consistent in a single direction, (b) when direction changes response profile no longer tracks the toolpath and response profile changes (c) profile would remain constant if head can rotate to allow the nozzle to track the toolpath in X and Y

In response to this, a method was devised to allow rotation of the head allowing the profile created by the nozzle to remain consistent and track the vector of the advancing tool-path (Figure 5.31c). A 4th axis system was devised to allow 360° rotation of the nozzle (Figure 5.32). This design incorporated the stainless-steel head insert which carries the Luer lock adaptor, nozzle and electrolyte tube push fits used throughout this work (see section 3.1 for full definition). The insert holder is fabricated from ABS to form the electrical isolation barrier and allows connection to the stepper motor which is controlled in the same manner as the main axis.

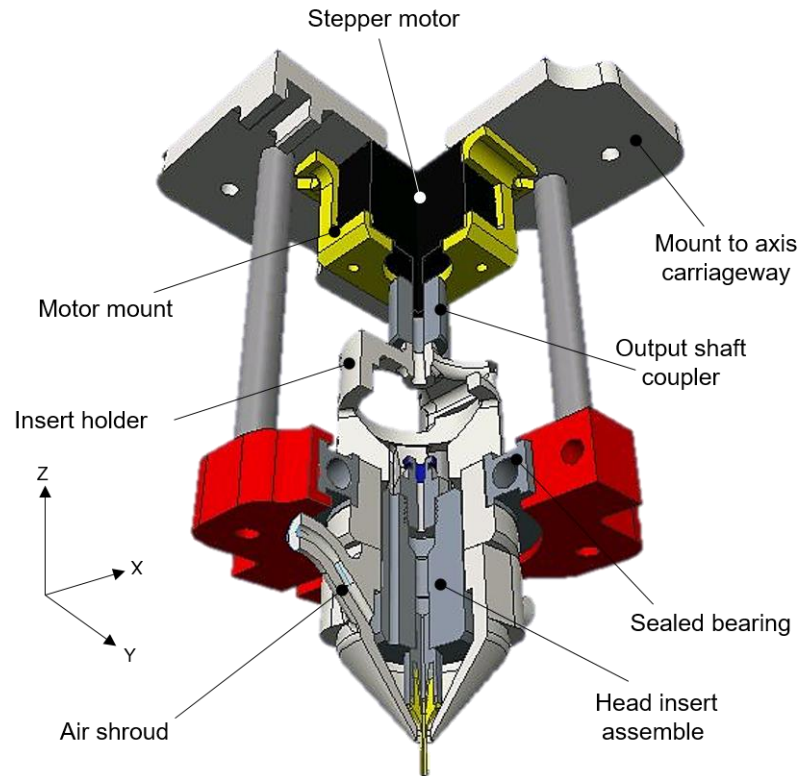


Figure 5.32: Schematic of rotary head design detailing the key features which allow tool articulation

The insert holder is press-fitted into the bearing in order to maintain stability throughout rotation. The air shroud used is a common component as described in section 3 but with the air inlets re-designed to allow clearance in rotation. The head is then mounted to the x-axis carriageway (Figure 5.33).

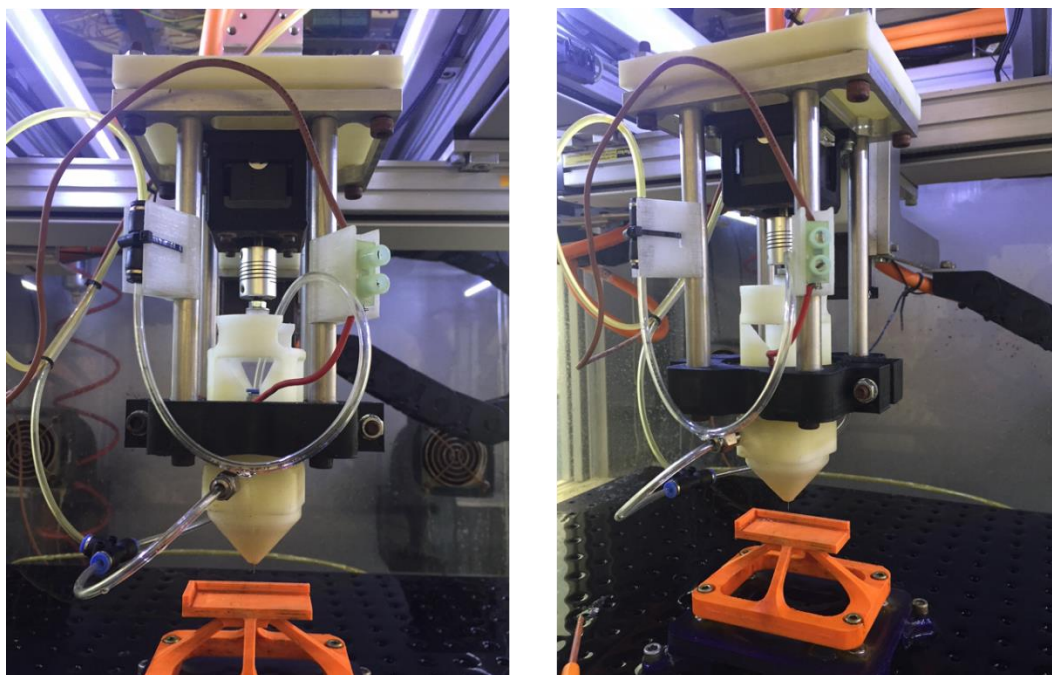


Figure 5.33: Rotary head mounted on the x-axis of the generation 2 machine tool

It was decided to control rotation of the tool rather than the sample fixture for a number of reasons:

- Maintain the machine architecture intent of isolating electronic components and moving parts above the natural electrolyte drain direction and main working area
- Ease of interchangeable heads within each, and across both, machine tools without disruption to the machine architecture.
- Reduce any latency and backlash in rotational translation through minimising rotational inertia and simplifying the rotational mechanism
- Simplifying control system and CAM implementation through the rotational axis being permanently coupled to the nozzle axis and independent from sample placement allowing consistent datums

- Maximising machine work volume by allowing rotation of the nozzle anywhere within the work envelope

It is also possible to exploit the functionality of the rotary head further by indexing the nozzle into different positions as regards the direction of travel. An example of this would be the *CPE* nozzle (Figure 5.18b). When used in the intended direction produces a triangular type tool path (Figure 5.21). However, once the nozzle is rotated by 90° it will then produce a completely different profile more akin to an *STE* nozzle (Figure 5.21) and an infinite number of differing profiles in-between. These changes can be carried out dynamically as a function of the toolpath program allowing a constantly changing and evolving profile as per the surface design intent.

5.4.2. Methodology

To demonstrate the viability of the rotary head with a modified nozzle a tangential control routine was implemented in the control software to continuously monitor the direction of the toolpath in the X-Y plane and assign a constant angle of the nozzle axis with relation to the direction vector of the tool path. Three simple toolpaths were designed to test the articulation of the head and the resultant profile produced. Toolpaths forming a circle, a square and a triangle. In each case the intended orientation of the nozzle is set initially in line with the Y axis. This allows investigation of how the resultant geometry created is affected by travelling in a constant curve, at trajectories between the X-Y planes and in the X-Y plane and the associated effects when turning tight corners in the toolpath. The features were machined over three passes with NaI20 electrolyte (see chapter 6) using a 1 mm STE nozzle, a traverse speed of 0.5 mm/s, IEG of 0.3 mm and current

density of 100 A/cm². The pattern was repeated with the rotary head engaged and with it dis-engaged.

The multi-tooling effect of indexing the nozzle was then investigated by using both the CPE nozzle design and the OSPE nozzle design. For each nozzle, a striation was machined with the head dynamically changing rotation as a function of the toolpath. The rotary head is connected in the software to a virtual gearbox which takes input from the positional increments of the X and Y axis. Therefore, the nozzle changes orientation from 0° through to 90° over the length of the striation, in this case 15 mm. The results were then imaged in-line with section 3.6. and the results presented.

5.4.3. Application of rotary head in constant profiling mode

In Figure 5.34 the resultant profiles can be seen when machining with an *STE* nozzle (Figure 5.34a). 3D surface maps of the features created with the rotary head engaged can be seen in Figure 5.34b, c, d. Profiles were extracted from the toolpaths at the points shown on the maps numbered 1-7 and the comparison is shown in the profile graphs Figure 5.34e, f, g between the rotary head engaged and dis-engaged. When considering the surface maps, the impact of the rotary head is acutely obvious. With the rotary system engaged the feature profiles can be seen to generate the expected profiles from section 5.3 in every direction.

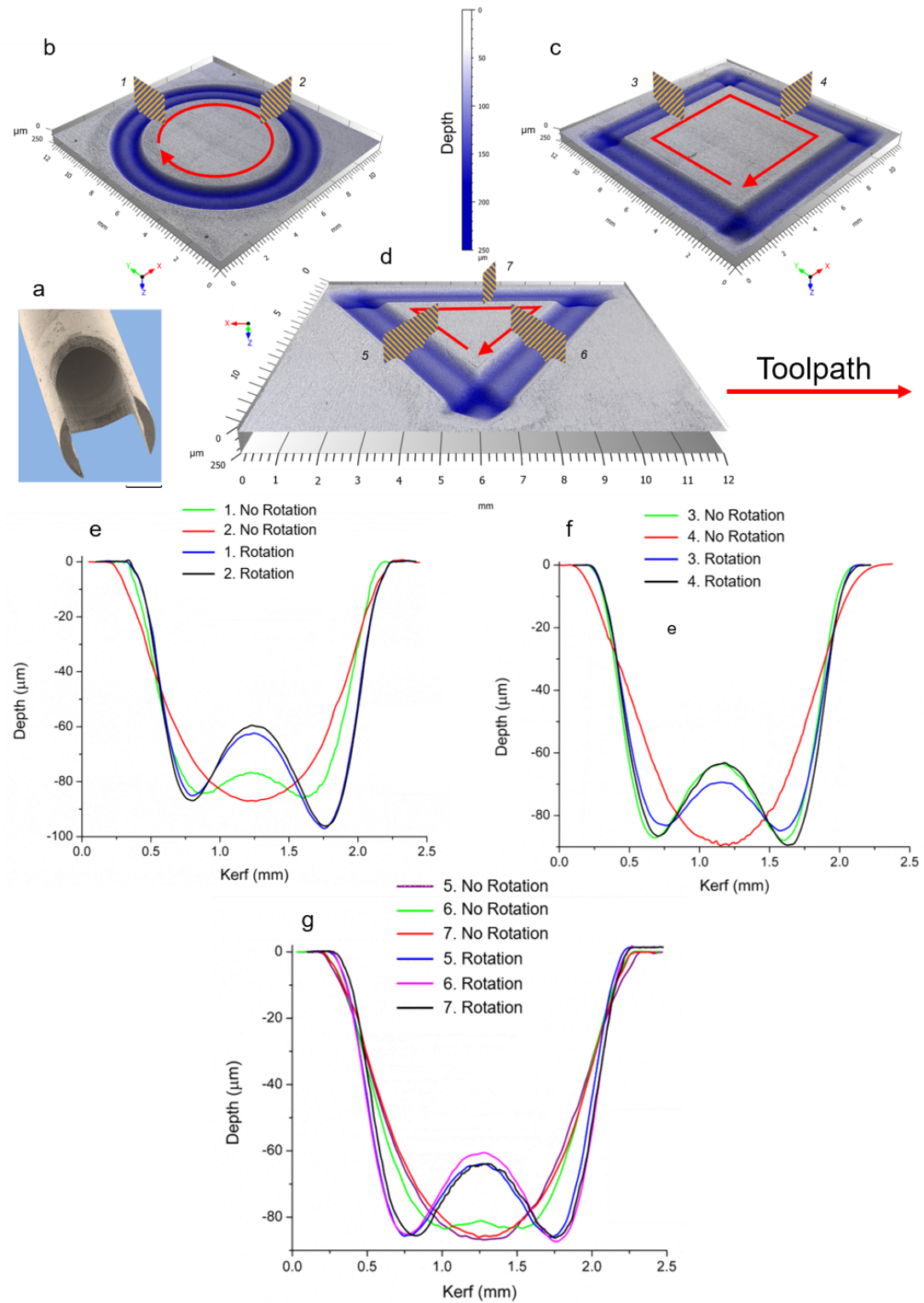


Figure 5.34: 3D surface reconstructions from constant profiling experiments using an STE nozzle (a), (b), (c) and comparison of profiles with and without rotary head (1-7) at extracted points denoted on the 3D surface.

From the extracted profiles with the rotary head disengaged and using the STE nozzle, profiles can be observed to be variable as expected. The profile extracted from the circle (Figure 5.34e) at section 1 show a reduced impact of the STE nozzle on the profile geometry with the two valleys created by the nozzle being closer than expected and a much less pronounced central peak than would be expected using the NaI20 electrolyte. This is due to the nozzle remaining in a fixed position, so the nozzle is essential at a slight angle to the toolpath vector at the point where the profile has been extracted. Thus, the energy distribution over the surface is not representative of what the nozzle is creating but by a combination of nozzle and direction of travel (Figure 5.35a). Due to the diameter of the circle feature and the diameter of the nozzle it never achieves a profile representative of the nozzle. At profile slice two, the nozzle produces a typical bell type curve as the nozzle is now essentially un-modified in its influence on the resultant profile.

In comparison the profiles with rotation achieve an expected profile as the nozzle orientation is constantly adjusted to form a tangential direction with the curve (Figure 5.35b) and maintain a constant profile. There is a noticeable effect when the curve feature is generated which is not seen across the rotary profiles from the square (Figure 5.34c) and the triangle (Figure 5.34d) which bear almost identical profiles at each extracted section (3-7).

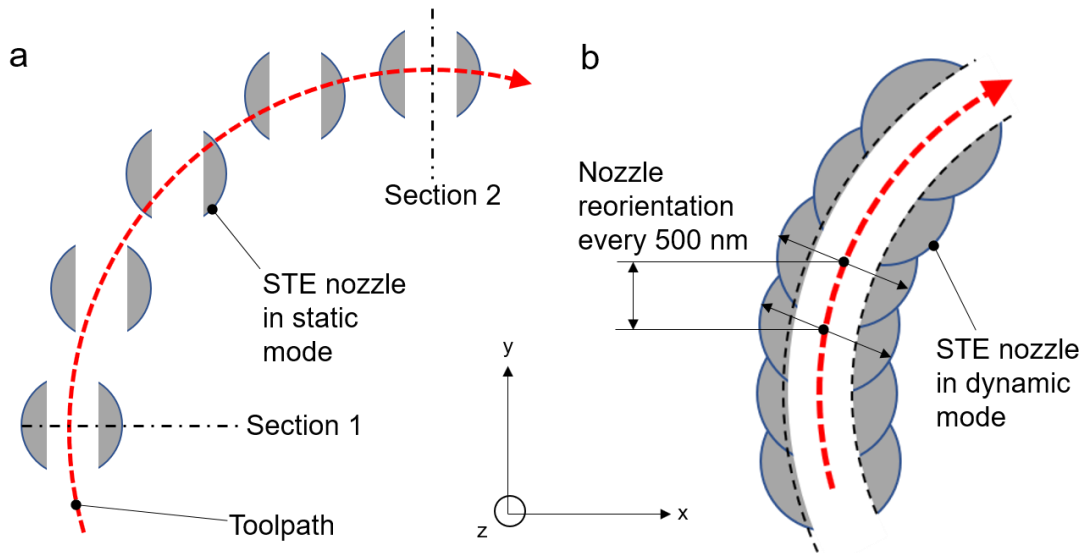


Figure 5.35: Comparison of toolpath vector and nozzle orientation (a) without rotary head and (b) with rotary head engaged

The valley closest to the centre of the curve is deeper and wider than the valley closest to the outside of the circle, $\approx 10 \mu\text{m}$ deeper and $\approx 80 \mu\text{m}$ wider. The areas (as seen in the previous section) show 1.1% difference between the profiles extracted from Figure 5.34g 5,6,7 with rotation ($119100 \mu\text{m}^2 \sigma < 1\%$) and the area of the profiles of the circle (Figure 5.34e 1, 2) with rotation ($120500 \mu\text{m}^2 \sigma < 1\%$). Therefore, the global energy applied to the IEG is the same, but the localised energy is being re-distributed to favour the inside valley making the outside valley shallower and thinner. This is due to the speed differential between the inside and outside of the edges of the feature. The inside edge travelling marginally slower to allow the curve to form. As noted in Chapter 4, a slower traverse speed leads to an energy increase seen at the surface therefore a greater removal rate, hence the inner valley is deeper. In Figure 5.34f the profiles form three similar profiles. The toolpath from where section 3 is taken being in the Y direction, therefore the non-rotational profile mimics the rotational one. Only in the X direction does it then differ, the non-rotational profile adopting the typical

Gaussian profile. The profiles from the triangle (Figure 5.34g) demonstrate the profiles taken from the three slices (5-7) bearing no resemblance between the rotated and non-rotated profiles. The rotated profiles maintaining the constant profile. The un-rotated profiles in two cases (profiles 5 and 7) create the bell type curve as found with the standard nozzle as the orientation of the nozzle is masking any effects of the modified energy distribution. The profile from section 6 is more akin to from the circle in section 1, where the nozzle is no longer following the toolpath therefore the centre peak is reduced, and the valleys are closer together. It can also be seen in Figure 5.34c, d where the toolpaths intersect at the corners in order to keep a sharp edge of the inside shape a radius is not created instead the toolpath exceeds the feature distance then adjusted to start the next line prior to the start of the feature. This means these areas have double the amount of interaction with the jet in opposing directions so eradicating the central feature and instead creating a square and triangular pocket.

5.4.4. Application of rotary head in dynamic profiling mode

When the tooling is applied in dynamic mode whereby the software gearbox is engaged to rotate the head through 90° over 15 mm travel in the X direction the profile can be seen to constantly change between two defined profiles (Figure 5.36). In Figure 5.36a the OSPE nozzle is used set initially as shown with the point set off to one side to create the profile as previously demonstrated for this nozzle. As the nozzle traverses in the x direction so the orientation of the nozzle incrementally changes as a function of the distance travelled. The deepest part of the profile, corresponding with the point of the nozzle tip, can be observed to curve from the left of the profile to the centre. As the point approaches the centre

so the profile becomes deeper by $\approx 20\text{ }\mu\text{m}$ and material removal across the kerf is more localised to the centre however, the overall dissolution kerf remains constant throughout the channel.

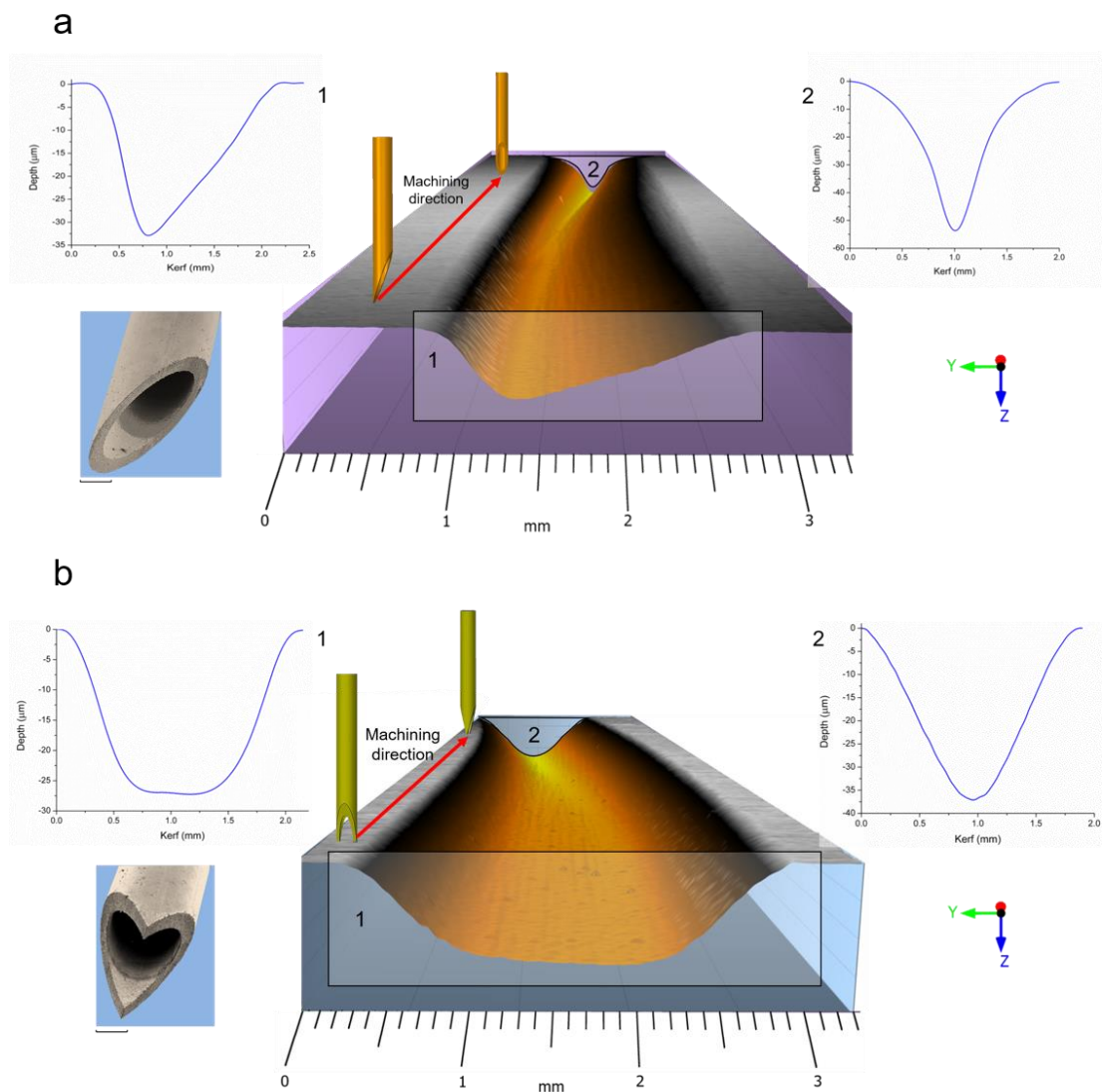


Figure 5.36: Demonstration of rotary head in dynamic mode carrying out 90° rotation over 15 mm channel (a) with OSPE nozzle and (b) with CPE nozzle. Scale bars are 0.5 mm

Figure 5.36b demonstrates an evolving channel shape using the CPE nozzle. In this case the nozzle is initially set to give a wide, flat bottom profile more akin to the STE type profile and then rotated to achieve the profile associated with the

CPE nozzle being a triangle type profile. Again, an increase in depth occurs due to the energy density modulation as the profile becomes more pointed. In this case however it is interesting to note the nozzle is not absolutely vertical when initially set, seen in the first profile as the cut floor not being level. This leads to runout in the system across the toolpath creating a curvature in the channel rather than a straight channel as seen in Figure 5.36a.

5.4.5. Validation of rotary head in application

Utilising the OSPE nozzle (Figure 5.18d) with the rotary head engaged features were machined into 0.8 mm thick medical grade scalpel blades to demonstrate the application (Figure 5.37).

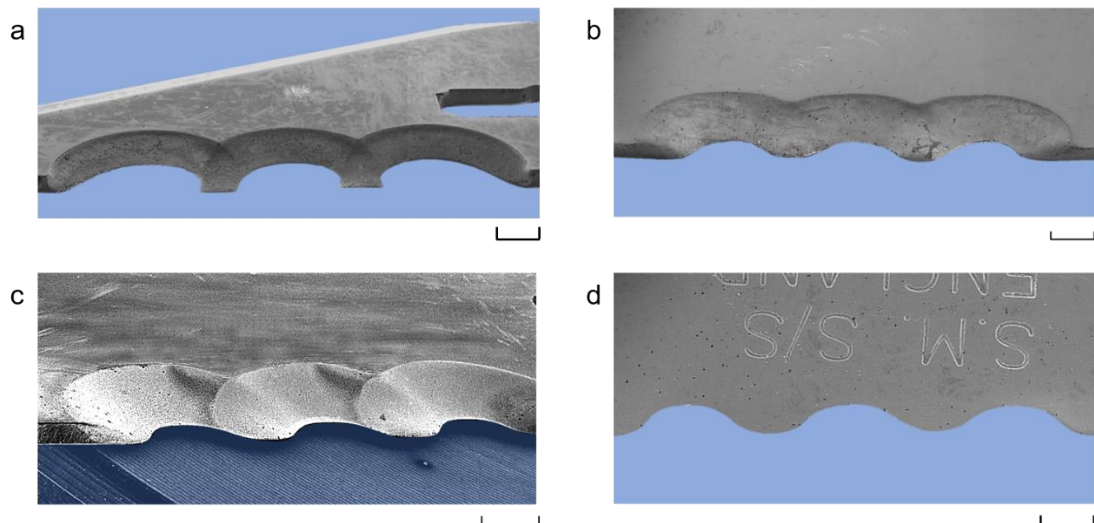


Figure 5.37: Utilising the OSPE nozzle with the rotary head to apply edge shaping to medical grade stainless steel. SEM images of (a) saw-tooth design at 65° (b) serrated edge at 65° (c) serrated edge at 80° and (d) reverse side of serrated edge. All scale bars 1 mm

Different toolpaths were adopted to create differing cutting type features. The saw tooth type feature Figure 5.37a and the more typical serrated edge in Figure 5.37b were each created with 8 successive passes taking a total of ≈ 5 minutes

to create each sample. The IEG being reduced by 30 μm after each pass. Figure 5.37c and d show the quality of the edge that is created without any secondary finishing process being carried out and no surface damage as expected.

5.5. Chapter summary of key findings

The motivation behind this chapter was to propose and develop innovative solutions to enhance the geometrical flexibility and precision in EJM through electro-mechanical means inspired by the findings of the literature review. This has been achieved through manipulation of the resistance found in-jet, ergo, the current density distribution across the surface through altering the mechanical influences on the electrical properties of the IEG.

The key findings of this chapter were:

- Through simple articulation of the incident jet it is possible to locally modulate in-jet resistance therefore distorting the energy distribution perceived at the work surface thus effecting the resultant form and finish which differs greatly from that found in alternative energy beam processes.
- The position of the trailing edge of the jet dominates the surface finish created in push / pull modes and as such in push mode smoother more polished surfaces can be achieved.
- The use of low incident angles between the jet and surface enables increases in depth and reduction in kerf due to a confluence of current pathways produced by electrolyte jet approach and the restricted contour of the nozzle tip addressing the surface.

- Discrete changes to resistance in-jet were affected by geometric modification of the nozzle apertures allowing modulation of the current density profile and thus allowing flexibility of the resultant profile shape.
- The design impact factor (DIF) was introduced to enable the assessment of the design of nozzle tip elements, both area of the tip contour facing the incident surface and its distance from the surface.
- Alongside increased flexibility precision improvements were found over the standard nozzle such as reductions in side wall taper, reduced kerf and flat cut base more analogous with traditional cutting profiles.
- A 4th axis system was devised which allowed the rotational positioning of the nozzle with respect to the toolpath vector. Thus maintaining a constant profile to be created regardless of the toolpath geometry
- A further methodology was developed allowing for dynamic tooling whereby the profile can be modulated as a function of position within the toolpath.

6. Enhanced geometrical flexibility and precision through electrochemical innovation

6.1. Introduction

To further the enhancements of precision and profile geometrical flexibility it was highlighted by the literature review (section 2.4) that electrochemistry has a significant influence on the resultant features. The electrochemistry of EJM is an area which is underdeveloped and presents opportunity when compared to the level of investigation in general ECM. It was observed in the literature review that even considering the common subtractive mode electrolytes sodium chloride (NaCl) and sodium nitrate (NaNO_3), they both display differing removal characteristics. NaCl is aggressive and so provides good MRR but poor precision in the form of poor kerf control. NaNO_3 having the opposite traits of good precision but lesser MRR by comparison. It was also noted that additions to the bulk electrolyte could cause specific changes to the resultant profile, often due to material considerations (section 2.3.6).

Therefore, the possibility to manipulate the electrochemistry through electrochemical innovation resulting in changes in precision and resultant geometry presents itself as a worthwhile research avenue to achieve the aims of this thesis.

The following chapter details investigations to understand and develop innovations concerned with manipulation of electrochemical properties within the IEG and the underlying process mechanics for enhanced feature flexibility, precision and process function.

6.2. Generation of a transitory electrochemical masking effect

6.2.1. Introduction

The modifications to the nozzle tip detailed in section 5.3 enable variation of the machined profile away from the typical profile attributed to the Gaussian energy distribution profile. This modulation of the resistance in-jet allows the response profile geometry to achieve not only application specific profiles but, more favourable profiles with reduced side wall taper and flat cut floors analogous to more conventional machining methods. It is proposed that these enhancements can be further exploited by coupling with an enhanced electrolyte designed to amplify the effect. Electrolyte feedstocks have been investigated in order to enhance resultant finish in EJM (see section 2.4). However, electrochemistry manipulation to alter characteristics within the IEG has not been a design criterion and subject to optimisation in previous studies.

6.2.1.1. Profile fidelity enhancements

The relationship between current density and current efficiency is exaggerated for EJP techniques due to large spatial current density differentials which were exploited in section 5.3. This causes localised regions where current density exceeds the well-understood activation threshold and thus the onset of machining (see sections 2.3.2 and 2.4). Rounded profile features and significant side wall taper are observed due to the extremes in current density found across the jet when using conventional (NaNO_3 and NaCl) electrolytes. This is problematic since material removal/deposition rate is proportional to current density.

The effect of electrolyte composition has been reported to affect dimensional accuracy in the more established practice of electrochemical machining (ECM) (see section 2.4.). However, these innovations, although effective in general ECM, are not so applicable to EJM. This being due to the aforementioned large spatial current density differentials across the jet diameter.

Previous attempts to negate this deleterious effect and therefore improve the dimensional accuracy and aspect ratio of the deterministic feature were outlined in the literature review (see section 2.5.6) covering the innovation of hybrid EJM processes.

It is hypothesised that significant process enhancements can be achieved by exploiting in-jet electrochemical reactions through doping of conventional electrolytes as opposed to altering process architecture. In this case the use of Sodium Iodide (NaI) is introduced as a doping agent into a NaNO₃ based electrolyte, noting from section 2.4 NaNO₃ that is already known to possess the best precision characteristics. Under electrolysis with inert electrodes Sodium Iodide is known to readily oxidise to iodine [284] :



It is proposed that when considering the standard electrode potential of nickel $\text{Ni}_{(\text{s})} \rightarrow \text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^{-} = 0.25 \text{ V vs. SHE}$ (as taken from Chapter 4) in comparison to Iodide ($\text{E}^{\circ} 2\text{I}^{-}_{(\text{aq})} \rightarrow \text{I}_{2(\text{aq})} + 2\text{e}^{-} = 0.621 \text{ V vs. SHE}$) [285], the propensity of Iodide to readily oxidise is greater, therefore this reaction will preferentially divert energy away from anodic dissolution. This would therefore generate a competing

reaction at the anode which would cause an increase in the faradaic impedance (see section 2.3.4). The supplied energy to the IEG would be required to exceed the energy that is required for the conversion to iodine in order to initiate material removal. This would effectively remove the low current density areas having a filtering effect and so creating an electrochemically induced temporary mask. It is proposed that when coupled with modified nozzles, predefined and high-fidelity profile geometries can be created. This study aims to demonstrate that a step change in process fidelity and flexibility can be achieved through optimisation of the electrochemistry specific to jet processes.

6.2.1.2. Current efficiency

Evaluating the experimental volume of material removal across a range of current densities allows comparison to the theoretical maximum removal obtained through Faraday's law (see section 2.3.6). Thus giving, η , the current efficiency for a particular electrolyte solution (Equation 21).

$$\eta = \frac{M}{\left(\frac{A}{zF}\right) I} \quad \text{Equation 21}$$

Where M is the experimentally observed mass removal, A , the incident surface area, z the assumed dissolution valence, F the Faraday constant and I the current.

Consideration of the energy efficiency profile across a range of current densities and for varying concentrations of NaI would allow the characterisation of the effects of the dopant on the current available for dissolution.

In section 5.3.4 secondary machining zones were identified in EJM at the periphery of the jet where current density is lowest. In order to enhance the precision of the process it is desirable to elevate the activation current density for the electrolyte to enable work piece dissolution.

Iodide would not usually present itself as a viable alternative to nitrate and chloride electrolytes due to the higher cost and negligible increase in conductivity over comparable solutions. However, if the hypothesis is correct that through addition of the dopant to form an anodic film, a transitory masking effect is created when an electrical potential is applied, it would justify the inclusion of NaI. It is proposed that the evolution of the anodic film would require an energy transfer resulting in reduced current available to invoke machining. This could negate some of the deleterious effects observed when using other common electrolytes in low current density regions.

6.2.2. Methodology

The experimental procedure in all experiments was carried out on the generation 2 machine tool details of which can be found in Chapter 3. Inconel 718 was selected as the substrate in this case due to the sensitivity of this material to current density modulation and the effect on the resultant surface finish as demonstrated in Chapter 4.

Throughout these experiments, and for simplification, the doped electrolytes will be referred to as NaI, with the corresponding percentage (of the ionic strength), of the sodium iodide component following it as shown in Table 6.1

Table 6.1: Electrolyte composition and conductivity for the range of concentrations used within this study. All measurements taken at 22°C (σ 0.2 °C)

Electrolyte	Component Composition (M)	Ratio	Overall Electrolyte Ionic Strength and Molar Concentration (M)	Electrolyte Conductivity (ms/cm ⁻¹)
NaCl	2.3 : 0		2.3	165.4 (σ 0.1%)
NaNO ₃	2.3 : 0		2.3	136.6 (σ 0.03%)
NaNO ₃	1.8 : 0		1.8	116 (σ 0.1%)
NaNO ₃ + 5 % NaI (NaI5)	2.185 : 0.115		2.3	137.7 (σ 0.1%)
NaNO ₃ + 10 % NaI (NaI10)	2.07 : 0.23		2.3	139.7 (σ 0.1%)
NaNO ₃ + 15 % NaI (NaI15)	1.955 : 0.345		2.3	141.8 (σ 0.1%)
NaNO ₃ + 20 % NaI (NaI20)	1.84 : 0.46		2.3	143.3 (σ 0.2%)
NaNO ₃ + 30 % NaI (NaI30)	1.61 : 0.69		2.3	145.6 (σ 0.1%)
NaNO ₃ + 40 % NaI (NaI40)	1.38 : 0.92		2.3	149.4 (σ 0.1%)

During surface processing and electrolyte efficiency experimentation, the electrolyte velocity was maintained at 16 m/s (1 mm I.D. nozzle), 25 m/s (0.5 mm I.D. nozzle) and 16 m/s (0.25 mm I.D. nozzle). For the refresh rate experimentation, detailed later, jet speed was varied from 4 m/s to 29 m/s (the upper and lower bounds of machine capability). The IEG was set initially at 0.25 mm for the modified and 1 mm I.D. nozzle and 0.5 mm in all other cases. For surface structuring a constant applied current of 900 mA ($J = 100 \text{ A/cm}^2$) for 1 mm nozzle, 900 mA ($J = 400 \text{ A/cm}^2$) for the 0.5 mm nozzle and 200 mA ($J = 400 \text{ A/cm}^2$) for 0.25 mm nozzle. Where J is the predicted mean current density at the nozzle. In the case of the electrolyte efficiency test, current density ranged from

20 A/cm² to 200 A/cm². The refresh rate and incident iodide concentration were both appraised at 100 A/cm². The electrical potential was left to float as this was seen to vary dependant on the nozzle geometry, electrolyte conductivity, and surface geometry, and therefore subsequent resistance. Where nozzle translation was used, speed was maintained at 0.5 mm/s, except for experiments reported in Figure 6.9 where 0.1mm/s was used.

The resultant machined profiles were imaged and analysed as per the described method in section 3.5.1, 3.6.1 and 3.7.2. The analysis was carried out to obtain depth, width, area, overcut and side wall slope (taper) of each of the resultant profiles as defined in section 3.8.

6.2.2.1. Current efficiency testing

To obtain experimentally derived material removal, an array of 5x5 dimples was machined at varying current density levels up to 200 A/cm². Each dimple was created using a specific bouncing toolpath (Figure 6.1) to maintain fidelity to experimental parameters, with a dwell time of 4 seconds using a standard 0.5 mm I.D. nozzle.

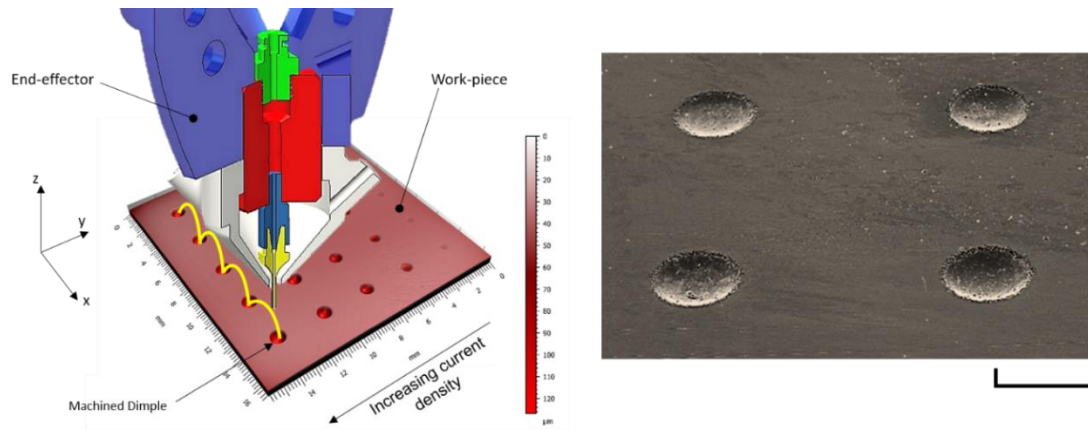


Figure 6.1: Schematic of the toolpath used to create dimples and accompanying example SEM image of the resultant features created. Scale bar is 1 mm

The dimple arrays were then scanned using a focus variation microscope in the same manner as the machined profiles, to obtain the volume of material removed for each current density with different electrolytes; NaNO_3 , NaCl and the doped electrolyte series. Electrolyte compositions are outlined in Table 6.1. From the extracted volumes, the experimental material removal can be calculated by incorporation of the material density (Equation 21).

6.2.2.2. Surface processing

In the same manner as section 5.3.3 standardised stainless steel, cylindrical, straight walled nozzles (Figure 6.2a) with internal diameters (I.D.) of 1 mm, 0.5 mm, 0.25 mm and 0.15 mm were used to demonstrate the electrolyte and as the base for the modified nozzle tip geometries. The *STE* nozzle design (Figure 6.2b) was employed to highlight areas where the hybrid electrolyte is advantageous in reducing secondary machining zones over a conventional electrolyte. The *STE* modified nozzle with an I.D. of 1 mm was employed to create multiple pass striations for comparison of response profiles.

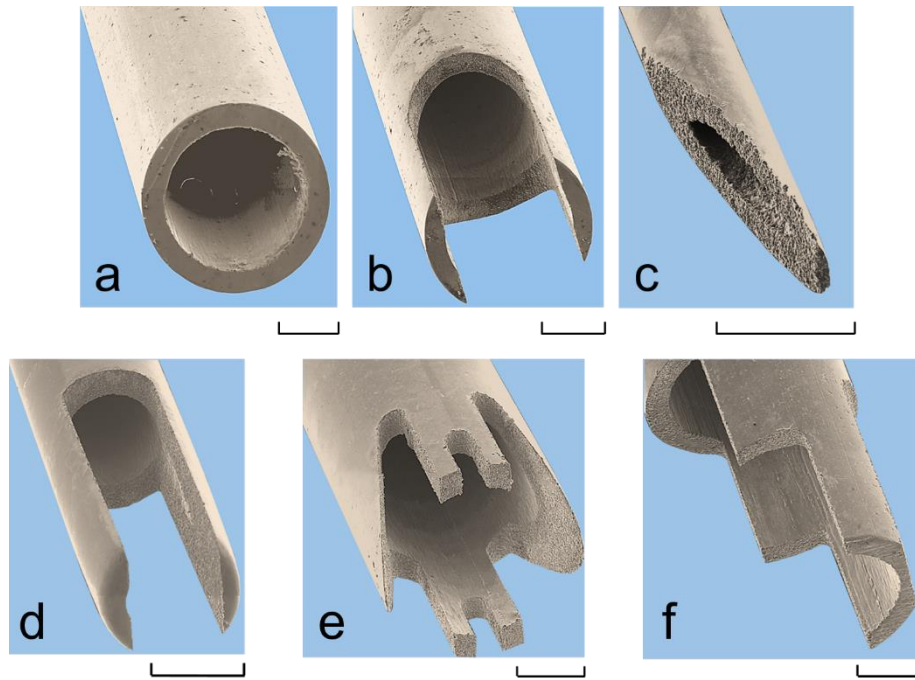


Figure 6.2: Nozzle types used within this study (a) standard nozzle (b) 1mm I.D. symmetrical twin element nozzle (STE), (c) 0.25 mm I.D. off-centre single point nozzle design (OSPE), (d) 0.5 mm I.D. STE nozzle, (e) 1 mm I.D. double channel cut nozzle (DCC) and (f) 1 mm I.D. steps nozzle design. All scale bars 500um.

Figure 6.2d - f shows a range of nozzles used to demonstrate the capability of this methodology to create surface structures with the modified nozzle tips and enhanced electrolyte demonstrating the scalability of the methodology. Figure 6.2c being a 0.25 mm I.D. nozzle cut with off-centre single point element (OSPE). Figure 6.2d being an STE design except in this instance cut into a 0.5 mm nozzle. Figure 6.2e and f are complex nozzle designs cut into 1 mm I.D. nozzles to achieve a specific cut with a secondary, smaller indent at the base of the cut and minimised taper.

6.2.3. Surface Processing

6.2.3.1. Enhanced Precision

In Figure 6.3 an effect of NaI addition to the electrolyte can be observed. In Figure 6.3b iodine can be seen to be forming under the jet impingement area as a dark cloud, in comparison to Figure 6.3a, where only NaNO_3 was used. Here no coloration of the thin film area is observed. It is interesting to note that iodine saturation within the electrolyte thin film, is visible up to 2 mm from the nozzle axis, where the iodide is oxidised. This is well within the resistive thin film area, where the current developed is extremely low and material removal will not occur.

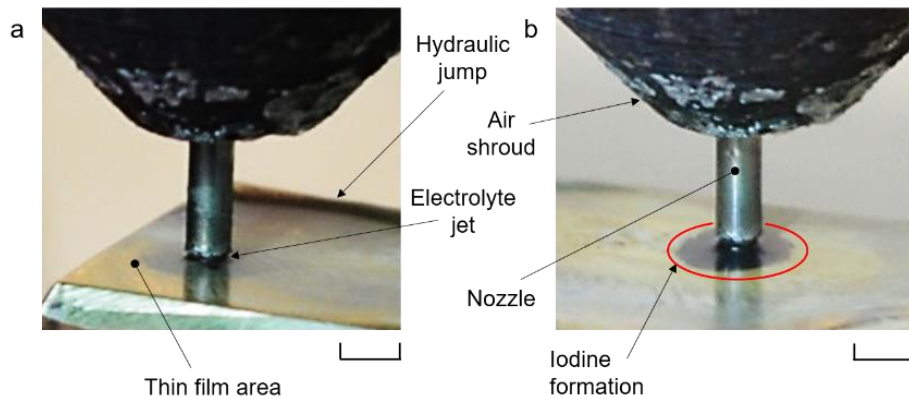


Figure 6.3: Photographs of the interaction zones whilst machining at 20 A/cm^2 (a) with NaNO_3 (2.3 M) and (b) NaI_2O (2.3 M), showing the formation of the iodine radial about the jet zone. Scale bars are 2 mm

The justification for the selection of NaI as a dopant can be seen in Figure 6.4 where exemplar 3D surface maps generated from areal scans of dimples are presented along with the corresponding 2D dimple profiles. Figure 6.4a demonstrates a dimple created with a 1.8 M solution of NaNO_3 showing the contour lines corresponding to the colour-scale changes. In Figure 6.4b identical

process parameters were used but NaI was added to the electrolyte solution, to make a 2.3 M solution (NaI20, Table 6.1).

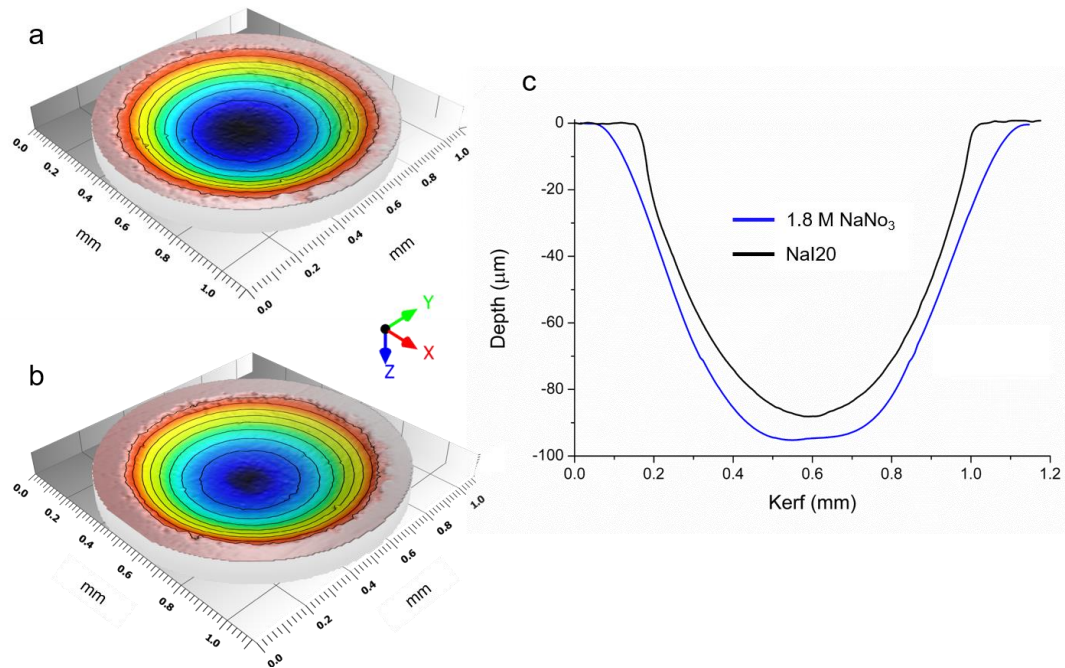


Figure 6.4: 3D surface map of compared machined dimples (a) using a 1.8 M solution of NaNO_3 and (b) with NaI20, (c) comparison of the extracted 2D profiles from the dimples.

Prior research [105] has identified that a reduction in electrolyte concentration leads to an increase in precision. However, in this case, although the concentration and conductivity has increased in Figure 6.4b with the addition of NaI, a 10% reduction in area of the dimple profile from $62541 \mu\text{m}^2$ ($\sigma < 1\%$) to $56128 \mu\text{m}^2$ ($\sigma < 1\%$) has occurred, recalling Table 6.1. This change in area can be observed in Figure 6.4c, the reduction in rounding at the surface to feature interface on NaI20 compared to 1.8M NaNO_3 and the reduction in depth.

In Figure 6.5 SEM of dimples machined with 200 A/cm^2 using three different electrolytes NaNO_3 (a), NaCl (b) and NaI10 (c) are shown. These are accompanied with respective surface scans. The obvious difference is observed in the SEM images at the shoulder interface precision (P) of the dimple to

substrate surface. Comparing the red contour band of all three images the enhanced electrolyte shows a thinner more defined band at which the same gradient occurs at a shallower depth range.

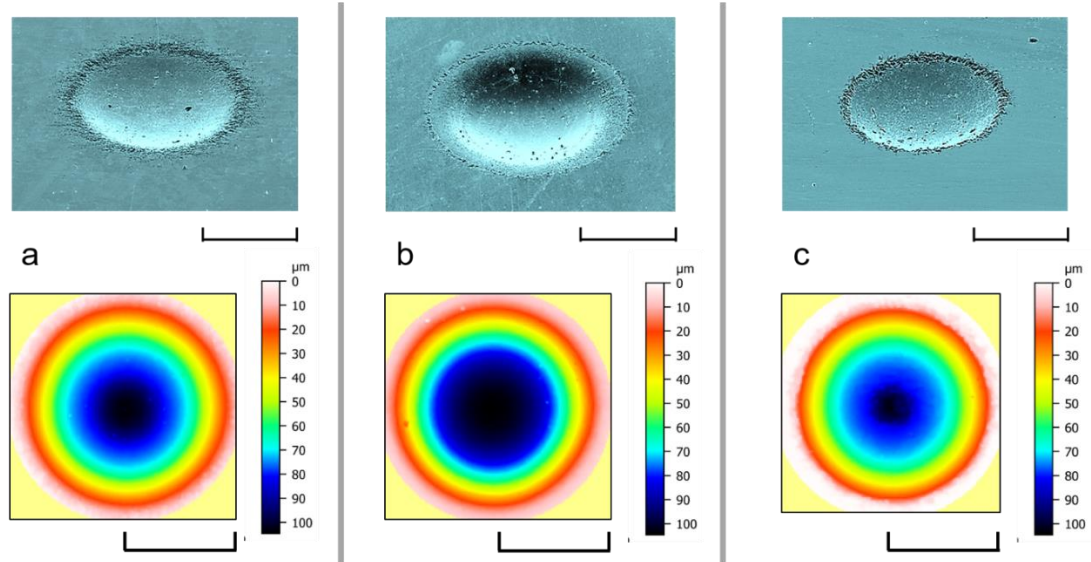


Figure 6.5: Tinted SEM images tilted at 60° of machined pits and associated contour information from surface scans of dimples machined at 200 A/cm² in (a) NaNO₃ (b) NaCl (c) NaI10. Scale bars 500 μm

When the precision of the three samples is compared, the enhanced electrolyte shows a mean side wall slope of 0.29 μm / μm ($\sigma = 0.01 \mu\text{m}$) achieving a 58% increase when compared to the NaCl electrolyte and 45% when compared to the NaNO₃ electrolyte. It is worth noting that chloride, although exhibiting the worst geometry definition of the three electrolytes, achieves a greater machining depth of 104 μm ($\sigma < 1 \%$) compared to 92 μm ($\sigma 1.7 \%$) for the NaNO₃ and 90 μm ($\sigma 2 \%$) for the NaI10. This is a result of the consistently higher current efficiency of this electrolyte across a broad range of current densities.

The resultant profiles seen in Figure 6.6, machined with the standard nozzle at 100 A/cm², continues to demonstrate the same trend in the enhancement of the

geometry definition at the dimple shoulder despite the reduction in applied energy. A reduction in overcut of 59% is seen when NaI20 is used ($2607 \mu\text{m}^2$ σ 5.8%) as compared to NaCl ($6377 \mu\text{m}^2$ σ <1%). A 43% reduction is also observed when compared to NaNO_3 ($4544 \mu\text{m}^2$ σ 6%).

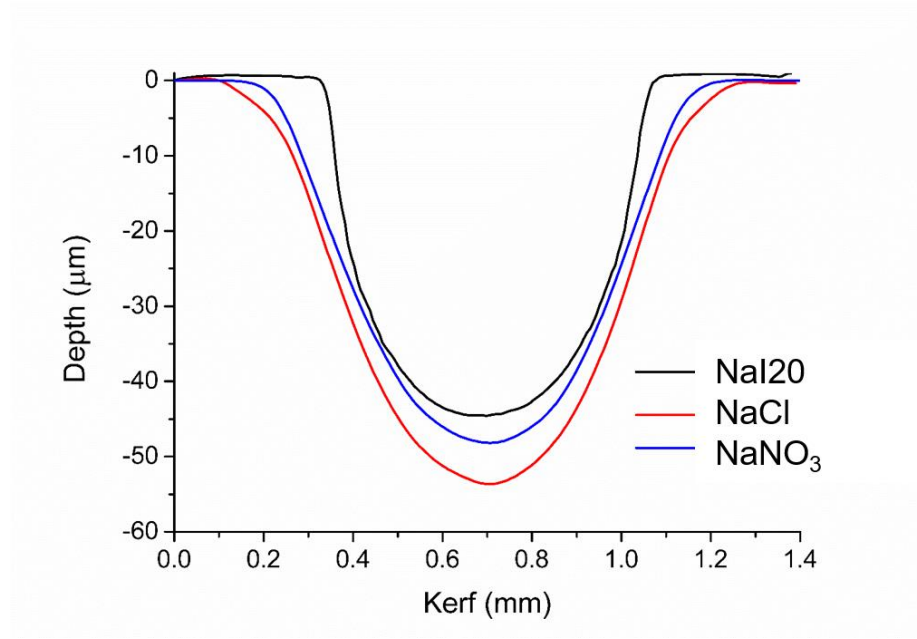


Figure 6.6: Comparison of machined profiles using 3 different electrolytes. Profile scans taken from the dimples produced using a standard nozzle at 100 A/cm^2 .

This change in the removal profile in comparison to NaNO_3 occurs at all current densities tested in this study. This is consistent with the hypothesis for this work that some energy will be preferentially utilised in oxidation of the dopant as opposed to direct machining. It should be noted that for this reason, iodide enhanced electrolytes are not recommended in applications whereby high material removal rates are sought over process dimensional accuracy. This is demonstrated in Figure 6.7 where the precision metric obtained from dimples at 200 A/cm^2 is compared to the material removal rate (MRR) across the range of electrolytes tested.

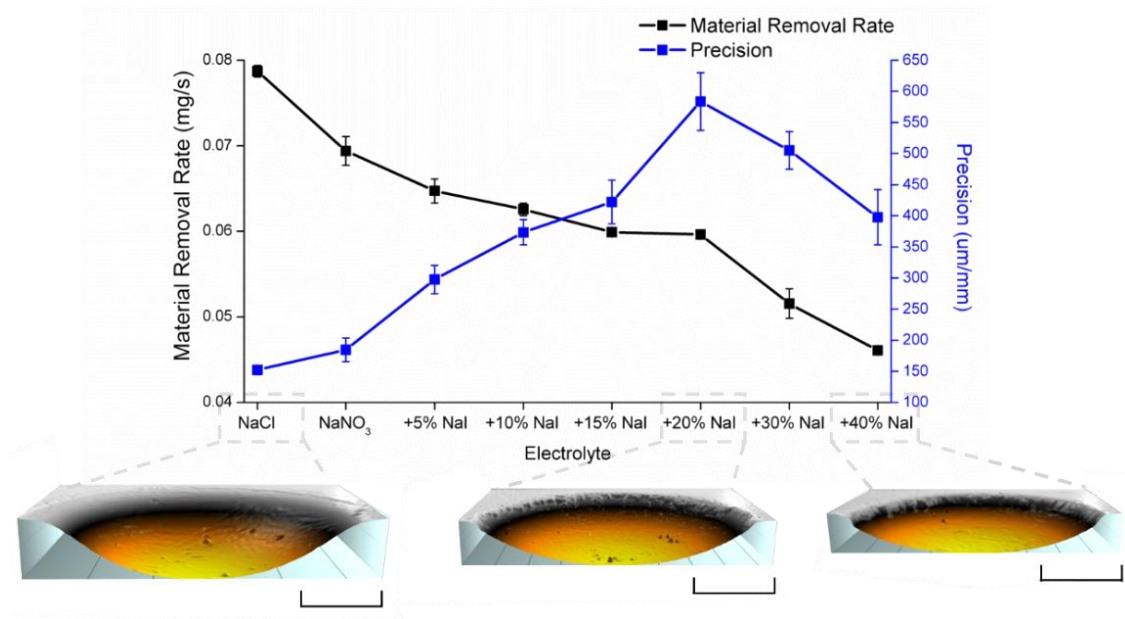


Figure 6.7: Comparison of material removal and precision across the variation of electrolytes at 200 A/cm² Reconstructed and sectioned 3D images of exemplar machined dimples from the samples machined with NaCl, NaI20 and NaI40 all represented on the same scale. All scale bars are 250 μm

The trend can be seen whereby NaCl demonstrates the highest removal rate at 0.078 mg/s ($\sigma < 1\%$) then decreasing by 8% to 0.069 mg/s ($\sigma 2.4\%$) with the use of NaNO₃. MRR is reduced by the introduction, and increasing NaI concentration, culminating in a reduction of 34% in the MRR compared to the straight NaNO₃ solution with NaI40 having an MRR of 0.046 mg/s ($\sigma < 1\%$). Therefore, under these process conditions, for every 1% increase in NaI added there is approximately a 1.2% decrease in MRR. Conversely, the precision of the feature shoulder is seen to increase from NaCl showing the lowest slope at 152 μm/mm ($\sigma 4\%$) to a 25% increase with the use of NaNO₃ (190.8 μm/mm $\sigma 7\%$). Culminating with a 206% increase in P when a 20% addition of NaI is used (583.6 μm/mm $\sigma 7\%$) compared to a straight NaNO₃ solution and 284% increase when compared to NaCl. Feature shoulder precision can be seen to improve by 50% for every 5% extra ratio of NaI that is added up to this point, beyond which

precision appears to decrease at this current density level. As material removal becomes reduced at this current density level, the dimple profile area drops to $47200 \mu\text{m}^2$ ($\sigma < 1\%$) for NaI40 compared to $55700 \mu\text{m}^2$ ($\sigma < 1\%$) for NaI20, meaning the side wall slope is very low and is reflected in the evaluated precision the side-wall slope dominating the shoulder precision. Increasing the applied energy would lead to increasing P values.

6.2.3.2. Enhanced feature generation

The application of more complex nozzle designs to affect a distinct profile demonstrates the enhancements that are achievable through implementation of the doped electrolyte. When the electrolytes are coupled with modified nozzle tips, the increase in fidelity of the response profile to the nozzle tip geometry is exaggerated. In the case of Figure 6.8a, an STE nozzle is used over 4 passes. Several distinct areas of change are observed. Firstly, a reduction in width by 10% to 1.74 mm ($\sigma < 1\%$) with the NaI10 electrolyte. Secondly, the slope on the side walls can also be seen to increase by 34% to $0.35 \mu\text{m}/\mu\text{m}$ ($\sigma 2.4\%$). Furthermore, the radius at the shoulder and apex of the troughs is reduced giving a reduction in overcut of 14% from $40181 \mu\text{m}^2$ ($\sigma 2.2\%$) to $34496 \mu\text{m}^2$ ($\sigma 1.8\%$).

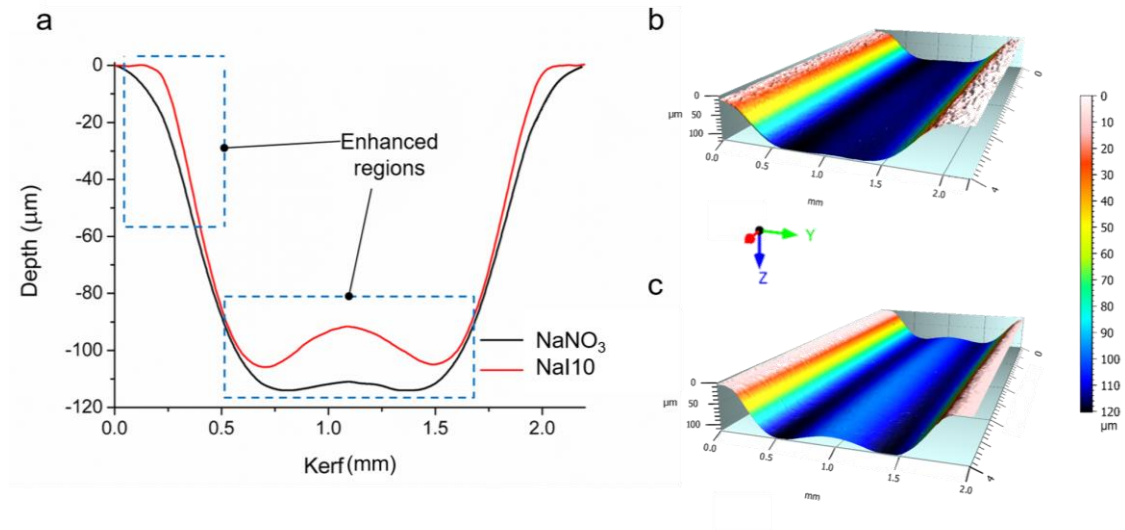


Figure 6.8: (a) Comparison of NaNO₃ and NaI10 profiles produced with an STE nozzle used over 4 passes demonstrating the increase feature fidelity in discrete areas that can be achieved when used with a modified nozzle and hybrid electrolyte. (b) 3D reconstruction of a sample cut with an STE nozzle and NaNO₃ (c) 3D reconstruction of a sample cut with an STE nozzle and NaI10

Figure 6.8 shows that even when used with an enhanced electrolyte there is a still a limit to the precision of the geometry that can be achieved. It is apparent though, that these features influence the overall profile created since they are significantly different to those generated with the equivalent NaNO₃ electrolyte. Again, it is demonstrated that the fidelity to the intent from the nozzle design is also influenced by secondary factors which includes hydrodynamic and changing resistance profiles as the cut feature evolves (see section 5.3.5). This is in contrast to other energy beam techniques where the end-effector geometry directly denotes the response profile.

In Figure 6.9, the innovation demonstrated previously is deployed for the purpose of demonstrating the new capabilities available to EJP practitioners. Here, Inconel 718 is processed using a number of nozzles with NaI10 electrolyte to investigate the application of previously generated geometries on a smaller scale

and to investigate the fidelity of features that can be achieved using complex nozzle designs.

The principle of nozzle design is applied to create an *OSPE* type geometry on a 250 μm nozzle (Figure 6.9a) and *STE* geometry on a 500 μm nozzle (Figure 6.9b). In doing so the scalability of this technique is highlighted. Using smaller nozzles leads to reduced kerf width while maintaining the desired profile. Utilising higher jet speeds, current densities ($\sim 400 \text{ A/cm}^2$) and slower head traverse speeds ($\sim 0.1 \text{ mm/s}$) to obtain enhanced precision features with these smaller nozzles, Figure 6.9e.

New nozzle designs were also realised to test the ability of the process to maintain profile fidelity. Figure 6.9e-k show a surface scan transposed into a 3D image and accompanying SEM images. This demonstrates how response profiles can be combined, through superimposition, to create an application-ready surface, for example, in microfluidic reactors, biomimetic surfaces or mechanical interlocking interfaces. Complete surface processing was undertaken in under 45 minutes including nozzle changes. The use of additional tooling was not required. All four profiles seen in Figure 6.9a–d were taken from this sample and demonstrate both the depth and profile achieved by a single pass.

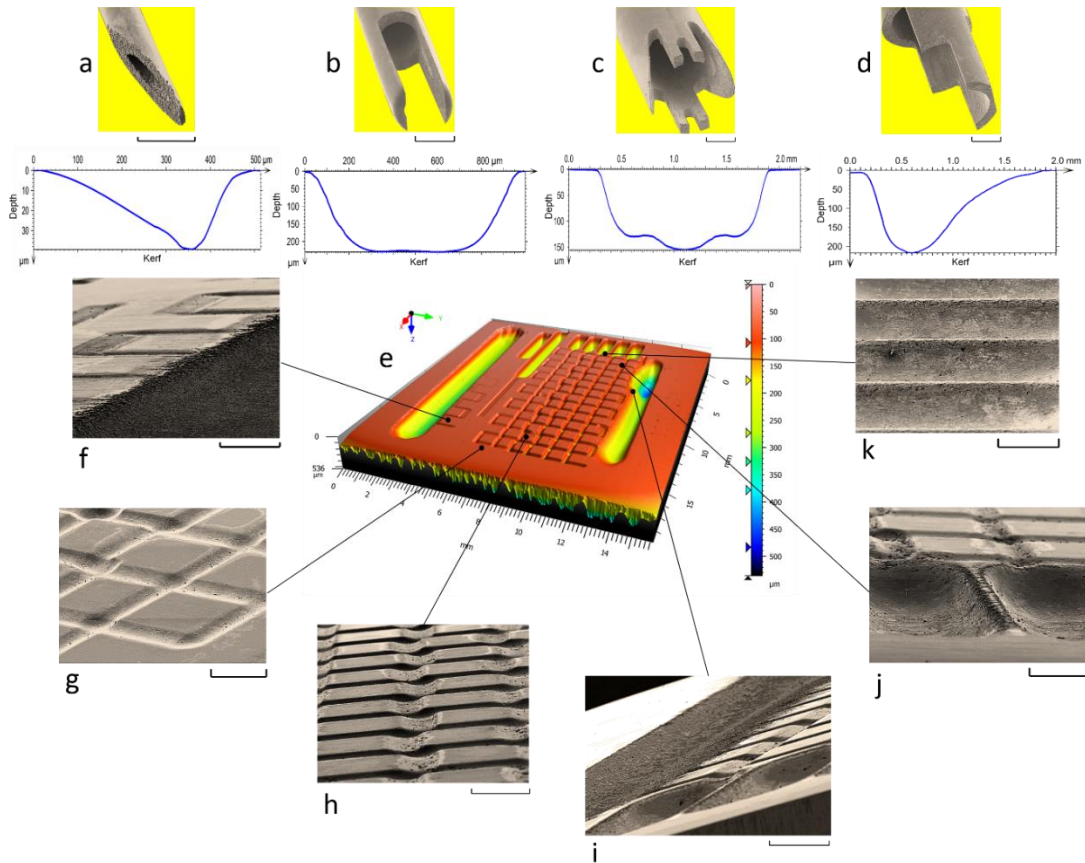


Figure 6.9: All features were machined using Na10 and applied to varying nozzle designs at differing scales (a) 250 μm I.D. nozzle cut with an OSPE geometry and the resultant profile shown below. (b) 500 μm I.D. nozzle with resultant geometry below. (c, d) 1 mm nozzle cut with an intentionally complex pattern to test the fidelity of the profile that can be created with the resultant profile below. (e) Shows a scanned surface map converted into a 3D image where all the above nozzles have been used to create features. (f) From the trench created by nozzle (c). (g) and (h) using nozzle (a) in two differing directions giving a different effect in both directions. (i) Deep pits created by nozzle (b) next to patterning created by nozzle (a) going into deep trench created by nozzle (d). (j) Nozzle (a) leading from pits created by nozzle (b). (k) Ribs created by nozzle (b). All scale bars are 500 μm .

Figure 6.10 shows the application of the enhanced electrolyte with a standard 150 μm nozzle to create repeated surface structures with sharp angular interfaces. Although the rounded base is still prevalent due to the use of a standard nozzle, sharpness of the feature shoulder and reduced taper at the top section of the profile relating to the increase in the precision metric is obvious. The slight undercut and curved top edge created in one direction occurs due to the electrolyte interaction with the already machined geometry. Upon successive machining passes the recessed regions are exposed diverting ejecting fluid flow.

This effect can be minimised or exploited by careful consideration of the toolpath and associated process parameters.

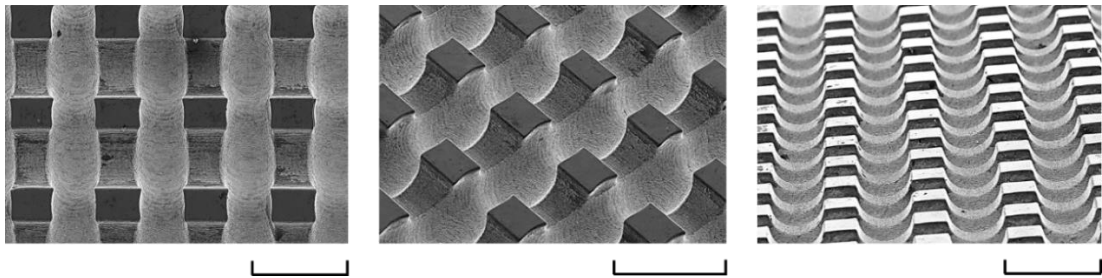


Figure 6.10: SEM images of repeating surface structures developed to demonstrate process capability for enhanced adhesion. Machining undertaken with a 0.15 mm I.D. nozzle. All scale bars are 500 μm

6.2.4. Process mechanics

From the results obtained through experimentation, the enhancement to precision and fidelity of the resultant features created is obvious through the range of NaI-doped electrolytes used. The removal effects in the first instance appear to concur with the original hypothesis. However, noting the increasing conductivity of the NaI-doped electrolytes (Table 6.1) as the concentration increases, the resultant profiles demonstrate a counterintuitive trend of significantly reducing MRR. The mechanism involved therefore requiring greater investigation.

6.2.4.1. Current filtering

Improvements can start to be explained by consideration of current efficiency characteristic of each electrolyte (Figure 6.11a). Here individual electrolyte current efficiency has been obtained from experimental comparison to theoretical values as outlined in section 6.2.1. There is a stark difference in current efficiency at the lower current densities ($< 60 \text{ A/cm}^2$) between the electrolytes. In

comparison to NaCl, all the NaNO₃ based electrolytes exhibit a much lower efficiency at low current densities. It is worth noting that it was deemed at this point not to take the inclusion of NaI further than 40% due to low MRR at these current density levels and the cost implications for large-area processing.

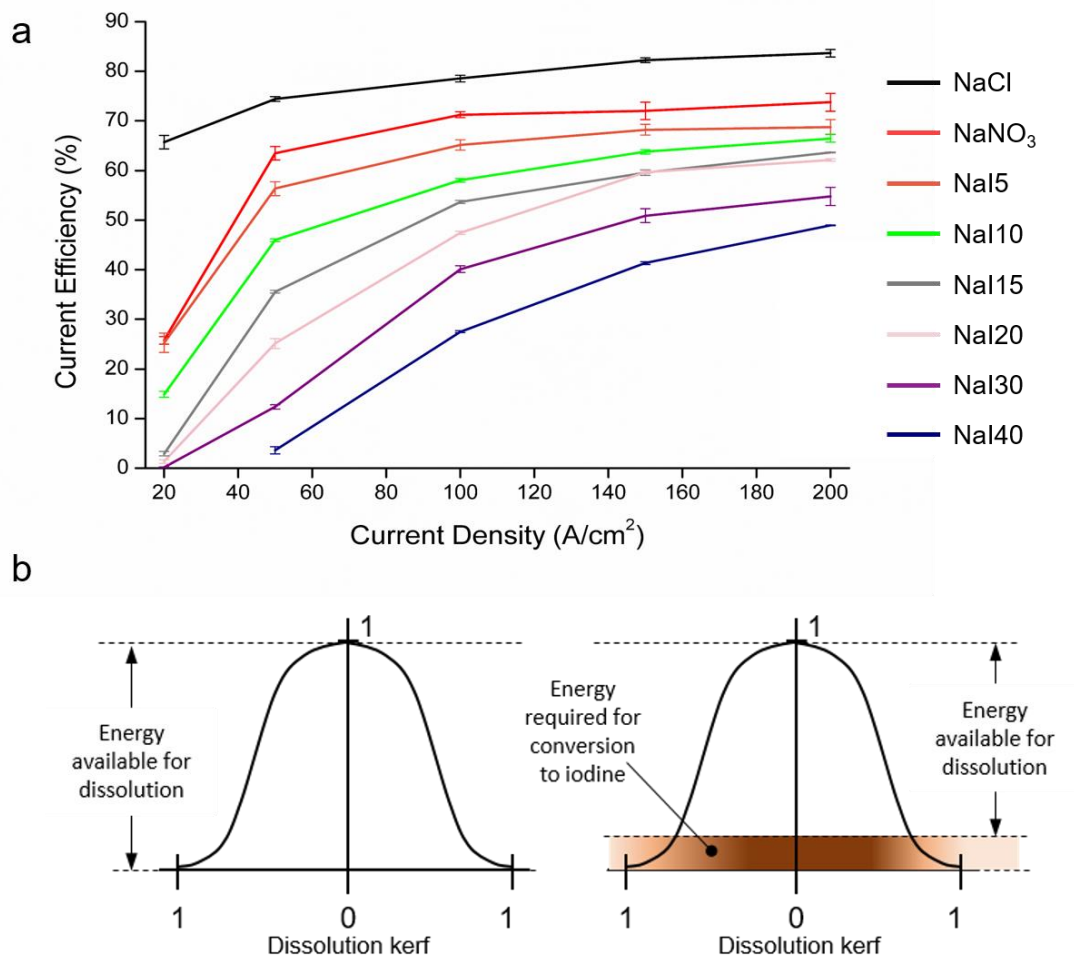


Figure 6.11: Energy filtering mechanism description (a) comparison of electrolyte efficiency across the range of electrolytes tested including increasing ratios of NaI (b) description of the mechanism occurring leading to exclusion of current levels at discrete points in the energy distribution, the machined profile being the mirror of the energy density curve.

At 20 A/cm², NaI20 exhibits an efficiency of 1.3% ($\sigma < 1\%$) in comparison to NaNO₃ at 26% ($\sigma < 1\%$) efficiency, and NaCl at 66% ($\sigma < 1.3\%$) efficiency. In comparison, at 200 A/cm², NaI20 exhibits an efficiency of 62% ($\sigma < 1\%$), when compared to NaNO₃ at 73 % ($\sigma < 1.8\%$), and NaCl at 84% ($\sigma < 1\%$).

Since the current efficiency at low mean current density is lower for the NaI-doped electrolytes, the threshold energy required for material removal is not achieved at the periphery of the feature. Hence, material removal is inhibited in these secondary machining zones, and a sharper edge definition is observed, shown by the highlighted regions in Figure 6.8a. This can then be compared to the higher current density areas at the centre of the pit where the efficiency differential between electrolytes is markedly reduced. Therefore, the energy density profile will demonstrate a steeper slope for the enhanced electrolyte resulting in less overcut as shown by the mechanism schematic in Figure 6.11b whereby the resultant machined profile will be a mirror of the energy density curve.

This phenomenon can be further observed in Figure 6.12, where 3 lines were machined with mean current densities increasing from 4 A/cm² to 50 A/cm² in 3 mm steps at 0.5 mm/s. The lines were machined with NaNO₃, NaI₂₀ and NaI₄₀.

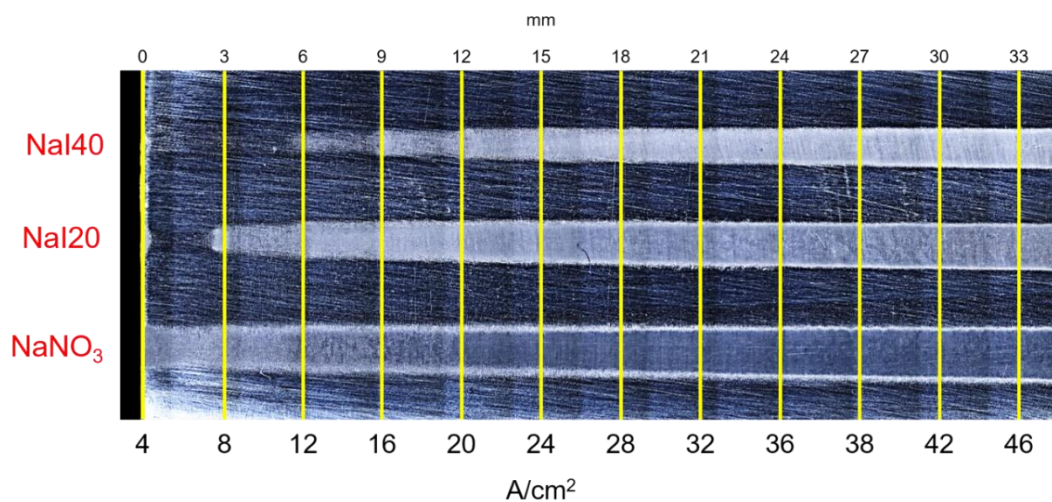


Figure 6.12: Optical micrograph of three machined lines all using the identical toolpaths and machine parameters but with differing electrolytes, to demonstrate the point at which the applied current exceeds the energy filter required to initiate dissolution of the material.

It can be observed from Figure 6.12 that as the current density increases from left to right, the filtering effect of the NaI addition, to achieve masking, can be clearly seen. The NaNO_3 (control) line showing an initial light texturing effect at 4 A/cm^2 as the dissolution energy required for the material is reached. From that point on the texturing continues to become more defined to 32 A/cm^2 where the mechanism has stabilised and becomes a consistent width. In comparison, the lines for NaI20 and NaI40 demonstrate different regimes. The Gaussian energy distribution is obvious as surface texturing starts to appear at the point where the energy distribution is highest in the centre of the jet and filling out to the width of the final line as current increases, noting the reduced width of the textured area in comparison to the NaNO_3 throughout. The NaI20 line surface initiating dissolution at 8 A/cm^2 and achieving a consistent line width by 36 A/cm^2 . The NaI40 line starts to achieve dissolution a step further on than the NaI20 line at 12 A/cm^2 , although with a much lighter and thinner texturing. In line with this, the NaI40 electrolyte does not achieve a consistent line until 1 step beyond the NaI20 at 38 A/cm^2 . The difference in dissolution kerf, pertaining to precision can again be observed with the NaNO_3 line having a final width of 1.97 mm in comparison to the NaI20 of 1.69 mm and the NaI40 of 1.45 mm demonstrating a 26% reduction for the NaI40 electrolyte.

It can be established that the reduction in current efficiency is not dependent on electrolyte conductivities. This assertion is supported by the measured conductivities (Table 6.1), and the known linear relationship between electrical potential as defined by Ohms law. In addition, equimolar ionic strength solutions were used throughout this study, with all electrolytes having similar theoretical activity coefficients.

These results unequivocally prove the hypothesis to be correct that addition of an NaI dopant will cause a transitory filtering effect due to competing anodic reactions. The energy required for this change in oxidation state noted in the hypothesis, occurring at the anode surface is understood to be responsible for the restriction of the current available for anodic dissolution of the substrate due to increased faradaic impedance. This is a preferential route offering less resistance in comparison to the oxidation of the substrate surface, so limiting current efficiency (Figure 6.11b). Therefore, as concentration increases these, in this case beneficial, side reactions have an increasing effect on the Faraday efficiency seen in the process.

This competing electrode reaction suppresses the anodic dissolution of the nickel-based substrate, leading to the experimental observation (Figure 6.12) of a varying decomposition potential of the anode below which the current efficiency approaches 0%. This cut-off point is different for each electrolyte tested and increases with iodide concentration as more energy is diverted to the preferential activity of oxidising iodide to iodine. The addition of iodide at varying concentrations therefore leads to superior edge definition and reduced overcut. It should be noted that this effect is also dependent upon the work piece material electrode potential in comparison to the standard electrode potential of the conversion from iodide to iodine. Also, the increase in conductivity goes some way to offset the reduced MRR so maintaining a balance between the increase in precision and MRR is vital.

Refresh rate

In order to further assess the mechanism leading to increased precision, a series of experiments were conducted varying the electrolyte jet speed across the range

available; 4, 10, 19, 27 and 29 m/s. Considering Figure 6.13, where resistance and removed profile area are compared to jet speed, a second influencing mechanism can be identified in relation to the current filtering effect, relating to the iodide concentration at the work surface. It is shown in Figure 6.13a that as the electrolyte jet speed is increased there is negligible change in the in-process resistance experienced in the IEG, for NaNO_3 electrolytes, beyond the initial increase up to 10 m/s associated with a transition in debris clearance regimes as noted in section 5.2.3. In comparison, the NaI-doped electrolytes have higher, and increasing, resistance with jet speed. This is counterintuitive since the conductivity of these electrolytes exhibits the opposite resistance trend. This is attributed to the readiness with which the transitory iodine mask forms in these electrolytes. At the highest jet speed, with a constant J of 100 A/cm^2 , the NAI40 electrolyte shows a 62% increase from $162 \text{ } \Omega$ ($\sigma 2.2\%$) to $263 \text{ } \Omega$ ($\sigma 3.6\%$).

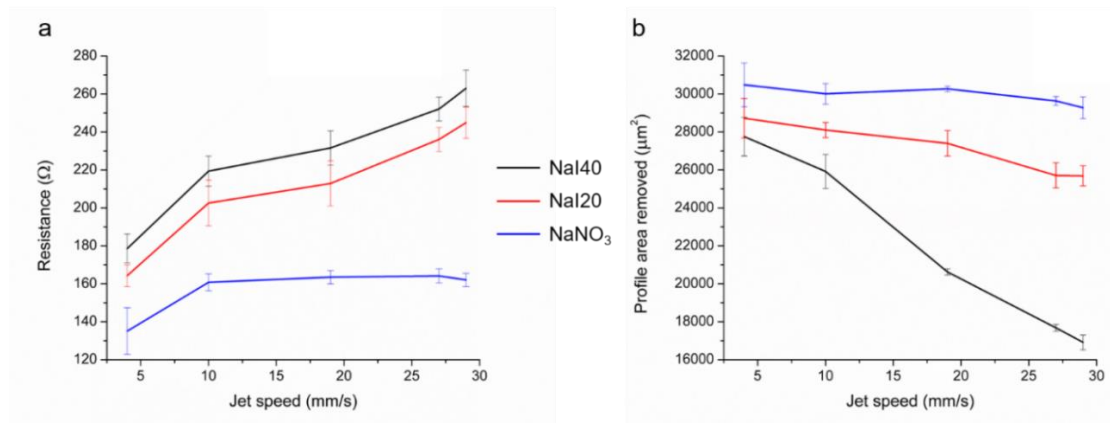


Figure 6.13: impact of variation of electrolyte jet speed on (a) in-process resistance and (b) profile area removed with differing electrolytes

In conjunction with this, in Figure 6.13b the relationship with jet speed to the area removed can be observed. The NaNO_3 electrolyte displays a negligible change in area removal of 4% ($\sigma 2\%$) over the range of jet speeds, the NaI20 in

comparison demonstrates a 9% (σ 2%) reduction in area from the lowest to highest jet speeds. However, the NaI40 experiences a drop of 39% (σ 2%) over the jet speed range having an area 42% (σ 2.2%) less than NaNO_3 at 29 m/s. From these results, the second influencing mechanism can be elucidated; the refresh rate. It is clear that the concentration of iodide present in the feedstock is not the only contributing factor, but also the rate at which it is refreshed at the surface. The higher the iodide refresh rate (consistent with increased jet speed), the greater the proportion of energy diverted from material removal to iodide oxidation.

6.3. Electrolyte Multiplexing for enhanced process flexibility

6.3.1. Introduction

As observed in the literature review and demonstrated in Chapter 4 and section 6.2 differing electrolytes used in EJM can produce significantly different form and finish with the same applied energy. The purpose of this work is to exploit these characteristic differences through hardware additions designed into the generation 2 EJP machine tool to enhance the process capability of electrochemical jet techniques.

A high degree of variation of surface features along different length scales has been demonstrated throughout this thesis to be possible using EJM through variation of parameters and by mechanical design. Furthermore, by utilising differing electrolytes it is possible to vary the deterministic mesoscale through electrolyte selection and the addition of dopants to the electrolyte in order to increase precision of machined features as demonstrated in section 6.2. It is also

possible to effect the non-deterministic microscale surface finish through manipulation of the electrolyte in response to the chosen workpiece material [272]. From this research it can be observed that different electrolytes exhibit different traits in material removal rate (MRR), precision and surface finish. Often a single electrolyte is incapable of satisfying all process design criterion and instead is selected as a compromise. This research is intended to build upon this prior knowledge to develop machining strategies that utilise the different advantages found with differing electrolytes for the optimisation of feature generation. Through demonstration of applying differing electrolytes concurrently and sequentially, the electrolyte can be considered as analogous to tooling changes in conventional machining. Thus, application of this methodology allows for greater flexibility and efficient machining strategies.

6.3.2. Methodology

As part of the Generation 2 machine tool (see section 3.4) an electrolyte multiplexing system was incorporated as per the design requirements (Figure 6.14). Four separate 12 litre electrolyte supply tanks (ST) are used each with an CNC solenoid. Two tanks share a single precision gear pump. These lines are fed into a 3/2-way valve which can either feed the nozzle or be diverted to a large bore pipe connected to waste. The effect of this means the electrolyte lines can be easily purged allowing for quick change over of electrolyte type. This can be achieved in less than 3 seconds (measured by changing between clear and coloured electrolyte) including nozzle clearance.

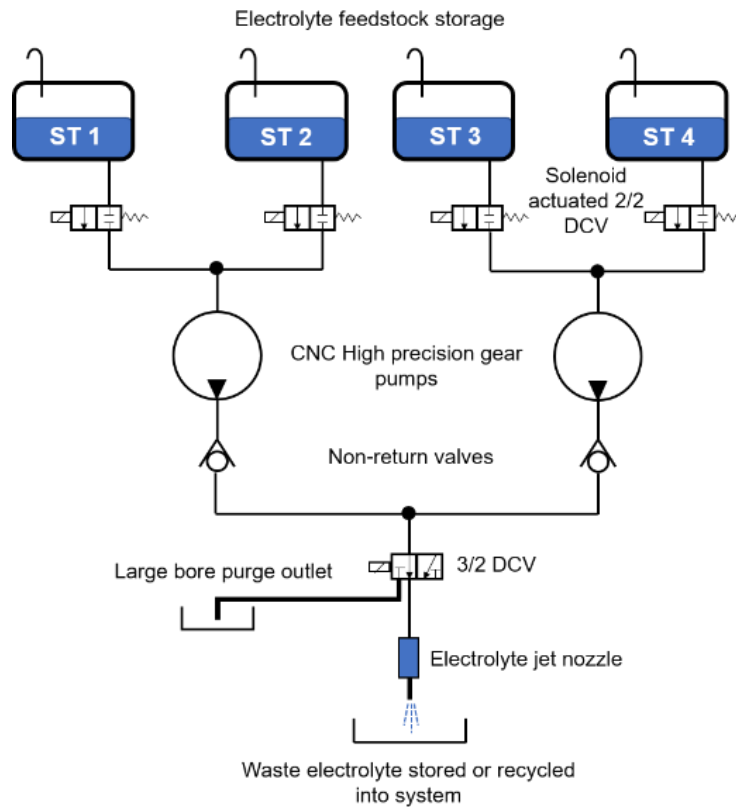


Figure 6.14: Schematic of the multiplexing system used in this study which allows rapid electrolyte exchange.

Utilising this configuration means it is possible to mix and vary electrolyte composition as part of the machining program. Each pump is controllable and operable independently over the full range of the possible flow rates. Therefore, each pump allows the electrolyte to be proportionally supplied creating dynamic mixing of electrolyte composition ‘in flight’.

To demonstrate this new capability a series of experiments were designed. Different electrolytes were applied in series to establish a best practice for meso-scale feature generation. This requires a quick switch between electrolyte on successive passes so makes use of the purging system. A second set of experiments was developed to demonstrate how this methodology could be used to create a functionally graded surface by fading between electrolytes within the

same toolpath. As described in Chapter 3, all parameters are set by the main control program remaining constant during the form and finish experiments reported here. Current density was set at 250 A/cm^2 , when used with a stainless-steel nozzle of $500 \text{ }\mu\text{m}$ internal diameter. IEG was set initially at 0.5mm . Nozzle traverse speed was 0.5 mm/s and for these experiments pump flow rate was set to achieve a jet speed of 29 m/s .

For the assessment of form and finish, multiple striations were created with two passes in opposite directions over a coincident toolpath machined into an Inconel 718 workpiece noting the resultant form and finish is well understood from Chapter 4. Table 6.2 shows the sample designation with the definition of the electrolytes used in each case and the sequential order in which they are used over successive passes in alternating directions over the same tool path. The electrolytes were maintained at 22°C and a 2.3 M concentration throughout. The electrolytes selected for this investigation include both NaCl and NaNO_3 electrolytes for which in the previous sections, the differing attributes, have been clearly demonstrated. Also selected is the NaI20 hybrid electrolyte reported in section 6.2 for its ability to increase precision specific to EJM. The drawback of NaI20 is the lower material removal compared to that found in NaNO_3 and NaCl . For the functionally graded surface demonstration both NaCl and NaNO_3 were used.

Table 6.2: Sample designation with defined electrolytes and sequential processing order

Sample designation	Electrolytes	Forward pass	Reverse pass
NaCl	2.3 M Sodium Chloride (NaCl)	NaCl	NaCl
NaCl/NaI20	2.3 M Sodium Chloride (NaCl), 2.3 M 80% Sodium Nitrate + 20% Sodium Iodide (NaI20)	NaCl	NaI20
NaI20	2.3 M 80% Sodium Nitrate + 20% Sodium Iodide (NaI20)	NaI20	NaI20
NaI20/NaCl	2.3 M Sodium Chloride (NaCl), 2.3 M 80% Sodium Nitrate (NaNO ₃) + 20% Sodium Iodide (NaI20)	NaI20	NaCl
NaCl/NaNO ₃	2.3 M Sodium Chloride (NaCl), 2.3 M Sodium Nitrate (NaNO ₃)	NaCl	NaNO ₃
NaNO ₃ /NaCl	2.3 M Sodium Chloride (NaCl), 2.3 M Sodium Nitrate (NaNO ₃)	NaNO ₃	NaCl
NaNO ₃	2.3 M Sodium Nitrate (NaNO ₃)	NaNO ₃	NaNO ₃

Both electrolytes were fed to the nozzle at the same flow rate through the same pump but dispensed at different times along the toolpath. Each line of the surface was created in the same direction following the same programmed tool path and solenoid control for each line.

All parameters were maintained as previously described except current density which was reduced to 100 A/cm² to limit material removal as this intended to demonstrate changing surface texture effects rather than form. The solenoids were then set to open and close as a function of time with respect to the known traverse speed giving a repeatable pattern. As the nozzle traversed back to the beginning of the next line with a 0.5mm step over, the electrolyte lines are purged in time for the succeeding electrolyte.

Imaging and analysis of the feature geometry and surface finish was carried out as described in section 3.6.1 and 3.7.2 and described as per the metrics outlined in section 3.8.

6.3.3. Results and Discussion

6.3.3.1. Form

Considering Figure 6.15, the difference in resultant profile shape due to the electrolyte type can be observed. Using a NaCl electrolyte gains the greatest performance removing a mean area of $50090 \mu\text{m}^2$ ($\sigma < 1\%$) and mean depth of $87.2 \mu\text{m}$ ($\sigma < 1\%$) across all samples tested. In comparison, the resultant profile of the NaI20 electrolyte achieves 18% less maximum depth ($71.4 \mu\text{m}$ $\sigma < 1\%$) and 22% less area ($39305 \mu\text{m}^2$ $\sigma < 1\%$) across the range of samples analysed.

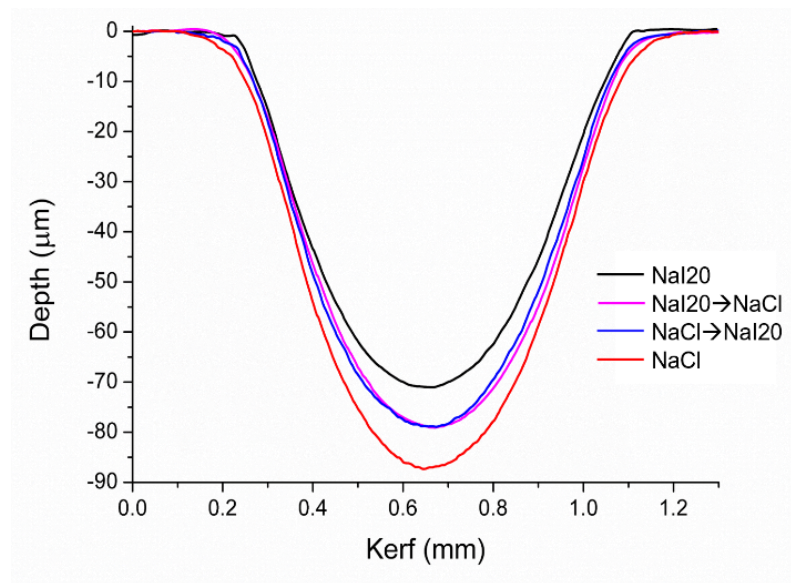


Figure 6.15: Exemplar resultant profiles from striations machined with two passes of the same electrolyte and two passes with differing electrolytes applied sequentially in this case NaI20 and NaCl

It was demonstrated in the previous section that this type of electrolyte achieves a narrower dissolution kerf, in this case achieving a 14% reduced width in comparison to NaCl and achieves a sharper interface between the cut area and

the workpiece surface. When the differing electrolytes are applied sequentially it can be observed that the resultant profile is a compromise between the precision of NaI20 and material removal performance of NaCl. The width of the striation being 6% more than NaI20 but 9% less than NaCL.

The depth is also 10% deeper (mean 78.7 μm $\sigma < 1\%$) than NaI20, but, 11% shallower than NaCl. It is worth noting that the sharp intersection between striation wall and workpiece surface is somewhat lost due to the flatter current efficiency profile found with NaCl (see section 2.4). This enables material dissolution even at low current densities found at the peripherals of the jet which in turn overwrites the enhanced precision obtained using NaI20. This compromise is achieved without creating a specific electrolyte type simply through sequential application. However, there is little difference in form between which order the electrolytes are applied which is also seen in Figure 6.16. Here NaNO_3 is applied sequentially with NaCl and compared to the previous results.

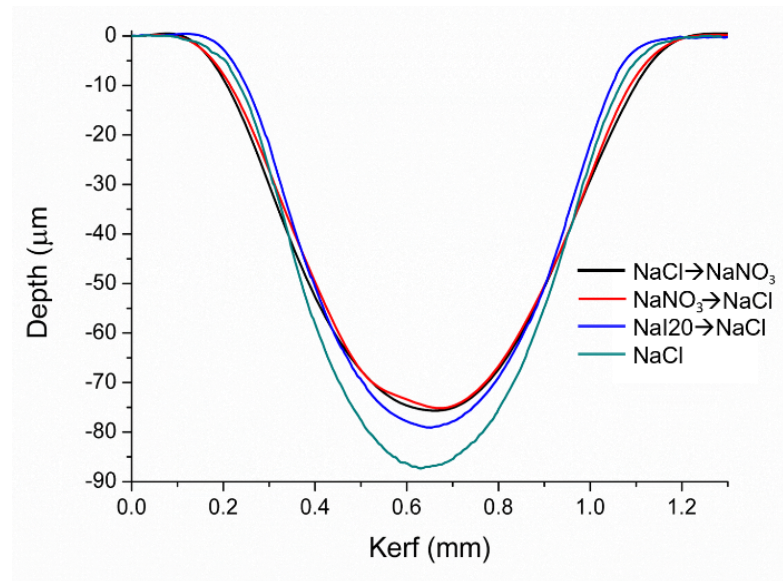


Figure 6.16: Exemplar resultant profiles from striations machined with two passes of NaCl and two passes with differing electrolytes applied sequentially in this case NaI20, NaCl and NaNO₃

Again, the differing current efficiency profiles as described in section 6.2.4 of the individual electrolytes denote the shape of the resultant profile when combined. The NaNO₃ sequentially applied with NaCl gives a much steeper side wall and lower radius intersection with the un-machined surface albeit with a mean striation cut width of 1.14 μm (σ 2%), 8% wider than NaCl and 19% wider than the NaI20/NaCl combination. The NaNO₃/NaCl combination produces a similar depth to NaI20/NaCl with 2% less depth at 77 μm (σ <1%) and 13% less than the twin pass of NaCl.

6.3.3.2. Surface Finish

Although a good compromise is found between performance and precision when using electrolytes sequentially there is little dependence on the order in which the electrolytes are applied to affect changes to the resultant profile. This is not the case with the resultant finish.

In Figure 6.17 the difference in surface finish is visually obvious. The optical images demonstrate the NaI20/NaCl striation (Figure 6.17a) to have a much higher lustre finish than the NaCl/NaI20 striation associated with NaCl electrolytes (Figure 6.17b). The exposure of the grain boundaries can also be seen as inter-granular corrosion has occurred again a trait of NaCl electrolytes when used with Ni-based alloys. In comparison the NaCl/NaI20 demonstrates the surface finish associated with NaNO₃ producing a dark tainted surface albeit with a proposed higher integrity surface as no inter-granular corrosion is present which can be associated with a change of mechanical properties at the near surface [286].

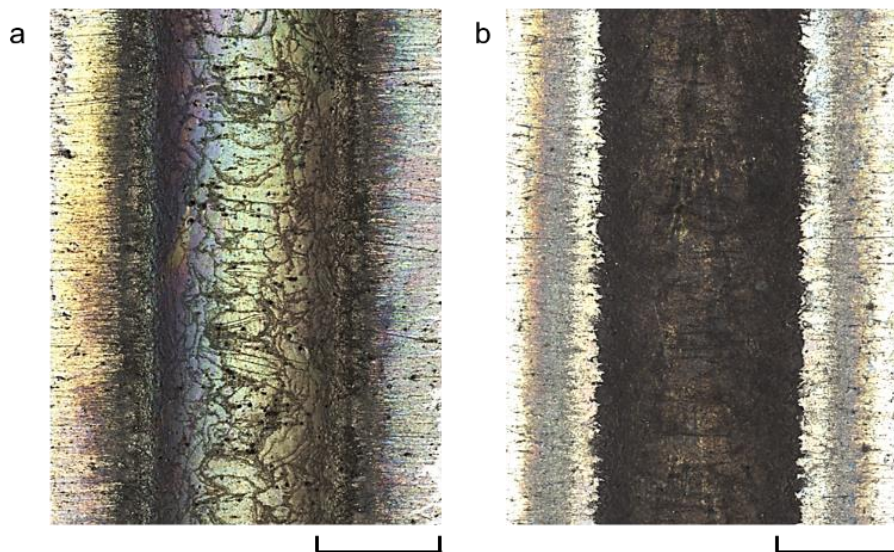


Figure 6.17: Optical images of the sequentially machined striations under identical lighting conditions (a) NaI20/NaCl and (b) NaCl/NaI20. All scale bars are 500 μm

This is supported by the profile roughness (R_a) figures extracted from the samples in Figure 6.17. The NaCl/NaI20 striations having a mean surface roughness of 0.11 μm (σ 11%) which reduces by 40% when the electrolyte order is reversed to 0.07 μm (σ 10%). This is comparable to the profile roughness (R_a) from the

twin pass of NaCl achieving $0.07\text{ }\mu\text{m}$ (σ 6%) and NaI20 $0.1\text{ }\mu\text{m}$ (σ 17%) which demonstrates the resultant finish is not a compound effect.

6.3.3.3. Graduated surfaces

Manipulating the multiplex electrolyte system and the correspondent resultant surface finish of differing electrolytes, a graduated surface finish can be simply created (Figure 6.18). As part of the toolpath program, it is possible to run the feed pumps, separately and concurrently, and open and close valves supplying the feedstocks as a function of the toolpath. This allows for discrete surface finishes to be applied as per the component design intent.

In the case of Figure 6.18, a repeating single direction linear toolpath was used. Figure 6.18a being the optical image of the surface created showing the regularity and therefore predictability of the fade between electrolytes as the solenoids open and close. Alongside the change in surface roughness from NaCl, producing a surface roughness (S_a) of $0.13\text{ }\mu\text{m}$ (σ 22%) to $0.23\text{ }\mu\text{m}$ for NaNO_3 (σ 15%), there is an optical difference. The surface transforming from a high lustre finish commonly associated with using NaCl (Figure 6.18b) with Ni alloys [18], to a matte finish due to the adherent oxide formation associated with Ni alloys machined with NaNO_3 (Figure 6.18d) at this current density level. The transition being seen in Figure 6.18c. The latency in the system, when the purge function is not used, can be seen when noting the point at which the solenoid controlling the NaNO_3 is opened when compared to the point which it becomes the dominant texture. This occurs at approximately 6 mm after the solenoid is opened (equating to approximately 12 s), although a slight darkening of the surface appears much quicker. Even with both solenoids open the texture from the NaNO_3 supply remains dominant once established.

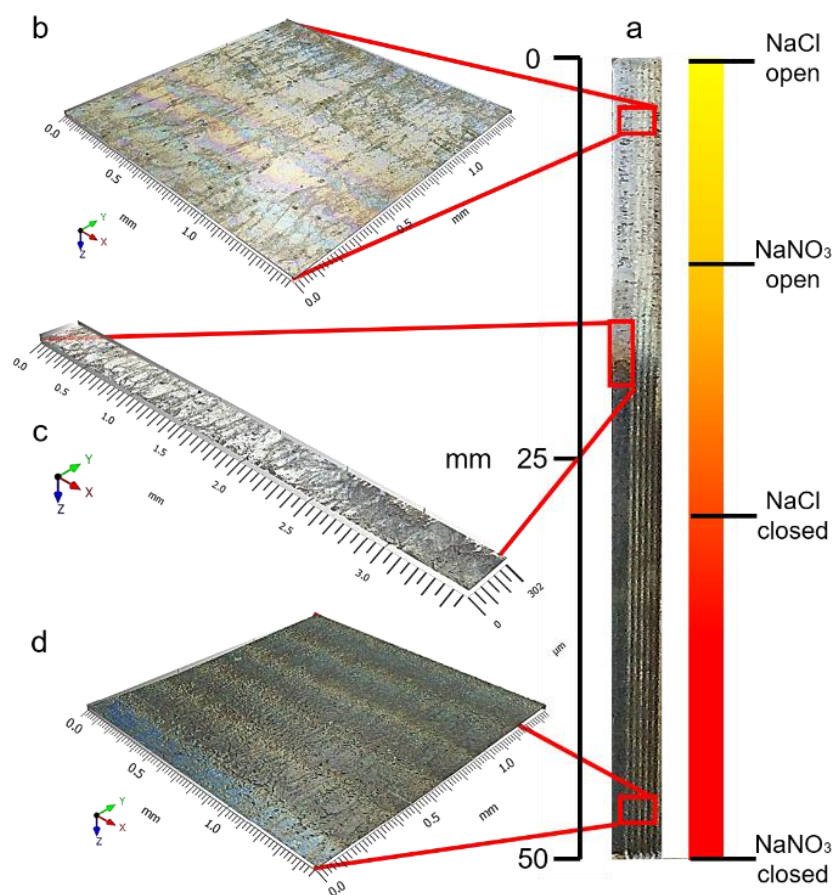


Figure 6.18: Graduated surface textures as a function of faded electrolytes (a) optical image of overall surface demonstrating the contrasting texture as the applied electrolytes open and close (b) extracted 3D reconstruction of the surface texture created with NaCl (c) extracted 3D reconstruction of the point of fade where NaNO₃ becomes the dominant texture (d) extracted 3D reconstruction of the surface created with NaNO₃

6.4. Chapter summary of key findings

The purpose of this chapter was to explore the possibilities of exploiting characteristics and innovations pertaining to the electrochemistry in the IEG to enhance precision and geometrical flexibility of the resultant profile. Inspired by the findings of the literature review, this has been achieved through using additives to the electrolyte in the form of a dopant to compound profile enhancement through implementation of a transitory electrochemical mask. This

has then been coupled with hardware innovations in the Gen. 2 machining centre along with dissolution characteristics of Inconel found in Chapter 4 in common electrolytes to allow enhancement of the feature flexibility of EJM.

The main findings of the chapter are as follows:

- An iodide-doped electrolyte was developed and demonstrated to create a transitory masking effect leading to a limitation of low-level current associated so increasing precision.
- Significant precision improvements, such as lower side wall taper and superior feature shoulder resolution are achieved due to modulated activation thresholds.
- The process mechanisms of current filtering and re-fresh rate are introduced to explain the enhanced effects of sodium iodide in a doped electrolyte.
- A new hardware methodology was introduced which allows the simultaneous or concurrent use of multiple electrolyte types extending the flexibility of the process and functionality of the machine tool
- An ideal combination of electrolytes (NaCl / NaI20) is defined which when applied sequentially analogous to a roughing and finishing strategy found in conventional machining techniques.
- The differing finishing characteristics of each electrolyte can also be exploited demonstrating the generation of not only discrete areas of surface roughness but graduated surfaces that repeatedly produce differing optical properties.

7. Ultra-precise electrochemical jet processing

7.1. Introduction

In each of the prior sections 5.2, 5.3 and 6.2 it has been seen that advances are made not only in the type of profiles created, but in each case advancements have been made that aid the overall precision of EJM. Whether this be increasing depth, reducing kerf or minimising the radius at the surface-to-cut interface. Identified through the literature review in section 2.3.5, the kerf in EJP is generally considered to be controlled by the development of the stagnation region below the nozzle as defined in Figure 2.11.

It was hypothesised that by combining the machining modes from the angle of address, modified nozzle tips and transitory masking, that most effected improvements of the geometry of the resultant machined profile, a compounded effect could be achieved beyond what is expected from the standard configuration (Figure 7.1a) termed ultra-precise electrochemical jet processing (Figure 7.1b). This would demonstrate the dissociation of the dissolution regime, from the hydrodynamic regime developed by the impinging jet stream. The aim being to minimise overcut towards that of the I.D. of the nozzle, reduce deleterious effects at the edge of the profile and maximise depth therefore achieving the best possible aspect ratio. It is proposed that the combination of these innovations, the compound effect of each process enhancement will be greater than the individual contributions. This would bring EJM in line with other surface structuring processes identified in section 2.6 such as laser ablation, micro-EDM, abrasive water-jet micro-machining (AWJ-MM) and electrochemical micro-machining (ECMM).

7.1.1. Machining mode effect

To quantify the contribution or effect that each mode has on the resultant profile and compare this to the cumulative machining mode it is necessary to derive a metric to allow easy comparison, termed the machining mode effect (MME)

Equation 22:

Machining mode effect (MME)

$$\begin{aligned} &= \left[\frac{(K_{baseline} - K_{mode\ 1})}{K_{baseline}} \right] + \left[\frac{(D_{mode\ 1} - D_{baseline})}{D_{baseline}} \right] \\ &+ \left[\frac{(P_{mode\ 1} - P_{baseline})}{P_{baseline}} \right] \\ &+ \left[\frac{(CWS_{mode\ 1} - CWS_{baseline})}{CWS_{baseline}} \right] \end{aligned} \quad \text{Equation 22}$$

Utilising the defined metrics in section 3.8.1 which are used to define the changes in profile form, where CWS is the mean cut-wall slope, D is the profile depth, P is the precision of the feature shoulder interface and K is the profile kerf. The metric can be used to assess the individual contribution to changes in the separate areas of the profile that describe the geometry made by changes to the machining mode. It also describes the overall effect that combining features gives in improvement of the geometry giving a final MME for each machining mode. The metrics generated for the standard configuration (Figure 7.1a) is denoted as the baseline and all other measurement of improvement are normalised with respect to this value. For an ideal machining scenario, with a fixed current and traverse speed, K should be minimised, while D, P and CWS should be maximised. An increased MME represents an improved set of machining conditions and

precision. Where the machining mode has a negative effect on a metric in comparison to the baseline it is denoted as a negative value.

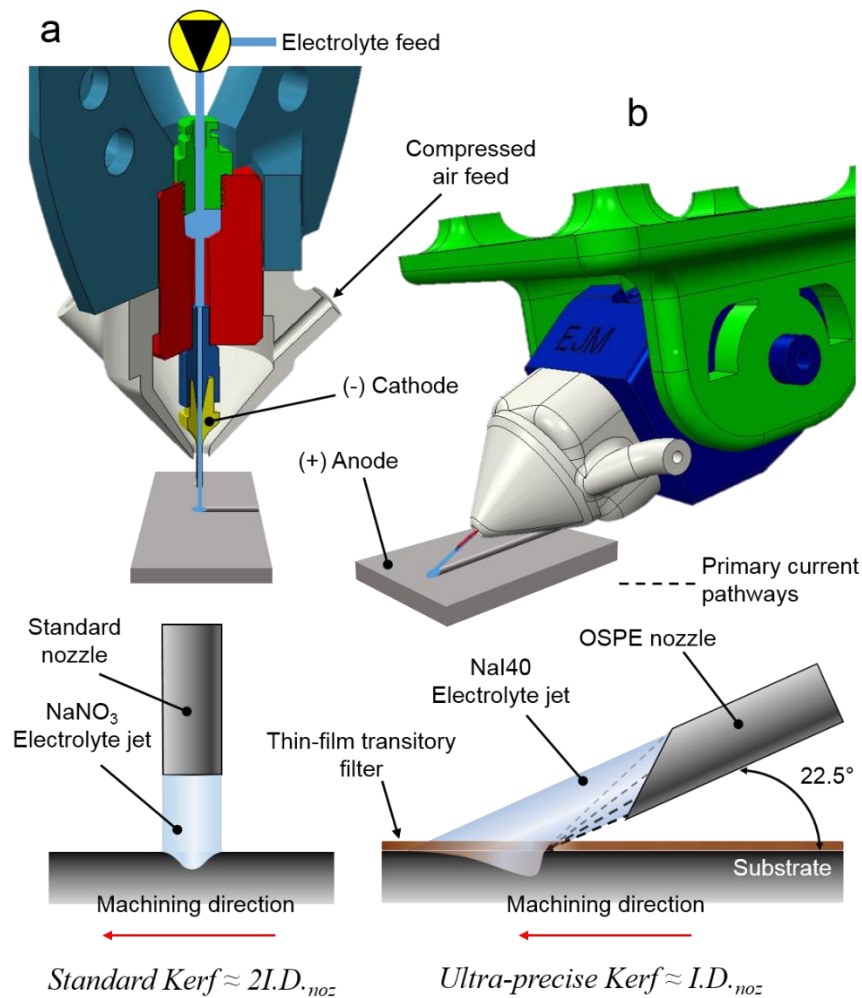


Figure 7.1: (a) The conventional perpendicular machining mode (baseline). (b) The contrasting arrangement used here, which exploits nozzle tilting, thin-film transitory filtering and modulation of energy density. This makes use of an off-centre single point element (OSPE) nozzle, to generate features $\approx$ nozzle internal diameter ($I.D.$).

7.1.2. Methodology

Machined striations were created in an In718 workpiece allowing the known material response from Chapters 4 and 6 when utilising the doped NaNO₃ electrolyte. Beginning with the baseline standard configuration, augmentations

were made in a piece-wise manner shown in Table 7.1. Machining effect comparison was undertaken using nozzles of equivalent I.D. (250 μm), and demonstrated using a 60 μm nozzle I.D. This shows the scalability of augmentations hereby proposed. This includes using a standard (STD) nozzle and OSPE nozzle from section 5.3. However, in this case the OSPE nozzle is orientated so that the single point current focussing feature is aligned with the trailing edge of the jet (Figure 7.2), so when the head is articulated to 22.5° the focussing feature is closest to the workpiece surface as noted in section 5.2.

Table 7.1: Machining modes and description used within this study

Baseline	Standard nozzle, $\theta = 90^\circ$, NaNO_3
Mode 1 – Electrolyte	Standard nozzle, $\theta = 90^\circ$, NaI40 (see section 6.2)
Mode 2 – Nozzle	OSPE nozzle, $\theta = 90^\circ$, NaNO_3 (see section 5.3)
Mode 3 – Angle of address	Standard nozzle, $\theta = 22.5^\circ$ (push mode), NaNO_3 (see section 5.2)
Mode 4 – Compound	OSPE nozzle, $\theta = 22.5^\circ$ (push mode), NaI40

The striations were machined using two current densities (200 and 400 A/cm^2). Demonstration of the effects at two different current densities is critical since material removal phenomena adopt distinct regimes with increasing current density. V_{jet} is set at 25 m/s and V_{noz} is set at 0.5 mm/s and IEG is initially set at 0.3 mm across all experiments.

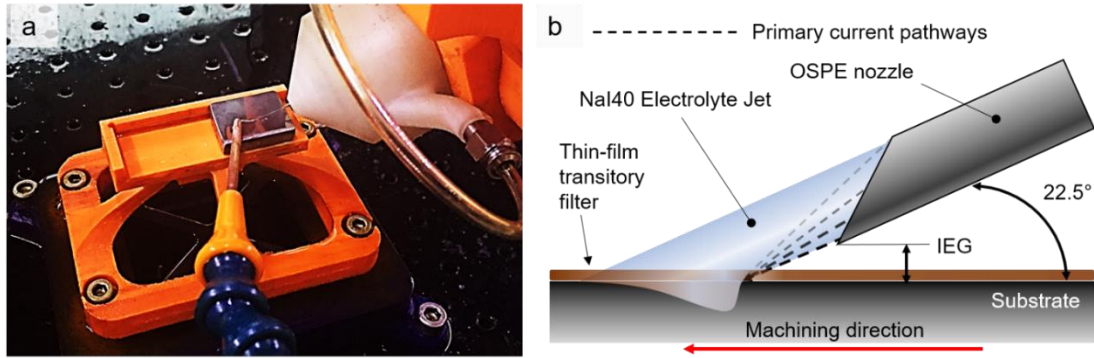


Figure 7.2: 0.06 mm I.D. OSPE nozzle orientation set at 67.5° in the generation 2 platform (b) schematic of machining mode definitions

7.1.3. Results

Exemplar resultant profiles from the different modes can be observed in Figure 7.3 when machined with 400 A/cm^2 and a 0.25 mm I.D. nozzle. It can be observed from the response profiles in Figure 7.3a that each machining mode results in a differing profile geometry. In this case the reduction in kerf is demonstrated for each mode. Considering overcut to be defined as the total dissolution kerf minus the I.D. of the nozzle, it is shown that by compounding all the modes (mode 4) 80% of the overcut generated by the baseline mode is removed (reduced from $243 \text{ }\mu\text{m}$, $\sigma 3.4\%$ (baseline) to $49 \text{ }\mu\text{m}$, $\sigma 8.4\%$ (mode 4)) (Figure 7.3b). Each mode demonstrates individual geometric enhancements. Mode 1 with the addition of NaI40 obtains a 96% improvement in precision at the cut to surface interface ($0.084 \text{ }\mu\text{m}/\mu\text{m}$ to $0.166 \text{ }\mu\text{m}/\mu\text{m}$) albeit at the expense of profile maximum depth showing a reduction of 11% ($34.32 \text{ }\mu\text{m}$ $\sigma 0.9\%$ to $30.52 \text{ }\mu\text{m}$ $\sigma 0.9\%$). In comparison when a shaped nozzle is used (mode 2) overall kerf is reduced from $493 \text{ }\mu\text{m}$ ($\sigma 1.7\%$) to $425 \text{ }\mu\text{m}$ ($\sigma 1.1\%$), feature shoulder precision increased by 51% to $0.128 \text{ }\mu\text{m}/\mu\text{m}$ ($\sigma 3.0\%$), and the side-wall slope is increased by 20% (0.3

$\mu\text{m}/\mu\text{m}$ $\sigma < 1\%$), compared to the baseline of $0.25 \mu\text{m}/\mu\text{m}$ ($\sigma 2.3\%$). The application of angle of address in mode 3 would appear to make one of the largest single contributions, achieving a 40% reduction in kerf to $366 \mu\text{m}$ ($\sigma 1.8\%$), and a 30% increase in depth to $44.8 \mu\text{m}$ ($\sigma 2.3\%$), and a 70% increase in cut-side-wall slope to $0.44 \mu\text{m}/\mu\text{m}$ ($\sigma 2.8\%$).

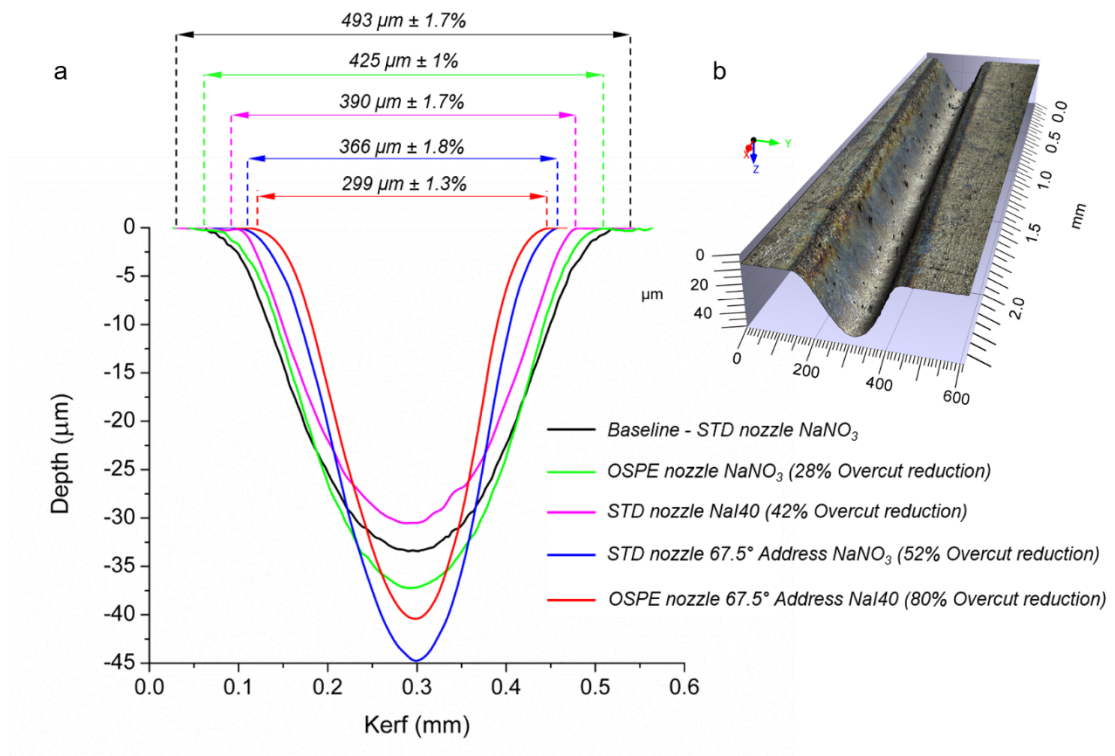


Figure 7.3: Exemplar resultant profiles showing the changes in geometrical features with different machine modes (a) Profiles machined with $400 \text{ A}/\text{cm}^2$ and 0.25 mm I.D. nozzle showing the kerf of the machined striation observing the $187 \mu\text{m}$ reduction in kerf possible when the machine modes are used together (b) reconstructed 3D image with optical overlay of a striation machined with ideal compound profile

Through the application of the MME (Equation 21), it is possible to assess the contributions each mode makes to the overall improvement of the profile geometry. Considering Figure 7.4, the individual effect that each mode has on kerf reduction, maximum depth increase, feature shoulder precision and cut side-

wall slope can be seen alongside the changing effect due to the change in applied mean current density. The overall effects are reduced as J is increased. From the 200 A/cm² trials, the effect of combining all the modes in fact slightly reduces the overall effectiveness on geometry improvement. This is due to the inclusion of NaI40 which noted from the result in mode 1, displays a negative effect on the maximum depth (supported by the findings in section 6.2). This correlates to the amount the effect on depth is reduced in the combined mode 4. However, the inclusion of NaI40 does have a further effect of increasing precision by 172% (σ 2.5%) and reducing dissolution kerf to 252 μ m (σ <1%). This effectively eradicates overcut achieving a 99% reduction.

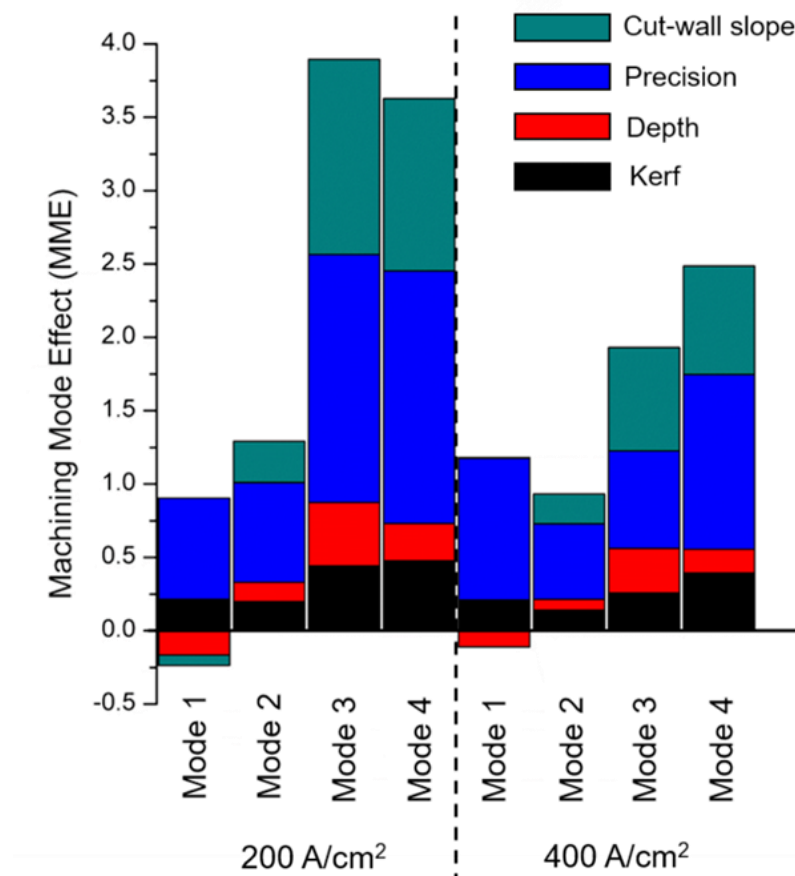


Figure 7.4: Stacked bar chart showing the overall effect of each machining mode on profile geometry and contribution to enhancement of individual profile features for a 250 μ m I.D. nozzle

At a current density of 200 A/cm^2 , the contribution to MME is dominated by the nozzle profile and angled address. Here, the tilted OSPE nozzle significantly enhances the precision of the cut. In addition, this serves to increase the depth of cut. The application of NaI4O electrolyte to this configuration reduces the depth of cut, which results in an increased cut-wall slope.

Thus, under these machining conditions, there is no benefit of exploiting the transitory masking technique, beyond the effects exhibited by applying the OSPE nozzle and adjusting the angle of address. This behaviour can be attributed to the oxidation reaction as described in section 6.2, which takes place in NaI4O electrolyte during processing. The iodide oxidation reducing the material removal rate (MRR) across the jet profile and not only at the periphery. Therefore, the effect is to be expected since the percentage difference of energy density at the jet periphery at low current density, as compared to higher current density, is reduced.

When a current density of 400 A/cm^2 is applied, the contribution of these effects changes. While the combination from the OSPE and tilted arrangements results in the most significant response at this energy density, the apparent effect of transitory filtering decreases. This is most obvious with respect to the reduced kerf width. In addition, the deleterious effect of reducing depth is reduced to the degree whereby the aggregated effect of all process enhancements results in an overall increased MME.

The methodology was also demonstrated at a reduced scale employing a 0.06 mm I.D. nozzle (Figure 7.5). Although difficulties in manufacture of the OSPE nozzle at this scale without deforming the jet aperture and blockage and precision

deficiencies generated from the head mounting meant it was difficult to carry-out a meaning full study at this scale. Features using modes 1 and the baseline could reliable be generated, modes 2, 3 and thus mode 4 displayed poor accuracy and repeatability (Figure 7.5c, d)

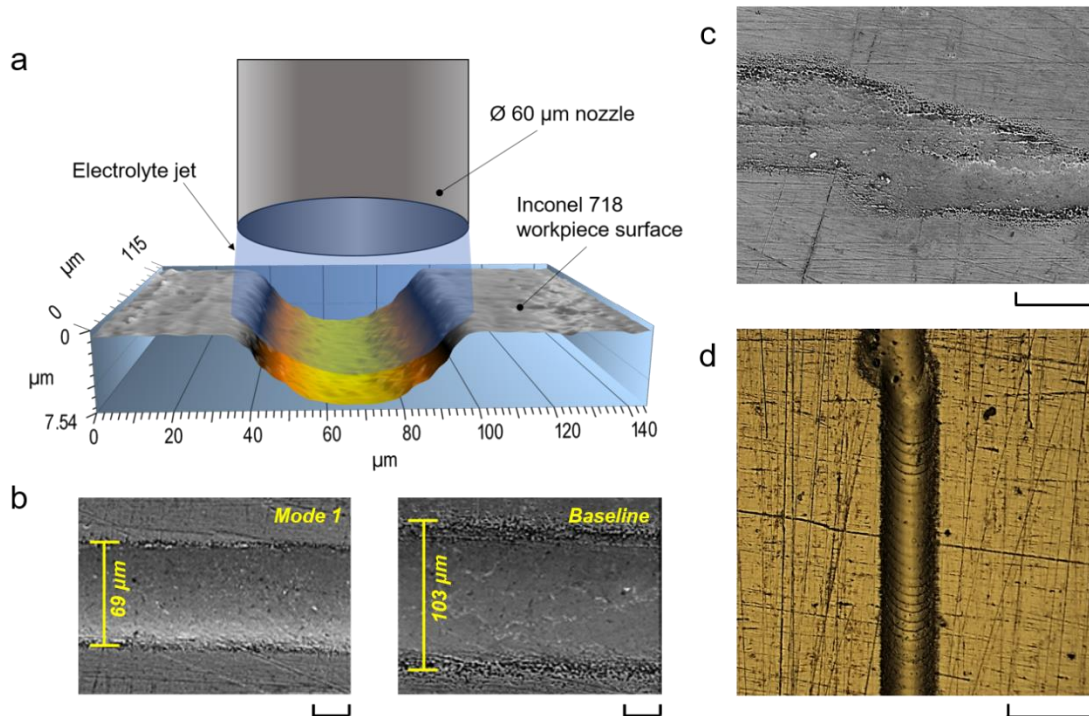


Figure 7.5: EJM with a 60 μm I.D. nozzle (a) surface 3D reconstruction of striation machined with a “to scale” jet imposed for comparison (b) SEM images of the striation created with mode 1 and the baseline demonstrating the kerf reduction (scale bars 25 μm) (c) SEM image of a striation which has deformed and jumped to one side likely due to nozzle blockage (scale bar 50 μm) and an optical image of again another machining fault showing the fragility of the process in its current guise at this scale (scale bar 100 μm)

However even with mode 1, reduction in kerf is observed. At $400\text{A}/\text{cm}^2$ the overcut is reduced by 78%, to the value of 9 μm with giving a kerf of 69.8 μm (σ 2.3%) (Figure 7.5a, b) and at $200\text{ A}/\text{cm}^2$ a reduction of 97% to 1.48 μm giving a kerf width of 61.48 μm ($\sigma < 1\%$). This represents a significant enhancement over the state-of-the-art. CWS is increased by 46%, from 0.24 $\mu\text{m}/\mu\text{m}$ (σ 4.8%) to 0.36

$\mu\text{m}/\mu\text{m}$ (σ 3.1%) for $400 \text{ A}/\text{cm}^2$ and increased by 40%, from $0.13 \mu\text{m}/\mu\text{m}$ (σ 5%) to $0.19 \mu\text{m}/\mu\text{m}$ (σ 7.8%). These observations correlating with formative experimentation at increased scale.

7.2. Chapter summary

Innovations from Chapters 5 and 6 were coupled together to create a level of precision not seen before in EJP. It has been demonstrated here, that through combination of advanced machining modes in EJM, precision can be enhanced beyond that observed in individual modes.

The main findings of this chapter were as follows:

- A compounding effect on precision and performance in EJM is achieved through combining electrochemical and electromechanical innovations made in previous chapters.
- The machining mode evaluation (MME) metric was developed to define the contribution that multiple innovations make to the overall enhancement of the feature geometry. The specific contribution from a given machining mode is shown to be dependent on available energy.
- It was demonstrated that overcut in the response profile, traditionally defined by the stagnation region, can be reduced by upto 99%, so achieving kerfs approaching the nozzle I.D. thus demonstrating complete dissociation from this boundary condition

8. Conclusion

Electrochemical jet machining is a novel and yet emergent manufacturing technology. A derivative of electrochemical machining, it demonstrates the advantages of ease of material removal in traditionally difficult to machine metals, as the material properties of hardness and toughness do not influence machinability, along with zero thermal loading of the material microstructure. EJM specifically displays further advantages over ECM of not requiring any masking technology to preferentially remove material, no tooling costs as the electrolyte jet is responsible for material removal, thus no wear of the nozzles is observed. This is accomplished via a simplistic machine architecture as the machining mechanisms do not impart forces into the machine structure. Alongside this the technology required to affect material removal is minimal and simplistic in nature leading to low-cost processing mechanism.

However, EJM currently displays several drawbacks that inhibit wider integration in process chains in comparison to alternative processing methods, thus restricting EJM in realising process maturity.

This thesis reports investigations from a fundamental perspective demonstrating the advancement of EJM beyond the state-of-the-art. This was achieved by consideration of the aims of the research (chapter 1.1) and identified knowledge gaps (chapter 2.8). Through greater understanding of the dissolution mechanisms in complex alloys (chapter 4), increased flexibility of the process in hardware application thus, resultant feature geometry (chapter 5) and increased precision beyond what has been previously reported (chapter 6 and 7), a step change in the capability of EJM and thus significant contribution to the field has

been achieved. A summary of the major contributions of this thesis are given in the following sections.

8.1. Machining of high value alloys

In line with the aims of this thesis of “*Fundamental analysis of complex alloy response*” and the research gap identified from the literature review of understanding of key material response of Inconel 718 and Titanium Ti-6Al-4V, from the research carried out in chapter 4 these conclusions can be drawn:

The dissolution mechanism specific to EJM of complex alloys has been elucidated

An in-depth investigation into the effects on dissolution of complex alloys as a function of EJM specific parameters was carried out. The findings support prior general ECM knowledge of the association of energy with material removal and surface finish. However, for the first-time distinct dissolution regimes were identified and characterised specific to EJM. This demonstrated the effect of the process on the surface structure of both Inconel 718 and Titanium Ti-6V-4Al as a function of applied energy. Described as sporadic, selective, equilibrium and aggressive dissolution regimes (Figure 4.5), so called because of the perceived effect on the surface related to the breakdown of the individual material elements. This allows idealised process parameters to be selected to achieve the desired finish. The concept of element “wash-out” was identified and described, demonstrating a secondary material removal mechanism of erosion that had not previously been reported, this being specific to complex alloys. It was found that constituent material elements such as inert phases or corrosion resistant elements do not dissolve at the same rate as the material bulk, therefore are

washed out of the bulk rather than dissolved as the material around it is removed. This can lead to increased material removal rates and is especially pertinent to Inconel 718 with its large niobium carbide precipitates found at grain boundaries which was observed to lead to pitting. This is integral to jet-based processes due to the impinging jet and not found in typical ECM.

Electrochemical equivalence cannot be used alone in describing material removal rate and consideration of the anode redox potential must be observed.

Although a materials ECE forms the basis of Faradays law, and as such the fundamental of many proposed processing models, from this work, for modern complex alloys, it has been found to not be wholly representative in EJM. The nature of modern alloys is such that they are often designed specifically for corrosion resistance. This is the case with Inconel 718. From calculation of Inconel's ECE it would suggest a far higher MRR than Ti-6V-4Al. Through experimental work carried out here, this was found not to be the case. However, when we consider the redox potential of both Inconel 718 and Ti-6V-4Al it can be observed that titanium is much more readily oxidizable than Inconel therefore will yield greater material loss under electrochemical conditions, which supports the findings here. There are also other contributing factors identified through this work, such as the formation of oxides which hinder the dissolution process. Again, due to the nuances of the EJM process it was shown that materials processed by EJM are much more susceptible to the formation of oxide layers from impinging oxygen entrapment than would be expected in ECM. The material removal effect is therefore much more complex in EJM than would be expected in ECM and strategies to overcome this must be considered.

8.2. Electromechanical innovation

As defined in the knowledge gaps a key boundary condition associated with EJM is the Gaussian distribution of energy in the IEG thus limiting the flexibility of the features that can be created. From the research and development of hardware innovations within this thesis, this is demonstrated to no longer be the case.

In-jet energy distribution can now be modulated achieving flexibility in profile formation.

For the first time it was demonstrated that process resistance could be altered discretely, in-jet, therefore allowing modulation of the energy distribution. Traditionally the energy distribution found within the IEG was described as Gaussian type distribution thus, achieving a bell type removal profile as found in typical energy beam processes. Through the research presented here it was hypothesised and demonstrated that this traditional boundary condition need not be the case. Considering the spatial influences within the IEG, an entirely novel approach to EJM was conceived. Initially variation of the angle of address of the jet was investigated (chapter 5.2), finding that the profile shape changed dependant on angle of jet address. Utilising two modes of approach, normal convention and push/pull convention, for the first time, thinner, deeper profiles were created without changing machining parameters. The resultant profile was found to differ from, and form the opposite asymmetric shape, to that created by other energy beam processes. The process mechanics were fully elucidated showing that the distance between discrete points on the nozzle and the changing attitude of the nozzle tip with respect to the surface were responsible. Building on these initial findings, nozzle tips were modified to create discrete areas of

variation in the IEG within the jet itself (chapter 5.3). This was intended to cause changes in localised resistance, replicating the findings from the angle of address experiments whilst maintaining a perpendicular jet and a constant global resistance. As resistance is directly related to current as described by Ohms law, as such the current density profile is altered. This leads to controlled flexibility in the resultant machined profile not seen before in EJM. Profiles were created entirely counterintuitive to the typical bell-type removal profiles, varying the positioning of the depth maxima of the profile and achieving multiple valleys within the same profile. This level of flexibility achieving the aims of this thesis for EJM and allows single step creation of complex machined profiles.

The Design Impact Factor (DIF) is introduced

To understand the effects of nozzle modification, the DIF equation was developed (chapter 5.3.3). The main influencing factors of area of a nozzle feature facing the surface and the distance from the workpiece surface were combined into an equation to allow the assessment of the impact of a nozzle design. Unlike traditional die-sinking ECM where the tool is wholly responsible for the shape of the machined feature, this is not the case in EJM as it is a combined interaction with the jet and in relation to other features on the nozzle tip. The DIF allows a true assessment of the relationship between nozzle design features and the profile that will be generated and is intended to form the basis for future process modelling in this area.

A new approach of constant and dynamic tooling was created for complex channel profiling.

To utilise the novel approach of increased flexibility afforded by modulating the energy distribution, further hardware innovation was required. A rotary head 4th axis system was introduced as a new approach, allowing the profile created by the modified nozzle tip to remain constant regardless of toolpath vector and minimise any error from design intent (chapter 5.4). Further to this it was demonstrated for the first time in electrochemical processes that a constantly evolving feature profile could be created over a defined toolpath within a single pass through utilisation of the control software, the rotary head and shaped nozzle tips.

8.3. Electrochemical Innovation

Further to the discussed knowledge gaps (chapter 2.8) achievable precision of the process is noted as a key research area, increasing of which would bring it in-line with competing technologies and make it a viable alternative.

Kerf definition is now dissociated from hydrodynamic influence.

For the first time in EJM, it was shown that the formation of the stagnation zone under an impinging jet and the following creation of the radial wall jet need not define the kerf of features created (chapter 6.2). This has been a long-established boundary condition in EJM that within acceptable EJM processing conditions the kerf of a cut will be ≈ 2 times the nozzle I.D. due to hydrodynamic effects. Through the introduction of sodium iodide as a doping agent never before seen in EJM, conflicting anodic reactions are created. Thus, the applied energy goes through

filtering mechanism due to the introduction of NaI. The doping agent preferentially requiring energy for the facile route of iodide to iodine conversion, so diverting energy available for material removal. The effect of this is to remove areas of low current from the current density distribution found at the periphery of the impinging jet area so minimising overall machining kerf. This reduction of the specific area at the shoulder of the profile means the radius is minimised so achieving a much sharper more defined edge to the feature which has not previously been achieved in EJM and reduction in overcut up to 60% albeit at the expense of depth of cut. Thus, it is unequivocally shown that the generation of the stagnation region need no longer be a consideration in the precision of EJM thus dissociating precision from hydrodynamic considerations.

Machine technicity enhancement for increased processing flexibility through electrolyte multiplexing.

The manipulation of nuances associated with different electrolytes and their removal traits has been largely ignored in EJM. For the first time it was demonstrated that the individual advantages of Sodium Chloride, Sodium Nitrate and doped electrolytes as demonstrated in section 6.2 could be utilised with a new methodology of electrolyte multiplexing. One of the key drivers throughout this thesis as defined in both the aims of the thesis and identified in the knowledge gaps, is architecture development and increasing process and hardware flexibility. Thus, the introduction of an enhanced machine technicity through more complex machine architecture achieves this. Utilising sequential processing of NaCl to affect large area material removal, followed by NaI₂O to enhance the precision of features generated, created an efficient processing strategy akin to traditional roughing and finishing machining strategies. It was further

demonstrated that the system could be employed to create dynamic surface textures. This enables a graduated surface finish over a large area to be created by utilising the surface finish achievable through different electrolyte application. This demonstrates a low-cost alternative to other processing technologies to efficiently change the surface qualities such as optical appearance and lustre of a surface.

8.4. A new approach

Breaking with tradition, through this work, a new approach to EJM was pioneered. This demonstrated that the boundary conditions of the energy distribution within the jet and development of the stagnation region beneath the jet need not dictate the precision achievable in EJM and combining innovations can have a compounding effect.

A new metric, Machining Mode Evaluation (MME) is developed

To identify and quantify where improvements have been made in introducing different machining innovations, a new metric was developed (chapter 7.1.1). The MME is designed to consider improvement within specific regions of the resultant machined profile, such as depth, kerf, feature shoulder radius, and then combine them to identify if an overall improvement in the resultant profile has been achieved. Using metrics specific to the type of profile generated by an energy beam (chapter 3.8) combined in a single equation, gives a simple way to evaluate not only singular process innovations but different combinations and obtain quantitative information as to the best combinations and the influences they have as a function of changing process parameters.

Through a combination of innovations, a new approach to EJM has been explicated.

Through combining innovations detailed throughout this thesis, an entirely new approach to processing by electrochemical jet techniques was expounded. Utilising angle of jet address at 22.5° (chapter 5.2) to focus the electric field, a shaped nozzle, in this case the OSPE, (chapter 5.3) to confine the electric field to a single point on the nozzle and the doped electrolyte NaI20 to filter out the low current density areas at the peripheral of the jet (chapter 6.2) a step change in the precision of EJM is achieved (chapter 7). This approach culminating in the eradication of overcut as defined as the kerf matching the nozzle I.D. This exceeds the previously achieved increases in precision throughout the thesis by any single innovation and demonstrates the compounding approach of combining these innovations to achieve a greatly enhanced process. Instead restriction and manipulation of the energy distribution within the IEG is shown to fulfil one of the primary identified knowledge gaps of increasing precision in-line with competing processes.

In order to highlight some of the applications of the work presented in this thesis, in combination with external collaborators, EJM was demonstrated as an alternative to laser processing. Firstly, in producing repeating surface texture for the reduction of wear in automotive cylinder liners in a non-conventional material Al-Si (Appendix 6). The knowledge in processing a complex alloy gained through this work proved invaluable to produce features preferential to those created by

laser. Secondly, in producing large area non-deterministic surface texturing for enhanced implant osseointegration. Three distinct topographies were derived from the findings in Chapter 3.8.3 and assed for cell uptake full details of which can be found in Appendix 7. Lastly, as there is a common architecture between EJM and electrochemical jet deposition as noted in the thesis introduction and literature review with the term EJP. As such the approach of in-jet energy modulation was applied and demonstrated to change the profile shape of deposited copper features which can be seen in Appendix 5

This thesis has made important contributions to the advancement and implementation of electrochemical jet processing techniques through fundamental innovations allowing a step-change in process flexibility, geometric form flexibility and precision. As such has fulfilled the identified research gaps. The findings throughout this work demonstrate that electrolytic jet processes need not be restricted by common boundary conditions developed from in-common processing technologies and EJM specific process mechanics can be employed to achieve results beyond what has been expected from consideration of the literature. This thesis is intended to exemplify the advantages of EJM over comparison technologies and demonstrate that continued development of the technology highlights its place as a viable and competitive micro-machining technology.

8.5. Future work

Several areas of suggested further work have been identified by the investigations in this thesis.

It was noted in Chapter 3.8.3 that jet speed appeared to have little influence on the form or performance of removal. However, all the evidence from the literature in the response of the diffusion layer for example to increasing applied energy, would suggest that variation of jet speed should have a larger influence than is demonstrated through this work. Although some variation is seen at very low flow rates and on the internal geometry of features in Chapter 5. It would seem likely that a hypothesis could be formed that variation of jet speed would have the same effect on surface finish that current density has. This could provide a more efficient avenue for optimising surface finish than increasing current density. Alongside this the assessment of the effects on profile geometry especially when geometry steps are overlaid and so the jet is interacting with prior geometry (as seen in Chapter 6) is also worthy of investigation to further the development and implication of EJM.

Although by and large additive mode EJP has not been demonstrated throughout this thesis several of the hardware innovations are applicable to additive mode. The application of modified nozzle tips is briefly shown in appendix 5 purely as a demonstrator of the possibilities. With on-going chemical development to the feedstock electrolytes, the use of profiled nozzles may move this technology into a more reliable methods of large scale layered 3D structure creation. As is demonstrated the use of an STE nozzle enables creation of a much flatter top to the deposition negating the need for a secondary process step to allow further

layers to be applied evenly. This coupled with the constant profiling technique (section 5.4) may enable greater scope for the technology and enables a further research avenue.

Reduction in feature size presented in section has introduced a new avenue in the development of EJM. This requires an entirely new set of considerations regarding the process and hardware. Considerations to filtration, electrolyte supply, isolation from external vibration factors, nozzle tip manufacture, material effects and introduced hydrodynamic flow effects at the microscale are required to be investigated. As it has been shown that the kerf of machined features approaching the nozzle I.D. the reliability, accuracy and repeatability become more susceptible to external influences. However, the rewards of a low-cost technology capable of a sub 50 μm kerf justify the research direction.

The sensitivity of the response profile to changes in nozzle tip design and approach angle is seen in Chapter 5 highlights further innovations that can be made in this area. Segmenting the nozzle into separate insulated elements around the circumference to create a multi-mode nozzle would allow each element to have individual potentials applied, therefore creating greater control over the energy distribution. For example, this would enable a more even profiles when creating curved features as the potential at the inside elements of the curve could be reduced to allow for the longer dwell and would enable further flexibility of the profile without changing the nozzle.

To enable further exploitation of the ability to modulate the energy density distribution and allow a further step-change in micro-machining capability the use of a more complex form of nozzle translation should be investigated. Such

alternatives as incorporation of the rotating head and changing nozzle address into a single head assemble with a further two degrees of freedom mounted on the stacked x, y, z axis. Or, use of a robotic arm or snake-like actuation to allow complete control of address and add further competency in achieving 3D micromachining is worthy of further investigation.

References

1. Ehl, R.G. and A.J. Ihde, *Faraday's electrochemical laws and the determination of equivalent weights*. Journal of Chemical Education, 1954. **31**(5): p. 226.
2. Kunieda, M., *Influence of Micro Indents Formed by Electro-chemical Jet Machining on Rolling Bearing Fatigue Life*. ASM, PED, 1993. **64**: p. 693-699.
3. Yu, Y.Q., J.S. Zhao, B.H. Li, and J.W. Xu, *Experimental Study of Pulsed Electrolyte Jet Machining for Small Hole*. Key Engineering Materials, 2010. **458**: p. 307-312.
4. Hackert, M., G. Meichsner, and A. Schubert, *Fast Micro Structuring with Electrolyte Jet Machining*, in *Proceedings of Fourth International Symposium on Electrochemical Machining Technology*. 2007, Fraunhofer: Chemnitz. p. 123-128.
5. Natsu, W., T. Ikeda, and M. Kunieda, *Generating complicated surface with electrolyte jet machining*. Precision Engineering, 2007. **31**(1): p. 33-39.
6. Bocking, C.E.B., S.I. Dover, and G. Bennett. *An investigation into the suitability of high speed selective jet electrodeposition for rapid tooling*. in *First National Conference on Rapid Prototyping and Tooling Research*. 1995. MEP.
7. Kunieda, M., R. Katoh, and Y. Mori, *Rapid Prototyping by Selective Electrodeposition Using Electrolyte Jet*. CIRP Annals - Manufacturing Technology, 1998. **47**(1): p. 161-164.
8. Rajput, M.S., P.M. Pandey, and S. Jha, *Micromanufacturing by selective jet electrodeposition process*. The International Journal of Advanced Manufacturing Technology, 2015. **76**(1): p. 61-67.
9. Qiao, G., T. Jing, N. Wang, Y. Gao, X. Zhao, J. Zhou, and W. Wang, *High-speed jet electrodeposition and microstructure of nanocrystalline Ni-Co alloys*. Electrochimica Acta, 2005. **51**(1): p. 85-92.
10. White, F., M., *Fluid Mechanics*. 2nd Edition ed. 1987: Mc Graw-Hill. 732.
11. Yoneda, K. and M. Kunieda, *Processing shape simulation in the electrolytic solution jet machining*. Electrical Processing Journal, 1995. **29**(62): p. 8.

12. Rajurkar, K.P., D. Zhu, J.A. McGeough, J. Kozak, and A. De Silva, *New Developments in Electro-Chemical Machining*. CIRP Annals - Manufacturing Technology, 1999. **48**(2): p. 567-579.
13. Bilgi, D.S., V.K. Jain, R. Shekhar, and S. Mehrotra, *Electrochemical deep hole drilling in super alloy for turbine application*. Journal of Materials Processing Technology, 2004. **149**(1–3): p. 445-452.
14. Buchanan, P.D., *Electroplating the Platinum Metals*. Platinum Metals Review, 1981(25): p. 32-42.
15. Meleka, A.H. and D.A. Glew, *Electrochemical machining*. International Metals Reviews, 1977. **22**(1): p. 229-252.
16. McGeough, J.A., *Advanced Methods of Machining*. 1988, UK: Chapman and Hall Ltd.
17. De Barr, A.E. and D.A. Oliver, *Electrochemical machining*. 1968: American Elsevier Pub. Co.
18. Wilson, J.F., *Practise and Theory of Electrochemical Machining*. 1971, USA: John Wiley & Sons, Inc. 221-224.
19. Kozak, J., K.P. Rajurkar, and R. Balkrishna, *Study of Electrochemical Jet Machining Process*. Journal of Manufacturing Science and Engineering, 1996. **118**(4): p. 490-498.
20. Ikeda, T., W. Natsu, and M. Kunieda, *Electrolyte Jet Machining Using Multiple Nozzles*. IJEM, 2006. **11**: p. 7.
21. Hackert, M., G. Meichsner, and A. Schubert, *Simulation of the Shape of Micro Geometries generated with Jet Electrochemical Machining*, in *COMSOL Conference*. 2008: Hanover.
22. Schubert, A., M. Hackert, and G. Meichsner, *Simulating the Influence of the Nozzle Diameter on the Shape of Micro Geometries generated with Jet Electrochemical Machining*, in *COMSOL Conference*. 2009: Milan.
23. Glaysher, G.H., N.P. Allen, and M.H. Farmer, *Electrolytic shaping - Improvements in and relating to the removal of metal from a workpiece*, in *PatBase*. 1953, National Research Development Corporation: UK.
24. Nannichi, A., *1st Report : Experimental Study on the Electrolytic Nozzling Micro-holes in Copper Study on the Electrolytic Process of Nozzling Micro-holes in Metals*. Journal of the Japan Society of Precision Engineering, 1961. **27**(323): p. 781-787.
25. Ippolito, R., S. Tornincasa, G. Capello, and G.F. Micheletti, *Electron-Jet Drilling — Basic Involved Phenomena*. CIRP Annals - Manufacturing Technology, 1981. **30**(1): p. 87-90.
26. Unvala, B.A., D.B. Holt, and A. San, *Jet Polishing of Semiconductors: III . Polishing and Shaping of Si, Ge, GaAs, and Slices*. Journal of The Electrochemical Society, 1972. **119**(3): p. 318-319.
27. Schmidt, P.F. and M. Blomgren, *Potential Measurements during Jet Etching of P-Type Ge and P-Type Si*. Journal of The Electrochemical Society, 1959. **106**(8): p. 694-700.
28. Sen, M. and H.S. Shan, *A review of electrochemical macro- to micro-hole drilling processes*. International Journal of Machine Tools and Manufacture, 2005. **45**(2): p. 137-152.
29. Winton, P. and J. Mitchell-Smith, *Use of electrochemical jet drilling in the aerospace industry*. 2017, Personal communication.
30. Fletcher, J. and G. Oliver, *Scanning nozzle plating system*, in *Google Patents*, NASA, Editor. 1974, Google Patents: United States
31. Melcher, R.L., L.T. Romankiw, and R.J. VON Gutfeld, *Method for maskless chemical and electrochemical machining*, in *Google Patents*. 1981, International Business Machines Corporation: USA.

32. von Gutfeld, R.J., M.H. Gelchinski, L.T. Romankiw, and D.R. Vigliotti, *Laser-enhanced jet plating: A method of high-speed maskless patterning*. Applied Physics Letters, 1983. **43**(9): p. 876-878.
33. Gelchinski, M.H., L.T. Romankiw, D.R. Vigliotti, and R.J. Von Gutfeld, *Laser-enhanced jet-plating and jet-etching: high-speed maskless patterning method*, in *Google patents*. 1985, International Business Machines Corporation (IBM): USA.
34. Datta, M., L.T. Romankiw, D.R. Vigliotti, and R.J. von Gutfeld, *Jet and Laser-Jet Electrochemical Micromachining of Nickel and Steel*. Journal of The Electrochemical Society, 1989. **136**(8): p. 2251-2256.
35. Datta, M. and L.T. Romankiw, *Application of chemical and electrochemical micromachining in the electronics industry*. Journal of The Electrochemical Society, 1989. **136**(6): p. 285 - 292.
36. Alkire, R.C. and T.J. Chen, *High-Speed Selective Electroplating with Single Circular Jets*. Journal of The Electrochemical Society, 1982. **129**(11): p. 2424-2432.
37. Bocking, C.E., *High speed selective jet electrodeposition of gold and gold alloys using single circular jets*, in *Chemical and Materials*. 1994, Loughborough University: Loughborough.
38. Bocking, C. and D.B. Cameron, *The Use of High Speed Selective Jet Electrodeposition of Gold for the Plating of Connectors*. Transactions of the IMF, 1994. **72**(1): p. 33-40.
39. Dover, S.J., A. Rennie, and G. Bennett. *Rapid prototyping using electrodeposition of copper*. in *Solid Freeform Fabrication Symposium*. 1996. Austin, Texas, USA: University of Texas.
40. Dover, S.J., A. Rennie, and G. Bennett. *The wear of High Speed Selective Jet Electrodeposition electrodes when used as EDM tools*. in *Proceedings of the Second National Conference on developments in rapid prototyping and tooling*. 1996. Mechanical Engineering Publications Ltd.
41. Liu, W., S. Ao, Y. Li, Z. Liu, Z. Wang, Z. Luo, Z. Wang, and R. Song, *Jet electrochemical machining of TB6 titanium alloy*. The International Journal of Advanced Manufacturing Technology, 2016. **90**(5-8): p. 2397-2409.
42. Bocking, C., *High Speed Selective Jet Electrodeposition*. Transactions of the Institute of Metal Finishing, 1991. **69**(4).
43. Schubert, A., M. Hackert-Oschätzchen, G. Meichsner, M. Zinecker, and A. Martin, *Evaluation of the influence of the electric potential in jet electrochemical machining*, in *International Symposium on Electrochemical Machining Technology (INSECT)*. 2011: Vienna, Austria. p. 47-54.
44. Hackert-Oschätzchen, M., S.F. Jahn, and A. Schubert. *Design of Electrochemical Machining Processes by Multiphysics Simulation*. in *COMSOL conference*. 2011. Stuttgart, Germany.
45. Hackert-Oschätzchen, M., R. Paul, M. Kowalick, A. Martin, G. Meichsner, and A. Schubert, *Multiphysics Simulation of the Material Removal in Jet Electrochemical Machining*. Procedia CIRP, 2015. **31**: p. 197-202.
46. Hackert-Oschätzchen., M., A. Martin, G. Meichsner, and A. Schubert, *Evaluation of Gap Control Strategies in Jet Electrochemical Machining on Defined Shape Deviations*, in *INSECT 2014*, D. Bahre. and A. Rebschlagel, Editors. 2014: Saarbrücken, Germany. p. 23-34.
47. Hackert-Oschätzchen, M., R. Paul, A. Martin, G. Meichsner, N. Lehnert, and A. Schubert, *Study on the dynamic generation of the jet shape in Jet Electrochemical Machining*. Journal of Materials Processing Technology, 2015. **223**: p. 240-251.
48. Rajput, M.S., P.M. Pandey, and S. Jha, *Modelling of high speed selective jet electrodeposition process*. Journal of Manufacturing Processes, 2015. **17**(0): p. 98-107.

49. Goffin, N.J., R.L. Higginson, and J.R. Tyrer, *The use of holographic optical elements (HOE's) to investigate the use of a flat irradiance profile in the control of heat absorption in wire-fed laser cladding*. Journal of Materials Processing Technology, 2015. **220**: p. 191-201.
50. Kaur, A., C. Ribton, and W. Balachandaran, *Electron beam characterisation methods and devices for welding equipment*. Journal of Materials Processing Technology, 2015. **221**: p. 225-232.
51. Bilbao-Guillerna, A., R.T. Eachambadi, G.B.J. Cadot, D.A. Axinte, J. Billingham, F. Stumpf, S. Beuer, and M. Rommel, *Novel approach based on continuous trench modelling to predict focused ion beam prepared freeform surfaces*. Journal of Materials Processing Technology, 2018. **252**: p. 636-642.
52. Chillman, A., M. Hashish, and M. Ramulu, *Energy Based Modeling of Ultra High-Pressure Waterjet Surface Preparation Processes*. Journal of Pressure Vessel Technology, 2011. **133**(6): p. 061205.
53. Srinivasu, D.S., D.A. Axinte, P.H. Shipway, and J. Folkes, *Influence of kinematic operating parameters on kerf geometry in abrasive waterjet machining of silicon carbide ceramics*. International Journal of Machine Tools and Manufacture, 2009. **49**(14): p. 1077-1088.
54. Kawanaka, T., S. Kato, M. Kunieda, J.W. Murray, and A.T. Clare. *Selective surface texturing using electrolyte jet machining*. in *Procedia CIRP*. 2014.
55. Kawanaka, T. and M. Kunieda, *Mirror-like finishing by electrolyte jet machining*. CIRP Annals - Manufacturing Technology, 2015. **64**(1): p. 237-240.
56. Bard, A.J. and L.R. Faulkner, *Electrochemical methods: fundamentals and applications*. 2nd ed. 2001, New York: Wiley.
57. Qiu, Y., *Dissolution mechanisms: theoretical and experimental investigations*, in *Pharmacy*. 2015, University of Iowa. p. 131.
58. Bocking, C., *High Speed Selective Jet Electrodeposition of gold and copper*. GEC Journal of Research, 1992. **9**(3): p. 12.
59. Natsu, W., S. Ooshiro, and M. Kunieda, *Research on generation of three-dimensional surface with micro-electrolyte jet machining*. CIRP Journal of Manufacturing Science and Technology, 2008. **1**(1): p. 27-34.
60. Kai, S., H. Sai, M. Kunieda, and H. Izumi, *Study on Electrolyte Jet Cutting*. Procedia CIRP, 2012. **1**(0): p. 627-632.
61. McGeough, J.A., *Electrochemical Machining*, in *Kirk-Othmer Encyclopedia of Chemical Technology*. 2000, John Wiley & Sons, Inc.
62. Klocke, F., A. Klink, D. Veselovac, D.K. Aspinwall, S.L. Soo, M. Schmidt, J. Schilp, G. Levy, and J.-P. Kruth, *Turbomachinery component manufacture by application of electrochemical, electro-physical and photonic processes*. CIRP Annals, 2014. **63**(2): p. 703-726.
63. Kunieda, M., K. Mizugai, S. Watanabe, N. Shibuya, and N. Iwamoto, *Electrochemical micromachining using flat electrolyte jet*. CIRP Annals - Manufacturing Technology, 2011. **60**(1): p. 251-254.
64. Lipiec, P., D. Wyszynski, and S. Skoczypiec, *Primary Research on Jet ECM Processing of Difficult to Cut Materials*. Key Engineering Materials, 2013. **554-557**: p. 1793-1799.
65. Leese, R.J. and A. Ivanov, *Electrochemical micromachining: An introduction*. Advances in Mechanical Engineering, 2016. **8**(1): p. 168781401562686.
66. Cagnon, L., V. Kirchner, M. Kock, R. Schuster, G. Ertl, W.T. Gmelin, and H. Kuck, *Electrochemical Micromachining of Stainless Steel by Ultrashort Voltage Pulses*. Zeitschrift für Physikalische Chemie, 2002(217): p. 14.
67. Kozak, J., D. Gulbinowicz, and Z. Gulbinowicz, *The mathematical modeling and computer simulation of pulse electrochemical micromachining*. Engineering Letters, 2008. **16**(4): p. 556-561.
68. Ahn, S.H., S.H. Ryu, D.K. Choi, and C.N. Chu, *Electro-chemical micro drilling using ultra short pulses*. Precision Engineering, 2004. **28**(2): p. 129-134.

69. Karakus, C. and D. Chin, *Metal Distribution in Jet Plating*. Journal of The Electrochemical Society, 1994. **141**(3): p. 691-697.
70. Fitzgerald, J.A. and S.V. Garimella, *A study of the flow field of a confined and submerged impinging jet*. International Journal of Heat and Mass Transfer, 1998. **41**(8): p. 1025-1034.
71. Caggese, O., G. Gnaegi, G. Hannema, A. Terzis, and P. Ott, *Experimental and numerical investigation of a fully confined impingement round jet*. International Journal of Heat and Mass Transfer, 2013. **65**: p. 873-882.
72. Kristiawan, M., A. Meslem, I. Nastase, and V. Sobolik, *Wall shear rates and mass transfer in impinging jets: Comparison of circular convergent and cross-shaped orifice nozzles*. International Journal of Heat and Mass Transfer, 2012. **55**(1-3): p. 282-293.
73. Hall, J.W. and D. Ewing, *On the dynamics of the large-scale structures in round impinging jets*. Journal of Fluid Mechanics, 2006. **555**: p. 439.
74. Meslem, A., V. Sobolik, F. Bode, K. Sodjavi, Y. Zaouali, I. Nastase, and C. Croitoru, *Flow dynamics and mass transfer in impinging circular jet at low Reynolds number. Comparison of convergent and orifice nozzles*. International Journal of Heat and Mass Transfer, 2013. **67**(0): p. 25-45.
75. Hackert-Oschätzchen, M., G. Meichsner, M. Zinecker, A. Martin, and A. Schubert, *Micro machining with continuous electrolytic free jet*. Precision Engineering, 2012. **36**(4): p. 612-619.
76. Rajput, M.S., P.M. Pandey, and S. Jha, *Modelling of high speed selective jet electrodeposition process*. Journal of Manufacturing Processes, 2015. **17**: p. 98-107.
77. Alkire, R.C. and J.B. Ju, *The Effect of an Impinging Fluid Jet on Mass Transfer and Current Distribution in a Circular Through-Hole*. Journal of The Electrochemical Society, 1987. **134**(5): p. 1172-1180.
78. Chanson, H., *Current knowledge in hydraulic jumps and related phenomena. A survey of experimental results*. European Journal of Mechanics - B/Fluids, 2009. **28**(2): p. 191-210.
79. Liu, Z., H. Nouraei, M. Papini, and J.K. Spelt, *Abrasive enhanced electrochemical slurry jet micro-machining: Comparative experiments and synergistic effects*. Journal of Materials Processing Technology, 2014. **214**(9): p. 1886-1894.
80. Liu, Z., H. Nouraei, J.K. Spelt, and M. Papini, *Electrochemical slurry jet micro-machining of tungsten carbide with a sodium chloride solution*. Precision Engineering, 2015. **40**: p. 189-198.
81. Fan, H., Y.P. Zhao, and S.K. Wang, *Technical Study of Jet Electrodeposition in Manufacture of Metal Parts*. Key Engineering Materials, 2015. **667**: p. 259-264.
82. Bannard, J., *Electrochemical machining*. Journal of applied electrochemistry, 1977. **7**: p. 1-29.
83. Hackert, M., G. Meichsner, and A. Schubert. *Generating Micro Geometries with Air assisted Electrochemical Machining*. in *EUSPEN 10th International Conference*. 2008. Zurich
84. Krain, H.R., A.R.C. Sharman, and K. Ridgway, *Optimisation of tool life and productivity when end milling Inconel 718TM*. Journal of Materials Processing Technology, 2007. **189**(1): p. 153-161.
85. Schirra, J. and D. Viens, *Metallurgical factors influencing the machinability of Inconel 718*. Superalloys 718, 625, 706 and Various Derivatives, 1994: p. 827-838.
86. Schubert, A., M. Hackert-Oschätzchen, A. Martin, S. Winkler, D. Kuhn, G. Meichsner, H. Zeidler, and J. Edelmann, *Generation of Complex Surfaces by Superimposed Multi-dimensional Motion in Electrochemical Machining*. Procedia CIRP, 2016. **42**: p. 384-389.

87. Hackert-Oschätzchen, M., G. Meichsner, H. Zeidler, M. Zinecker, and A. Schubert, *Micro Machining of Different Steels with Closed Electrolytic Free Jet*, in *AIP Conference Proceedings*. 2011, AIP Publishing. p. 1337-1343.
88. Rosenkranz, C., M.M. Lohrengel, and J.W. Schultze, *The surface structure during pulsed ECM of iron in NaNO₃*. *Electrochimica Acta*, 2005. **50**(10): p. 2009-2016.
89. Stern, M. and H. Wissenburg, *The electrochemical behavior and passivity of titanium*. *Journal of the Electrochemical Society*, 1959. **106**(9): p. 755-759.
90. Klocke, F., M. Zeis, A. Klink, and D. Veselovac, *Experimental Research on the Electrochemical Machining of Modern Titanium- and Nickel-based Alloys for Aero Engine Components*. *Procedia CIRP*, 2013. **6**: p. 368-372.
91. Geetha, M., A.K. Singh, R. Asokamani, and A.K. Gogia, *Ti based biomaterials, the ultimate choice for orthopaedic implants – A review*. *Progress in Materials Science*, 2009. **54**(3): p. 397-425.
92. Lu, X. and Y. Leng, *Electrochemical micromachining of titanium surfaces for biomedical applications*. *Journal of Materials Processing Technology*, 2005. **169**(2): p. 173-178.
93. Datta, M., *fabrication of an array of precision nozzles by through-mask electrochemical micromachining*. *Journal of The Electrochemical Society*, 1995. **142**(11): p. 3801-3805.
94. Liu, W., S. Ao, Y. Li, Z. Liu, H. Zhang, S.M. Manladan, Z. Luo, and Z. Wang, *Effect of Anodic Behavior on Electrochemical Machining of TB6 Titanium Alloy*. *Electrochimica Acta*, 2017. **233**: p. 190-200.
95. Pramanik, A., *Developments in the non-traditional machining of particle reinforced metal matrix composites*. *International Journal of Machine Tools and Manufacture*, 2014. **86**: p. 44-61.
96. Kunieda, M., N. Shibuya, and K. Mizugai, *Study of Electrolyte Jet Machining of Cemented Carbide*, in *Proceedings of the 37th International MATADOR Conference*, S.L. Hinduja, L., Editor. 2012, Springer London. p. 83-86.
97. Mizugai, K., N. Shibuya, and M. Kunieda, *Study on Electrolyte Jet Machining of Cemented Carbide*. *International Journal of Electrical Machining*, 2013. **18**: p. 23-28.
98. Hackert-Oschätzchen, M., A. Martin, G. Meichsner, M. Zinecker, and A. Schubert, *Microstructuring of carbide metals applying Jet Electrochemical Machining*. *Precision Engineering*, 2013. **37**(3): p. 621-634.
99. Miyoshi, K. and M. Kunieda, *Fabrication of Micro Rods of Cemented Carbide by Electrolyte Jet Turning*. *Procedia CIRP*, 2016. **42**: p. 373-378.
100. Hackert-Oschätzchen, M., N. Lehnert, A. Martin, and A. Schubert, *Jet Electrochemical Machining of Particle Reinforced Aluminum Matrix Composites with Different Neutral Electrolytes*. *IOP Conference Series: Materials Science and Engineering*, 2016. **118**: p. 012036.
101. Hackert-Oschätzchen, M., N. Lehnert, M. Kowalick, C. Scherf, A. Martin, and A. Schubert, *Analysis of an electrochemical machining process for particle reinforced aluminium matrix composites*, in *COMSOL conference*. 2016: Munich, Germany.
102. Bannard, J., *On the electrochemical machining of some titanium alloys in bromide electrolytes*. *Journal of Applied Electrochemistry*, 1976. **6**(6): p. 477-483.
103. Guodong, L., L. Yong, K. Quancun, and T. Hao, *Selection and Optimization of Electrolyte for Micro Electrochemical Machining on Stainless Steel 304*. *Procedia CIRP*, 2016. **42**(Supplement C): p. 412-417.
104. Bhattacharyya, B., *Chapter 7 - Influencing Factors of EMM*, in *Electrochemical Micromachining for Nanofabrication, MEMS and Nanotechnology*. 2015, William Andrew Publishing. p. 123-143.
105. De Silva, A.K.M., H.S.J. Altena, and J.A. McGeough, *Influence of Electrolyte Concentration on Copying Accuracy of Precision-ECM*. *CIRP Annals - Manufacturing Technology*, 2003. **52**(1): p. 165-168.

106. Ryu, S.H., *Micro fabrication by electrochemical process in citric acid electrolyte*. Journal of Materials Processing Technology, 2009. **209**(6): p. 2831-2837.
107. Yang, Y., W. Natsu, and W. Zhao, *Realization of eco-friendly electrochemical micromachining using mineral water as an electrolyte*. Precision Engineering, 2011. **35**(2): p. 204-213.
108. Meakin, J.D., *Nontoxic Technique for Electrolytically Polishing and Thinning Gold*. Review of Scientific Instruments, 1964. **35**(6): p. 763-763.
109. Booker, G.R. and R. Stickler, *Large-Area "Jet" Electrolytic Polishing of Ge and Si*. Journal of The Electrochemical Society, 1962. **109**(12): p. 1167-1171.
110. Bannard, J., *On the electrochemical machining of some titanium alloys in bromide electrolytes*. Journal of Applied Electrochemistry, 1976. **6**: p. 477-483.
111. Datta, M. and D. Harris, *Electrochemical micromachining: An environmentally friendly, high speed processing technology*. Electrochimica Acta, 1997. **42**(20): p. 3007-3013.
112. Schubert, N., M. Schneider, and A. Michaelis. *Investigation of anodic dissolution of cobalt in alkaline solution*. in *7th International Symposium on Electrochemical Machining Technology (INSECT)*. 2011.
113. Landolt, D., *Throwing Power Measurements during High Rate Nickel Dissolution under Active and Transpassive Conditions*. Journal of The Electrochemical Society, 1972. **119**(6): p. 708-712.
114. Bannard, J., *The use of surface-active additives in electrochemical machining electrolytes*. Journal of applied electrochemistry, 1974. **4**: p. 117-124.
115. Thiemig, D., A. Bund, and J.B. Talbot, *Electrocodeposition of nickel nanocomposites using an impinging jet electrode*. Journal of the Electrochemical Society, 2007. **154**(10): p. D510-D515.
116. Osborne, S.J., W.S. Sweet, K.S. Vecchio, and J.B. Talbot, *Electroplating of copper-alumina nanocomposite films with an impinging jet electrode*. Journal of the Electrochemical Society, 2007. **154**(8): p. D394-D399.
117. Weber, J. and K. Koeberle, *Method and device for producing a galvanic layer on a substrate surface*, in *PatBase*. 2004, Bosch GMBH: Germany.
118. Shaodian, S. and G. Tao, *Electrochemical marking machine for generating random patterns and texts by jet flow*, in *PatBase*. 2014, Wuxi Huazhen New Energy Technology Co Ltd: China.
119. University, H.P., *An electrochemical processing system and method for three-dimensional metal microstructures (machine translation)*, in *PatBase*. 2016, Henan Polytechnic University: China.
120. Kunieda, M., *Electrolyte jet cutting device and the electrolyte jet machining method*, in *Google Patents*. 2017, University of Tokyo: Japan.
121. Sen, M. and H.S. Shan, *Analysis of hole quality characteristics in the electro jet drilling process*. International Journal of Machine Tools and Manufacture, 2005. **45**(15): p. 1706-1716.
122. Sen, M. and H.S. Shan, *Electro jet drilling using hybrid NNGA approach*. Robotics and Computer-Integrated Manufacturing, 2007. **23**(1): p. 17-24.
123. Hackert, M., G. Meichsner, M. Zinecker, and A. Schubert. *Micro turning with closed electrolytic free jet*. in *International Symposium on Electrochemical Machining Technology (INSECT)*. 2010. Brussels: Brussel University Press.
124. Kock, M., V. Kirchner, and R. Schuster, *Electrochemical micromachining with ultrashort voltage pulses—a versatile method with lithographical precision*. Electrochimica Acta, 2003. **48**(20): p. 3213-3219.
125. Kozak, J., K.P. Rajurkar, and Y. Makkar, *Study of Pulse Electrochemical Micromachining*. Journal of Manufacturing Processes, 2004. **6**(1): p. 7-14.
126. Rajurkar, K.P., J. Kozak, B. Wei, and J.A. McGeough, *Study of Pulse Electrochemical Machining Characteristics*. CIRP Annals, 1993. **42**(1): p. 231-234.

127. Joshi, S.S. and D. Marla, 11.15 - *Electrochemical Micromachining*, in *Comprehensive Materials Processing*, S.H.F.B.J.V.T. Yilbas, Editor. 2014, Elsevier: Oxford. p. 373-403.
128. Martin, A., C. Eckart, N. Lehnert, M. Hackert-Oschätzchen, and A. Schubert, *Generation of Defined Surface Waviness on Tungsten Carbide by Jet Electrochemical Machining with Pulsed Current*. *Procedia CIRP*, 2016. **45**: p. 231-234.
129. Kunieda, M., *Electrolyte jet processing device and electrolyte jet processing method*. 2013, National University Corporation Tokyo.
130. Kunieda, M., S. Ooshiro, and N. Iwamoto, *Manufacturing Dimpled Saw Wires Using Electrolyte Jet Machining*. *Journal of the Japan Society for Precision Engineering*, 2010. **76**(5): p. 572-576.
131. Alkire, R. and J.B. Ju, *High Speed Selective Electroplating with Impinging Two-Dimensional Slot Jet Flow*. *Journal of The Electrochemical Society*, 1987. **134**(2): p. 294-299.
132. Puipe, J.C., R.E. Acosta, and R.J. von Gutfeld, *Investigation of Laser-Enhanced Electroplating Mechanisms*. *Journal of The Electrochemical Society*, 1981. **128**(12): p. 2539-2545.
133. Von Gutfeld, R.J., L.T. Romankiw, and R.E. Acosta, *Laser-Enhanced Plating and Etching: Mechanisms and Applications*. *IBM Journal of Research and Development*, 1982. **26**(2): p. 136-144.
134. Gelchinski, M.H., L.T. Romankiw, D.R. Vigliotti, and R.J. von Gutfeld, *Electrochemical and Metallurgical Aspects of Laser-Enhanced Jet Plating of Gold*. *Journal of The Electrochemical Society*, 1985. **132**(11): p. 2575-2581.
135. Gutfeld, R.J.v., *Laser-enhanced plating and etching for microelectronic applications*. *IEEE Circuits and Devices Magazine*, 1986. **2**(1): p. 57-60.
136. DeSilva, A.K.M., P.T. Pajak, D.K. Harrison, and J.A. McGeough, *Modelling and Experimental Investigation of Laser Assisted Jet Electrochemical Machining*. *CIRP Annals - Manufacturing Technology*, 2004. **53**(1): p. 179-182.
137. Pajak, P.T., A.K.M. Desilva, D.K. Harrison, and J.A. McGeough, *Precision and efficiency of laser assisted jet electrochemical machining*. *Precision Engineering*, 2006. **30**(3): p. 288-298.
138. Zhang, H., J. Xu, and J. Wang, *Investigation of a novel hybrid process of laser drilling assisted with jet electrochemical machining*. *Optics and Lasers in Engineering*, 2009. **47**(11): p. 1242-1249.
139. Hua, Z. and X. Jiawen, *Modeling and Experimental Investigation of Laser Drilling with Jet Electrochemical Machining*. *Chinese Journal of Aeronautics*, 2010. **23**(4): p. 454-460.
140. Zhang, H., J.W. Xu, and J.M. Wang. *Green laser drilling assisted with jet electrochemical machining of nickel-based superalloy*. in *3rd International Conference on Engineering and Technologies and Ceeusro, ICETC2009, November 19, 2009 - November 21, 2009*. 2010. Changzhou, Jiangsu, China: Trans Tech Publications Ltd.
141. Zhang, Z.Y., M.X. Cai, Q.Y. Feng, and Y.B. Zeng, *Comparison of different laser-assisted electrochemical methods based on surface morphology characteristics*. *International Journal of Advanced Manufacturing Technology*, 2014. **71**(1-4): p. 565-571.
142. Katoh, R., M. Yoshida, and M. Kunieda. *Rapid prototyping of metal parts with electrolyte jet chemical machining*. in *Japanese Society for Precision Engineering Spring meeting*. 1997.
143. Kalpakjian, S. and S. Schmid, *Manufacturing Engineering & Technology*. 2013: Pearson Education.
144. Rajurkar, K.P., G. Levy, A. Malshe, M.M. Sundaram, J. McGeough, X. Hu, R. Resnick, and A. DeSilva, *Micro and Nano Machining by Electro-Physical and*

- Chemical Processes*. CIRP Annals - Manufacturing Technology, 2006. **55**(2): p. 643-666.
145. Mishra, S. and V. Yadava, *Laser Beam MicroMachining (LBMM) – A review*. Optics and Lasers in Engineering, 2015. **73**: p. 89-122.
 146. Liu, Q., Q. Zhang, M. Zhang, and J. Zhang, *Review of size effects in micro electrical discharge machining*. Precision Engineering, 2016. **44**: p. 29-40.
 147. Carou, D., E.M. Rubio, J. Herrera, C.H. Lauro, and J.P. Davim, *Latest advances in the micro-milling of titanium alloys: a review*. Procedia Manufacturing, 2017. **13**: p. 275-282.
 148. Folkes, J., *Waterjet—An innovative tool for manufacturing*. Journal of Materials Processing Technology, 2009. **209**(20): p. 6181-6189.
 149. Chen, X., N. Qu, H. Li, and Z. Xu, *Electrochemical micromachining of micro-dimple arrays using a polydimethylsiloxane (PDMS) mask*. Journal of Materials Processing Technology, 2016. **229**: p. 102-110.
 150. Romankiw, L.T., *A path: from electroplating through lithographic masks in electronics to LIGA in MEMS*. Electrochimica Acta, 1997. **42**(20): p. 2985-3005.
 151. Murray, J.W.H., *Damage, contamination and surface treatment of electrical discharge machined materials*, in *Faculty of Engineering*. 2014, University of Nottingham.
 152. Fasasi, A.Y., S. Mwenifumbo, N. Rahbar, J. Chen, M. Li, A.C. Beye, C.B. Arnold, and W.O. Soboyejo, *Nano-second UV laser processed micro-grooves on Ti6Al4V for biomedical applications*. Materials Science and Engineering: C, 2009. **29**(1): p. 5-13.
 153. Schaller, T., L. Bohn, J. Mayer, and K. Schubert, *Microstructure grooves with a width of less than 50 μm cut with ground hard metal micro end mills*. Precision Engineering, 1999. **23**(4): p. 229-235.
 154. Haghbin, N., J.K. Spelt, and M. Papini, *Abrasive waterjet micro-machining of channels in metals: Comparison between machining in air and submerged in water*. International Journal of Machine Tools and Manufacture, 2015. **88**: p. 108-117.
 155. Mehrpouya, M., H. Lavvafi, and A. Darafsheh, *Microstructural Characterization and Mechanical Reliability of Laser-Machined Structures*. 2018: p. 731-761.
 156. Yoon, H.-S., C.-S. Kim, H.-T. Lee, and S.-H. Ahn, *Advanced scanning paths for focused ion beam milling*. Vacuum, 2017. **143**: p. 40-49.
 157. Raju, L. and S.S. Hiremath, *A State-of-the-art Review on Micro Electro-discharge Machining*. Procedia Technology, 2016. **25**: p. 1281-1288.
 158. Kumar, P., M. Kumar, V. Bajpai, and N.K. Singh, *Recent advances in characterization, modeling and control of burr formation in micro-milling*. Manufacturing Letters, 2017. **13**: p. 1-5.
 159. Hallmann, S., P. Glockner, C. Daniel, V. Seyda, and C. Emmelmann, *Manufacturing of Medical Implants by Combination of Selective Laser Melting and Laser Ablation*. Lasers in Manufacturing and Materials Processing, 2015. **2**(3): p. 124-134.
 160. Murray, J.W. and A.T. Clare, *Morphology and Wear Behaviour of Single and Multi-layer Electrical Discharge Coatings*. Procedia CIRP, 2016. **42**: p. 236-239.
 161. Hashish, M., *WaterJet Machining Process*, in *Handbook of Manufacturing Engineering and Technology*, A.Y.C. Nee, Editor. 2015, Springer London: London. p. 1651-1686.
 162. Shipway, P.H., G. Fowler, and I.R. Pashby, *Characteristics of the surface of a titanium alloy following milling with abrasive waterjets*. Wear, 2005. **258**(1-4): p. 123-132.
 163. Axinte, D.A., B. Karpuschewski, M.C. Kong, A.T. Beaucamp, S. Anwar, D. Miller, and M. Petzel, *High Energy Fluid Jet Machining (HEFJet-Mach): From scientific and technological advances to niche industrial applications*. CIRP Annals, 2014. **63**(2): p. 751-771.

164. Schubert, A., J. Edelmann, S. Gross, H. Zeidler, G. Meichsner, M. Hackert, N. Wolf, and J. Schneider. *Micromanufacturing of hard to machine materials by physical and chemical ablation processes*. in *International conference on advances in materials and processing technologies*. 2011.
165. Liu, H.T., *Waterjet technology for machining fine features pertaining to micromachining*. Journal of Manufacturing Processes, 2010. **12**(1): p. 8-18.
166. Kong, M.C., D. Axinte, and W. Voice, *Aspects of material removal mechanism in plain waterjet milling on gamma titanium aluminide*. Journal of Materials Processing Technology, 2010. **210**(3): p. 573-584.
167. Hwang, Y.-L., C.-L. Kuo, and S.-F. Hwang, *The coating of TiC layer on the surface of nickel by electric discharge coating (EDC) with a multi-layer electrode*. Journal of Materials Processing Technology, 2010. **210**(4): p. 642-652.
168. Lim, H.S., Y.S. Wong, M. Rahman, and M.K. Edwin Lee, *A study on the machining of high-aspect ratio micro-structures using micro-EDM*. Journal of Materials Processing Technology, 2003. **140**(1-3): p. 318-325.
169. Barman, S., Vijay, Nagahanumaiah, and A.B. Puri, *Surface Texture and Elemental Characterization of High Aspect Ratio Blind Micro Holes on Different Materials in Micro EDM*. Procedia Materials Science, 2014. **6**: p. 304-309.
170. Uhlmann, E., M. Röhner, M. Langmack, and T.-M. Schimmelpfennig, *Micro-electrical Discharge Machining*. 2015: p. 81-105.
171. Boden, S.A., Z. Moktadir, D.M. Bagnall, H. Mizuta, and H.N. Rutt, *Focused helium ion beam milling and deposition*. Microelectronic Engineering, 2011. **88**(8): p. 2452-2455.
172. Sun, J., X. Luo, J.M. Ritchie, W. Chang, and W. Wang, *An investigation of redeposition effect for deterministic fabrication of nanodots by focused ion beam*. Precision Engineering, 2012. **36**(1): p. 31-36.
173. Tan, H., W. Shang, F. Zhang, A.T. Clare, X. Lin, J. Chen, and W. Huang, *Process mechanisms based on powder flow spatial distribution in direct metal deposition*. Journal of Materials Processing Technology, 2018. **254**: p. 361-372.
174. Yamazaki, T., *Development of A Hybrid Multi-tasking Machine Tool: Integration of Additive Manufacturing Technology with CNC Machining*. Procedia CIRP, 2016. **42**: p. 81-86.
175. Liang, L., J. Yuan, X. Li, F. Yang, and L. Jiang, *Wear behavior of the micro-grooved texture on WC-Ni 3 Al cermet prepared by laser surface texturing*. International Journal of Refractory Metals and Hard Materials, 2018. **72**: p. 211-222.
176. Momma, C., B.N. Chichkov, S. Nolte, F. von Alvensleben, A. Tünnermann, H. Welling, and B. Wellegehausen, *Short-pulse laser ablation of solid targets*. Optics Communications, 1996. **129**(1): p. 134-142.
177. Huang, H., H.Y. Zheng, and G.C. Lim, *Femtosecond laser machining characteristics of Nitinol*. Applied Surface Science, 2004. **228**(1-4): p. 201-206.
178. Hung, C.-H., F.-Y. Chang, T.-L. Chang, Y.-T. Chang, K.-W. Huang, and P.-C. Liang, *Micromachining NiTi tubes for use in medical devices by using a femtosecond laser*. Optics and Lasers in Engineering, 2015. **66**: p. 34-40.
179. Leong, K.H., *Femtosecond lasers for manufacturing*, in *Industrial Laser Solutions for Manufacturing*. 2002, LFW International.
180. Schaeffer, R., *Commercially available ultrafast-pulse lasers: An update*, in *Industrial Laser Solutions for Manufacturing*. 2014, LFW International.
181. Munda, J., M. Malapati, and B. Bhattacharyya, *Control of micro-spark and stray-current effect during EMM process*. Journal of Materials Processing Technology, 2007. **194**(1-3): p. 151-158.
182. Ahmad, S., M. Mustafa, and J. Akhtar, *On selective electroplating of gold in fabrication of MIC's*. Microelectronics Reliability, 1981. **21**(5): p. 727-730.

183. El-Sayed, H., M.T. Greiner, and P. Kruse, *Selective electroplating of copper lines on pre-patterned tantalum oxide thin films*. Applied Surface Science, 2007. **253**(22): p. 8962-8968.
184. Leester-Schädel, M., T. Lorenz, F. Jürgens, and C. Richter, *Fabrication of Microfluidic Devices*. 2016: p. 23-57.
185. Lin, Y.S., C.H. Yang, C.Y. Wang, F.R. Chang, K.S. Huang, and W.C. Hsieh, *An aluminum microfluidic chip fabrication using a convenient micromilling process for fluorescent poly(DL-lactide-co-glycolide) microparticle generation*. Sensors (Basel), 2012. **12**(2): p. 1455-67.
186. Naqiuddin, N.H., L.H. Saw, M.C. Yew, F. Yusof, T.C. Ng, and M.K. Yew, *Overview of micro-channel design for high heat flux application*. Renewable and Sustainable Energy Reviews, 2018. **82**: p. 901-914.
187. Kewalramani, G.V., A. Agrawal, and S.K. Saha, *Modeling of microchannel heat sinks for electronic cooling applications using volume averaging approach*. International Journal of Heat and Mass Transfer, 2017. **115**: p. 395-409.
188. Bai, L., Y. Fu, M. Yao, and Y. Cheng, *Enhancement of mixing inside ionic liquid droplets through various micro-channels design*. Chemical Engineering Journal, 2018. **332**: p. 537-547.
189. Kuang, Z., J. Li, S. Edwardson, W. Perrie, D. Liu, and G. Dearden, *Ultrafast laser beam shaping for material processing at imaging plane by geometric masks using a spatial light modulator*. Optics and Lasers in Engineering, 2015. **70**: p. 1-5.
190. Momma, C., S. Nolte, G. Kamlage, F. Von Alvensleben, and A. Tünnermann, *Beam delivery of femtosecond laser radiation by diffractive optical elements*. Applied Physics A: Materials Science and Processing, 1998. **67**(5): p. 517-520.
191. Kim, H.-Y., J.-W. Yoon, W.-S. Choi, K.-R. Kim, and S.-H. Cho, *Ablation depth control with 40 nm resolution on ITO thin films using a square, flat top beam shaped femtosecond NIR laser*. Optics and Lasers in Engineering, 2016. **84**: p. 44-50.
192. Smarra, M., M. Janitzki, and K. Dickmann, *Beam Shaping in Ultra-short Pulse Laser Processing for Enhancing the Ablation Efficiency*. Physics Procedia, 2016. **83**: p. 1145-1152.
193. Kell, J., J.R. Tyrer, R.L. Higginson, J.C. Jones, and S. Noden, *Laser weld pool management through diffractive holographic optics*. Materials Science and Technology, 2012. **28**(3): p. 354-363.
194. Rung, S., J. Barth, and R. Hellmann, *Characterization of Laser Beam Shaping Optics Based on Their Ablation Geometry of Thin Films*. Micromachines, 2014. **5**(4): p. 943-953.
195. Goffin, N., F. Lisco, G. Claudio, J. Tyrer, and E. Woolley, *Annealing of Thin-film Cadmium Telluride Photovoltaics Using Holographically Controlled Laser Processing*. Energy Procedia, 2016. **102**: p. 70-79.
196. Venkatesh, V.C., *Parametric Studies on Abrasive Jet Machining*. CIRP Annals - Manufacturing Technology, 1984. **33**(1): p. 109-112.
197. Venkatesh, V.C., T.N. Goh, K.H. Wong, and M.J. Lim, *An empirical study of parameters in abrasive jet machining*. International Journal of Machine Tools and Manufacture, 1989. **29**(4): p. 471-479.
198. Hashish, M., *The Effect of Beam Angle in Abrasive-Waterjet Machining*. Journal of Engineering for Industry, 1993. **115**(1): p. 51-56.
199. Xu, X., A.D.D. Ratta, J. Sosonkina, and J. Melngailis, *Focused ion beam induced deposition and ion milling as a function of angle of ion incidence*. Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena, 1992. **10**(6): p. 2675-2680.
200. Tokarev, V.N., J.I.B. Wilson, M.G. Jubber, P. John, and D.K. Milne, *Modelling of self-limiting laser ablation of rough surfaces: application to the polishing of diamond films*. Diamond and Related Materials, 1995. **4**(3): p. 169-176.

201. George, D.S., A. Onischenko, and A.S. Holmes, *On the angular dependence of focused laser ablation by nanosecond pulses in solgel and polymer materials*. Applied Physics Letters, 2004. **84**(10): p. 1680-1682.
202. Palmer, J.A., K.L. McDaniel, M.F. Harris, R. Lumia, and M.L. Griffith. *The effects of varying substrate angle on feature quality in femtosecond laser ablation of ferrous alloys*. 2004.
203. Yang, P., G.R. Burns, J.A. Palmer, M.F. Harris, K.L. McDaniel, J. Guo, G.A. Vawter, D.R. Tallant, M.L. Griffith, and T.S. Luk, *Microfabrication with Femtosecond Laser Processing - (A) Laser Ablation of Ferrous Alloys, (B) Direct-Write Embedded Optical Waveguides and Integrated Optics in Bulk Glass* 2004, Sandia National Laboratories: New Mexico. California, USA.
204. Groenendijk, M. and J. Meijer, *Microstructuring using femtosecond pulsed laser ablation*. Journal of Laser Applications, 2006. **18**(3): p. 227-235.
205. Guo, W., Z.B. Wang, L. Li, D.J. Whitehead, B.S. Luk'yanchuk, and Z. Liu, *Near-field laser parallel nanofabrication of arbitrary-shaped patterns*. Applied Physics Letters, 2007. **90**(24): p. 243101.
206. Leitz, K.-H., H. Koch, A. Otto, and M. Schmidt, *Numerical simulation of process dynamics during laser beam drilling with short pulses*. Applied Physics A, 2011. **106**(4): p. 885-891.
207. ElTobgy, M.S., E. Ng, and M.A. Elbestawi, *Finite element modeling of erosive wear*. International Journal of Machine Tools and Manufacture, 2005. **45**(11): p. 1337-1346.
208. Lozano Torrubia, P., D.A. Axinte, and J. Billingham, *Stochastic modelling of abrasive waterjet footprints using finite element analysis*. International Journal of Machine Tools and Manufacture, 2015. **95**: p. 39-51.
209. Takaffoli, M. and M. Papini, *Numerical simulation of solid particle impacts on Al6061-T6 Part II: Materials removal mechanisms for impact of multiple angular particles*. Wear, 2012. **296**(1-2): p. 648-655.
210. Yoneda, K. and M. Kunieda, *Numerical Analysis of Cross Sectional Shape of Micro-Indents Formed by the Electrochemical Jet Machining (ECJM)*. Journal of The Japan Society of Electrical Machining Engineers, 1995. **29**(62): p. 1-8.
211. Otto, A., H. Koch, R.G. Vázquez, Z. Lin, and B. Hainsey, *Multiphysical Simulation of ns-Laser Ablation of Multi-material LED-structures*. Physics Procedia, 2014. **56**: p. 1315-1324.
212. Torrubia, P.L., J. Billingham, and D.A. Axinte, *Stochastic simplified modelling of abrasive waterjet footprints*. Proc Math Phys Eng Sci, 2016. **472**(2186): p. 20150836.
213. Mieszala, M., P.L. Torrubia, D.A. Axinte, J.J. Schwiedrzik, Y. Guo, S. Mischler, J. Michler, and L. Philippe, *Erosion mechanisms during abrasive waterjet machining: Model microstructures and single particle experiments*. Journal of Materials Processing Technology, 2017. **247**: p. 92-102.
214. ten Thijs Boonkamp, J.H.M. and J.K.M. Jansen, *An analytical solution for mechanical etching of glass by powder blasting*. Journal of Engineering Mathematics, 2002. **43**(2): p. 385-399.
215. Ghobeity, A., J.K. Spelt, and M. Papini, *Abrasive jet micro-machining of planar areas and transitional slopes*. Journal of Micromechanics and Microengineering, 2008. **18**(5): p. 055014.
216. Ghobeity, A., T. Krajac, T. Burzynski, M. Papini, and J.K. Spelt, *Surface evolution models in abrasive jet micromachining*. Wear, 2008. **264**(3-4): p. 185-198.
217. Kong, M.C., S. Anwar, J. Billingham, and D.A. Axinte, *Mathematical modelling of abrasive waterjet footprints for arbitrarily moving jets: Part I—single straight paths*. International Journal of Machine Tools and Manufacture, 2012. **53**(1): p. 58-68.
218. Billingham, J., C.B. Miron, D.A. Axinte, and M.C. Kong, *Mathematical modelling of abrasive waterjet footprints for arbitrarily moving jets: Part II—Overlapped*

- single and multiple straight paths*. International Journal of Machine Tools and Manufacture, 2013. **68**: p. 30-39.
219. Bilbao Guillerna, A., D. Axinte, and J. Billingham, *The linear inverse problem in energy beam processing with an application to abrasive waterjet machining*. International Journal of Machine Tools and Manufacture, 2015. **99**: p. 34-42.
 220. Bilbao-Guillerna, A., D.A. Axinte, J. Billingham, and G.B.J. Cadot, *Waterjet and laser etching: the nonlinear inverse problem*. R Soc Open Sci, 2017. **4**(7): p. 161031.
 221. Cadot, G.B.J., *Experimental and numerical investigations of diamond and related materials controlled-depth machining using pulsed laser ablation*, in *Faculty of Engineering*. 2017, University of Nottingham: Nottingham.
 222. Han, Z., Z. Mu, W. Yin, W. Li, S. Niu, J. Zhang, and L. Ren, *Biomimetic multifunctional surfaces inspired from animals*. Advances in Colloid and Interface Science, 2016. **234**: p. 27-50.
 223. Malshe, A., K. Rajurkar, A. Samant, H.N. Hansen, S. Bapat, and W. Jiang, *Bio-inspired functional surfaces for advanced applications*. CIRP Annals - Manufacturing Technology, 2013. **62**(2): p. 607-628.
 224. Bruzzone, A.A.G., H.L. Costa, P.M. Lonardo, and D.A. Lucca, *Advances in engineered surfaces for functional performance*. CIRP Annals - Manufacturing Technology, 2008. **57**(2): p. 750-769.
 225. Bhushan, B. and Y.C. Jung, *Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction*. Progress in Materials Science, 2011. **56**(1): p. 1-108.
 226. Liu, K. and L. Jiang, *Bio-inspired design of multiscale structures for function integration*. Nano Today, 2011. **6**(2): p. 155-175.
 227. Valencia-Lazcano, A.A., T. Alonso-Rasgado, and A. Bayat, *Characterisation of breast implant surfaces and correlation with fibroblast adhesion*. J Mech Behav Biomed Mater, 2013. **21**: p. 133-48.
 228. Zhang, F., J. Chan, and H.Y. Low, *Biomimetic, hierarchical structures on polymer surfaces by sequential imprinting*. Applied Surface Science, 2008. **254**(10): p. 2975-2979.
 229. Hansen, H.N., R.J. Hocken, and G. Tosello, *Replication of micro and nano surface geometries*. CIRP Annals - Manufacturing Technology, 2011. **60**(2): p. 695-714.
 230. Scholz, S.G., C.A. Griffiths, S.S. Dimov, E.B. Brousseau, G. Lalev, and P. Petkov, *Manufacturing routes for replicating micro and nano surface structures with bio-mimetic applications*. CIRP Journal of Manufacturing Science and Technology, 2011. **4**(4): p. 347-356.
 231. Ahuir-Torres, J.I., M.A. Arenas, W. Perrie, and J. de Damborenea, *Influence of laser parameters in surface texturing of Ti6Al4V and AA2024-T3 alloys*. Optics and Lasers in Engineering, 2018. **103**: p. 100-109.
 232. Yu, Z., G. Yang, W. Zhang, and J. Hu, *Investigating the effect of picosecond laser texturing on microstructure and biofunctionalization of titanium alloy*. Journal of Materials Processing Technology, 2018. **255**: p. 129-136.
 233. Schlie, S., E. Fadeeva, A. Koroleva, A. Ovsianikov, J. Koch, A. Ngezahayo, and B.N. Chichkov, *Laser-based nanoengineering of surface topographies for biomedical applications*. Photonics and Nanostructures - Fundamentals and Applications, 2011. **9**(2): p. 159-162.
 234. Voisey, K.T., C.A. Scotchford, L. Martin, and H.S. Gill, *Effect of Q-switched Laser Surface Texturing of Titanium on Osteoblast Cell Response*. Physics Procedia, 2014. **56**: p. 1126-1135.
 235. Ohtsu, N., T. Kozuka, M. Yamane, and H. Arai, *Surface chemistry and osteoblast-like cell response on a titanium surface modified by a focused Nd:YAG laser*. Surface and Coatings Technology, 2017. **309**: p. 220-226.

236. Obeidi, M.A., E. McCarthy, L. Kailas, and D. Brabazon, *Laser surface texturing of stainless steel 316L cylindrical pins for interference fit applications*. Journal of Materials Processing Technology, 2018. **252**: p. 58-68.
237. Moradi, S., S. Kamal, P. Englezos, and S.G. Hatzikiriakos, *Femtosecond laser irradiation of metallic surfaces: effects of laser parameters on superhydrophobicity*. Nanotechnology, 2013. **24**(41): p. 415302.
238. Aguilar-Morales, A.I., S. Alamri, and A.F. Lasagni, *Micro-fabrication of high aspect ratio periodic structures on stainless steel by picosecond direct laser interference patterning*. Journal of Materials Processing Technology, 2018. **252**: p. 313-321.
239. Martínez-Calderon, M., A. Rodríguez, A. Dias-Ponte, M.C. Morant-Miñana, M. Gómez-Aranzadi, and S.M. Olaizola, *Femtosecond laser fabrication of highly hydrophobic stainless steel surface with hierarchical structures fabricated by combining ordered microstructures and LIPSS*. Applied Surface Science.
240. Klokkevold, P.R., P. Johnson, S. Dadgostari, J.E. Davies, A. Caputo, and R.D. Nishimura, *Early endosseous integration enhanced by dual acid etching of titanium: a torque removal study in the rabbit*. Clinical Oral Implants Research, 2001. **12**(4).
241. Wennerberg, A.A., T. Andersson, B. Krol, J. J., *A histomorphometric study of screw-shaped and removal torque titanium implants with three different surface topographies*. Clinical Oral Implants Research, 1995. **6**(1): p. 6.
242. Wennerberg, A., A. Ektessabi, T. Albrektsson, C. Johansson, and B. Andersson, *A 1-year follow-up of implants of differing surface roughness placed in rabbit bone*. The International journal of oral & maxillofacial implants, 1997. **12**(4): p. 486-494.
243. Ghosh, S. and S. Abanteriba, *Status of surface modification techniques for artificial hip implants*. Sci Technol Adv Mater, 2016. **17**(1): p. 715-735.
244. D'Lima, D.D., S.M. Lemperele, P.C. Chen, R.E. Holmes, and C.W. Colwell, *Bone response to implant surface morphology*. The Journal of Arthroplasty, 1998. **13**(8): p. 928-934.
245. Le Guehennec, L., A. Soueidan, P. Layrolle, and Y. Amouriq, *Surface treatments of titanium dental implants for rapid osseointegration*. Dent Mater, 2007. **23**(7): p. 844-54.
246. Bocking, C., S.J. Dover, and G. Bennett, *An investigation into the suitability of high speed selective jet electrodeposition for rapid tooling*, in *First national conference on rapid prototyping and tooling research*. 1995, MEP. p. 157 - 173.
247. Ikinamo, *Micro Electrolyte Jet Machining Technologies [online video]*. 2016: YouTube.
248. Schubert, A., M. Hackert-Oschätzchen, G. Meichsner, and M. Zinecker, *Design and realization of micro structured surfaces for thermodynamic applications*. Microsystem Technologies, 2011. **17**(9): p. 1471-1479.
249. Schubert, A., R. Neugebauer, D. Sylla, M. Avila, and M. Hackert, *Manufacturing of surface microstructures for improved tribological efficiency of powertrain components and forming tools*. CIRP Journal of Manufacturing Science and Technology, 2011. **4**(2): p. 200-207.
250. Kato, S., T. Kawanaka, H. Sai, and M. Kunieda, *Injection Molding Transcription of Micro Surface Structure Machined by EJM*, in *Japan Society for Precision Engineering*. 2013: Academic lecture Conference Paper Collection. p. 867-868.
251. Yang, X., X. Liu, Y. Lu, S. Zhou, M. Gao, J. Song, and W. Xu, *Controlling the Adhesion of Superhydrophobic Surfaces Using Electrolyte Jet Machining Techniques*. Sci Rep, 2016. **6**: p. 23985.
252. Singh, T. and A. Dvivedi, *Developments in electrochemical discharge machining: A review on electrochemical discharge machining, process variants and their hybrid methods*. International Journal of Machine Tools and Manufacture, 2016. **105**: p. 1-13.

253. Thellaputta, G.R., P.S. Chandra, and C.S.P. Rao, *Machinability of Nickel Based Superalloys: A Review*. Materials Today: Proceedings, 2017. **4**(2, Part A): p. 3712-3721.
254. Singh, P., H. Pungotra, and N.S. Kalsi, *On the characteristics of titanium alloys for the aircraft applications*. Materials Today: Proceedings, 2017. **4**(8): p. 8971-8982.
255. Williams, D.B. and C.B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*. 1996, Springer US.
256. Moroni, G., W.P. Syam, and S. Petrò, *A simulation method to estimate task-specific uncertainty in 3D microscopy*. Measurement, 2018.
257. Helmlí, F., *Focus Variation Instruments*, in *Optical Measurement of Surface Topography*, R. Leach, Editor. 2011, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 131-166.
258. Danzl, R., F. Helmlí, and S. Scherer, *Focus Variation – a Robust Technology for High Resolution Optical 3D Surface Metrology*. Strojniški vestnik – Journal of Mechanical Engineering, 2011. **2011**(03): p. 245-256.
259. Abramoff, M.D.M., Paulo J.; Ram, Sunanda J., *Image processing with ImageJ*. Biophotonics international, 2004. **11**(7): p. 36-42.
260. Schindelin, J., I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D.J. White, V. Hartenstein, K. Eliceiri, P. Tomancak, and A. Cardona, *Fiji: an open-source platform for biological-image analysis*. Nature Methods, 2012. **9**: p. 676.
261. Joblove, G.H. and D. Greenberg, *Color spaces for computer graphics*. SIGGRAPH Comput. Graph, 1978. **3**(12): p. 5.
262. Leach, R., *Characterisation of Areal Surface*. 2013, Berlin, Germany: Springer-Verlag. 353.
263. Leach, R.K., *The measurement of surface texture using stylus instruments*, in *Measurement Good practice Guide*. 2014, National Physics Laboratory.
264. Blateyron, F., *The Areal Field Parameters*, in *Characterisation of Areal Surface Texture*, R. Leach, Editor. 2013, Springer-Verlag: Berlin, Germany. p. 15-43.
265. Blateyron, F., *New 3D Parameters and Filtration Techniques for Surface Metrology*, in *Quality Magazine*. 2007.
266. Blateyron, F. *3D Parameters and New Filtration Techniques* in *Symposium proceeding of Japan Society of Precision Machining (JSPE)*. 2006. JSPE.
267. Waterworth, A., *Quantitative characterisation of surface finishes on stainless steel sheet*. 2006, University of Huddersfield. p. 222.
268. Kumar, S., D. Singh, and N.S. Kalsi, *Experimental Investigations of Surface Roughness of Inconel 718 under different Machining Conditions*. Materials Today: Proceedings, 2017. **4**(2, Part A): p. 1179-1185.
269. El-Taib Heakal, F., A.A. Ghoneim, A.S. Mogoda, and K. Awad, *Electrochemical behaviour of Ti–6Al–4V alloy and Ti in azide and halide solutions*. Corrosion Science, 2011. **53**(9): p. 2728-2737.
270. Klocke, F., A. Klink, D. Veselovac, D.K. Aspinwall, S.L. Soo, M. Schmidt, J. Schilp, G. Levy, and J.-P. Kruth, *Turbomachinery component manufacture by application of electrochemical, electro-physical and photonic processes*. CIRP Annals - Manufacturing Technology, 2014. **63**(2): p. 703-726.
271. McGeachie, J., E. Smith, P. Roberts, and M. Grounds, *Reaction of skeletal muscle to small implants of titanium or stainless steel: a quantitative histological and autoradiographic study*. Biomaterials, 1992. **13**(8): p. 562-568.
272. Speidel, A., J. Mitchell-Smith, D.A. Walsh, M. Hirsch, and A. Clare, *Electrolyte Jet Machining of Titanium Alloys Using Novel Electrolyte Solutions*. Procedia CIRP, 2016. **42**: p. 367-372.
273. Speidel, A., A.H.A. Lutey, J. Mitchell-Smith, G.A. Rance, E. Liverani, A. Ascari, A. Fortunato, and A. Clare, *Surface modification of mild steel using a combination*

- of laser and electrochemical processes. *Surface and Coatings Technology*, 2016. **307, Part A**: p. 849-860.
274. Schreiber, A., C. Rosenkranz, and M.M. Lohrengel, *Grain-dependent anodic dissolution of iron*. *Electrochimica Acta*, 2007. **52**(27): p. 7738-7745.
 275. Cook, N.H., S.P. Loutrel, and M.C. Meslink, *Increasing Electrochemical Machining Rates*. 1967, Massachusetts Institute of Technology. p. 124.
 276. Tobias, C.W., M. Eisenberg, and C.R. Wilke, *Diffusion and Convection in Electrolysis - A Theoretical Review*. *Journal of the electrochemical society*, 1952. **99**(12): p. 7.
 277. Landolt, D., P.F. Chauvy, and O. Zinger, *Electrochemical micromachining, polishing and surface structuring of metals: fundamental aspects and new developments*. *Electrochimica Acta*, 2003. **48**(20): p. 3185-3201.
 278. Jang, H., C. Park, and H. Kwon, *Photoelectrochemical analysis on the passive film formed on Ni in pH 8.5 buffer solution*. *Electrochimica Acta*, 2005. **50**(16): p. 3503-3508.
 279. Ebbing, D.D. and S.D. Gammon, *General chemistry*. 9th ed ed. 2010: Belmont, CA Brooks/Cole.
 280. Chen, X., Z. Xu, D. Zhu, Z. Fang, and D. Zhu, *Experimental research on electrochemical machining of titanium alloy Ti60 for a blisk*. *Chinese Journal of Aeronautics*, 2016. **29**(1): p. 274-282.
 281. Baxter, A.C., *Electrochemical Machining*, in *Mechanical Engineering*. 1967, The University of Warwick: Warwick. p. 96.
 282. Walker, J.C., T.J. Kamps, J.W. Lam, J. Mitchell-Smith, and A.T. Clare, *Tribological behaviour of an electrochemical jet machined textured Al-Si automotive cylinder liner material*. *Wear*, 2017. **376–377, Part B**: p. 1611-1621.
 283. Prakash, A. and K. Struik, *Roughness measurement of highly polished, mirror-finished surfaces*. *Precision Engineering*, 1981. **3**(4): p. 215-219.
 284. Dewanjee, M.K., *Radioiodination: Theory, Practice, and Biomedical Applications*. 2012: Springer US.
 285. Dean, J.A., *Lange's Handbook of Chemistry*. Fifteenth ed. 1999, New York: McGraw-Hill, Inc. 1291.
 286. Khan, Z., S. Fida, F. Nisar, and N. Alam, *Investigation of Intergranular Corrosion in 2nd stage gas turbine blades of an aircraft engine*. *Engineering Failure Analysis*, 2016. **68**: p. 197-209.
 287. McIlroy, C. and P.D. Olmsted, *Disentanglement effects on welding behaviour of polymer melts during the fused-filament-fabrication method for additive manufacturing*. *Polymer*, 2017. **123**: p. 376-391.
 288. Dargay, J., D. Gately, and M. Sommer, *Vehicle ownership and income growth, worldwide: 1960-2030*. *The Energy Journal*, 2007: p. 143-170.
 289. King, J., *The King Review of low-carbon cars Part I: the potential for reducing CO2 emissions from road transport*. 2008. **23**(08): p. 2011.
 290. IAI, *Improving sustainability in the transport sector through weight reduction and the application of aluminium-model*. 2008, IAI.
 291. Ifeu, H. and U. Lambrecht, *Energy savings by light-weighting–II. Final report for the International Aluminium Institute*. Institute for Energy and Environmental Research, Heidelberg, 2004.
 292. Chen, M. and A. Alpas, *Ultra-mild wear of a hypereutectic Al-18.5 wt.% Si alloy*. *Wear*, 2008. **265**(1-2): p. 186-195.
 293. Chen, M., T. Perry, and A. Alpas, *Ultra-mild wear in eutectic Al-Si alloys*. *Wear*, 2007. **263**(1-6): p. 552-561.
 294. Das, S., T. Perry, and S. Biswas, *Effect of surface etching on the lubricated sliding wear of an eutectic aluminium–silicon alloy*. *Tribology Letters*, 2006. **21**(3): p. 193-204.

295. Dienwiebel, M., K. Pöhlmann, and M. Scherge, *Origins of the wear resistance of AlSi cylinder bore surfaces studies by surface analytical tools*. Tribology International, 2007. **40**(10-12): p. 1597-1602.
296. Slattery, B., T. Perry, and A. Edrisy, *Microstructural evolution of a eutectic Al-Si engine subjected to severe running conditions*. Materials Science and Engineering A, 2009. **512**(1-2): p. 76-81.
297. Walker, J., W. Rainforth, and H. Jones, *Lubricated sliding wear behaviour of aluminium alloy composites*. Wear, 2005. **259**(1): p. 577-589.
298. Holmberg, K., P. Andersson, and A. Erdemir, *Global energy consumption due to friction in passenger cars*. Tribology International, 2012. **47**: p. 221-234.
299. Etsion, I., *State of the art in laser surface texturing*. J. Tribol., 2005. **127**(1): p. 248-253.
300. Ronen, A., I. Etsion, and Y. Kligerman, *Friction-reducing surface-texturing in reciprocating automotive components*. Tribology Transactions, 2001. **44**(3): p. 359-366.
301. Ryk, G., Y. Kligerman, and I. Etsion, *Experimental investigation of laser surface texturing for reciprocating automotive components*. Tribology Transactions, 2002. **45**(4): p. 444-449.
302. Andersson, P., J. Koskinen, S.e. Varjus, Y. Gerbig, H. Haefke, S. Georgiou, B. Zhmud, and W. Buss, *Microlubrication effect by laser-textured steel surfaces*. Wear, 2007. **262**(3): p. 369-379.
303. Borghi, A., E. Gualtieri, D. Marchetto, L. Moretti, and S. Valeri, *Tribological effects of surface texturing on nitriding steel for high-performance engine applications*. Wear, 2008. **265**(7): p. 1046-1051.
304. Costa, H. and I. Hutchings, *Hydrodynamic lubrication of textured steel surfaces under reciprocating sliding conditions*. Tribology International, 2007. **40**(8): p. 1227-1238.
305. Costa, H. and I. Hutchings, *Some innovative surface texturing techniques for tribological purposes*. Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 2015. **229**(4): p. 429-448.
306. Gao, L., P. Yang, I. Dymond, J. Fisher, and Z. Jin, *Effect of surface texturing on the elastohydrodynamic lubrication analysis of metal-on-metal hip implants*. Tribology International, 2010. **43**(10): p. 1851-1860.
307. Kovalchenko, A., O. Ajayi, A. Erdemir, G. Fenske, and I. Etsion, *The effect of laser surface texturing on transitions in lubrication regimes during unidirectional sliding contact*. Tribology International, 2005. **38**(3): p. 219-225.
308. Pettersson, U. and S. Jacobson, *Influence of surface texture on boundary lubricated sliding contacts*. Tribology International, 2003. **36**(11): p. 857-864.
309. Podgornik, B. and M. Sedlacek, *Performance, characterization and design of textured surfaces*. Journal of Tribology, 2012. **134**(4): p. 041701.
310. Ramesh, A., W. Akram, S.P. Mishra, A.H. Cannon, A.A. Polycarpou, and W.P. King, *Friction characteristics of microtextured surfaces under mixed and hydrodynamic lubrication*. Tribology International, 2013. **57**: p. 170-176.
311. Vladescu, S.-C., A.V. Olver, I.G. Pegg, and T. Reddyhoff, *The effects of surface texture in reciprocating contacts – An experimental study*. Tribology International, 2015. **82**, Part A: p. 28-42.
312. Yu, H., X. Wang, and F. Zhou, *Geometric shape effects of surface texture on the generation of hydrodynamic pressure between conformal contacting surfaces*. Tribology Letters, 2010. **37**(2): p. 123-130.
313. Costa, H.L. and I.M. Hutchings, *Hydrodynamic lubrication of textured steel surfaces under reciprocating sliding conditions*. Tribology International, 2007. **40**(8): p. 1227-1238.
314. Podgornik, B. and M. Sedlacek, *Performance, Characterization and Design of Textured Surfaces*. Journal of Tribology, 2012. **134**(4): p. 041701-041701-7.

315. *ASM Handbook, Volume 2 - Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*. 2nd ed. 2000, Materials Park, Ohio: ASM International.
316. Kligerman, Y., I. Etsion, and A. Shinkarenko, *Improving Tribological Performance of Piston Rings by Partial Surface Texturing*. Journal of Tribology, 2005. **127**(3): p. 632-638.
317. Capulli, M., R. Paone, and N. Rucci, *Osteoblast and osteocyte: Games without frontiers*. Archives of Biochemistry and Biophysics, 2014. **561**(Supplement C): p. 3-12.
318. Florencio-Silva, R., G.R.d.S. Sasso, E. Sasso-Cerri, M.J. Simões, and P.S. Cerri, *Biology of Bone Tissue: Structure, Function, and Factors That Influence Bone Cells*. BioMed Research International, 2015. **2015**: p. 421746.
319. Denhardt, D.T. and M. Noda, *Osteopontin expression and function: role in bone remodeling*. J Cell Biochem Suppl, 1998. **30-31**: p. 92-102.
320. Shibata, Y. and Y. Tanimoto, *A review of improved fixation methods for dental implants. Part I: Surface optimization for rapid osseointegration*. Journal of Prosthodontic Research, 2015. **59**(1): p. 20-33.
321. Coelho, P.G., R. Jimbo, N. Tovar, and E.A. Bonfante, *Osseointegration: Hierarchical designing encompassing the micrometer, micrometer, and nanometer length scales*. Dental Materials, 2015. **31**(1): p. 37-52.

Appendix:

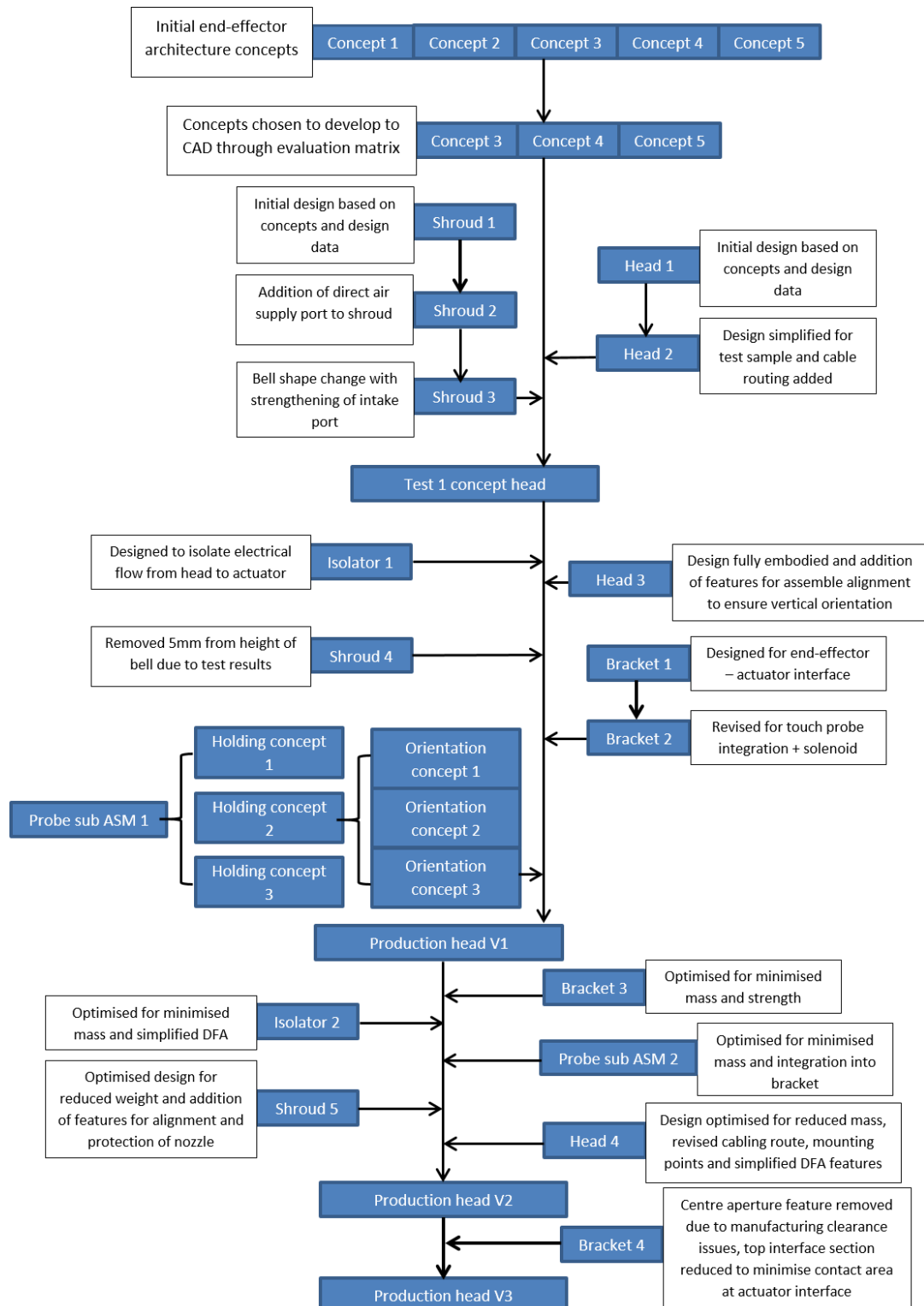
1. Statement of requirements (SoR) for EJP machine tool

Req. #	Requirement
1	Machine must be capable of controlled material removal utilising the EJM process
2	The machine must be capable of machining on a sub millimetre scale
3	The machine should be capable of creating a pre-defined pattern
4	The machine should be modular in design to allow for future expansion
5	The machine should have 3 axis (x, y, z)
6	The machine should be safe in operation and avoid direct user interface
7	The machine in its entirety should meet all relevant safety standards and practice in-line with HSE and UoN health and safety manual
8	All systems should be integrated as far as practicable and should include: • Controlled spatial movement of end-effector • Controlled and variable electrolyte flow • Controlled and variable electrical power (current and voltage)

9	Nozzle spatial feedback should be provided
10	End-effector should be capable of a minimum traverse speed of 50 $\mu\text{m/s}$
11	Current density should be aimed to be able to achieve a resolution of 2 A/cm^2
12	Head design should include: • Nozzle I.D. of 200 μm • Be interchangeable to allow for different jet sizes • Incorporate a compressed air shroud co-axially to the electrolyte jet
13	End-effector should be controlled to a resolution of 1 μm in x and y axis and 100 μm in z.
14	The control system should reflect the resolution possible in repeatability and accuracy
15	Jet access to the component should be maximised
16	Provision of a storage facility for supply of solution
17	Supply pressure from the electrolyte tank should range from 0.3 Mpa to 0.5 Mpa
18	Machine must be capable of a minimum 30-minute continuous machining run time

19	Provision should be made for removal of solution and debris from the work interface
20	Method must be provided to capture waste solution
21	The work envelope should be 200 x 200 x 200 mm
22	There should be ease of workpiece unloading / loading (placement) considering the scale of components
23	The following systems should have dynamic capability as far as possible to allow for continual change of parameters during operation: • Axis control • Electrolyte flow • Electrical current
24	Jet nozzle should be treated as a consumable
25	Control system should include a traditional style CNC GUI
26	All PC to Machine interfaces should utilise modern communication interfaces (USB and / or Ethernet) to allow control from any modern laptop or PC

2. Example of design iteration map



Example of a design iteration map used in the design and evolution of the generation 1 platform, in this case for a re-design of the end effector

3. Machine upgrades Gen. 1 to Gen. 1.5

Nozzle touch sense – Removed due to IP consideration.

Multiple electrolyte control – Introduction of an extra electrolyte tank and rinse tank holding deionised water has meant quick selection of a different electrolyte types and automatic cleaning regimes of the pump and electrolyte lines can be implemented. Controlled by solenoids from an output on the machine CPU which is activated as part of the control program has meant ease of operator use in machining different materials requiring different electrolytes and aid in housekeeping of the machine and components.

Head development – Throughout the development of the Generation 1 machine continual modifications of the head geometry and design have been required to fit innovations and simplification of architecture. For example, the removal of the external touch probe system (seen in Figure 3.4) to set the IEG distance, being replaced by the touch sense system meant the head design could be vastly simplified. The incorporation of 3D printing techniques allowed rapid design and assessment of varying components within the head. Both the head bracket and shroud seen in Figure 3.6, being designed and manufactured by fused filament fabrication (FFF) [287] allowing for simplistic designs with optimised configurations. When coated with enamel paint, and due to the load exerted on the head, these make serviceable components that are low cost, water and air tight, and inherently provide corrosion resistance and electrical isolation due to their polymer construction.

Component upgrades – Throughout the course of the generation 1 machine development limitations, and material and component failure arose as the

technique was refined. Material wise it was found that only high grade stainless steel (grade 316, 2205 Duplex and Superduplex) and polymers were suitable for any component within the machine tool. Even outside the direct interaction zone of the jet, the atomised electrolyte plume would reach and corrode any un-coated metallic component within the machine tool body. Where components were required to be light weight and load-bearing, aluminium alloy was used with a coating applied to avoid oxidation. The main power supply to the IEG was also an area that required significant improvement as the process developed with increasing demands on power and remote capability in terms of reaction speed and resolution to commands produced as part of the main control program. This exemplifies one of the main ethos of the design development that all peripheral controls should be computer numerically controlled (CNC) and controllable dynamically by the tool path specific master control program.

Machine architecture – In the same manner as component upgrades, as the process developed so the machine architecture was required to change with it. This was made feasible by the adherence to the original design requirement of the machine adopting a modular design in order to allow for changes due to research outcomes. The main changes being the addition of a secondary module to house the expanding peripheral control systems, PSU, electrolyte tanks and fixturing for the controller and modification of the z-axis and machine table to allow the motion, accuracy and resolution now required.

4. Key improvements over Gen. 1.5 platform

Fluid management (architecture schematic shown in figure App 1) – *Removed due to IP consideration*

Air management (system architecture is shown in Figure App 3) – *Removed due to IP consideration.*

Removed due to IP consideration

Figure App1: Schematic of the fluid management system incorporated in generation 2 machine tool

Removed due to IP consideration

Figure App 2: Example of a looping program architecture used for peripheral control in this case for the electrolyte recirculation system

Control (System architecture shown in Figure App 4) – For the Generation 2 machine design the emphasis was on complete automation of all core and peripheral functions alongside maximising operator usability. To this ends all functions, including those that were previously manual, such as setting polarity, can now be controlled as a function of the master control program for an individual part. Via a CAN-bus expansion system all peripheral systems are connected to the machine CPU either directly to the I/O ports (digital or Analogue) or the via contactors in the case of polarity, nozzle touch sense and 12 V pump supply.

Removed due to IP consideration

Figure App 3: air flow management (a) schematic of compressed air system (b) excerpt from 3D model showing extraction system sectioned (c) image of extraction system and compressed air system during machine construction

Contactors are now also used for the emergency stop system whereby the E-stop button controls the contactors which allows power to flow to the 24 V, 12 V and nozzle PSU's alongside the axis drivers. This means that if the E-stop button

is activated the entire machine is instantly cut dead. The axis is now driven by servo motors rather than steppers used in the generation 1, giving superior resolution and smoothing of the translation movement. This was deemed necessary due to the direct relation between dwell of the jet and material removal, therefore any latency or oscillation in the translation will directly impact on the created feature geometry and surface roughness.

Removed due to IP consideration

Figure App 4: Generation 2 Control and power architecture schematic

5. Application of energy modulation in deposition

It was demonstrated that modifications to the electrolyte jet nozzle tip to affect changes in in-jet resistance are also applicable in deposition mode.

A simplistic parameter window was developed that showed that formed structure morphology and precision is highly dependent on the energy experienced within in the IEG and a balance must be found between current density, traverse speed and electrolyte concentration.

Utilising the defined parameters OSPE and STE nozzle designs were employed to create layered structures distinct from that found when a standard nozzle is used. This shows potential for future development as a layer based additive manufacturing technology.

However, the morphology of the structures is still found to be quite poor and prone to peripheral artefacts when non-acidified solutions are used. Further development of the electrolyte chemistry and refinement of processing parameters especially relating to dynamic application is required to create repeatable and reliable structures.

Dynamic process window definition

Experimental studies were carried out utilising the generation 1 research platform (see section 3.1). A 0.5 mm I.D. nozzle was employed, and electrolyte jet speed was set at 16 m/s. The IEG was initially set at 0.5 mm. Tracks of 15 mm length were deposited on polished copper substrate (in this case the cathode) to allow analysis at different points along the tracks. Current densities investigated were skewed to the lower end of the machines capabilities. This decision was

made from observations by prior research [38]. The feed rate and the concentrations used can be seen in Table 5.1

Within these tests, the higher end of current density was not used with the lowest copper concentration because the voltage supplied had reached its maximum point, hence no further current would be supplied as the resistance of the solution was too high. Attempting to run the highest current density would result in a greater risk of arcing between the nozzle and the cathode as the easier current pathway was external to the jet. This would jeopardise the experiment as the nozzle would become deformed in the process, affecting the form of the impinging jet, potentially skewing results and creating data unrepresentative of the process as intended.

Table 5.1: Parameters used for track depositions

Parameter	Magnitude
Nozzle travers speed (mm/s)	0.2, 2, 20
CuSO ₄ .5H ₂ O Concentration (Moles)	0.01, 0.1, 1
Current Density (A/cm ²)	4, 9, 15, 40

In almost all cases current densities beyond 9 A/cm² led to poor feature definition and a rougher finish with more dendritic copper artefacts being formed on the surface rather than contributing to the bulk. It appears there is a cut-off point of a combination of feed rate and current density, at which few or no dendritic structures form as can be seen in Table 5.2. The formation of dendritic structures is clear in the 3D surface maps seen in Figure App 5, in which sharp towers appear. These findings agree with work previously carried out by Bocking in 1994 [5] for spot deposition. It was stated that with similar parameters, beyond 5 A/cm²,

structures with higher porosity formed. It was found that in every deposit at 20mm/s as well as many deposits with 0.01M copper sulphate concentration that the copper deposit would not cover the impingement region, giving rise to isolated deposition regions. This is thought to be due to the lack of energy density available to reduce dissolved metal cations in comparison the same sporadic occurrence of deposition occurred when a concentration of 0.1M copper sulphate was used but this instead is due to the lack of cations present in the electrolyte to be converted.

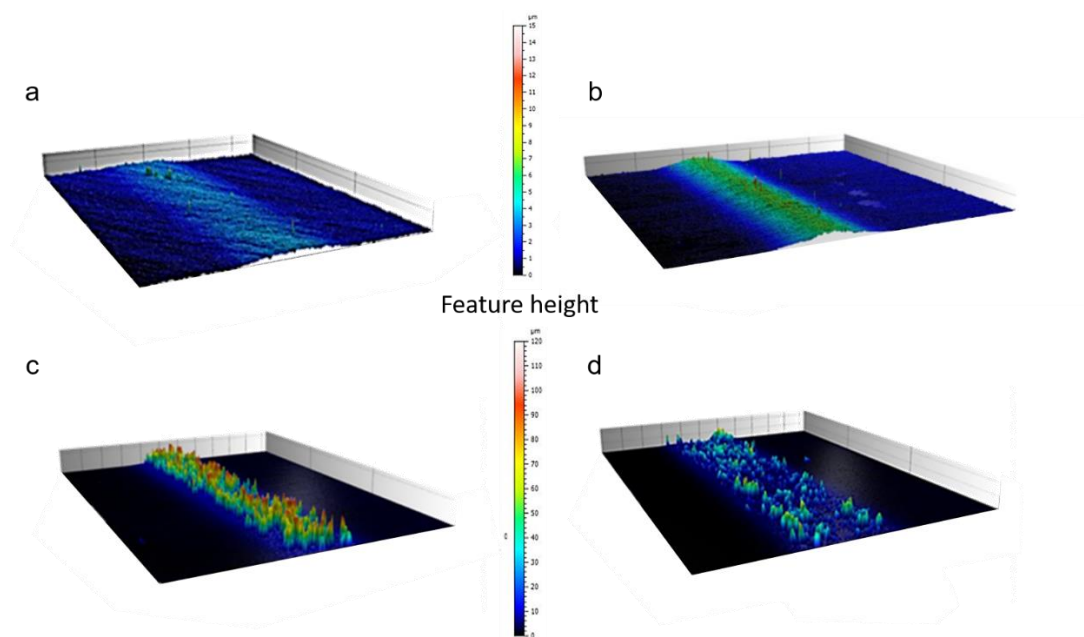


Figure App 5 Morphology and roughness at 0.2mm/s feed rate, 0.1M CuSO_4 concentration. a) 4.4 A/cm^2 b) 9.3 A/cm^2 c) 15.2 A/cm^2 d) 39.2 A/cm^2 . Note increased height scale on c and d

Table 5.2: Qualitative information of deposition structure with varying parameters

Parameters		Current Density (A/cm ²)			
Copper concentration (M)	Feed rate (mm/s)	4	9	15	40
0.01	0.2	Nodular, incomplete surface	Nodular	Nodular	N/A
0.01	2	Nodular, incomplete surface	Nodular	Nodular, incomplete surface	N/A
0.1	0.2	Nodular	Nodular	Nodular, dendritic	Nodular, dendritic
0.1	2	Smooth	Smooth	Nodular	Nodular, dendritic
1	0.2	Smooth	Smooth	Merged	Nodular, dendritic
1	2	Smooth	Smooth	Smooth	Nodular

The higher the concentration of the electrolytes used, the more likely a deposit is to be smooth as is seen in Table 5.2. This pattern also follows the trend noted by Bocking in 1994 [5], stating that a higher concentration enables a greater usable current density. Above this usable current density deposits tend to form nodular and dendritic structures.

It can be observed that with increased current density the width of the tracks increases. Using the 0.1 M copper sulphate solution, the width of the deposit plateaued as current density increased. However, with the 1 M solution, this width continues to increase. This increase continues to the extent that the more concentrated solution produced a larger width than the 0.1 M solution when it was traversing at ten times the feed rate. This is likely due to the increased maximum

current density, which therefore increases plating rate. The trend of increased plating rate was documented by Bocking 1992 [8] when using a sulfuric acid based copper solution.

These initial findings demonstrate the balance that is required between ionic strength and the available energy within the jet in order to achieve precise and homogeneous deposited structures.

A process window was selected of 1 M concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, feed rate of 2 mm/s and current density of 4 A/cm² and an IEG of 0.5 mm. These parameters were modified to suit a 1 mm I.D. nozzle and employed with the OSPE and STE nozzles (Figure 5.18) with 100 passes over the same toolpath but with a lift in the Z direction of 0.02 mm every two passes in order to maintain the intended IEG as the deposition grew.

Results

Examples of the resultant profiles of these depositions can be seen in Figure App. 6 It is immediately obvious the modified current density field has impacted on the shape of the deposition. There are acute similarities between the additive and subtractive resultant profiles with a shift in the maximum feature height from the centre as expected from a standard nozzle to one side with the OSPE nozzle (Figure App 6a). With the STE nozzle (Figure App 6b) the maxima of the feature is widened from that expected resembling that of a multi-pass feature with a blunt feature tip rather than a sharper peak as expected with a typical Gaussian current distribution.

The OSPE nozzle achieving a deposition rate of 470 nm per layer and the STE nozzle achieving 550 nm per layer. This corresponds to increased resistance

found with the OSPE nozzle in comparison to the STE nozzle seen in Figure App 6b and demonstrates a direct correlation between resistance within the IEG and deposition rates.

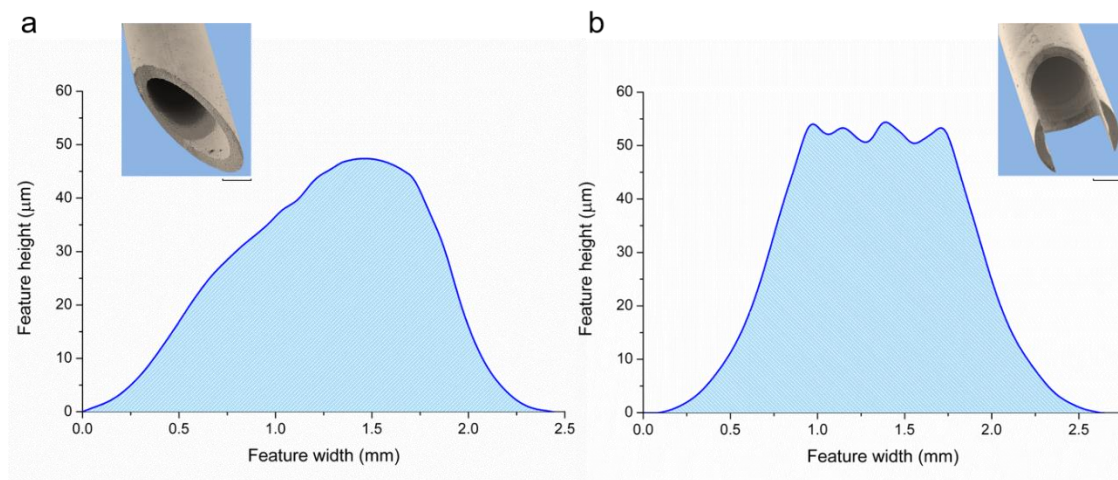


Figure App.6: Exemplar profiles of additive features generated with modified nozzles (a) OSPE nozzle (shown in insert) (b) STE nozzle (shown in insert). Scale bars are 500 μm

It can be seen however in Figure App 7 that the microstructure of the depositions is quite poor and inhomogeneous with isolated copper artefacts created on the surface. Although the deposits are adherent to the surface and structurally solid, further development of the chemistry and processing parameters is required to make 3D additive structuring a variable free-form fabrication technique. Research is currently being undertaken to this end through the use of organic and non-organic additives in order to improve and control the resulting micro-structure .

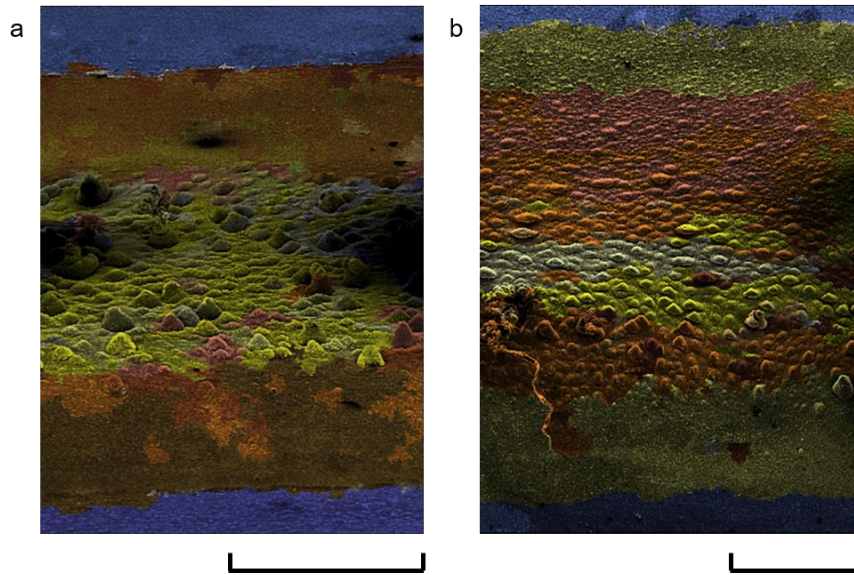


Figure App 7: Coloured SEM images of deposition structures (a) STE nozzle design (b) OSPE nozzle design

6. Tribological behaviour of an electrochemical jet machined textured Al-Si automotive cylinder liner material tribological testing methodology

Introduction

Projected increases in worldwide automotive vehicle numbers [288] place an ever increasing emphasis on improvements to vehicle fuel economy and reduction of environmental emissions in an effort to achieve sustainability [289]. Vehicle lightweighting technology is one means to achieve this objective [290, 291] and has seen increasing research and development of aluminium alloys and composites for use in engine applications, in particular the wear resistant eutectic Al-Si system [292-297]. Holmberg et al [298] suggested that on average, 45% of energy losses in a typical internal combustion engine are used to overcome friction within the piston assembly. This has led in recent years to intensive

research into the applicability of surface texturing to the cylinder bore surfaces. Early work by Etsion et al. [299-301] into the applicability of laser surface texturing to automotive contacts has led to a significant body of literature on the applicability of this technique for improving frictional performance of reciprocating engine components [302-312]. However, the applicability of surface texturing for enhanced tribological properties is not universal and improvements in frictional response of sliding couples are sensitive to both the texture geometry as well as the contact environment. Dimple size (depth, diameter) has been identified as a key variable of texturing performance as well as the areal coverage of the feature density [313, 314]. Hence the precision of the application process is critical. The sliding parameters that the contact operates under, namely the lubrication regime, fluid viscosity and contact geometry also strongly determine if texturing is beneficial or detrimental to the overall friction and wear performance [311].

Application of surface textures in this field, has in the most part been demonstrated by laser micro-machining. However, as noted in section 2.6, laser surface texturing of metallic surfaces is prone to a number of drawbacks. The microstructure in the immediate vicinity of textured features is often altered as a result of the heat energy input. Concurrently, the presence of surface lips or burs around features can compromise friction and wear performance without a further machining step to remove them [302, 305, 307-309, 311]. As noted in section 2.6 this can somewhat be overcome using femto second lasers. However, the intended application in the automotive sector greatly influences the capital expenditure required to implement such a system.

This study investigates the applicability of subtractive mode EJP to surface texture a hyper-eutectic Al-Si alloy for lubricated reciprocating tribological testing

and compares the feature generation to that created by laser for the same application.

Methodology

This investigation was carried out in conjunction with the national centre for advanced tribology, Southampton (nCATS) who carried out the tribological testing and analysis. The methodology for this can be found in appendix 6.

A hyper-eutectic A390 Al-Si alloy, nominal composition indicated in Table App 6.1, was obtained from MS International GmbH, Germany, in the form of a cylinder liner blank. Rectangular samples 58 x 20 x 4mm were prepared using an electro-discharge machine (Sodick SLC600G), such that the long dimension was parallel with the cylindrical liner axis. Samples were then parallel flat lapped using a Kemet 15 lapping machine with 25 μm diamond suspension. Surfaces for tribological testing were further polished using the same lapping procedure down to a 6 μm diamond suspension finish. To expose the load bearing primary silicon colonies from the matrix, each sample was immersed in a 10% NaOH solution for 180 seconds before being cleaning in de-ionised water.

Table App 6.1: Nominal weight percentage of a A390 alloy [315]

Al-Si	Si	Cu	Mg	Zn	Al
wt %	17.0	4.5	0.6	0.5	Bal.

Considering the analysis carried out in chapter 4 and noting the electrode potential of Aluminium ($E^0 \text{ Al(s)} \rightarrow \text{Al}^{3+}_{(\text{aq})} + 3e^{-1} = 1.662 \text{ V vs SHE}$) when compared to titanium ($E^0 \text{ Ti(s)} \rightarrow \text{Ti}^{2+}_{(\text{aq})} + 2e^{-1} = 1.63 \text{ V vs SHE}$), to achieve an aspect ratio of 0.1 it would be expected that a similar current density too that used

in titanium to could be employed ($\approx 400 \text{ A/cm}^2$). This is taking into account initial testing that found a $0.15 \text{ }\mu\text{m}$ nozzle would generate $\approx 400 \text{ }\mu\text{m}$ diameter dimple. The wider than normal diameter likely due to passivation effects similar to titanium (see Chapter 4) and the inert silicon inclusions resisting machining. However, a further two factors need to be considered to ascertain the required applied parameters. Firstly, as seen in the machining of titanium in Chapter 4, the low resistivity of aluminium leads to enhanced machining of aluminium elements. This means when machining Al substrates more energy is available at the anode surface due to the ease of transition of charge through the substrate. Thus, less energy is required for similar removal than titanium. Secondly, seen in the machining of In718 (Chapter 4) the precipitate wash-out can have a large effect on enhancing MRR. In Al-Si the silicon inclusions are large, therefore wash-out is also likely to mean again much less energy is required to achieve the correct depth and may lead to a high level of feature size variance. These factors alone make it difficult to theoretically define the required energy. Due to this an initial test was used to determine the correct energy requirement. A series of holes was machined in an array using a fixed dwell but varied J values from 100 A/cm^2 through to 400 A/cm^2 . From this it was found that the correct depth can be achieved with just 220 A/cm^2 considerable less than that expected (Figure App 6.1), although the variance to the profile shape caused by the inert inclusions is obvious and expected being similar to that found in the literature review in MMC's (see section 2.3.6)

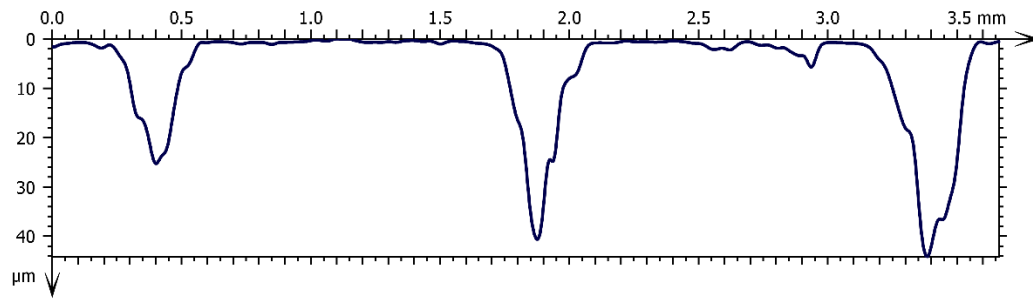


Figure App 6.1: Extracted profile section of aspect ratio tests with actual parameters used in the centre

The process parameter sets for both laser and EJP are shown in Table App 6.2. These remained constant across all samples.

Table App 6.2 EJP and Laser parameter set

EJP parameters		Laser parameters	
Electrolyte	NaCl @ 2.3 mol.	Laser	2 kW IPG Ytterbium doped, CW, fibre
IEG	500 μm	Wavelength	1070 nm
Nozzle Size (I.D.)	152 μm	Inclination	15°
Dwell Time	1.5 s.	Dwell	5 ms
Current Density	220 A/cm ²		
Electrolyte Flow Rate	80 ml/min		

The laser processing was carried out at the University of Southampton on a 3-axis laser with a pre-programmed toolpath. Dimple depth was selected based on an ϵ -ratio (depth/diameter) of 0.1, which had been previously reported in the literature to be the optimum ratio of low friction performance [300, 316]. A dimple spacing distance of 5D was created, where D is the dimple diameter. For processing by EJP a fixed current and floating voltage was used to machine a 12 x 19 array of dimples ($\varnothing$ 420 μm x Depth 42 μm) created using a bouncing type tool path, Figure App 6.2 , taking $\approx$ 20 minutes per sample. Between each dwell

point used to create the dimple, the end-effector arcs rapidly away from the surface to ensure dissolution only develops at the desired point. This occurs by rapidly increasing stand-off therefore the in-jet resistance, so no stray current can affect dissolution and maintains pattern precision. Repeatability of the array positioning relative to the workpiece was maintained throughout the generation of all samples by use of the touch sense datum system. This allows the start point (X, Y) and nozzle stand-off (Z) to be set relative to the workpiece surfaces using the nozzle for positional feedback.

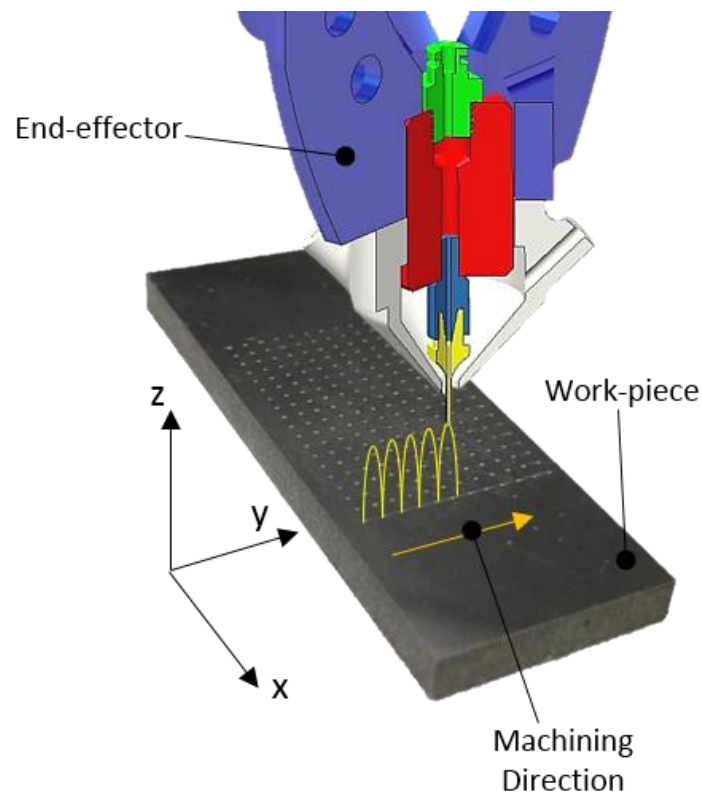


Figure App 6.2: Schematic of EJP sample generation tool path including actual machined sample

Textured samples we tested in a lubricated reciprocating sliding line contact configuration against a 52100 G5 roller bearing element (6mm diameter, 16mm length, Bearing Boys, UK) using a Phoenix Tribology TE77 high frequency

reciprocating tribometer. Prior to assembly, both the flat liner samples and cylindrical roller bearing elements were ultrasonically cleaned and de-greased in a solution of 60–80 petroleum ether and weighted using a precision balance to within 1×10^{-5} g. The liner was then immersed in a bath of unformulated synthetic polyalphaolefin (PAO, SpectraSyn 4, ExxonMobil) with a kinematic viscosity of 4 cSt at 100°C. The dynamic viscosity of the lubricating fluid was determined for the test temperature as 0.0316 Pa.s using an Anton Paar MCR302 viscometer at 21.7°C and shear rates between 10 to 1000 reciprocal seconds. A normal load of 50N (corresponding to an initial Hertzian line contact pressure of 141.9 MPa) was applied to the counter surface and reciprocating sliding at a stroke length of 25mm conducted at frequency increments of 1 Hz every 40 seconds between 1–16 Hz. Once complete, the normal load was incremented 50N and the frequency sweep repeated, up to a maximum normal load of 200N. The test was repeated using an un-textured liner sample prepared in the same way outlined above. Average friction coefficient data was plotted against a mid-stroke Hersey Number to generate Stribeck curves in order to determine changes in trends arising from the surface texturing during different lubrication regimes.

Results

The results of the laser processing can be seen in Figure App 6.3a, b and compared to the EJP created dimple (Figure App 6.3c). Figure App 6.3a, shows the laser created dimple demonstrating that the thermally loaded surface through ablation leads to edge burs. Figure App 6.3b shows the laser created dimple after post processing to remove the burs, noting that this compromises the Si particle condition. In comparison the dimple created by EJP (Figure App 6.3c) demonstrates clean burr-free edges requiring no post processing. The Si particle

distribution is also un-disturbed as the preferential machining using short processing times preferentially removes the matrix alloy leaving behind the carbide in the same manner as the findings of In718 in chapter 3.8.3.

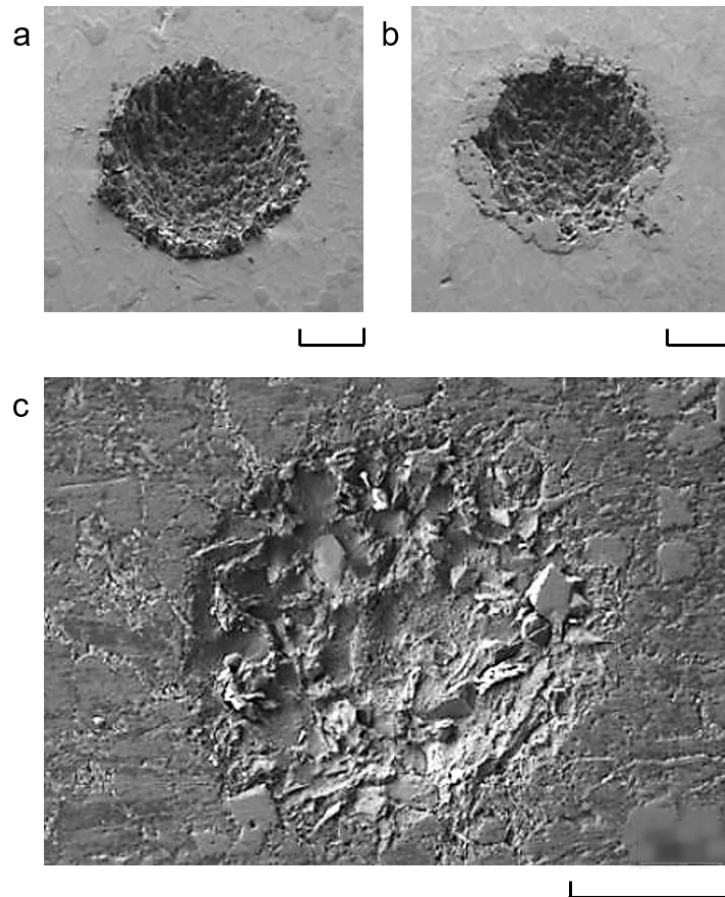


Figure App 6.3: comparison of features created for reduced wear surface by (a) laser (b) laser after post process edge removal (c) by EJP with Si particle remaining. All scale bars are 100 μm

The machined texture pattern was a rectangular array of hemispherical dimples, measured at $1.50 \pm 0.01\text{mm}$ intervals (Figure App.6.4). The average dimple radius was measured to be $210 \pm 4\mu\text{m}$, whilst the corresponding dimple depth was measured to be $40 \pm 3\mu\text{m}$. This corresponded to a depth/diameter ratio, ϵ , of 0.095 and a surface dimple area coverage of 6.2%. The colour depth map and line profile in Figure App.6.4b and c clearly showed the absence of any burs or

lips at the edge of each dimple, however the centre of the dimple appeared more uneven and less hemispherical.

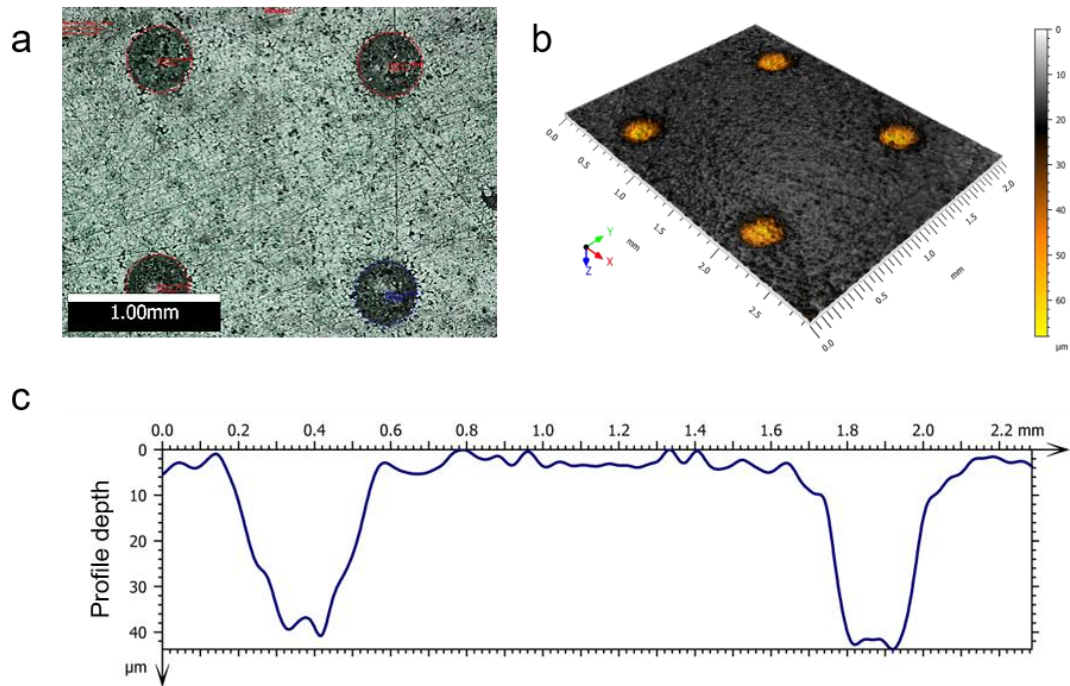


Figure App.6.4: Analysis of dimple array (a) optical image, (b) surface reconstruction depth map and (c) profile of created dimples

Higher magnification inspection using SEM, Figure App.6.5, revealed an etched cavity with a rough surface, corresponding to the angular morphology of primary silicon particles. Indeed, some such particles were still present within the feature.



Figure App.6.5: Angled SEM image of dimple revealing the etched structure around the inclusion (scale bar 200 μm)

Inspection of the surfaces post the wear tests (Figure App.6.6), show the created dimples have maintained their form showing no signs of deterioration and the revealed silicon still remaining intact in the dimple bases. It can be seen however that there are noticeable topographical differences arising from the texturing. A discontinuity in the surface damage can be observed in the space between the textured lines according to the direction of the sliding mechanism. The reciprocating sliding direction being horizontal (Figure App.6.6a). The most significant amount of wear appears to have taken place between the textured features, parallel to the sliding direction, in the centre of both Figure App.6.6a and b. However, closer inspection of the surface topography (Figure App.6.6c and d) indicates that this area is in fact raised above the surrounding surface. Inspection of the worn counter surface did not reveal any such discontinuity as a result of the textured pattern, presenting an evenly worn, flat surface of width $1.08 \pm 0.27\text{mm}$. Higher magnification SEM images in Figure App.6.6b suggests differences in the surface morphology around the primary silicon particles. It can be seen from Figure App.6.6c, taken from within the raised area, that the primary silicon particles are no longer raised above the surrounding matrix, being flush with the surrounding material. In contrast, Figure App.6.6d, which was taken from an area next to a textured feature in the same horizontal plane, indicating that the primary silicon particles retain their step height difference from the etching phase, being raised above the surrounding matrix.

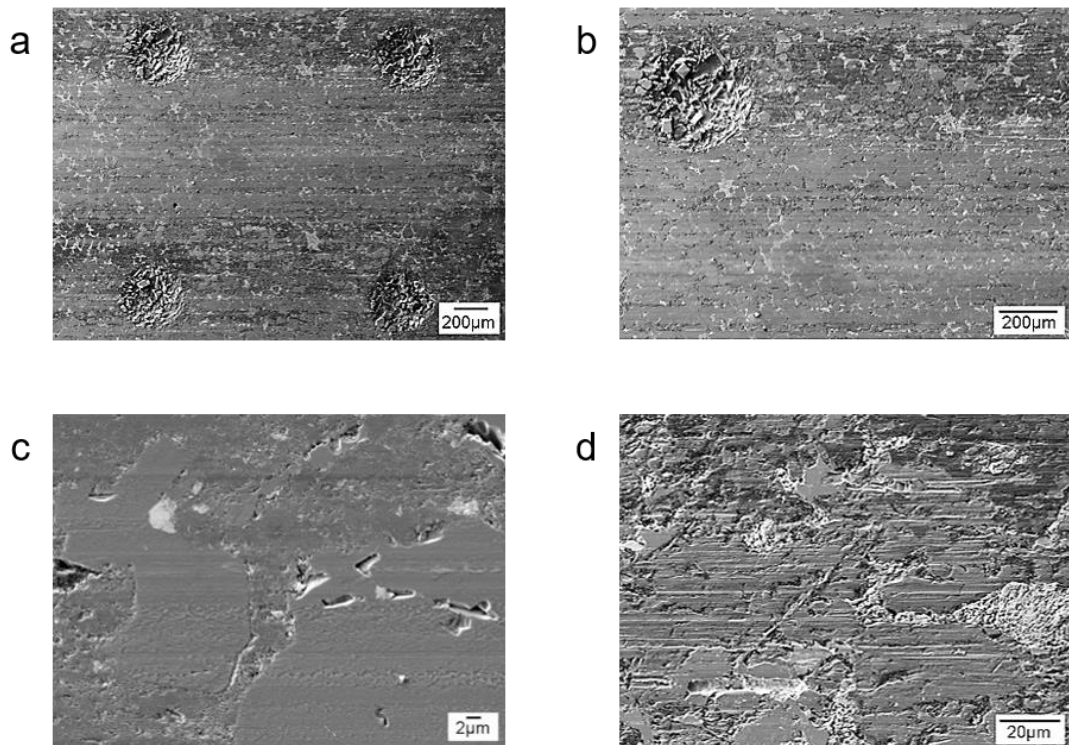


Figure App.6.6: SEM images of the worn textured Al-Si surface after sliding wear tests at 100 N, 10 Hz demonstrating the different wear patterns created by the texture inclusion (a) and (b). Higher magnification images of the areas on the surface directly below the dimple (c) and to the right (d)

The interface of the raised area was examined in further detail with EDS (defined in section 3.5.2) (Figure App.6.7). The area corresponding to A exhibited the presence of Fe and Cr species only in the area of the raised tribo-layer, whilst the area next to a dimple marked as B showed no evidence of compounds associated with the composition of the counter-face material. Such a mechanism was similar to that proposed by Dienwiebel et al. [2007] [295] for tribological conditioning of an Al-Si surface, with wear debris particles re-embedding themselves into the relatively soft aluminium matrix, leading to friction induced dispersion hardening.

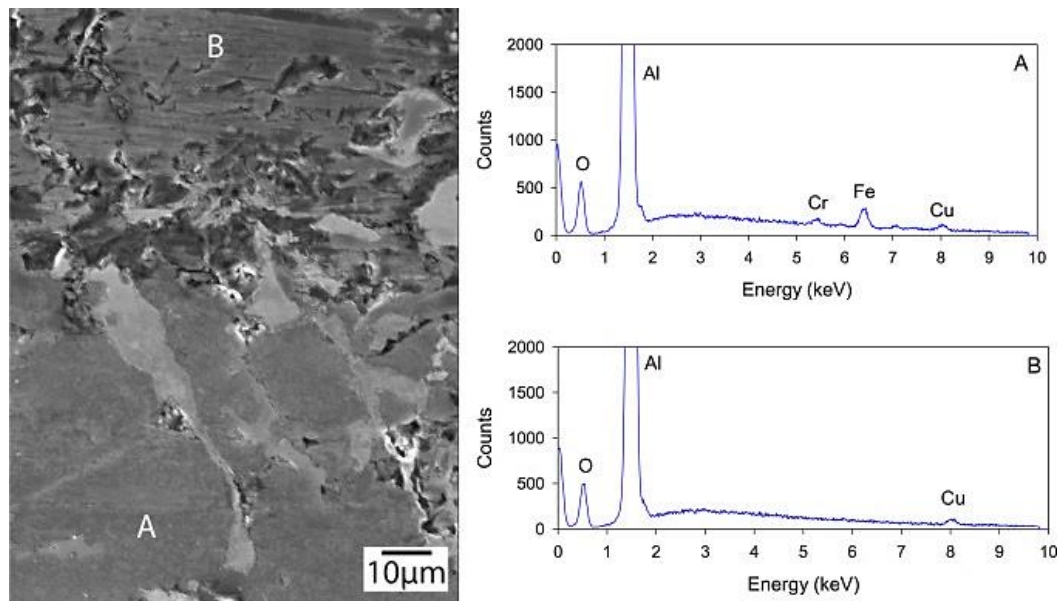


Figure App.6.7: SEM imaging from the transition area between wear regimes and EDS data from the areas marked A and B

This tribo layer was formed due to the silicon particles in these regions being effective as two body abrasives against the counter surface, causing an order of magnitude increase in mass loss from the counter surface. This was due to the similar hardness of the silicon particles (Hv 747) and the counter-surface (Hv 788). In traditional preparation of a bore lining, the mechanical honing of Al-Si alloys produces more rounded apexes on the silicon particles, an etched exposure of the silicon as used in this study tends to leave angular particles that are more effective at two body abrasion as they are microscopically individually harder than the ferrous counter surface matrix. Wear debris was subsequently transferred to the liner and formed a compacted tribo-layer around the silicon colonies, such that they no longer protruded above the surface.

Average coefficient of friction values for both textured and un-textured surfaces over the range of conditions tested initially are shown in Figure App.6.8. It can be seen that in the boundary to mixed lubrication regime, the textured surfaces

displayed a lower coefficient of friction for all conditions tested. In particular, at the 50N and 150N conditions, decreases in average coefficient of friction in the mixed lubrication regime were from 0.13 for the un-textured to 0.08 for the textured sample, approximately a 38.5% decrease.

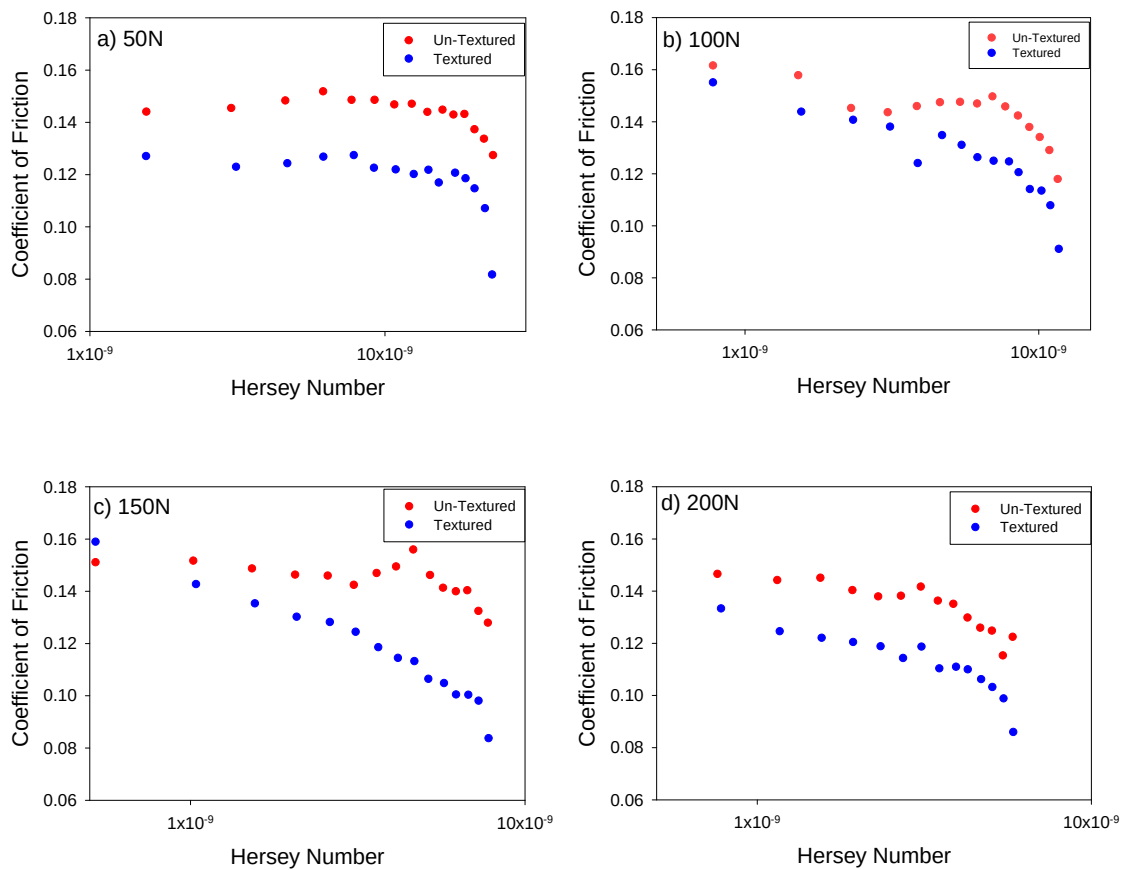


Figure App.6.8: Stribeck curves for textured and un-textured surfaces at a)50N; b)100N; c)150N and d)200N.

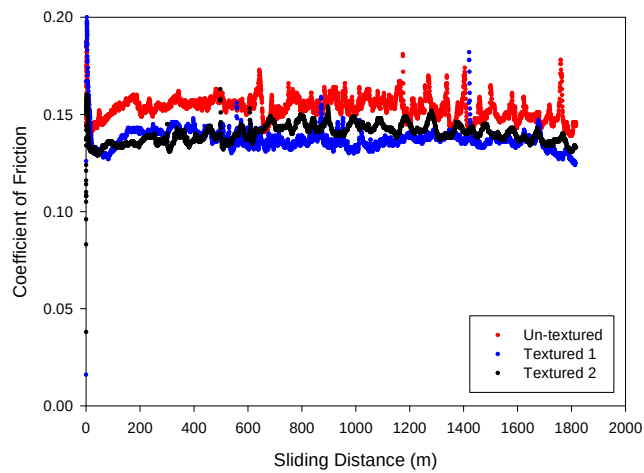


Figure App.6.9: Average coefficient of friction for tests conducted at 100N and 10Hz.

Wear testing within the boundary lubrication regime at a constant set of conditions (100N, 10Hz), Figure App.6.9, also resulted in a decrease in the average coefficient of friction of a textured surface (0.138 ± 0.009) compared to a un-textured surface (0.153 ± 0.006), although the decrease was less than that observed in the mixed lubrication regime, approximately 9.6% compared to 38.5%. Dimensionless wear coefficients, k , were calculated from equation (1), using the data in Table 2 and showed that the textured liner surfaces exhibited a lower wear rate, $8.25 \times 10^{-4} \pm 9.82 \times 10^{-5}$ compared to the un-textured surface, 12.58×10^{-4} . The measured mass loss from the counter face surface for each test was an order of magnitude greater than that recorded for the liner surfaces, Table 3. Unlike the liner wear coefficients, values for the counter surface from the un-textured test (9.16×10^{-3}) and the textured tests ($8.87 \times 10^{-3} \pm 4.08 \times 10^{-4}$) were remarkably similar.

Test	Mass Loss (g)	Volume loss (mm ³)	Sliding Distance (m)	Dimensionless wear coefficient, <i>k</i>
Un-Textured	0.00047	0.175	1816.86	12.58 x 10 ⁻⁴
Textured 1	0.00034	0.124	1814.69	8.95 x 10 ⁻⁴
Textured 2	0.00028	0.105	1816.85	7.56 x 10 ⁻⁴

Table 3. Liner wear data.

Test	Mass Loss (g)	Volume loss (mm ³)	Sliding Distance (m)	Dimensionless wear coefficient, <i>k</i>
Un-Textured	0.00476	0.610	1816.86	9.16 x 10 ⁻³
Textured 1	0.00494	0.633	1814.69	8.82 x 10 ⁻³
Textured 2	0.00464	0.594	1816.85	8.58 x 10 ⁻³

Table 4. Counter surface wear data.

Conclusion

Electrochemical jet machining was able to create a rectangular array of dimple features at a spacing of 1.5mm and ϵ ratio of 0.095, with a 6.2% surface area density. This was close to the optimal depth/diameter ratio of 0.1 and provided good repeatability in feature size and placement in a typically difficult to machine material. The topography within each feature did not exhibit a smooth hemispherical surface but a high degree of angularity. This was the result of selective electrochemical dissolution, preferentially removing aluminium from

around the primary silicon and intermetallic phases. It was observed that in some instances primary silicon particles were not completely detached from the surrounding matrix, however this did not appear to affect the tribological performance of the textured surfaces. Importantly, the electrochemical jet machining process resulted in the manufacture of hemispherical dimples that did not exhibit a heat affected zone, burrs or lips that are often a feature of ablative processes of metallic materials and can compromise friction and wear performance. This is advantageous as the electrochemical jet machining process can be used as a time-efficient one step finishing process for creating surface textures on aluminium-based cylinder liner materials for enhanced friction and wear performance.

The textured features on the Al-Si surface appeared to promote more effective lubrication between features along the plane of sliding, such that abrasive wear debris is removed from the contact in these regions. This mitigates the formation of a surface tribo-layer and concurrently reduces the contribution to the average friction coefficient. Under boundary and mixed lubrication regimes, EJP textured Al-Si surfaces all exhibited a reduction in average coefficient of friction values. The greatest decrease was observed in the mixed lubrication region of the Stribeck curve, where decreases of up to 38.5% occurred.

7. Stem cell differentia methodology

Introduction

Through the literature review it was noted that large area non-deterministic micro-structuring of bio-medical implants can elicit specific cell responses (see section 2.6.2). Specifically, the use of textured surfaces in skeletal implants has received a great deal of interest. The use of lasers to create these textured surfaces was identified through the literature review as being a credible alternative to the use of acid etching to generate the required surface topography and as such the focus of considerable research. However, the disadvantages identified of the mode of energy delivery to the surface as noted in section 2.6 can create detrimental effects to the integrity of the surface, especially when considering the re-cast layer formed, in some instances, constitutes the micro-texture formed. Alongside this, the technical complexity of the process leads to high capital expenditure and relatively low throughput in comparison to acid etching techniques. It has been demonstrated in Chapter 4 that EJP in subtractive mode is able to generate surface features in multiple length-scale surfaces due to nuances of the mode of energy delivery when combined with material traits. Throughout this thesis the controllability of the process in creating differing surface topographies through simple parameter and tool path adaptations is well demonstrated. Therefore, EJP could offer the flexibility and sustainability of laser textured surfaces without detrimental surface effects whilst maintaining the simplicity of acid etching. Therefore an investigation was devised to use a common skeletal implant material (Ti6AL-4V) identified in the literature as of interest in EJP (Sections 2.3.6 and 2.7.3) and using the material response knowledge gained in Chapter 4, to

apply large area surface texturing across the dissolution regimes identified so obtaining differing surface morphologies. These surfaces were then tested by the Bone and Joint research group (University of Southampton) for cell response. The premise being to identify if textures created by EJP could initiate different cell responses dependant on the topography created.

Surface processing

Titanium (Ti6Al-4V) was used as the substrate throughout this study due to its common use in structural skeletal implants (see Chapter 4 for further material details). 20 x 20 mm samples were sectioned from a 3 mm plate. No other preconditioning or polishing was carried out prior to machining with a surface roughness (Sa) of 3 μm .

Three parameter sets were devised based on the information gained in Chapter 4 (*Table App.7.1*) that achieve significantly different topographies due to increases in current density affecting material response. Six repeat samples were created for each batch including 6 control samples (Batch C).

On each sample the jet was rastered across the surface with a 60% step over (*Figure App.7.1*). Batch A and B process parameters are kept constant across the surface. Batch D required a 50% decrease in applied current for the first and last one mm of each translation across the surface (ramp in and out) to avoid unstable conditions damaging the surface of the workpiece as the nozzle enters and exits the workpiece.

Table App.7.1 Processing parameters for 3 batches of titanium samples based on finding in section 4:

Parameter	Batch A	Batch B	Batch D
Electrolyte / concentration	NaCl / 3 M	NaCl / 3 M	NaCl / 3 M
Nozzle I.D. mm	1	1	0.5
Applied current density (J) A/cm ²	35	112	285
Nozzle translation speed (v_{noz}) mm/s	0.5	0.5	0.5
Inter electrode gap (IEG) mm	0.75	0.75	0.75
Electrolyte jet speed (v_{jet}) m/s	16	16	25

Post machining, the samples were immersed in acetone and cleaned using an ultrasonic cleaner, then rinsed in cleaned again in an ultrasonic cleaner immersed in deionised water. Surface characterisation was carried out in line with Chapter 3.

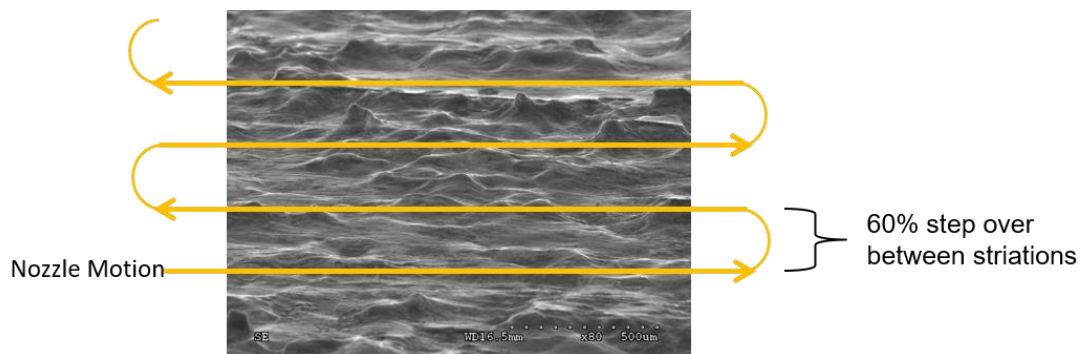


Figure App.7.1: Toolpath of nozzle with stepover to create the surface texture

Stem cell preparation

All cultures were conducted in basal media:

Basal medium contained α -MEM, 10% FCS and 1% Penicillin-Streptomycin (P/S) and was used to maintain human Bone Marrow Stromal/Skeletal Stem Cell cultures.

STRO 1+ Skeletal stem cell (SSC) isolation.

Bone marrow and femoral head samples were collected from patients who were undergoing hip replacement surgery either for hip fracture or electively and were haematologically fit to proceed with the procedure. Collection was undertaken with the local ethics committee approval (LREC194/99/1). If the bone marrow sample was insufficient, it was augmented by processing cancellous bone fragments obtained from the supplementary femoral neck. The fragments were acquired by taking pieces of the cancellous bone from the femoral neck with orthopaedic bone nibblers, while discarding the cortex. The bone marrow was repeatedly agitated in α -MEM to release the osteoprogenitor cells, which were then pelleted by centrifugation at 1100 rpm for 4 minutes at 18°C. The cell pellet was re-suspended in 25 ml of α -MEM and filtered through a 70 μ m cell strainer to remove bone debris. To remove the red blood cells, the cell suspension was gently layered onto Lymphoprep (Stemcell Technologies, 07801)) and centrifuged at 2200rpm (800g) for 40min at 18°C with the brake off. The cells were then removed from the interface layer and pelleted. To further select the STRO 1+ SSC fraction from adult bone marrow cells, the pellet was re-suspended in 2ml of MACS Blocking Buffer (17ml α -MEM, 2ml AB Serum human, 0.2g BSA, 1ml FCS) for 30 minutes, then rinsed in a chilled MACS buffer (1L

PBS, 5g BSA, 0.74448g EDTA), re-suspended once more in 1ml of STRO 1 hybridoma supernatant and incubated for 30 minutes. The cells were then washed in MACS buffer and re-suspended in 800 µl of MACS buffer and 200 µl of MACS Goat Anti-mouse IgM MicroBeads (Miltenyl Biotec – 130048401) for 15 minutes. The cells were then washed in MACS buffer and, to achieve further selection of STRO 1-enriched SSC fraction from bone marrow cell population, passed through MACS Separation Columns (Miltenyl Biotec – 130042401), before being seeded into tissue culture flasks in α -MEM, 10% FCS and 1% P/S at 37°C in 5% CO₂. When cells became 60-70% confluent, they were washed with PBS and released using Trypsin-EDTA. The cells were pelleted and resuspended in basal medium. Only passage 1 cells (unless otherwise specified) were used in all experiments.

Ti 6A-4V sample preparation for cell seeding.

Substrates were carefully transferred into culture plates and sterilised for a minimum of 24 hours in antibiotic-antimycotic solution (Life Technologies, Invitrogen, UK) diluted to 1% in PBS. The substrates were then transferred using sterile forceps into clean plates and washed 3 times in PBS prior to further use.

Cell seeding and culture

The STRO 1 cells were seeded at 220/cm² (500/ml x 4 ml) concentrations in 6-well plates, either directly onto tissue culture plastic (control groups) or the ample surfaces being tested. A 220/cm² cell seeding density has been shown previously within the UoS Bone and Joint Research Group and by the protocol optimisation experiments to be optimal to avoid early over confluence of the cells. The cells

were cultured for 21 days at 37°C in 5% CO₂. Medium was changed twice a week.

Cell health assessment

CellTracker™ Green (CTG) CMFDA and ethidium homodimer-1 were used to determine cell viability. Metabolically active cells with intact plasma membrane are stained green with CellTracker™ Green CMFDA, while damaged or dead cells with impaired plasma membrane integrity are stained red with ethidium homodimer-1. 50 µg of CTG was dissolved in 10 µl of Dimethyl sulfoxide (DMSO), along with 25 µg of ethidium homodimer, added to 5 ml of medium. This was added to the cells in the plate wells and culture undertaken at 37°C in 5% CO₂ for 1 hour. Subsequently, the medium containing the dye was removed, and fresh medium was added for 30 minutes to remove the remaining dye. The fluorescent imaging of the cells was then carried out, with substrates required to be reoriented to achieve visualisation of cells on the opaque material.

The viability of the cells was examined at 21 days only, due to concerns about the maintenance of sterility and preservation of intact culture conditions during the substrate transfers required for fluorescent imaging.

Imaging.

Imaging of the cell cultures was performed using a Zeiss Axiovert 200 inverted microscope with a Axiovert HR camera for white light imaging and an AxioCam MR camera for fluorescent imaging. Zeiss Axiovision software version 4.7 was used for image capture and analysis.

Molecular analysis of osteogenic gene expression

Total mRNA isolation to specify the amino acid sequence of the protein products for gene expression, was carried out using RNeasy Qiagen kit and according to manufacturer's protocol. The culture medium was removed, the cells were washed in PBS, trypsinised, pelleted and subjected to lysis with Buffer RLT Plus. The homogenised lysate was transferred to a gDNA Eliminator spin column and centrifuged. Equal volume of 70% molecular grade ethanol was added to the flow-through, and the sample transferred to an RNeasy spin column. Buffer RW1 and Buffer RPE were then sequentially passed through the spin column. mRNA was eluted with RNase-free water, and the amount was quantified in ng/μl on NanoDrop 1000 spectrophotometer.

For each sample, the mRNA amount needed for reaction was calculated and if necessary diluted in distilled H₂O to ensure equivalent mRNA across all samples. The resultant mRNA samples were treated with VILO reaction mix and VILO 10x superscript and spun down. Samples were reverse-transcribed using SuperScript first-strand synthesis system in a Veriti 96-well Thermal Cycler (Applied Biosystems) using "VILO RT" program. The resultant cDNA was diluted using distilled H₂O.

Quantitative RT-PCR

In order to qualitatively detect gene expression SYBR® Select Master Mix was used for the reverse transcriptase real time polymerase chain reaction (RT-PCR). Samples were run in triplicates on 96-well plates. Specific gene reaction mix contained SYBR® Select Master Mix, and forward and reverse gene primers (Table 7.2) diluted in distilled H₂O. This was then added to cDNA loaded into

wells. The Applied Biosystems® 7500 Real-Time PCR system was used for gene amplification and evaluation of the expression of β -actin, ALP, Collagen 1, OPN, OCN and Collagen 2 genes. β -actin was used as the house-keeping gene, while Collagen 2 was used as a negative control marker. Expression of the genes of interest was normalised to β -actin expression. As the SYBR Green method was employed, primer sequences for the genes were validated by dissociation curve/melt curve analysis. The efficiencies of amplification for the β -actin primers and primers for the bone marker genes of interest were established to be approximately equal. The comparative cycle threshold method was utilised for quantification of PCR amplification data. The relative transcript levels were expressed as mean $\pm$ S.D. and analysed and plotted as graphs using GraphPad Prism 6 for Mac OS X software.

Table 7.2 Primer sequences used for qPCR (Dr R. Tare, Bone and Joint Research Group).

Species	Gene	Primer pairs	Amplicon	
Human	β -Actin	F: 5' GGC ATC CTC ACC CTG AAG TA 3'	82	NM_001101
		R: 5' AGG TGT GGT GCC AGA TTT TC 3'		
	ALP	F: 5' GGA ACT CCT GAC CCT TGA CC 3'	86	NM_000478
		R: 5' TCC TGT TCA GCT CGT ACT GC 3'		
	Collagen 1a1	F: 5' GAG TGC TGT CCC GTC TGC 3'	52	NM_000088
		R: 5' TTT CTT GGT CGG TGG GTG 3'		
	OPN	F: 5' GTT TCG CAG ACC TGA CAT CC 3'	80	NM_001251
		R: 5' CAT TCA ACT CCT CGC TTT CC 3'		830
	OCN	F: 5' GGC AGC GAG GTA GTG AAG AG 3'	102	NM_001199
		R: 5' CTC ACA CAC CTC CCT CCT 3'		662
Mouse	Collagen 2a1	F: 5' CCT GGT CCC CCT GGT CTT GG 3'	58	NM_001844
		R: 5' CAT CAA ATC CTC CAG CCA TC 3'		
	β -Actin	F: 5' TTG CTG ACA GGA TGC AGA AG 3'	86	NM_007393
		R: 5' GTA CTT GCG CTC AGG AGG AG 3'		
	Collagen 1a1	F: 5' GCC AAG AAG ACA TCC CTG AAG 3'	102	NM_007742

	R: 5' TGT GGC AGA TAC AGA TCA AGC 3'		
OPN	F: 5' GCT TGG CTT ATG GAC TGA GG 3'	81	NM_001204
	R: 5' GGT CCT CAT CTG TGG CAT C 3'		203
OCN	F: 5' CTG ACC TCA CAG ATG CCA AG 3'	76	NM_001037
	R: 5' ACC TTA TTG CCC TCC TGC TT 3'		939

Surface topography assessment

Samples were taken from each of the three batches and analysed against a set of 3D and 2D measurement parameters. Batch A (*Figure App.7.2*) can be described as isotropic [265] as it displays no directionality to the created topography despite the repetitiveness of the toolpath (*Figure App.7.2 a*).

The dissolution mechanism can be described as “sporadic” in-line with Chapter 3.8.3. Demonstrated by the large-scale pitting and indiscriminate and non-deterministic point corrosion with little relation to material structure (*Figure App.7.2b, c*). This type of surface is defined by the mechanism of a limited decomposition voltage spasmodically breaking down the oxide films and Ohmic overvoltage being inherently un-stable across the surface. The surface has a comparatively high resultant roughness (S_a) of $18.9\ \mu\text{m}$ compared to the control and demonstrates a slightly spikey surface with a S_{ku} (see section 3.8.2 for definitions) value of 3.61. A few very deep pits can be seen with depths exceeding $100\ \mu\text{m}$ which generates a negative skew (S_{sk}) value of -0.838 meaning the bulk of the surface topography is slightly above the mean surface height.

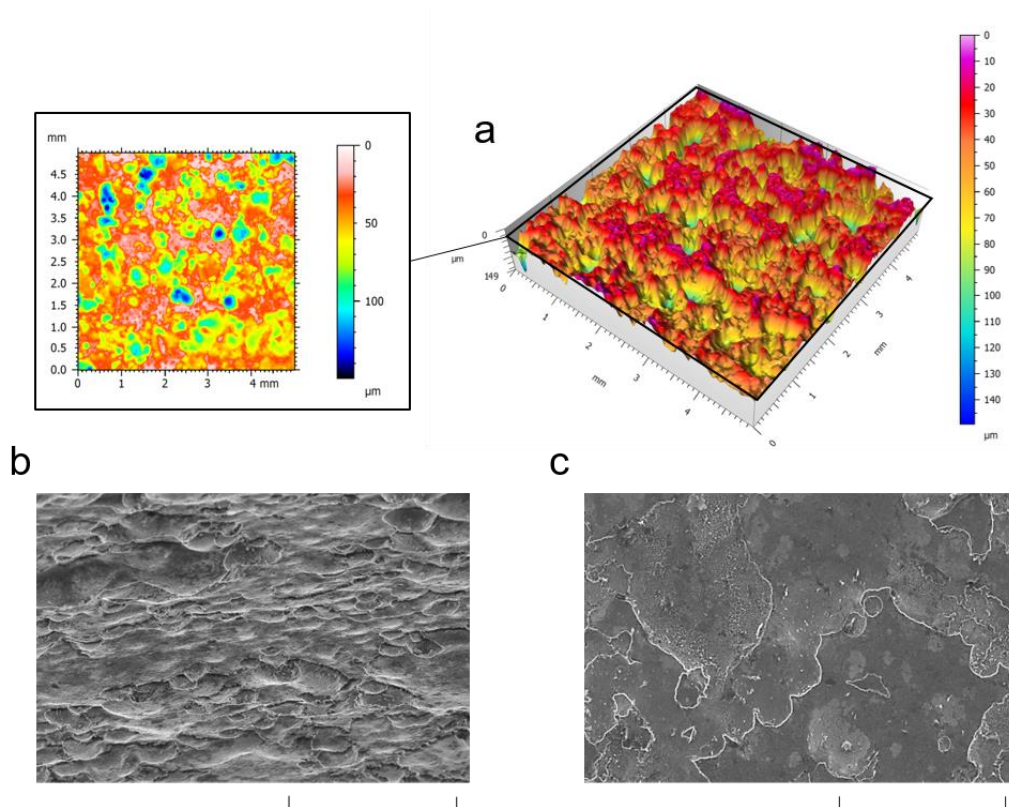


Figure App.7.2: Batch A Macro-scale surface topography analysis (a) Areal scan generated from surface analysis describing surface topography with 3D surface reconstruction showing depth colour scale bar (b) SEM image at x100 magnification with 75° tilt, scale bar 500 μm (c) SEM image at x100 magnification, scale bar 500 μm

When considering the nano analysis of the same surface (Figure App.7.3) but within one of the dissolution pits, the resultant topography is wholly attributed to material microstructure in line with surface composition. The SEM images (Figure App.7.3b, c) showing the vanadium rich β phase standing proud of the α phase pits denoting selective machining. These pits are however shallower giving a resultant Sa of 46.7 nm and the topography in general changes to a bumpier surface with Sku being 2.93. Grain boundaries are not well defined however it would appear grain orientation is contributing to the surface texture as seen in the larger 3D reconstruction in Figure App.7.3a.

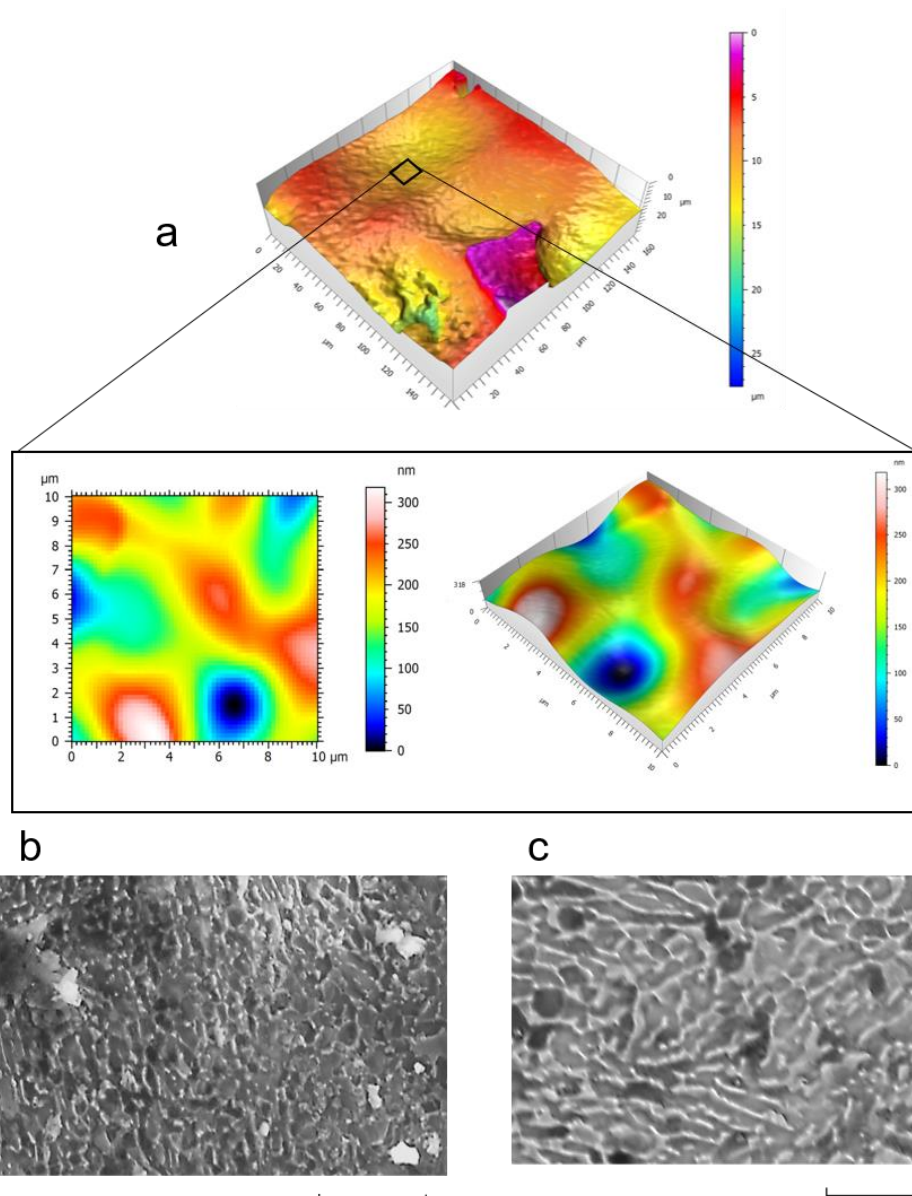


Figure App.7.3: Batch A micro analysis (a) 100x magnification surface scan giving 150 μm x 150 μm patch. 10 μm square patches extracted for analysis (b) SEM image from the side wall of the dissolution pit. Scale bar 20 μm (c) SEM close up image at the base of a pit. Scale bar 10 μm .

Observing Figure App.7.4 batch B achieves a very different surface topography. The topography still appears to be isotropic with the surface appearing to show no obvious direction. Here the anodic dissolution is described as selective demonstrating the obvious machining of grains due to orientation and composition at the interaction surface. Corrosion is still non-deterministic, but now more relatable to the material grain structure. Erosion by jet dynamics

causing elemental wash out is also now observable affecting the overall structure. The decomposition voltage is still variable although Ohmic overvoltage has been achieved to varying degrees across the surface leading to a spike / peak based morphology, the bulk of the material being below the mean height of the surface morphology (Ssk 0.0306). Overall roughness (Sa) has now increased to 35 μm with the depths of some of the valleys exceeding 300 μm . Although still maintaining a kurtosis value above 3 (Sku 3.11) it shows a more even distribution of the peaks than batch A.

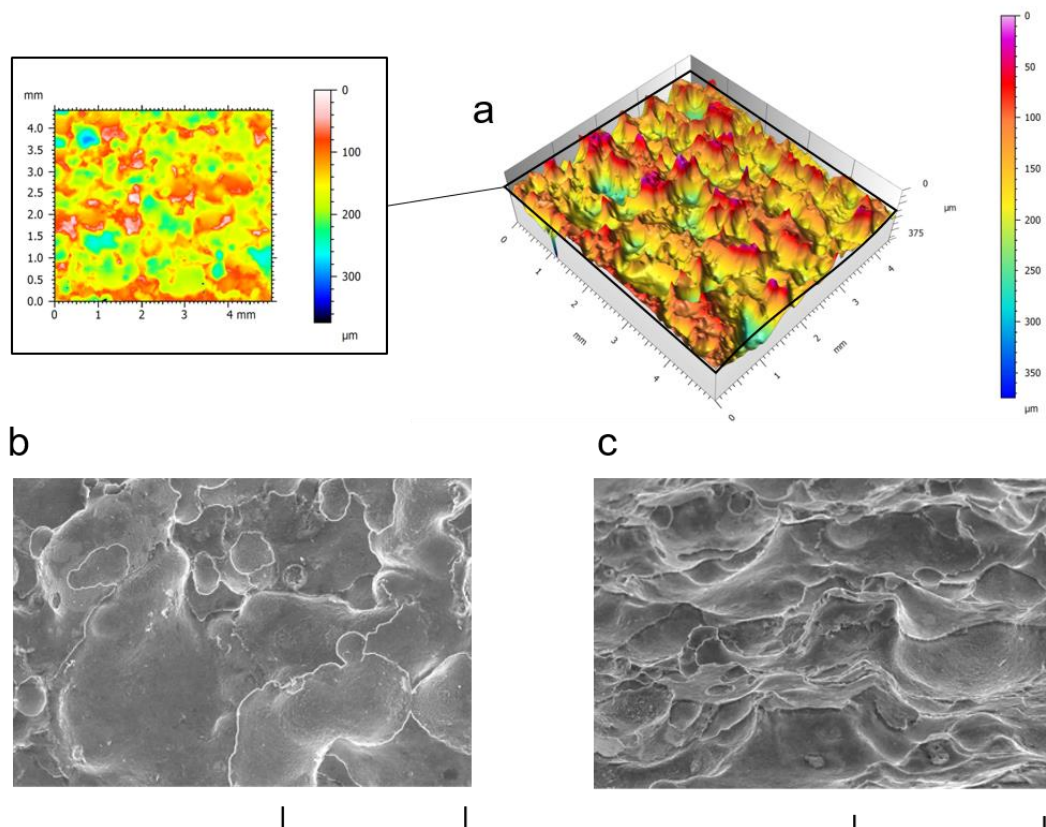


Figure App.7.4: Batch B Macro-scale surface topography analysis (a) Areal scan generated from surface analysis describing surface topography with 3D surface reconstruction showing depth colour scale bar (b) SEM image at x100 magnification, scale bar 500 μm (c) SEM image at x100 magnification with 75° tilt, scale bar 500 μm Cell differentia

The micro analysis demonstrates a rougher nano texture achieving a Sa of 52.5 nm. Skewness of the surface is now positive (Ssk 0.167) in the same respect as

the macro analysis showing the further selective machining of the α phase than batch A. However, the kurtosis is now leaning towards a bumpier type surface (Sku 2.75) rather than spikey as opposed to the macro analysis so this would suggest moving towards a more hierarchical two-tier surface texture.

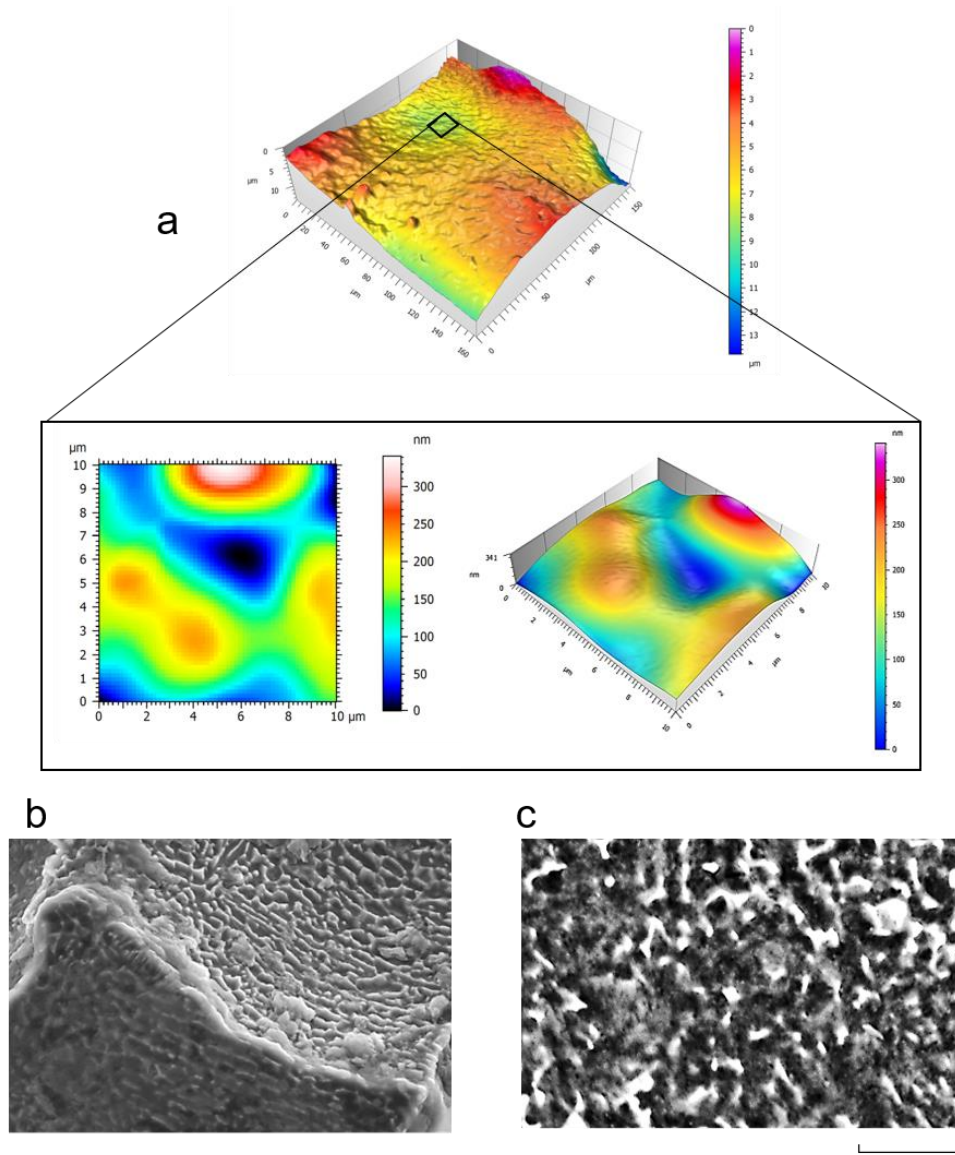


Figure App.7.5: Batch B micro analysis (a) 100x magnification surface scan giving 150 μm x 150 μm patch. 10 μm square patches extracted for analysis (b) SEM image from the side wall of the dissolution pit showing an intersection between grains. Titanium oxide can be seen present on the surface. Scale bar 20 μm (c) SEM close up image at the base of a pit. Scale bar 10 μm

Batch D macro analysis (Figure App.7.6) now reveals a further difference in the surface topography and can be considered anisotropic with obvious directionality

to the topography relating to the rastering motion of the nozzle. This is partly due to reduction in nozzle size to meet current density requirements and the larger specific material removal under the nozzle due to the increased applied current density. The mechanism of anodic dissolution can be described as in equilibrium, observed by the flatter topography between the peaks and the micro texture being less obvious in the SEM imaging (Figure App.7.6b and c). Overall the Sa value is now reduced to 16.4 μm . Therefore, decomposition voltage is generally met across all elements.

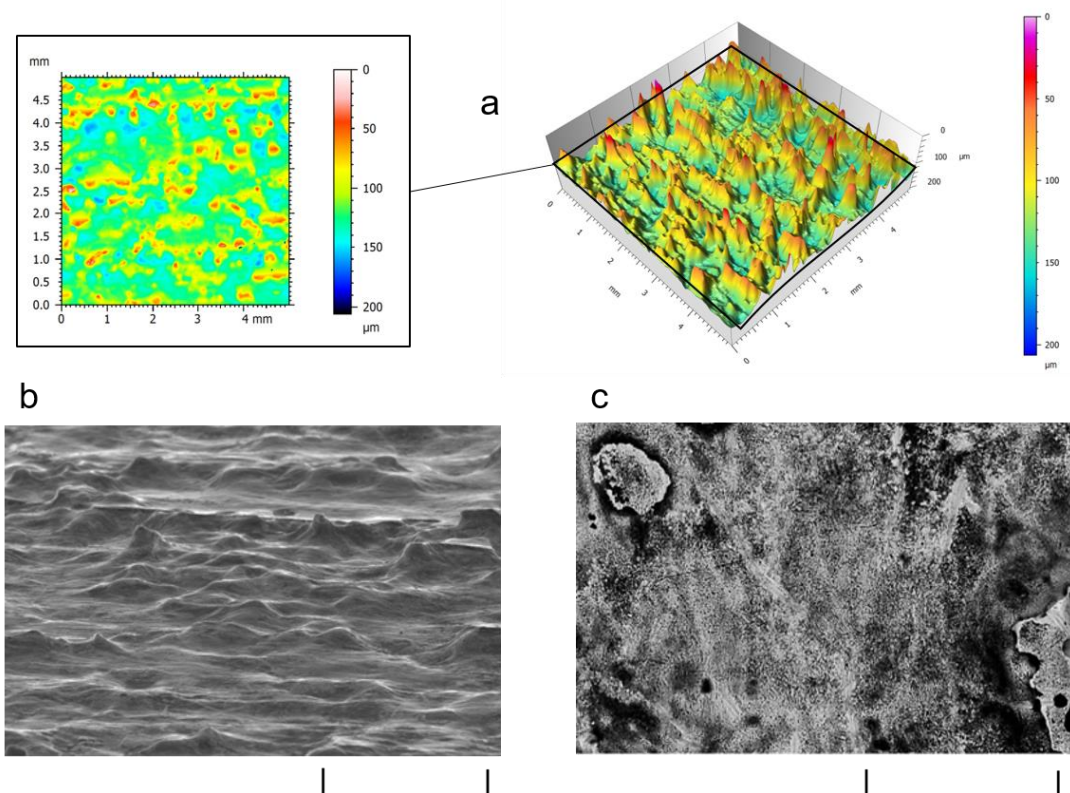


Figure App.7.6: Batch D Macro-scale surface topography analysis (a) Areal scan generated from surface analysis describing surface topography with 3D surface reconstruction showing depth colour scale bar (c) SEM image at x100 magnification with 75° tilt, scale bar 500 μm (d) SEM image at x100 magnification, scale bar 250 μm

The surface is also considered spikier and less uniform than batch B with a Sku value of 3.7 which is also supported by the Ssk value increasing to 0.8 which can be the opposite to that found in batch A.

The micro analysis (**Error! Reference source not found.**) supports the macro analysis in that the micro surface roughness (S_a) has now reduced in comparison to both batches A and B to 35.9 nm due to the dissolution mechanism with the α phase pits becoming shallower as the decomposition voltage of the vanadium in the β is reached allowing dissolution of both phases.

Machining at grain boundaries can be observed due to the etching effect, producing a much smoother finish and higher MRR in these areas seen in **Error! Reference source not found.**a and c.

The micro-surface is more now more evenly distributed similar to batch A (Sku 3.1) with a near perfect distribution of features albeit spikier than batch A, which is expected due to the more aggressive current density. Again, this is supported by the S_{sk} value of -0.5 with the bulk of the material being above the mean surface topography height.

Comparison of the volume parameters (see section 3.8.2) allows quantitative assessment of the changing material found in the peak, core and valley areas of the interaction surface. This can be observed to change between sample batches at the sub-micron scale (*Figure App.7.7*). Batch B shows the greatest overall surface depths (peak to valley). The surface is high in peaks above the core material volume and low in valley pits below the mean core. Both batch A and D demonstrate similar topography although batch D shows a flatter topography with a lower peak to valley figure due to a smaller material amount found in all three regions. This follows the machining regimes found whereby less preferential machining of the Aluminium heavy α phase occurs in batch D even in comparison to Batch A. Batch B indifference to batches A and D achieves fluid retention in

the deepest valleys on the surface showing the lowest Vvv value with the lowest 20% of surface volume having voids section depth of 80 μm compared to batch A and D having a void section depth of 115 μm and 185 μm respectively.

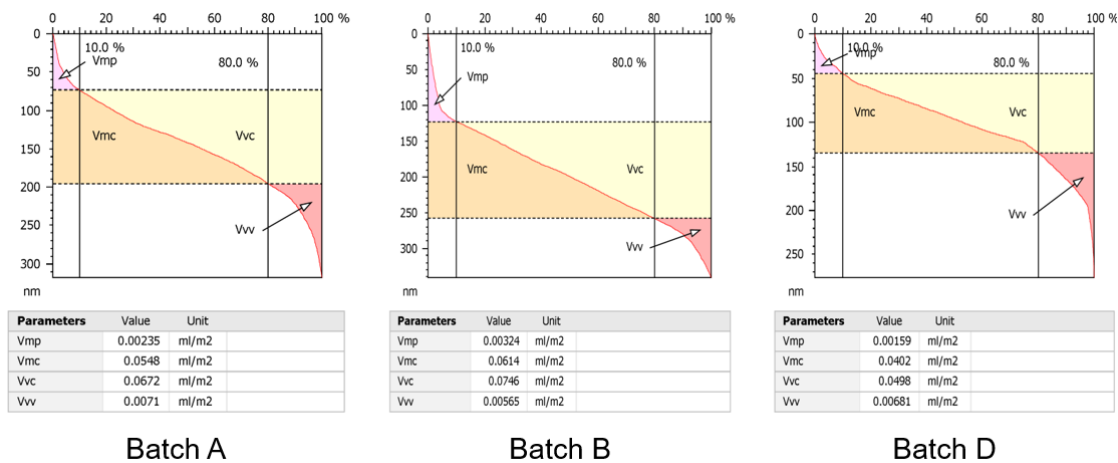


Figure App.7.7: Volume parameters shown on the bearing areal ratio curve taken from the micro analysis for sample batches A, B and D allowing direct comparison of the sub-micron-scale topography

Cellular response

Qualitative analysis

Observing Figure App.7.8 shows the cell topological behaviour after 21 days from fluorescent optical imaging which enables the dynamics of gene expression, protein expression and molecular interactions of the seeded cells to be observed. All skeletal stem cells shown are regarded as viable.

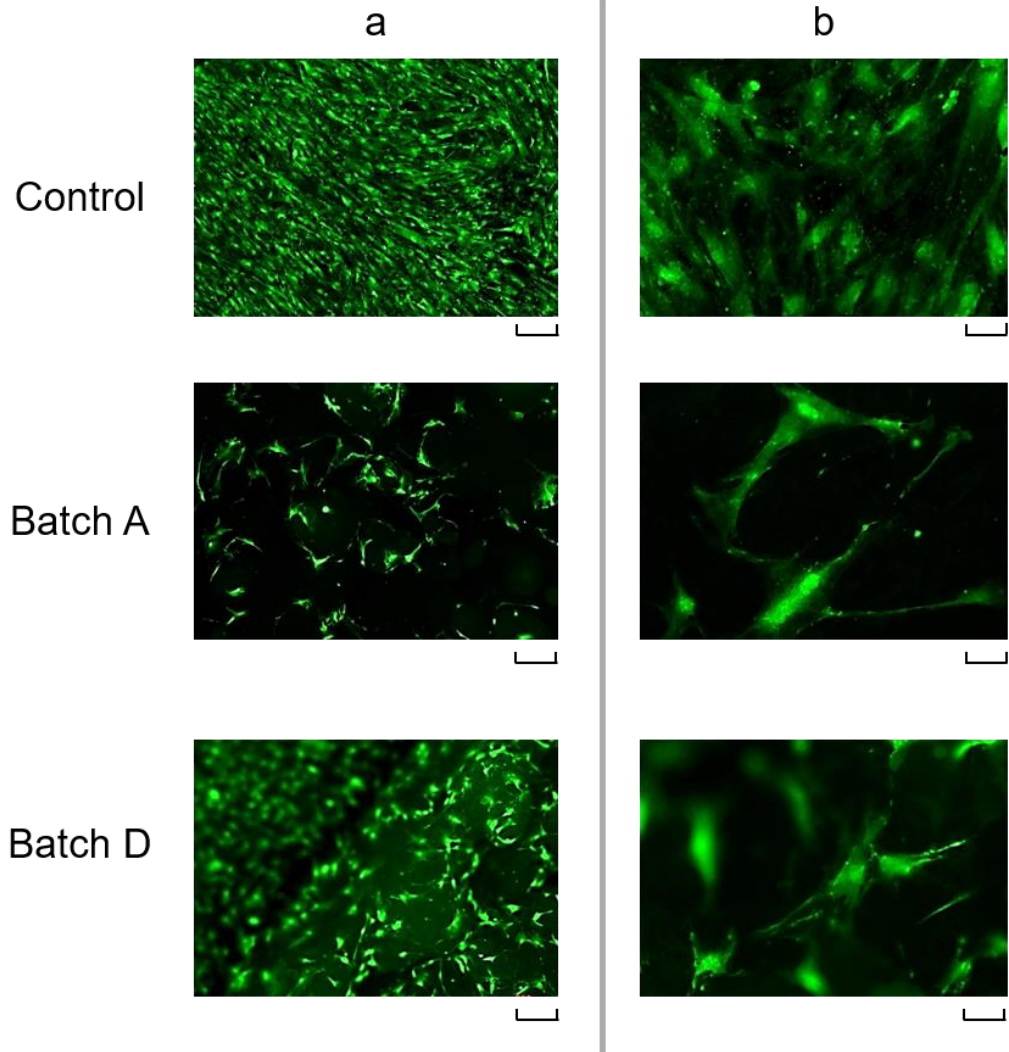


Figure App.7.8: 21 days live / dead cell imaging (a) x5 magnification all SSC's in field are viable. Scale bars are 200 μ m (b) x20 magnification cells have transformed with significantly greater spread and filopodia than control. Scale bars are 50 μ m

Images from batch B were not possible due to the poor response and uneven topography causing difficulty in capture within the focal plane. *Figure App.7.8a*, shows the surfaces imaged at 5x magnification, where a stark contrast to the control surface is obvious as the cells on the treated surfaces have transformed morphologically. This is acutely obvious in batch D where the in-focus section is within the treated area of the surface and the out of focus section is the control surface. At 20x magnification in *Figure App.7.8b* the changes in the cell structure are

acutely more defined as they change from spindle-like shaped cells with little interaction or grouping on the control surface to cells with significantly greater spread and multiple filopodia, suggestive of potential osteoblastic differentiation. Batch D particularly showing a distinctly higher density of filopodium.

Quantitative analysis

The outcome from the RT-PCR carried out at the University of Southampton reveals the gene expression after 21 days (*Figure App.7.9*). The values from the control surface are normalised and the outcome from the three batches are compared relative to the control. There is a promising enhancement of gene expression seen on batches A and D. This supports the differentiation of SSC's suggested by the morphological appearance of the cells in the fluorescent imaging and demonstrates further the poor result from batch B. Alkaline phosphatase (ALP) is seen to be increased across all batch samples with batch D showing over two times the amount in comparison to the control. ALP activity is thought to signify the presence of osteoblast progenitors and are considered pre-osteoblasts [317]. The maturity of osteoblasts however is signified by the presence of osteocalcin and collagen type 1 [318]. High levels of these in comparison to the control surface (seen across all three batches) would suggest the early onset of bone formation and integration of the implant in comparison to an un-machined surface alongside the morphological changes of becoming larger as seen in *Figure App.7.8*. Osteopontin (OPN) is known to enhance cell attachment and wound healing and bone re-modelling [319]. This is shown as markedly reduced in Batch B below the level of the control surface. This would render the surface created through the process parameters in batch B as

unsuitable for implant texturing as this would cause poor healing and eventual rejection and re-work of the implant.

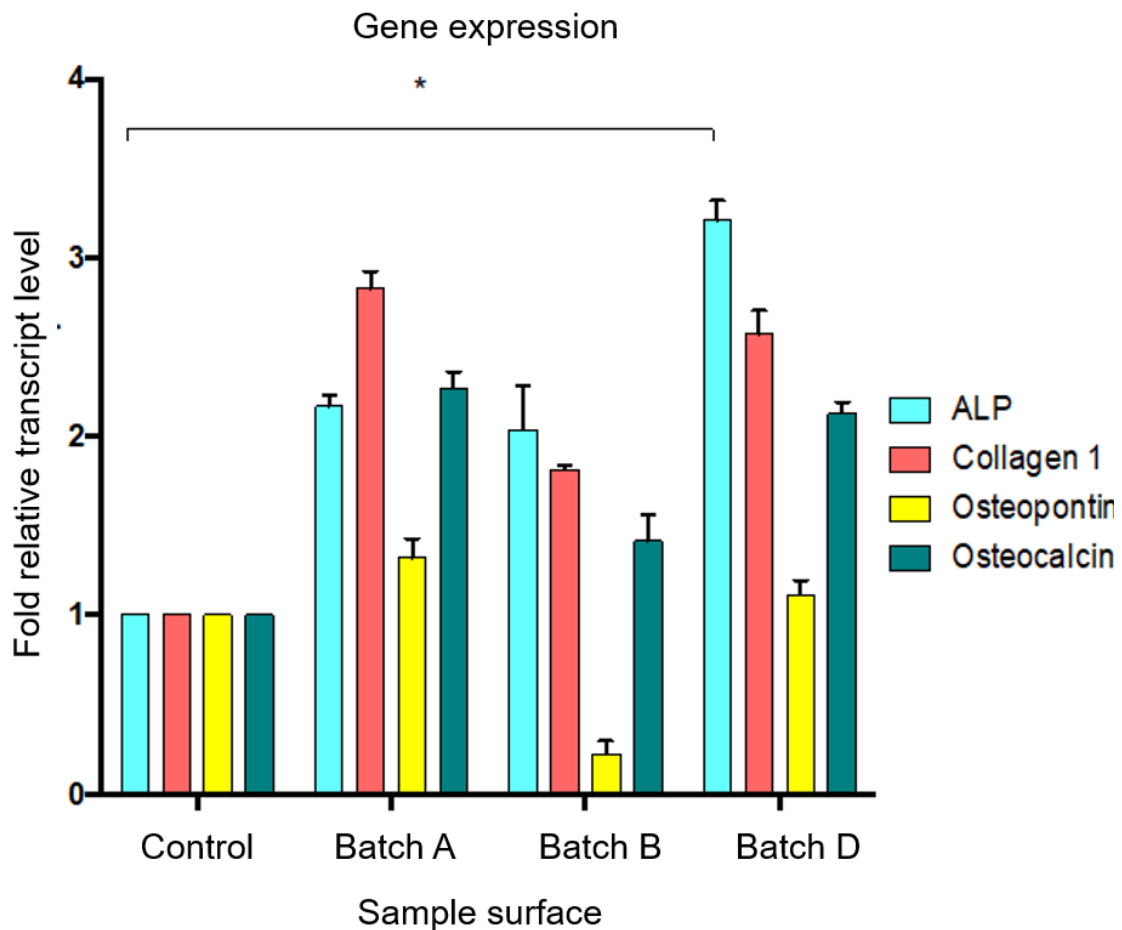


Figure App.7.9: Results of the RT-PCR with comparison of gene expression relative to that found on the un-machined control surface. Error bars being the standard deviation about the mean.

Discussion

From these initial results there is clear suggestion that the surface textures found in batches A and D show potential for enhancing the formation of osteoblasts, both earlier and more vigorously than an untextured surface. Comparing the results from the surface characterisation to the results from the cell trials, the area where batch B differs to batch A and D, and where batches A and D are similar, is the enlarged and deeper Vvv at the sub-micron scale found in these two

surfaces. Batch D which demonstrates the greatest potential has the highest frequency of valleys but also has a reduced surface roughness likely allowing the cells to migrate easier across the surface in comparison to the other surface with less large obstacles, albeit with a spikier nature, at the macro-scale, the valleys then providing an enhanced habitat. This follows prior findings that more than one scale of surface topography is responsible for enhanced osseointegration of implants [240, 320, 321]

Section summary

Through this initial investigation it is clear that subtractive mode EJP is capable of being a practical alternative to both laser and acid etching to deliver surface topographies on a typical implant material that will instigate a preferable cell response. It has been demonstrated here that the process response described in Chapter 4 delivers enough flexibility and variation in topography through variation of material response to cause changes in cell uptake. The deeper pitting in batches A and D seeming to promote the best cell response. The results presented here are in no way considered as optimised for the application of enhanced in-vivo response. A much deeper assessment across a wider parameter set would be required not only to confirm surface response but isolate cell response and therefore define a specific surface. However, it is intended, and achieves, the demonstration that EJP can be considered as an efficient low-impact method to apply large area surface texturing and a viable alternative process offering distinct advantages.