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Development of Dry Film Lubricants for Highly Loaded Contacts

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Preface

This thesis is submitted for the degree of Doctor of Philosophy at the University of Nottingham. The research work was carried out under the supervision of Dr. K. T. Voisey and Professor P. H. Shipway in the Faculty of Engineering.

It is certified that the work presented in thesis is original, and suitable references are made to any work from the literature or carried out elsewhere.

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Abstract

This thesis motivated by concerns over fretting damage in the aerospace engine disc dovetail joint in Ti6Al4V. The dovetail joint behaviour was investigated using a cylinder-on-flat contact geometry setup and fretting amplitude of 300 μm , a frequency of 2.5 Hz and load of 575 N was used. The thesis is concerned about an experimental investigation of the fretting behaviour of Ti6Al4V coated with a commercially available MoS₂-based dry film Lubricant (DFL).

Sample performance was determined via analysis of fretting loops, condition of coefficient of friction, Scanning Electron Microscopy (SEM) images of wear scars on plan view and cross section, Energy-dispersive X-ray spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) analysis.

To study the influence of contact geometry on fretting wear, tests were conducted using cylinders with radii of 15 mm, 80 mm and 160 mm with DFL thicknesses between 12 μm and 86 μm . All tests showed a high level of repeatability. Three stages phenomenological model of the polymer bonded dry film lubricant in the lifetime of the system were identified. In the first stage, the DFL wore with a volumetric rate that was proportional to the number of cycles (under a given load), until the thickness of the DFL was reached. In the second stage, a thin low friction surface layer existed, with its durability being proportional to the contact pressure. In the third stage, metal-metal contact resulted in short-term instabilities in the

coefficient of friction and the DFL system was regarded to have failed. A phenomenological model that predicts coating lifetime is developed, which can be applied regardless of contact geometry, thickness and loads.

The model was extended to a system in presence of a Cu-Ni-In underlayer, as DFL behaviour was determined and analysed using the same three stage approach. Higher roughness results in reduced rates of change in behaviour and a significant extension of the stage II duration over which the surface material is made up of a mixture of DFL and metal, accordingly, the high durability of the system with the Cu-Ni-In underlayer is primarily ascribed to the high roughness of the underlayer in its as-sprayed form onto which the DFL was deposited.

The effect of PTFE and graphite additives was determined. 4.77 wt. %, 9.08 wt. % PTFE and 4.76 wt. % graphite extended DFL lifetime. The PTFE appears to slow stage I, the wear of the DFL layer, but once the metallic surface is reached the mechanism of wear of DFL system appears unchanged. Lifetime of the graphite extended significantly with stage I and stage II maintaining lower coefficient of friction, that it was not possible to run tests to completion, even when the wear scar penetrates significantly through the metal. An alternative mechanism appears to be active, thus requires further investigation.

Publications

K. Barman, P. H. Shipway, K. T. Voisey and G. Pattinson, 2015, Fretting wear behaviour of MoS₂ dry film lubricant, Lubricant Tribology – Finnish Journal of Tribology, 33 (1), 14-20.

K. Barman, P. H. Shipway, K. T. Voisey and G. Pattinson, Evolution of damage in MoS₂-based dry film lubricants (DFLs) in fretting wear – the effect of DFL thickness and contact geometry (in preparation) - to be submitted in Tribology International.

K. Barman, P. H. Shipway, K. T. Voisey and G. Pattinson, The role of a thermally sprayed Cu-Ni-In underlayer in the durability of a dry-film lubricant system in fretting – a microstructural study (in preparation) - to be submitted in Tribology International.

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Chapter 1. Introduction

1.1 Background

Fretting wear, occurs when two contacting surfaces undergo relative oscillatory motion with small amplitude displacements, usually less than 70 micrometers [1]. It is an important issue for many engineering industries. It has long been a major problem to the aircraft and automotive industries. In the aero-engine, the combination of inflight loading, unloading during takeoff and inflight vibration can lead to fretting damage, such as wear and cracking. Ti alloys are used for discs and blades in the aero-engine industry, these components are joined with dovetail joints. Fretting fatigue in the dovetail joints can lead to catastrophic blade or disc failures by fracture [2]. Understanding how dry film lubricants can improve the fretting life of such components is the motivation of this thesis.

Fretting can be dominated by mechanical or chemical effects. This complexity has been a great problem to the researchers since the early

twentieth century, and remains a problem today, even after years of research, there is no definite reason for fretting wear. Strategies, such as, lubrication, coatings, surface modifications and design modification, have been employed successfully to particular fretting conditions [3].

Nowadays, one of the popular ways to prevent fretting wear is lubrication. The literature contains many investigations using lubricious surface coatings. In recent years, there has been a lot of improvement in the level of understanding of the tribology of surface coatings. At the same time, developments in coating technology have enabled the possibility of producing surface layers with properties that were previously unachievable.

1.2 Effect of Coating in fretting

The form of wear and fatigue-cracking, commonly known as fretting damage, is a common cause for concern in a wide range of loaded mechanical joints, and consequently, such examples seek to control the rates of fretting damage either by design or by material selection. The introduction of surface treatments or coatings to mating counterfaces has been a successful strategy against fretting damage.

Coatings can mitigate the fretting damage, by reducing the coefficient of friction or by reducing wear at the contacting surfaces. However, there is no general methodology for selecting specific coatings for fretting applications. It is very important to first understand the mechanism of the interacting surface between the substrate and coating in a fretting wear situation. The coating might behave differently in different environments.

Commercially produced coatings are available in a wide range with a variety of characteristics. The thickness of coating may vary from a few micrometers [4] to hundreds of micrometers [5].

1.3 Why dry film lubricant (DFL)?

Most industrial mechanical processes need lubrication to work properly. Lubricants reduce friction and protect against wear as long as a lubricant film separates the moving parts involved in the process. There are many soft or hard film coatings, multi-phase alloying and composite structuring have been developed to control wear and friction by improving materials and surfaces for better properties of friction and wear [6].

Hard coatings are not used more widely due to their high friction and if the coated surface is rough, then they can cause abrasion and rapid wear of the opposing surface. For example, very hard diamond-like carbon (DLC) coatings tend to be brittle, have poor adhesion, and are unsuitable for highly loaded applications [7]. The doped metal carbon: hydrogen (Me-C:H) coatings are much softer, but less brittle. They can be deposited with excellent adhesion [8] and can be used at moderately high loads. The coefficient of friction is low, typically 0.15, but these coatings are not true solid lubricants, as they do not provide an efficient transfer film on the opposing surface [7].

In order to provide optimum wear protection for rubbing mechanisms, it is necessary to use dry film lubricant coating with low friction and the ability to protect the uncoated opposing surface. MoS₂ and graphite, both

hexagonal-layer lattice materials, exhibit these properties [9]. Such solid lubricant coatings provide low friction, giving low wear rates, and the mechanical properties of the coatings combined with the good adhesion leads to very high load-bearing capacity [7].

1.4 Aims and scope of this research

Very often, a turbine engine component is failed and removed from service before it reaches its “full life”. One of the most common reasons is accumulated fretting damage in the dovetail slots of disks. This fretting damage is very difficult to characterize and analyze. Due to the long processing times and the high costs associated with replacing this hardware, it would be desirable to have a comprehensive set of tools to minimize sensitivity or repair fretting damage. This includes a number of elements including new design approaches to minimize contact stresses, coating systems to minimize fretting damage, and surface treatments to mitigate the effects of any fretting damage [10].

Research performed in this course of the thesis has aimed to improve the knowledge of the mechanism of fretting wear of existing molybdenum sulphide coating on Ti6Al4V substrate. Research focused on developing in-house setup for coating on the Ti6Al4V surfaces according to Rolls Royce standards. Work has been done to determine the behaviour of the existing DFL with or without a Cu-Ni-In underlayer. The existing DFL coating has been modified by adding different additives into DFL, such as, PTFE and graphite. The effect of these additives on DFL has been investigated. The

various experimental results obtained combine to build up a phenomenological model of how DFL affects fretting lifetime.

1.5 Objectives

- To develop an understanding of mechanism of wear failure of evolution of coefficient of friction of molybdenum sulphide coating;
- To investigate the effect of contact geometry and coating thicknesses on lifetime of molybdenum sulphide DFL coating;
- To determine the effect of Cu-Ni-In underlayer followed by DFL on Ti6Al4V;
- To determine the effect of PTFE and Graphite addition on the behavior of a molybdenum sulphide DFL coating;

1.6 Thesis overview

Chapter 2 provides a critical review of the published literature on fretting wear with a focus on wear mechanisms. The review presents the fundamentals and history of different solid lubricant coatings and discusses the different aspects of dry solid lubrication and methods to improve fretting wear.

Chapter 3 provides a detailed description of the materials, methods used to coating samples, procedures of tests carried out as well as the parameters and principles of the characterisation techniques used for the study of the prepared samples.

Chapter 4 presents the results of evaluation of coefficient of friction of MoS₂ dry film lubricant and characterisation of the wear surface and establish characterisation of the different stages of wear. The effect of coating thickness and effect of contact geometry on fretting wear is determined.

Chapter 5 presents the effect of a Cu-Ni-In underlayer on behavior of a molybdenum sulphide DFL. An explanation of the underlying mechanism is given.

Chapter 6 presents the results of PTFE and graphite additives on behavior of a molybdenum sulphide DFL.

Chapter 7 summarises the key work reported in Chapter 4, Chapter 5 and Chapter 6 and presents the conclusions of this thesis.

Suggestions for future work are given in Chapter 8.

Chapter 2. Literature Review

2.1 Titanium alloys

The interest in titanium as engineering material started approximately 80 years ago. The aeronautic industry gave special attention to this material due to its specific combination of properties such as, the high specific strength [11, 12], outstanding corrosion resistance due to the presence of a protective oxide on the surface [13-17] and strength at temperatures up to approximately 500 °C [12, 16, 18, 19]. It has high temperature capability in the range of 300-600 °C. Ti alloys also have high toughness making them useful materials with applications, from structural component in the aerospace [1] and automobile industries to corrosion resistance materials in the chemical and marine sectors and medical device manufacturing [16, 20].

In the aero-engine industry Ti alloys are especially important. The jet engine works by sucking air into the core through multiple compressors.

Squashed by the compressors, the air is forced into the combustion chamber, mixed with fuel which explodes to create a ferocious gas jet. This jet is met head on by the turbine blades, spinning them so fast, that each blade delivers the same power as the formula 1 engine [21]. Ti alloys are used for disks and blades from the fan to compressor stages where temperature do not exceed 500 °C [16, 18].

However, titanium alloys possess some disadvantages. In addition to their cost [16], their poor tribological performance makes fretting a concern [17]. In dry air titanium readily forms a hard, thin oxide layer. Fretting wear can easily disrupt the thin oxide layer and create hard debris particles which become abrasive [22], the relevant mechanisms are explained in section 2.2.

2.1.1 Ti6Al4V alloys

The first well developed and popular titanium alloy is the alpha-beta Ti6Al4V alloy. The nominal chemical composition of the alloy is listed in wt. percentage in Table 2.1 [23].

Table 2.1 Chemical composition of Ti6Al4V (Wt. %) [23]

Al	V	Fe	N	O	C	H	Ti
6.2	3.96	<0.20	<0.01	<0.03	<0.05	<0.003	Balance

The susceptibility of titanium alloys to fretting also may be because of a deformation or temperature-induced transformation from a two-phase, α (h.c.p.) plus β (b.c.c.), to a single phase α (h.c.p.) microstructure, which is a brittle structure. It has been reported that a superficial layer of 20-50 nm

crystallites of the α phase formed during fretting of a two-phase $\alpha+\beta$ structure [13].

2.1.2 Fan blade root

Figure 2.1 illustrates a dovetail joint [24] and location of fretting wear damage. The bottom of the blade is the area which holds the blade into disc as shown in Figure 2.1 [24]. Damage is observed in the blade and disc, when the two bodies are in contact and experience small amplitude oscillatory movements due to the poor tribological properties of Ti-alloys [25]. These surfaces are very susceptible to fretting and experience wear damage[19].

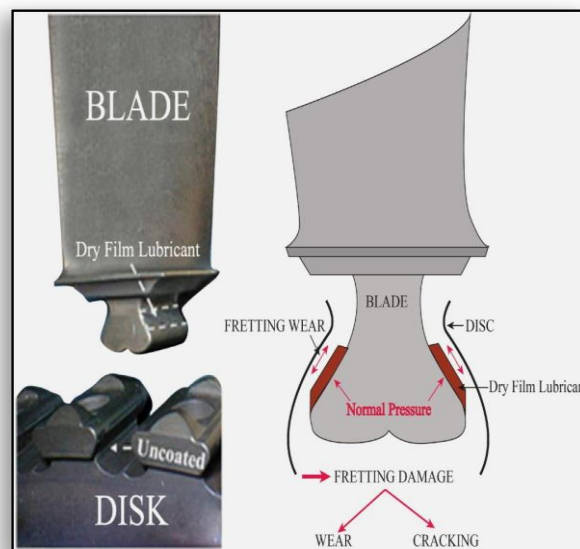


Figure 2.1 Titanium blade and disk showing the dovetail joint [24] and the schematic illustration of Blade/disk fretting wear damage in compressor blade.

To prevent the dovetail surfaces from fretting and fatigue, current practice is to use shot-peening combined with a plasma sprayed copper-nickel-indium (Cu-Ni-In) alloy coating followed by a dry film molybdenum disulphide lubricant on the fan blade [26-31]. The coating is applied to the blade root as the disk cannot be coated due to its geometry which is inaccessible to coating equipment [17].

2.2 Fretting

Tomlinson et al. [30] was the first to conduct a systematic study on fretting. He showed that fretting occurs when two surfaces in contact with each other are subjected to very small relative displacements, i.e., mechanical joints subject to vibration, including dovetail/failure joints, usually less than 70 μm [1]. Fretting may occur between contact surface which experience vibration or cyclic stress. Fretting is possible in all quasi-static loadings that experience vibration, consequently it concerns many industries such as helicopters, aircraft, trains, ships, trucks and electrical conductors [24]. In fretting, the centre of the contact never gets exposed directly to the environment. Extended metal interaction at high pressure, can significantly reduce penetration of air inside the contact and create oxygen depletion condition[19]. Godfrey et al. [32] examined the initiation of fretting and concluded that finely divided loose material produced from adhesion between the surfaces, extrudes from the contact area and reacts with oxygen, which acts as a secondary factor. It can cause localised damage or initiate fatigue cracks which lowers the fatigue strength of material [3]. The product is often characterized by the production of finely ground particles or debris. Such damage can be found between plates of

bolted or riveted assemblages in aircraft as well as joints, splines, bearings and couplings, all of which are vulnerable to fretting [22].

There are two key types of fretting damage, (a) fretting wear and (b) fretting fatigue. Fretting wear and fretting fatigue are driven by the rate of formation of third-bodies between the initial contact surfaces [33]. Fretting wear can be formed by any one of the basic wear mechanisms and can generate considerable amounts of very fine oxide debris [34, 35]. Fretting fatigue is combination of surface and bulk fatigue [36]. The mechanism of formation of cracks, often leads to multi-site damage initiate crack from a surface under stress and lastly the propagation of the crack due to combined effect of contact and bulk loading [37]. In this work, only fretting wear has been addressed; i.e. the process is only considered up to the limits at the point where damage initiate on the surface due to third body formation, exposing the metallic surface. Fretting fatigue is therefore not considered any further.

2.2.1 Mechanism of fretting wear

The theories on the mechanism of fretting wear can essentially be divided into two different groups: 1) mechanical and b) chemical.

A mechanical mechanism is when the adhesive welding of the contacting surfaces takes place, followed by a shearing action producing debris which is then or at a later stage oxidized [38]. It has been shown that small amplitudes ($<70\text{ }\mu\text{m}$) of motion are sufficient to cause damage and that the same effects can be produced by non-metallic materials. Oxidation was

therefore considered a secondary process because fretting could occur between metals and non-metals [22].

A different mechanical mechanism is where fretting can be considered to act in a similar fashion to the delamination theory of wear. It is based upon dislocation theory and the plastic deformation and fracture of metals near the surface. It was theorised that during rubbing of the contacting surface dislocations would be generated by plastic deformation. Oxide layers present would be ruptured to expose fresh metal. Continuous rubbing and production of dislocations would then lead to the formation of voids at a finite distance from the surface. With time, either by growth or shearing of the metal, voids would coalesce, finally resulting in a crack parallel to the surface [38]. When the crack reached a critical length, a platelet of material would be produced by shear of the material between crack and surface [22].

The chemical theory of fretting explains that the majority of metal surfaces are covered by oxides which could play a major part in the damage process. Oxides protect the surface from damage while they remained adhered, but become abrasive when they become loose. The mechanism of fretting wear damage in air is then due to repeated scraping off and reformation of surface oxide. The damage to readily oxidisable metal surfaces is far more severe in air or oxygen than under vacuum or inert atmosphere[22].

Fretting wear damage can occur by a combination of both chemical and mechanical effects. For example, The chemical damage results in removal

of surface oxide which can be followed by mechanical damage due to adhesive wear of the exposed metal [22].

2.2.2 Mechanism of fretting wear in titanium alloys

Many authors have proposed theories to explain Ti alloy wear mechanisms. One of the ideas is, formation of plastically deformed layer near the surface at the early stage of friction. Reigney et. al. [39] called these "Mechanically mixed layers (MML)" where Sauger et al.[40] and Sekkal [41] denoted them as "Tribologically Transformed Structure (TTS)". Aluminium, copper, iron and titanium alloys were extensively studied [42, 43]. The creation of TTS layers has been shown in Figure 2.2 [40, 44].

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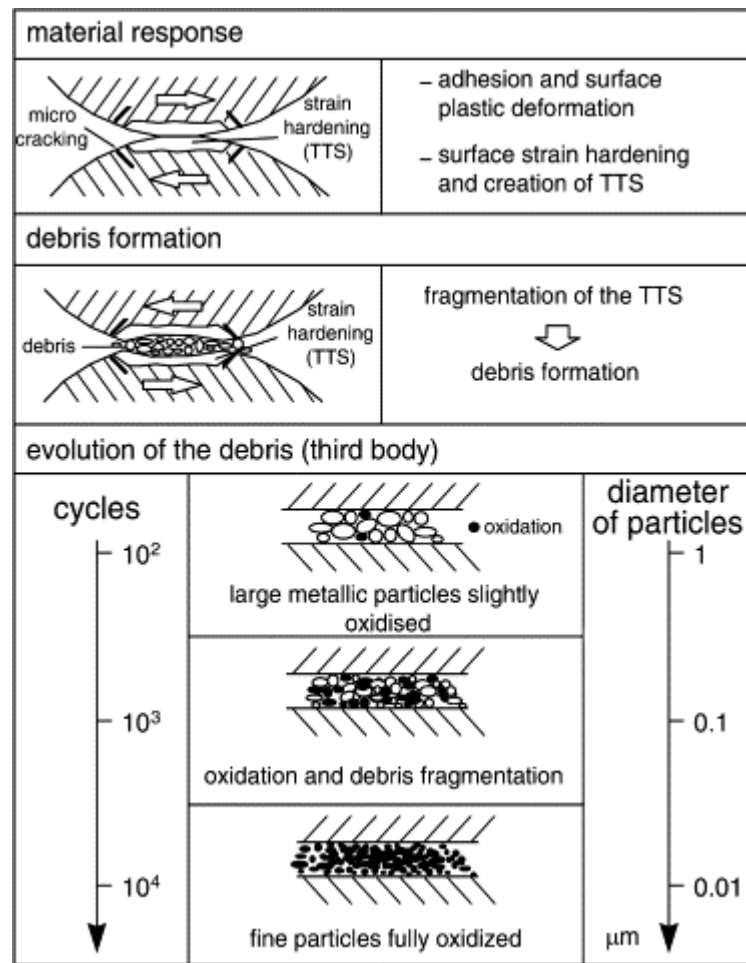


Figure 2.2 Creation and evolution of the third body through the contact interface [40, 44].

This layer is characterized by a very fine grain size, its high hardness and its structure to the wear debris. The wear mechanisms responsible for its initiation are still controversial. Rigney explained that, the local contacts cause plastic deformation under the surface, the accumulated strains help the formation of the substructures in the near- surface material, which becomes prone to shear instabilities. This encourages transfer of materials and complex mixing process at the interface which produces the MML, from which debris particles are generated [39]. In many studies, in environments with active components such as oxygen, nitrogen, the evidence of MML has been found by observation of intimate mixing of the

two counter parts [19]. Sauger et al. observed similar features but they did not mention the formation of TTS on counterparts or the role of oxygen or nitrogen [40]. Their mechanism was based on dynamic recrystallization, which was enabled by the plastic strain accumulation and high dislocation concentration, which is inspired by the work of Blanchard et al. [42]. Freimanis et al. [17] performed wear analysis on extended service jet engine disks and compressor blades. The wear analysis indicated that titanium from uncoated disk was transferred to the softer Cu-Ni-In coated dovetail surface on the blades. This transfer created titanium on titanium contact and consequently fretting wear.

Mary et al. [19] investigated temperature and mean pressure effects of the Ti17/ Cu-Ni-In interface fretting wear process which is depicted in Figure 2.3 [19] . Here Cu-Ni-In is being considered as a coating itself but in our present senario Cu-Ni-In considered as a underlayer of the top coating which is MoS₂.

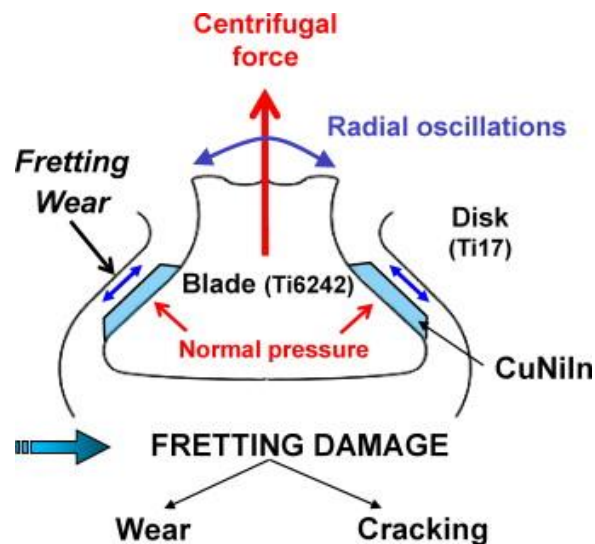


Figure 2.3 Illustration of blade/disk fretting wear damage in high temperature stages of turbine engines [19].

2.3 Prevention of fretting

Since fretting is intimately related to wear, corrosion and fatigue, the introduction of surface treatments or coatings is expected to be an ideal solution to fretting damage [45] and [46]. A wide variety of coatings and surface treatments to prevent fretting have been in use for many years.

There are few general ways to prevent fretting and fretting fatigue:

- a) Application of surface engineering
- b) Use of lubricants

2.3.1 Application of surface engineering

There are several surface modification techniques which have been identified as effective methods to enhance the ability of materials to resist fretting wear, such as, ion implantation (II), laser beam quenching (LBQ), shot peening (SP), laser shot peening (LSP), plasma nitriding (PN), plasma immersion ion implantation (PIII) and surface mechanical attrition treatment (SMAT) [1, 47-51]. Among these, shot peening and laser peening is a common method of surface treatment [26]. Shot-peening has been used on Ti6Al4V specimen to increase its fatigue life by increasing the crack initiation resistance by inducing residual compressive stresses [52]. Fu et al. discussed several advanced surface modification methods, such as, physical vapour deposition (PVD), chemical vapour deposition (CVD), ion implantation and plasma nitriding etc. [53].

2.3.1.1 Peening

Shot peening is an effective method of introducing compressive residual stresses into the metal surface to improve fatigue and fretting performance [54] in metals and alloys for the past six decades. Shot-peening is done by bombarding the material with hard, small steel balls which results in a rougher surface and compressive residual stress in the surface of the component. The in-depth compressive residual stress field and the associated work hardening [10] tend to prevent crack initiation by neutralising the effects of applied tensile stresses on the component [25]. It is a widely used, relatively inexpensive method suitable for small or large components.

The method has its own limitations. The process is semi-quantitative and depends on a metal strip gauge while determining the compressive stresses produced to provide an indication of shot peening intensity. The shot peening generates a rough surface relatively on soft metals like aluminium. The roughness needs to be removed before wear application and by this typical processes before it goes to the wear application [54]. Shot peening is a line of sight process.

Laser shock peening (LSP) is a surface treatment method, also called laser peening. High power, pulsed laser beam is used to impact compressive residual stresses on the surface by laser shock peening method [50]. Schematic diagram of laser peening method is shown in Figure 2.4 [54].

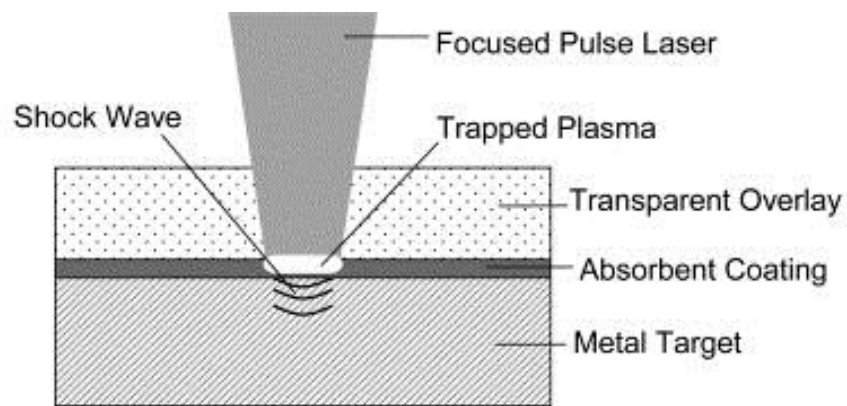


Figure 2.4: Schematic presentation of the laser peening method [54].

By the laser peening method, a greater depth of residual stress can be induced into the metal surfaces than by the shot peening method [54]. The residual compressive stress helps to increase the fatigue strength of engineering components [55]. Like shot peening, laser peening is a line of sight process.

Srinivasan et al. [50] observed the effect of LSP on fretting fatigue life of Ti6Al4V alloy subjected to contact loading that generates stresses within a range of 250-350 MPa, similar to the system occurring in gas turbine blade/ disk contacts. The fatigue lives for LSP treated specimens were increased 5, 10, 25 fold at stress levels compared to untreated specimen but it did not mitigate the formation of fretting cracks.

Liu et al. studied the effect of laser peening (LP) and shot peening (SP) on fretting fatigue in Ti6Al4V substrate [56]. The results showed The SP had near-surface stress of -750 MPa and a depth of compression of 0.25 mm. The LP had near-surface stress of -570 MPa and a depth of compression of

1.3 mm. Both LP and SP showed significant lifetime improvements, with the improvements for LP less than those for SP. King et al. also applied shot and laser shock peening in three-point bend and Dovetail Biaxial Rig samples on Ti6Al4V surface of fan blade roots [57]. Residual stress of 700-800 MPa was introduced and indicates the extra depth of compressive residual stress introduced by laser shock peening (1.5 mm) compared to shot peening (0.3 mm) improved the tolerance of components to fretting damage.

2.3.1.2 Other surface engineering techniques

The use of lasers of creating textured patterns on surfaces has received some attention. These textures contribute to improved reduction in friction acting as a lubricant reservoir, trapping wear debris [35, 58].

Fu et al. worked to improve the fretting wear and fretting fatigue resistance of Ti6Al4V alloy by using several types of surface treatments and thin films, including shot-peening, ion-beam-enhanced deposition (IBED) CrN films, shot-peening+ IBED CrN films as well as IBED Cu-Ni-In films [59] and results showed improvements of the fretting wear and fretting fatigue resistance of Ti-6Al-4V. These surface treatments helps in four different ways (a) induce a compressive residual stress, (b) decrease the coefficient of friction, (c) increase the hardness, (d) increases surface roughness.

Zhang et al. addressed the effects of multiple laser peening and laser peening intensity used in laser shock peening (LSP) on the residual stress,

micro-hardness and three-point bending fatigue performance of Ti-6Al-4V alloy [60] and the treatment showed a maximum 42% increase in the fatigue strength as compared with the as-received specimens.

Golden et al. [61] investigated two surface treatments, Laser Shock Processing (LSP) and Low Plasticity Burnishing (LPB). These are considered both with and without coatings [61] on Ti6Al4V surfaces. The addition of LSP and LPB to the dovetail specimens with no coatings greatly improved fretting fatigue strength as expected. DLC coating significantly improved the fretting fatigue lives by decreasing the coefficient of friction.

2.3.2 Temperature effect

Plenty of investigations have been performed under conditions of reciprocating sliding in different temperature conditions and other environments. Dutta noticed fretting is more severe at low ambient temperatures than at high temperatures in titanium alloys [62]. It is found that in mild steel in dry air the fretting damage was highest at -150 °C, gradually decreasing as the temperature rise to 0 °C, and then decrease as temperature increased and at 50 °C remained constant. The possible reason may be that the liquid water acts as lubricant but ice does not [62, 63].

Hurricks investigated the fretting wear behaviour of mild steel from room temperature to 200 °C and found fretting damage on mild steel decreases with increase of temperature within the range and reaches a constant value at 200 °C [64], which is consistent with Dutta's [62] observation in case of

Ti alloys. Hurricks also investigated the fretting wear behaviour of mild steel in air in a range of 200 °C to 500 °C and found above 200 °C the degree of fretting wear continuously decreases up to 500 °C [65]. It was also mentioned that between 500 °C and 600 °C, there is second transition temperature above which the wear rate increased.

The fretting wear of Ti6Al4V was investigated in air at temperatures up to 600 °C for the titanium alloy by Hamdy & Waterhouse [66]. It was found that the titanium alloy generally exhibited higher coefficients of friction which continued to increase at 10^6 cycles, oxide begins to form at 200 °C and is well developed at 400 °C and breakdown occurs due to substrate creep at 600 °C. Hamdy et al. also investigated fretting fatigue behaviour of Ti6Al4V at temperature up to 600 °C and showed fatigue becomes accelerated at the higher temperatures and leads to large accretions of platelets at 600 °C [67].

Hager et al. investigated fretting wear regimes in Ti6Al4V interfaces at room temperature which indicate mixed fretting wear initially, however, a cycle dependent transition to gross slip occurred in some tests [68].

2.3.3 Effect of wear debris / third body/ transfer film

Wear particle analysis to monitor and diagnosis machine condition faults is not new topic and it is been studied for several decades in the tribology world. It is a recognised effective and economic technique [69] to detect the actual condition of wear or the machine part. It also allows performance of preventive maintenance. The shape, size and surface

structure of the wear particles can indicate the nature of the wear process [70]. There are opposing viewpoints about the specific wear reducing roles of filler decomposition, polymer degradation, transfer film adhesion, and transfer film cohesion. There is a broad agreement that transfer films play a very important role in the tribology of polymers. Thin and uniform transfer films always accompany low wear sliding of polymers and transfer film adhesion for low wear rates [71-73]. However, Ye et al. [74] indicated there are three distinct transfer film morphologies that define the sliding regimes and wear response for an PTFE-alumina composite : (a) run-in (b) transition and (c) steady state. Debris are mechanically and chemically identical to the bulk in run-in period, in transition period the debris size reduces and helps improving dwelling time by reducing wear rate, in steady state period deposition oxide debris produce continuous transfer film island towards destruction. They also highlighted that the transfer film is not responsible for low wear rate, it evolves in response to the wear debris morphology and chemistry [74]. The bond strength of the transfer film with the counterface let to lower wear rate for all the composites [75].

In machinery, the condition of the wear state of critical components can be determined by the debris transported from the wear site by lubricant. Wear debris carry important information with them [76]. The most important information concerns the quantity of debris generated as a function of operating hours. It provides an excellent opportunity to monitor the trend of the extent of the wear and the wear rate, at which it is progressing. Size, outlined shape, edge detail, surface feature and colour are particularly important features to analyse the type of debris formation and the cause of wear and severity of the wear [76]. Usually, wear particle

morphology is assessed qualitatively based on microscopy observations [70]. Ye et al. [74] studied PTFE-alumina composites to determine the complex interplay involving transfer film adhesion, chemistry, debris morphology and mechanics. They mentioned, the progressive reduction of debris size over time reduces the wear rate increasing the life time of the protective surface. Fretting wear has the characteristic of forming considerable amounts of very fine oxide debris by any one of the basic wear mechanisms. i.e., oxidative, adhesive, surface fatigue and abrasive [35, 36]. Their behaviour is a significant factor in governing fretting wear [34]. The wear particles present in the contact zone, i.e., debris, can escape from areas of contact into adjacent rough grooves on the surface [35]. This means, increasing the roughness of the surface will give more opportunity for escape to the debris formed from the contact zone in to the rough holes on the surface. Depending on the ease of wear debris removal from the contact regions to the adjacent areas, fretting can either increase the separation or lead to breakage of the fretting surfaces [77].

Many papers have been discussing directly or indirectly the role played by wear particles presence at the contact zone [34, 78-82], [83], [84], [53] and [27, 28, 85] and two opposite effects were identified, i.e., reducing or increasing the wear. It was observed that allowing the presence of oxide debris in the interface by better surface finish or by supplying them directly into the contact may have either a beneficial effect [78], [79], [80] and [81] or a harmful effect [53, 84]. Depending on materials selection two opposite effects were also found by Shipilov [83], Varenberg et al. [35] studied the role of the oxide wear debris present during fretting. They allowed the wear particles to escape in to the micro-pores of a laser

textured surface. When the adhesive wear mechanism is dominant, oxide particles act like a solid lubricant and reduce the damage occurred by fretting. If abrasive mechanism is dominating then the oxide debris facilitate the wear process rather than protect against it. Wear by debris formation has been the most critical damage phenomenon under gross slip conditions but cracking is predominant under partial slip conditions [86].

Sabeya et al. [27] conducted experiments with Cu-Ni-In and Cu-Ni-In followed by MoS₂ on Ti6Al4V and showed that the internal third body is a mixture of coating and the substrate.

2.3.4 Lubricants

Another possible way to provide a useful mitigation of fretting is to use appropriate lubricants, such as, liquid, grease and solid lubricants [87]. However, lubricants are usually very difficult to apply in fretting contact because of their low durability [88].

There are five different possible mechanisms for using surface-modification methods to increase fretting resistance: (a) inducing a residual compressive stress, (b) decreasing the coefficient of friction, (c) increasing the surface hardness, (d) altering the surface chemistry, (e) increasing the surface roughness [53]. Based on the above possibilities, coating-selection method was proposed to select the most appropriate surface treatments or coatings to minimise the probability of fretting damage. According to the fretting failure modes and the ability to adjust and obtain the required surface properties coating selection can be done. Apart from this, the

intrinsic properties of the coatings, such as their density and mechanical and chemical properties as well as the adhesion condition with the substrate, also significantly affect the performance of the coatings under fretting conditions.

Zhou et al. reviewed the effects of many lubricants on fretting behaviour and found majority of experimental data was obtained under quite differing conditions. In order to select successful candidate of lubricant for a specific fretting application, representative lubricants, oil, grease, polymeric film and solid lubricant coating such as, molybdenum disulphide (MoS_2) with different physical states were used. Results indicate that the palliative effect on fretting should be analysed using the fretting regimes concept. In particular, solid lubricant is most efficient in the partial slip regime while grease and oil, particularly the latter, are more suitable in the gross slip regime [88].

According to different physical states, lubricants can be divided into three groups: (a) liquid lubricants (b) semi-solid lubricants (c) solid lubricants

2.3.4.1 Liquid lubricants

In earlier work [89], [88], [90], [91, 92] and [93], oil has been used to prevent fretting corrosion by restricting access of oxygen, while simultaneously reducing the coefficient of friction and adhesion of the wear surface. Imai et al. [94] has shown a significant reduction in fretting wear when using oil for a mechanically treated surface in gross slip regime.

Viscosity of oil is one of the most important parameters while considering fretting. Some works have shown that low viscosity oil is more effective than high viscosity oil in preventing fretting damage because of its easier penetration into the fretting contact area [88]. However, some research reported that high viscosity oil is more effective due to better restriction of oxygen access. McColl et al. [95] and Shima et al. [96] conducted experiments at low slip amplitudes. The coefficient of friction was higher than without lubrication as shown in Figure 2.5 [96], especially for oil with high viscosity due to inhibition of oxygen access. For low oil viscosity, when slip amplitude increases, steady state coefficient of friction decreases rapidly and it is much less than without lubrication. A similar phenomenon has also been observed by Kalin et al. [97].

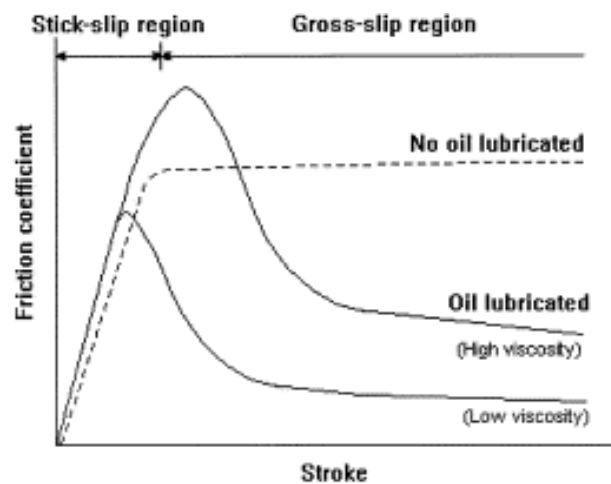


Figure 2.5 Schematic effect of slip amplitude on steady coefficient of friction, for tests with and without oil lubrication [96].

Oil lubrication film is very sensitive to normal contact pressure. Shima et al. [96] and Neyman [98] showed evidence that effectiveness of the lubrication film decreases and coefficient of friction increases with increasing normal load. Liquid lubricants have certain limitations which solid lubricant can overcome such as facility of expulsion from the gaps

between moving parts of a device, easy to use in different environmental condition or in high temperature application[99]. Neyman [98] showed evidence that effectiveness of the lubrication film decreases and coefficient of friction increases with increasing normal load. However, due to the very high stresses generated in the application considered in this thesis, liquid lubricants are not useful.

2.3.4.2 Semi-solid lubricants

Grease is one of the most important semi-solid lubricants used in tribo-systems [88]. It is thickened oil. The mechanisms of lubricant film formation are complicated and poorly defined. However, in fretting situations such as in electrical conductors and steel ropes, various greases have been found to be an effective palliative [92, 100].

The main purpose of grease lubrication is prohibiting oxygen access to the fretting contact area as well as lowering the coefficient of friction [93, 95]. Zhou et al. showed that the oxidation observed from the cross-section of aluminium wire of fretting fatigue emerging in the dry condition almost disappeared under grease lubrication conditions [101]. However, the difficulty with grease lies in its durability unless there is self-cleaning action of fretting which quickly removes any lubrication film, and have access to the inner regions of fretting contact without separating the surfaces is difficult for greases. Zhou et al. also showed that improvement due to grease lubrication could be possible if normal load and relative slip is small, and that lubricant protective effect tended to decrease with increasing load

and relative slip [101]. Therefore greases also are not suited to the application considered in this thesis.

2.3.4.3 Solid lubricants

Solid lubricant coatings were originally developed for aerospace applications and are presently widely used in many fields [102]. Solid lubricant coatings are generally used to reduce coefficient of friction [103], to control friction and wear under different application conditions, especially, problems of lubrication in applications where conventional fluid lubricants are ineffective and undesirable [102, 104] such as in environments at high vacuum or high temperature, or with highly-loaded contacts with velocities too low to generate fluid-film separation. Because of the environmental requirements, modern tribology is trying to reduce the use of liquid lubricant as much as possible by increasing the use of solid materials and coating with self-lubricating properties[104].

Most work with solid lubricants has concentrated on MoS₂ (in powder or film form), graphite (in powder form), polymeric film (e.g., polyvinyl chloride, polyimide, polystyrene, polytetrafluoroethylene) [89], [90], [91]. Later section will concentrate on solid lubricant coatings in detail.

2.4 Solid Lubricant Coatings

Typically solid lubricants are layer lattice crystals such as graphite, WS₂ and MoS₂. Superlubricity also happens in hexagonal boron nitride as it has tribological characteristics very similar to these observed in graphite

system [105]. Diamond-like carbon (DLC) [106-108], as well as the crystalline polymers such as polytetrafluoroethylene (Teflon) [109-111], soft inorganic compounds such as lead oxide, lime, talc, bentonite and malleable metals such as aluminium, copper, lead are effective solid lubricants [111-114]. All solid lubricants have common properties that they are plastic, elastic, malleable or fracturable [111], because of their solid phase, they lubricate, reduce friction as well as liquid lubricants. They can provide extremely low friction and wear coefficients under certain conditions, but solid lubricant coatings have disadvantages like limited lifetime and less easy to replace than a liquid lubricant.

Depending on their physical, chemical and structural and mechanical properties, solid lubricants can be categorised into two sub categories. 1) hard solid lubricants and 2) soft solid lubricants. In some cases where materials possess layered structures but have strong interlayer bonding, fluorination can be used to insert atoms or molecules into the gap between the planes, which widen the spacing, softening the material. Graphite fluoride or Ag_xNbSe_2 are examples of this kind [115]. Soft coatings are also considered to offer additional advantages, for example, compliance between mating components, so combinations of hard and soft coatings might be more desirable instead of only a hard coating [61]. Soft coatings such as Al-Bronze or Cu-Ni-In along with a solid lubricant such as MoS_2 provide the desired performance [31] but can wear out over time. These solid lubricants are applied as coatings on substrate. Table 2.2 [116] below provides some of the solid lubricants of each category.

Table 2.2 Classification of tribological coatings, depending on the nature of the constituting material [116]

Hard coatings Hardness higher than ≈ 10 GPa	Soft coatings Hardness lower than ≈ 10 GPa
Nitrides TiN, CrN, ZrN, BN, BaSO ₄	Soft metals Ag, Pb, Au, In, Sn, Cr, Ni, Cu
Carbides TiC, WC, CrC	Lamellar solids MoS ₂ , WS ₂ , Graphite H ₃ BO ₃ , HBN, GaS, GaSe
Oxides Al ₂ O ₃ , Cr ₂ O ₃ , TiO ₂ , ZnO, CdO, Cs ₂ O, PbO, Re ₂ O ₇	Halides sulfates, sulfur CaF ₂ , BaF ₂ , PbS, CaSO ₄ , BaSO ₄
Borides TiB ₂	Polymers PTFE, PE, Polyimide Polymer like DLC
DLC & Diamond a-C, ta-C, a-C:H, ta-C:H, CN X a-C:X(:H), (nc-)diamond	
DLC = diamond like carbon a= amorphous ta = tetrahedral amorphous X = a metal nc = nanocrystalline PTFE = polytetrafluoroethylene PE = polyethylene	

Coating design needs careful consideration of the relevant tribological contact mechanisms. Matthews et al. [117] explained four main factors influence the tribological behaviour as 1) hardness of the coating & substrate, 2) thickness of the coating, 3) roughness of the coating surface and 4) size and hardness of the debris in contact. In DLC or MoS₂ coatings, transfer of material from one surface to the other dominates the friction and wear behaviour which is beneficial in these coating where in other coating this mechanism could be disadvantageous [117].

Low friction with a low wear rate can be achieved from a hard, high shear strength surface. A hard, load supporting layer is needed to prevent

junction growth and bulk plastic deformation. In certain applications a thick, relatively soft film can assist in extending surface life by sliding any debris present, and removing this from the contact. Different sliding contacts can result from changing in coating parameters as can be seen in Figure 2.6 [118].

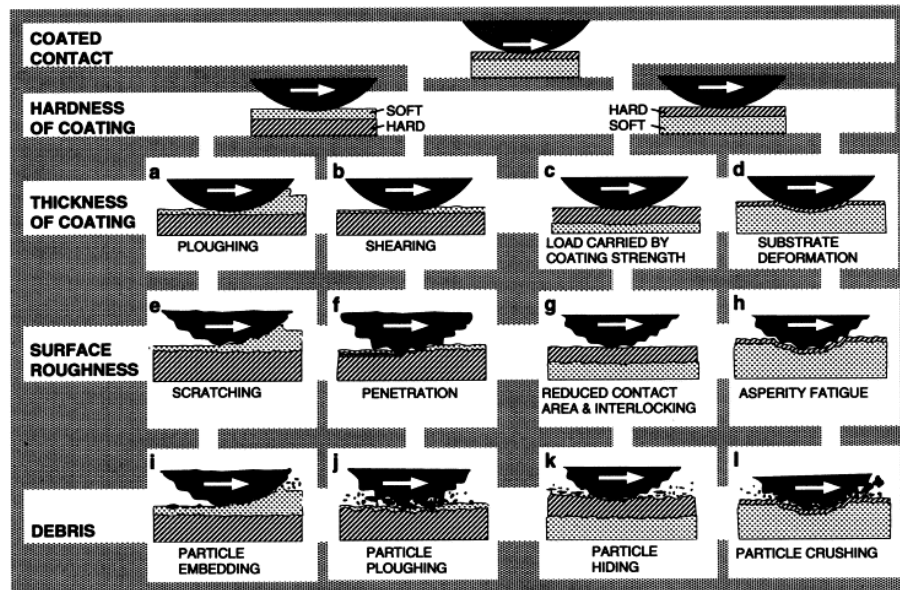


Figure 2.6 Macro mechanical contact conditions for different mechanisms that influence friction when a hard spherical slider moves on a coated flat surface [118]

2.4.1 Hard solid lubricants

Hard solid lubricants have hardnesses of more than 10 GPa whereas soft solid lubricants have the hardnesses of less than 10 GPa [104, 119]. The hard solid lubricants exhibit higher wear resistance along with low coefficients of friction when compared with soft solid lubricants, which can provide low coefficients of friction but their wear resistance is not always

high [116]. Hard solid lubricant coatings include some of the carbon-based coatings, such as, DLC and certain oxide. TiN, CrN, ZrN, BN, DLC are typical solid lubricant coatings [116].

2.4.2 Soft solid lubricants

Soft solid lubricant coatings include polymers, soft metals, such as Pb, In, Sn, Ag and Au. Other materials, such as CaF_2 or BaF_2 may also be included as they become soft at high temperatures [115]. Halides and sulphates of alkaline earth metals, and the well-known lamellar solids, including transition-metal dichalcogenides, such as MoS_2 , WS_2 and TaS_2 and the similar series of ditellurides and diselenides [115], along with materials such as talc ($\text{Mg}_3\text{Si}_2\text{O}_{10}(\text{OH})_2$) are soft solid lubricants. Graphite, boric acid, boron Nitride (BN_{hex}) also fall in this category [116], but for these, absorbed vapours, such as water or organic compounds are necessary to maintain low coefficients of friction [115]. Other inorganic materials, such as PbO , PbS or CdO can also act as soft solid lubricants under specific conditions [115].

2.4.2.1 Cu-Ni-In Coating

In the blade/disk contact, surfaces are usually covered by a thick soft metal layer of Cu-Ni-In coating. A solid lubricant coating is deposited on the top of Cu-Ni-In [19] followed by a topping with polymer bonded molybdenum sulphide coating, where Cu-Ni-In coating is done by the thermal spraying method, producing the lamellar structure and surface

roughness. A typical thermally sprayed Cu-Ni-In coating shown in Figure 2.7.

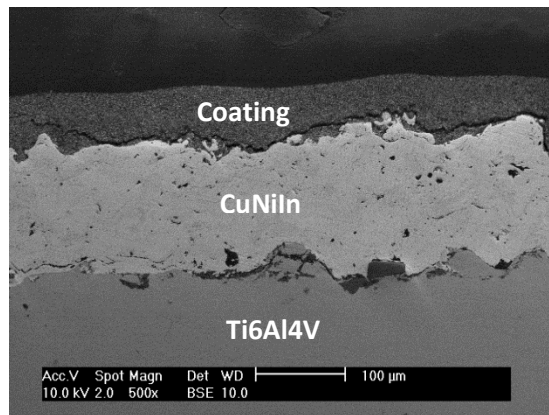


Figure 2.7 Typical thermally sprayed Cu-Ni-In underlayer sandwiched between Ti6Al4V substrate and a top coating layer

The surface roughness is important to ensure that the reservoirs of the dry film lubricant (DFL) are contained within the surface. The Cu-Ni-In coating is reported to have a great capability to accommodation by plastic deformation which limits nucleation and the propagation of cracks [27, 31, 59, 119, 120].

The thermal spraying method is one of the successful coating techniques for providing wear-resistant surfaces [121]. It is a line of sight process. Due to the low cost, simple equipment, flexible process and availability of field operation, thermal spraying is an important surface modification technique. Thermal spraying is probably the most promising method to produce the relatively thick surface layers to modify wear or corrosion properties without influencing the mechanical properties of substrate such as strength and ductility [122-124]. By this method, the build-up of the coating from individual particles results in a rough surface. Cu-Ni-In coating is thermally sprayed to generate this rough surface. Rajasekaran et

al. [125] studied the relative performance of Cu-Ni-In coatings on Ti6Al4V by plasma spray and D-gun spray process, where D-gun spray samples exhibited superior plain fatigue life than uncoated specimens whereas plasma spray samples shows similar values of residual stresses on the surface compared with the uncoated specimens.

Fridrici et al. [126] examined the fretting behaviour of a system with a DFL which was deposited onto a plasma sprayed Cu-Ni-In coating. The Cu-Ni-In was reported to have a Vickers Hardness of 170 kgf mm^{-2} and an as-sprayed roughness (Ra) of $8 \text{ }\mu\text{m}$. It was argued that this roughness promoted retention of the DFL layer. In addition, it was noted that the Elastic modulus of the Cu-Ni-In (60 GPa) was around a half of that of the titanium alloy substrate (119 GPa), and as such, the addition of the Cu-Ni-In reduced the contact stiffness and resulted in a larger contact area and a reduction in contact stress. Moreover, Sabeya et al. [27] noted that the function of the Cu-Ni-In coating is to accommodate plastic deformation which thus limits cracking in the substrate (component) material. More explicitly, Fouvry et al. [127] argued that "a major part" of the strain imposed through the interface of a fretting contact is "accommodated by plastic deformations through the bronze coating". It has also been noted [127] that the lifetime of such a system may not be related to the removal of the DFL to reveal the underlying metals, but instead it is associated with a total oxidation of the MoS_2 phase in the interfacial material. However, it has also been noted that the epoxy-based DFL is rapidly removed from such a system, and accordingly the fretting behaviour of titanium alloy against Cu-Ni-In -coated titanium alloys has been the subject of investigation [19, 31]. It was noted that, although the Cu-Ni-In itself can be

used “to act as a sacrificial barrier that protects both the blade and disk by preventing the Ti6Al4V surfaces from coming in contact with each other”[128], significant damage can be caused to the titanium alloy by fretting against the plasma-sprayed coating [24].

Cu-Ni-In enhances roughness of the surface and helps DFL retention and provides effective isolation between coating and substrate. Being a soft metal, it helps reduce friction, improving anti-wear ability as well as help increasing service lifetime of the equipment. However, Cu-Ni-In coating causes severe damage to the Ti-alloy counterpart due to adhesion mechanisms. When the adhesion occurs, Ti transfers on the Cu-Ni-In surface and accelerates wear by producing a Ti/Ti contact [19].

Most of these self-lubricating materials have been extensively studied in recent years, and some of them have been further optimized to provide better lubricity when used under specific conditions or in environments such as high temperatures [129-133]. There are other soft coatings which are well known as solid lubricant coating and will be discussed in detail separately.

2.4.3 Solid lubricant coatings composition

The usable solid lubricants includes sulphides such as molybdenum disulphide and tungsten disulphide, fluorides, such as polytetrafluoroethylene and graphite fluoride, graphite etc. be used individually or in combination of two or more [134]. It is usual to use a

combination of one or two components together usually embedded in a polymer or resin.

There is no restriction on synthetic resins to be used. In coating composition for lubrication, any synthetic resins can be used such as thermosetting resins, cold settings resins and two component curing resins. Resins can be miscible in water or oil. Well known examples of usable synthetic resins are epoxy resins, phenyl resins, amino resins, polyester resins, polyurethane resins, vinyl resins, polyamide-imide resins and silicon resins. The resins can be used single or combination of two or more [134].

From commercial standpoint, epoxy polymers or resins are among the most important of the nonvinyl polymers. They represent a special type of polyether prepared by a step-polymerisation reaction between an epoxide and a dihydroxy compound, usually bisphenol A, in presence of base. The commonest dihydroxy compound in commercial use is bisphenol A, giving pre-polymer structure.

2.4.3.1 Low friction coating composition

There are a few compounds that are used as friction coefficient adjusting additives which include carbon fibres, carbon black, silicon compounds, such as silicon dioxide, silicon carbide, silicon nitride and glass fibres, aluminium oxide, potassium titanate fibres [134]. An admixture of high temperature epoxy and molybdenum disulphide powder and a polyimide powder can produce a low friction coating. Fillers such as graphite powder, fibreglass fibres or polytetrafluoroethylene (TEFLON) in powder or fibre

form are added in amounts from 0 to about 5% by weight of the admixture to get low friction coefficients [135].

2.4.4 Molybdenum disulphide

Molybdenum sulphide is a well-known dry film solid lubricant which has a lamellar hexagonal structure [99, 136-139]. For MoS_2 , three chemical properties are responsible for its tribological behaviour, layered structure, Van der Waals interlayer interactions and structural anisotropy [99, 136]. The binding between adjacent layers is very weak. Each layer is composed by a plane of molybdenum atoms embedded between two layers of sulphur atoms. The Van der Waals interaction between two layers are small compared to the strength of Mo-S binding so the sliding of the plane happens [99, 102, 105, 112] which can be clearly seen in Figure 2.8 [115].

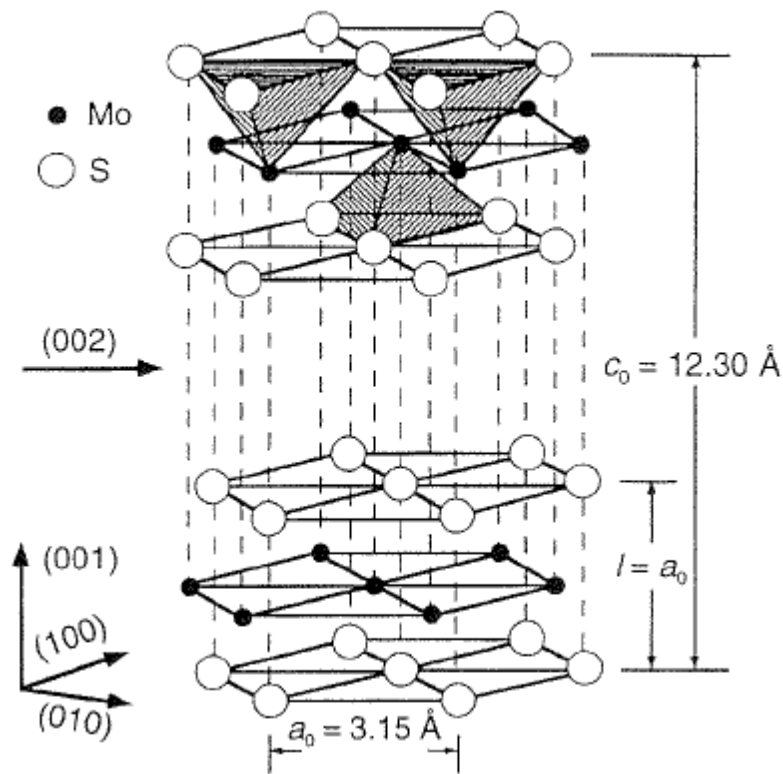


Figure 2.8 The crystal structure of MoS₂ 2H, indicating covalent (tetrahedral) in-plane bonding, and Van der Waals between plane bonds structure [115]

The mechanism of ultra-low friction of MoS₂ has been studied in several studies [136, 140]. It is generally explained that the three following conditions must be satisfied to achieve low friction: 1) built in MoS₂ transfer film on the contact surface 2) avoid contamination such as oxides and 3) reorientation of the (0001) basal planes of MoS₂ grains in the interface parallel to the sliding direction when friction induced.

In many industrial sectors, the MoS₂ is applied to a surface as a coating in the form of MoS₂ particles in a polymeric binder [141] (although MoS₂ can also be utilized as a low friction material in a wide range of forms [136, 142-145]). in the case of a polymer loaded with MoS₂ particles, the coating

is often applied on top of a soft, compliant, Cu-Ni-In layer [146] explained in section 2.4.2.1.

The polymer bonded molybdenum sulphide favours sliding and decreases the coefficient of friction [88, 147]. Winer [148] reviewed and evaluated the work presented in the literature over the past 50 years on the behaviour of MoS₂ as a lubricant [115, 148]. Most of the work with solid lubricants has concentrated on MoS₂, either in powder form or film form or with addition of other materials [7, 109, 115, 142-145, 147-174]. The best-performing and most flexible technique for preparing MoS₂ film is by physical vapour deposition (PVD) [115].

In presence of high vacuum or an inert atmosphere, pure and stoichiometric MoS₂ should satisfy the condition of superlubricity, where two contacting surfaces exhibit no resistance to sliding in the absence of any contamination [136, 175].

2.4.4.1 Methods of coating

Various processes have been applied for applying molybdenum sulphide in a film to the surface of metal for use to mechanical friction. Specifically molybdenum sulphide has historically been applied using following techniques:

- Burnishing
- Spray bonding
- Particle incorporation in liquid or greases
- Thin film coating

Burnishing typically produces poorly adherent, significantly contaminated, porous coating with and high variability in thickness. They are simple and cheap and can be applied in non-critical situations. The use of solid lubricants in oil or greases must be carefully evaluated on a case-by-case basis as some cases addition of oil MoS_2 or graphite is ineffective or even detrimental. Coatings of MoS_2 are usually deteriorate quickly in presence of liquid and burnished MoS_2 films may start cracking and bulging immediately after exposure to mineral oils [115]. The presence of oxidizing agents, particularly water vapour and oxygen, tends to reduce the wear life of the MoS_2 film. This behaviour is particularly true in the case of burnished films [148].

Spray bonding employs dispersion of the solid lubricant, with a binder, in a volatile solvent. In this case the material is sprayed on to the surface to be lubricated followed by drying and curing. Binder can be organic (e.g., alkyd, phenolic, epoxy, acrylic) or inorganic (e.g., silicate, phosphate, borate, ceramic) resin [115] followed by application of the mixture to the pre-treated surface for satisfactory results such as shot-peening, sand blasting etc. [138]. Presence of binder along with the coating thickness results in higher coefficient of friction than the lubricant phase alone would exhibit [115]. A comparison coefficient of friction coefficient and lifetime of burnished, spray-bonded and PVD MoS_2 in vacuum is given in Figure 2.9 [115].

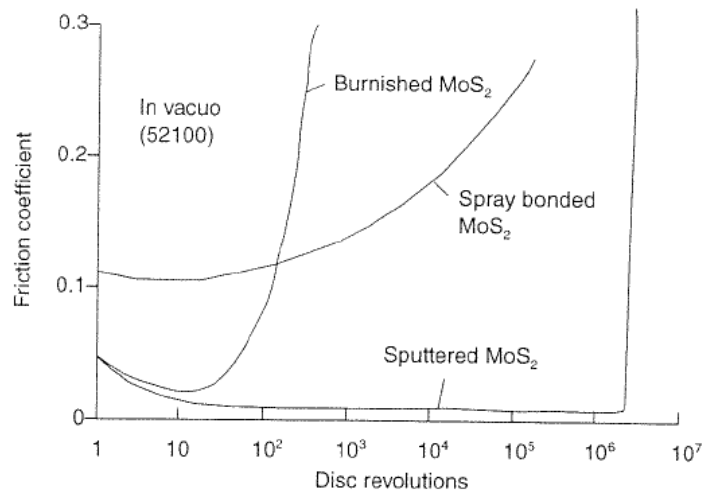


Figure 2.9 Friction coefficients of MoS₂ films deposited by various techniques [115]

Traditional wear resistant coatings have been generated by electroplating and thermal spraying techniques. Coatings achieved from these mechanisms are much thicker than other recently developed techniques such as vapour deposition method [117]. Cu-Ni-In coating thicknesses achieved by plasma spray method are typically 100-150 μm [24, 125]. For higher thickness the established coating is less dependent on the substrate to provide load support. It ensures that macro mechanical wear mechanisms are resisted [117].

2.4.4.2 Fretting behaviour of MoS₂

Various investigations into the fretting behaviour of MoS₂ have been reported [141, 142, 144, 145, 147, 163]. Xu et al. carried out fretting wear tests on MoS₂ solid lubricant using various normal loads and amplitudes and saw a rapid increase of CoF with higher loads [147]. Hu et al.

investigated the tribological properties of hot pressed MoS₂ coating on laser textured surface and found a significant increase in wear life compared to a burnished coating on textured steel surface [144], they also noted that the coefficient of friction could be low as 0.05. Ye et al. saw that MoS₂ based solid lubricant on steel had excellent anti-friction and wear-resistant performance [163] within a wide load range of 20 N to 800 N [141]. Holmberg et al. found that the use of MoS₂ coatings on steel and silicon substrates improved the fracture performance of the coated surfaces [142]. Sabeya et al. [27] conducted the experiment with MoS₂ and Cu-Ni-In + MoS₂ and found the contribution of polymer bonded solid lubricant MoS₂ on Cu-Ni-In coating strongly decreases the coefficient of friction over Cu-Ni-In alone from 0.7 to 0.5 at 6 N load, amplitude of $\pm 75\text{ }\mu\text{m}$ and frequency at 100 Hz. This confirms the high performance of the association of Cu-Ni-In + MoS₂. This system is able to dissipate energy while limiting the wear of the contacting materials [28]. Systematic investigations of fretting tests with MoS₂ powder have been conducted by Müller [89]. Wahl et al. [143] investigated the wear and friction of MoS₂ in a reciprocating sliding contact. 55 nm of MoS₂ on 35 nm TiN was deposited on steel substrate, where they observed the friction coefficient was insensitive to changes in coating thickness of MoS₂ until a significant underlying wear area was exposed. Ripoll et al. [58] studied fretting and evolution of coefficient of friction on laser textured Ti6Al4V surfaces followed by MoS₂ coating and analysed the surface by SEM & EDS. Sabeya et al. [27] performed a test for Cu-Ni-In + MoS₂ at ambient temperature at a constant frequency of 100 Hz over a period corresponding to 10⁶ cycles with the normal force range from 2.5 to 15 N with referred displacement amplitudes of ± 50 , ± 75 and $\pm 100\text{ }\mu\text{m}$.

2.4.4.3 Effect of thickness and contact geometry

A number of investigations have been carried out to examine both the sliding and the fretting behaviour of MoS₂-loaded polymeric films [141, 142, 145, 147, 163, 165, 176], with thermal effects being observed to be significant in controlling behaviour in certain sliding test configurations. Fridrici et al. [126] investigated the effect of contact geometry on fretting life of a surface engineered system (Cu-Ni-In with a top coat of MoS₂) by comparing results from cylinder-on-flat contacts with flat-on-flat contacts. They determined a unique Wohler like master curve to predict the life time of MoS₂ solid lubricant which proved to be independent of the contact geometry. Ye et al. [141] examined the behaviour of 30 µm thick MoS₂-based DFLs in reciprocating sliding against an uncoated steel ball (the DFL was applied directly to a steel substrate with no soft metallic interlayer). In this case, both the wear coefficient and coefficient of friction were observed to increase with decreasing contact pressure, indicating a sensitivity to contact geometry.

Some data regarding the evolution of the coefficient of friction (CoF) during fretting of MoS₂ containing DFL systems have previously been reported. A period of rapid change is often observed during an initial running-in stage which frequently produces an initial peak in the CoF, this is commonly followed by an essentially steady state secondary region during which the coating thickness progressively decreases (by wear) until a critical point is reached (the tertiary stage) where the CoF increases rapidly [177]. In recent work, Fouvry et al. [178] examined the fretting behaviour of a surface-engineered titanium alloy pair, both bodies had been shot peened,

but on one of the bodies in the fretting pair, a coating system had been applied (Cu-Ni-In with a $\sim 30\text{ }\mu\text{m}$ thick top coat of a MoS_2 -containing epoxy resin). They observed that the friction coefficient at the beginning of tests was low and rose in a relatively steady manner to the point when coating failure occurred (which they defined as being the point at which the CoF reached 0.35).

As well as the loss in thickness of the material, a number of researchers have also noted that degradation of such systems is also associated with the oxidation of MoS_2 to MoO_3 [127]. Indeed, Luo et al. described the degradation of an MoS_2 -containing epoxy resin in fretting as being a combination of abrasive wear, delamination and tribo-oxidation of the MoS_2 to MoO_3 , with the latter transformation being responsible for a gradual increase in CoF from 0.2 to 0.3 throughout the fretting tests [109]. Similar increases in CoF associated with this chemical degradation of MoS_2 have been reported elsewhere [141, 149].

Kim et al. investigated the effect of two different coating thicknesses of a polymer bonded MoS_2 on a Cu-Ni-In metallic layer (total thicknesses of 50-80 μm and 100-150 μm) and showed that durability of the system coating increased with increasing initial coating thickness [179]. Zhou and Vincent [180] investigated the effect of initial coating thickness (5 μm and 50 μm) of polystyrene coatings on a steel substrate in fretting using a ball-on-disc arrangement. Here, a sudden increase in CoF was observed after 10^3 cycles and 10^4 cycles for the 5 μm and 50 μm thick coatings respectively with this being explained by the real initial contact area increasing significantly with increasing coating thickness. A large increase in contact area will decrease

the induced shear stress, thereby helping to extend the life of coatings. Langlade et al. [181] conducted fretting tests with DFL coated steel (using two different types of DFL) with different coating thicknesses. They observed that significant increases in life resulted from increases in the DFL thickness, with the increase in lifetime increasing more rapidly with increasing coating thickness at the lower thicknesses. For example, for a PTFE / thermosetting resin DFL, the lifetime was observed to increase by around a factor of ten as the thickness was increased from 6 μm to 15 μm (across a range of pressures from 850 MPa to 1200 MPa), but then only by a factor of less than three with a further increase in thickness to 22 μm . In addition, they also observed a substantial increase in the steady-state CoF with increasing DFL thickness¹, although no hypothesis to explain this behaviour was offered. Kong et al. [165] investigated the wear life of $\sim 10 \mu\text{m}$ thick MoS_2 -bonded-films with different contact configurations on steel substrate, where the film failure was faster for increased contact pressure. It is also observed that the MoS_2 films were worn by fatigue for a ring-on-block test, they failed by oxidation of the film due to the higher surface temperature for a pin and V-block test where the contact pressure is high [165].

¹ There is some confusion in the paper with contradictions between the figures and the text. However, the text makes a clear statement in this regard, and thus it has been assumed that the figure (Figure 10) has been incorrectly labelled.

2.4.4.4 Limitations of MoS₂

The disadvantage of molybdenum disulphide is that, at temperatures above 300 °C sulphur is liberated which may have a corrosive effect in a humid environment. At high temperatures, MoS₂ diffuses into steel surfaces and causes stress corrosion [114, 182]. Molybdenum di-sulphide has a superior film forming ability and a migration property to the mating surfaces than graphite, but at high temperature molybdenum di-sulphide is not protective as a lubricating material because oxidative wear becomes excessive in an atmospheric temperature of more than 350 °C [183]. Presence of binder along results in higher coefficient of friction than the lubricant phase alone would exhibit [115].

2.4.5 Graphite

Graphite has lamellar structure and can be used as a solid lubricant coating. As graphite consists only of carbon the surfaces of the lamellae do not have a polar structure. Consequently pure graphite adheres poorly to metal surfaces and does not form load bearing films. External conditions strongly influence the lubricity of graphite but to improve the lubricity of the graphite it is needed to add other lubricants to graphite such as sodium fluoride[182]. Schachner [139] also discovered that fluorinated graphite constitutes a lubricant having outstanding dry-lubricating properties.

Kumar et al. [184] showed in ambient atmospheric conditions that the, coefficient of friction is found to systematically decrease for graphite. In oxygen atmosphere, this value is 0.24–0.3 and also increases with increase

in relative humidity. Increase in relative humidity provides passivation of interacting dangling bonds on the sliding surface. Jardi et al. [185] showed at "low" loads (2-15N), the friction coefficient and the transfer film forming tendency increased with increasing load, due to the modification of the morphology of the contact area. He observed under "high" loads (30.4 – 50.4N) the existence of a critical load at which a sudden decrease of both the coefficient of friction and the transfer film forming tendency is observed [185]. H. Unal et al. [186] evaluate the friction and wear performance of the pure polyamide 6, 5% and 15% graphite with polyamide 6 against stainless steel. The load was used 50N to 100N. CoF decreases with increasing load, but when the applied load increases to the limit load values of the polymer, the friction and wear will increase due to the critical surface energy of the polymer material. Addition of graphite resulted a large improvement in lowering friction coefficient and wear rate of PA polymer. The graphite hexagonal layers are linked by weak Van der Waals bonds, which may easily broke by shear force under sliding condition. The filler debris comes out during sliding and sticks on the surface due to repetitive sliding process. A uniform layer was formed on the worn surface and reduces adhesion between the material and the substrate, which helps to decrease the wear rate and the CoF.

Xin et al. added Graphite from 4-10 % by weight. 4-5% graphite addition decreased CoF and was 0.15 but at 8% graphite addition increased CoF to 0.2 and again decreased to 0.1 while added 10% of graphite under the load of 40N. At 160N, the coefficient of friction was maximum, 0.5 and decreased at 10% to 0.26. Wear rate was much higher in graphite than PTFE but in both cases wear rate is lower at lower load and increased at

higher load of 160N. As the load increases, the possibility of graphite comes out increases from the matrix and form a continuous and smooth transfer film which helps to lubricate more and as a consequence the CoF decreases [187].

Zhang et al. did experiments to enhance the wear resistance of epoxy by adding 10% graphite and PTFE separately. In these, pure epoxy has highest wear rate of $25.5 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The graphite was lowest $0.69 \times 10^{-6} \text{ mm}^3/\text{Nm}$ and the PTFE gave the wear rate of $7.07 \times 10^{-6} \text{ mm}^3/\text{Nm}$. The CoF was not mentioned in this paper [188]. You et al. investigated the effect of 5% graphite and 5% PTFE on glass fiber reinforced polyamide 6, where particle size of graphite was 25 μm and the PTFE was $<1 \mu\text{m}$. Single addition of 15% PTFE and graphite gives the CoF of 0.16 and 0.31 respectively and wear rate of $1.25 \times 10^{-5} \text{ mm}^3/\text{Nm}$ and $12.94 \times 10^{-5} \text{ mm}^3/\text{Nm}$ respectively [189].

2.4.6 Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene (PTFE) is known as a high performance engineering polymer as well as solid lubricant. PTFE is a low friction, high temperature, chemically inert and biocompatible material [74, 190]. This unique combination of properties makes PTFE popular in a several extreme applications. Unfortunately, its application as a solid lubricant in an extreme environment has been limited by its high wear rate [191-193]. At sliding speeds well below 5 mm/s, the coefficient of friction for PTFE is low ($\mu \sim 0.05$) and wear rates are moderate ($k \sim 10^{-5} \text{ mm}^3/\text{Nm}$) [194-196]. The low friction of PTFE is often associated with low adhesion [74], but

Makinson and Tabor [195] rejected this hypothesis based on the observation of molecularly thin, highly oriented and strongly adhered transfer films following low friction sliding. They concluded that low friction can be achieved from easy shear of PTFE lamellae at low shear rates. At high speed of 50 mm/s, coefficient of frictions are moderate ($\mu \sim 0.15 - 0.3$), wear rates are high ($k \sim 10^{-3} \text{ mm}^3/\text{Nm}$) and large particles of transfer films exhibit poorly adhered debris fragments [192, 193, 195].

Numerous hard fillers can diminish severe wear of PTFE, but typically this comes at the expense of its other beneficial properties, most notably friction [191, 192, 197-199]. The addition of 20-50 wt% microscale fillers (e.g. glass fiber, carbon fiber, bronze particles) can reduce wear rate of PTFE by greater than 100 X at higher speeds [191, 198-202]. Li et al. [203] showed that adding nanometer ZnO to PTFE greatly reduced the wear and the best anti-wear performance was obtained with 15 vol % nanometer ZnO than pure PTFE. Coefficient of friction of the composite reduces as loads and sliding velocity increases.

There are several papers that report on the effects of nano-fillers additives for their potential to reduce wear rate without abrading the beneficial transfer layer [74], but no systematic studies have been published on the effects of nano-sized PTFE particles. However, Dubey et al. used nano particle sizes of 50 nm, 150 nm, 400 nm and 12 μm and the particle concentrations were 4, 8 and 12 wt. % for their experiment [204]. They observed that the smaller the size of PTFE particles and the higher their concentration, the greater was the performance improvement [204]. However, an initial study by Tanaka and Kawakami [199] showed that

nano-fillers were ineffective fillers because of their extremely small size which disrupted the formation of large-scale debris. Small weight percents of nano fillers can have high densities and surface areas, consequently, they have potential for modifying certain properties of the polymer matrix with very low loadings [190]. Tanaka and Kawakami used nanoscale TiO_2 in a PTFE matrix for improved performance [199]. Burris and Sawyer [205] discovered a unique PTFE nanocomposite which demonstrated 1000 times reduction in wear rates with less than 1% filler loading. This change in wear rate relative to the filler loading remains unique in the tribological polymer nanocomposites even today [206]. Consequently, the particular material has been the subject of numerous follow-up studies of nanoscale polymer coating mechanisms [190, 207-209].

The filler has a great role in preventing wear of PTFE and other polymer composites and remains an important topic for further studies [74]. Blanchet and Kennedy [210] described two general wear rate determining factors for PTFE composites: (a) the prevention of initial removal of material from the composite, (b) the prevention of the secondary removal of material from the transfer film. Lancaster [197] proposed that fillers reduce initial removal of materials of the matrix by supporting the normal force. Briscoe [211] proposed that fillers help reduce secondary removal which increases adhesion between the transfer film and the counterface by inducing polymer degradation. Ricklin [212], Tanaka et al. [199], and Bahadur and Tabor [213] suggested similar mechanisms of primary wear reduction by preventing large-scale debris generation. Bahadur and Gong [214] supported Briscoe's [211] hypothesis but concluded that filler decomposition rather than polymer degradation increases bonding to the

counterface [214]. Gong et al. [215], Ye et al. [74] and Blanchet et al. [210], observed that fillers had no effect on the chemistry at the counterface and concluded that the wear behaviour is independent of counterface adhesion. Gong et al. [216] suggested that fillers offered to improve transfer film cohesion and therefore reduce secondary wear by prohibiting failure within the transfer film. Blanchet et al. [210] observed that severe wear of PTFE only occurs at high speeds and argues that the primary role of the filler must be most closely related to the prevention of initial removal of materials [191, 192, 212], this hypothesis supports that pre-deposited low wear transfer films do not reduce the wear rate of high wear PTFE-based materials [191, 217]. Ye et al. [74] elucidate the relationships between wear rate, debris size, and transfer film morphology via direct in situ observations of debris generation and transfer film formation for PTFE-alumina composites. Well-documented studies are available to show its exceptional wear reduction of PTFE-alumina composites with low filler loading [190, 207-209].

2.4.7 Influence of various fillers and synergistic effect

This section outlines the evidence for the importance of integrating various functional fillers in wear-resistant polymer and discusses the synergistic effects of various novel and traditional fillers on sliding wear of polymeric materials. Inorganic particles are well known to enhance the mechanical properties of polymers [218], and have been widely investigated in the past decades. In literature, it has been found that the particle size also has effect on fretting. Nano particle filled polymers (polymer nano-composites) are very promising materials for various applications. These nano fillers are

also expected to be able to strongly influence the wear performance of polymers and composites [218].

Zhang et al. [219] group investigated polyimide (PI) composite with additions of short carbon fibre (SCF), micro SiO_2 , graphite (Gr). The result revealed that single incorporation of graphite, short fibre and micro SiO_2 was harmful in order to improve the friction and wear behaviour of the polyimide composite. The CoF of the PI composites filled with SiO_2 , SCF and graphite was further reduced to CoF 0.05 and was most effective in improving the tribological properties of the PI composites. A combinative addition of Gr, SCF and micro SiO_2 showed the synergistic effect. SCF or micro SiO_2 particles can rub into graphite powder and act as favourable solid lubricants. The friction coefficient decrease continuously with increasing load. The load was used from 200N to 600N [219]. You et al. [189] showed that the addition of 3-5% graphite and 10-12% PTFE together shows the lowest CoF of 0.13-0.14 with similar wear rate as before. Graphite and PTFE shows synergistic effect of lower CoF on GA/PA6 composite. The used load was 40N. the wear rate of composites decreases with the increase of PTFE content [189]. Wang et al. [220] also showed synergism effect for SiO_2 , graphite and composite and has CoF <0.2 [220].

Addition of alkali phosphates leads to a synergistic improvement of the mixture consisting of graphite and alkali molybdate or alkaline sulphate. The preferred alkali phosphate is sodium phosphate. Alkali phosphate shows the excellent properties of improved resistance to abrasion, high load bearing capacity, constant physical properties independent from external conditions and gives good protection against rust [182]. As the

binder sodium meta-phosphate form the solid lubricant suitable for covering the sliding surface of the bearing [183]. Using higher amount of alkali phosphate generates a high coefficient of friction compared to the amount of alkali molybdate which generates a lower coefficient of friction[182].

Sodium fluoride does not give any influence to the lubricating property but it helps to keep the friction coefficient unchanged even if the temperature of the solid lubricant change upto 1 wt. percent of sodium fluoride within the compound and when about 3 wt. percent of sodium fluoride is mixed into graphite, it also improves the film forming ability in the dry friction [183]. The more sodium fluoride used (about 50 wt percent), the more the migrating amount of solid lubricant to the mating surface will increase which indicates the reverse effect.

X-R Zhang et al. [219] group investigated polyimide composite in addition of short carbon fiber, micro SiO_2 powders ($<15\text{ }\mu\text{m}$) and Graphite powder ($<1.5\text{ }\mu\text{m}$). The volume fractions of SiO_2 , graphite (Gr) and short carbon fiber (SCF) were 3%, 10% and 10%, respectively. The result revealed that single incorporation of three different additives was detrimental in order to improve the friction and wear behaviour of the polyimide composite. The friction of coefficient of PI composite filled with SiO_2 and SCF and Gr was further reduced to CoF 0.05 and was most effective in improving the tribological properties of the PI composites.

PI composite have been developed for special applications in which low friction, high wear resistance and good thermal conductivity under sliding

wear conditions against smooth steel counterparts were of great importance. It can be found that PTFE + 10 vol% Bronze + 10 vol% CF exhibits an excellent wear resistance property. In particular, the addition of bronze improves the tribological properties of the composite significantly because of its outstanding thermal conductivity. This is a good example to demonstrate the effectiveness of this kind of filler for the design of a wear resistant polymer composite [218].

Larsen et al. used CuO nanoparticles in epoxy resin and in epoxy containing PTFE. The coefficient of friction decrease when 0.4 vol % CuO added to PTFE containing resin but CoF increases when % of CuO increased. 7.5 vol % PTFE was added. Without PTFE, the CoF (μ) is roughly independent of the nano-CuO content. With PTFE the CoF was below 0.4 at 0.4 vol% [221]. Basavarajappa et al. [222] used glassy-epoxy composite mixed with SiC and graphite particles. It showed an increase in sliding velocity increased the specific wear rate. Applied load has more predominant effect than the effect of sliding distance [222]. Jacob et al. [223] added 1% optimum carbon nano tube (CNT) with epoxy resin composite. They also added 10% of MoS₂ and graphite with only epoxy resin, which shows better performance than pure epoxy but worse than multi component composites [223]. Unal et al. [186] evaluate the friction and wear performance of pure polyamide 6 wt.%, 5 wt.% and 15 wt.% graphite with polyamide 6 against stainless steel. The load used was 50N to 100N. CoF decreased with increasing load, but when the applied load increases to the limit load values of the polymer, the friction and wear will increase due to the critical surface energy of the polymer material. Addition of graphite resulted in a large improvement in lowering friction of

coefficient and wear rate of PA polymer. The graphite hexagonal layers are linked by the weak Van der Waals bonds, which may be easily broken by shear force under sliding conditions. The filler debris comes out during sliding and sticks on the surface due to repetitive sliding process. So a uniform layer was formed on the worn sample surfaces and reduced adhesion between the material and the substrate, which helped to decrease the wear rate and the CoF [186]. Xin et al. [187] added PTFE and graphite to the polyamide 6 polymer. PTFE lowered CoF and can be easily dragged out of polymer and form a third-body transfer-film, which reduces the direct contact of the substrate. This will help to reduce the CoF further and improve the abrasive resistance of the composite [187].

Wang et al. [220] added $<1.5\ \mu\text{m}$ graphite and $<50\ \mu\text{m}$ nano silica (5%) singly and both of them with basal fabric reinforced phenolic composite. Friction and wear behaviour was tested. The CoF of pure composite was more than 0.4, where graphite and composite has the CoF near 0.2 and SiO_2 and composite together showed 0.3. SiO_2 , graphite and composite showed CoF <0.2 . The wear rate of graphite, SiO_2 , composite and graphite + composite was within $15\text{-}20 \times 10^{-6}\ \text{mm}^2/\text{Nm}$. With increasing load until 600N, the wear rate increased continuously for BFC+ SiO_2 and pure BFC, but decreased with load for BFC+ SiO_2 +graphite and BFC+Gr. The CoF also decrease to <0.1 as the load increased for BFC+Gr and BFC+Gr+ SiO_2 but increased >0.3 for BFC+ SiO_2 [220].

Difallah et al. [224] added 40-63 μm graphite to ABS polymer in different percentage range of 0-7.5 % and tribological properties has been investigated. As the graphite content increased the CoF was lowered. At

7.5% graphite the CoF was <2.5 at 10000 cycles at constant load of 17N. the wear surface after 10000 cycles was smooth and small debris found along the sliding direction with less damage [224].

2.5 Polymer Coating

Fretting wear behavior of polymer is of relevance because DFLs are frequently incorporated into polymer binders.

2.5.1 Fretting Wear behaviour of polymer

The unavoidable consequence of friction in a sliding contact is wear. Wear of polymers is a complex process and the explanation of the wear mechanism can be given most efficiently by the three systems of classification done by Briscoe et al. [225] shown in Figure 2.10 [225].

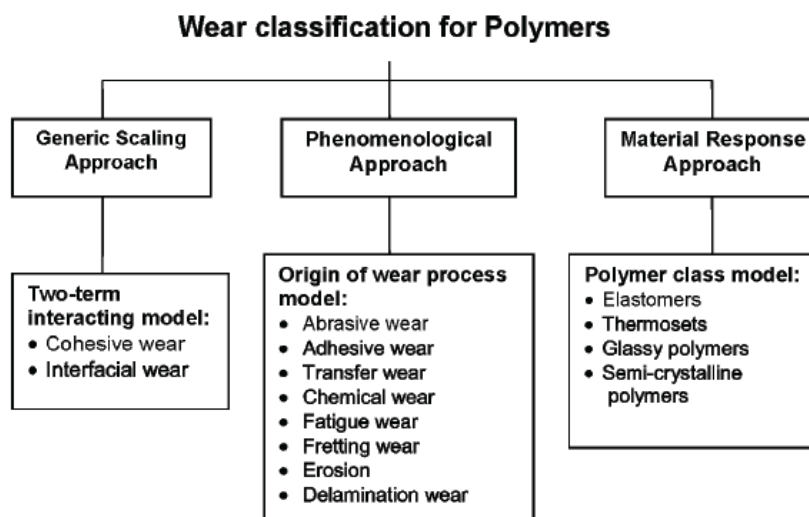


Figure 2.10. Simplified approach to classification of the wear of polymers [225]

Polymer wear is greatly influenced by what type of polymer is being used such as elastomer, amorphous, semi crystalline. The properties such as elastic modulus, tensile strength and the toughness (percentage elongation at failure) are also of particular importance, which changes remarkably as the type of polymer changes [226].

High tensile strength with a high elongation at failure promotes wear resistance in a polymer [226]. If other factors remain constant, some of the thermoplastic polymers with semi crystalline structures showed better performance than thermosets or amorphous thermoplastics in terms of wear resistance. This information leads to the concept that the surface hardness of the polymer is not the predominate factor for wear resistance but high polymer hardness might be harmful in dry sliding condition against the hard counterface as hardness usually associated with low toughness of polymer.

Wear and debris formation mainly observed under gross slip conditions lead to a wear volume which is shown to present a linear evolution with the cumulated dissipated energy [43].

The earliest works on polymer tribology started with sliding friction studies on rubbers and elastomer materials [227, 228]. Briscoe studied the polymers (thermosets and thermoplastics) and developed the two-term model of friction [211]. The two-term model depicts that frictional force is a result of the interfacial and cohesive work done on the polymer surface assuming the counterface is sufficiently harder than the polymer mating surface with mild or no elastic deformation, shown in Figure 2.11 [225].

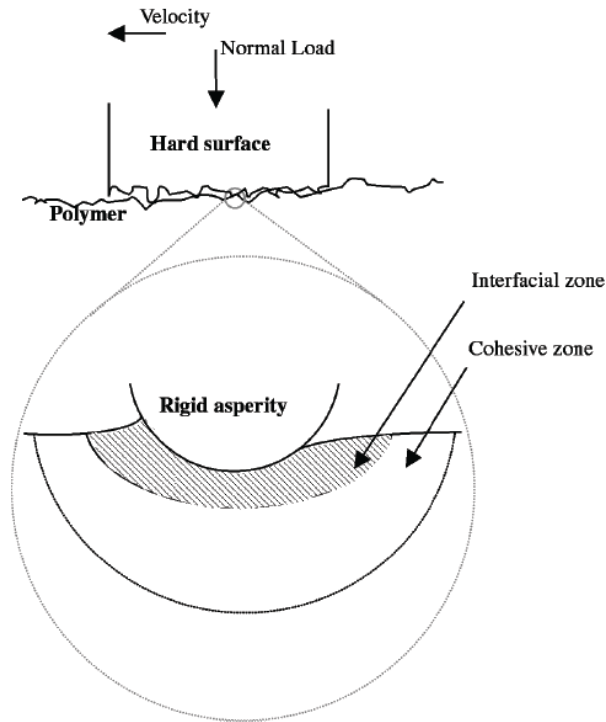


Figure 2.11 Two-term model of the wear processes. The distinction between interfacial and cohesive wear processes arises from the extent of deformation in the softer material (usually polymer) by a rigid, non-dissipative, asperity of the counterface. For interfacial wear, the frictional energy is dissipated mainly by adhesive interaction while for cohesive wear the energy is dissipated by adhesive and abrasive (sub surface) interactions [225]

The interfacial frictional process is consequence of adhesive interactions and it depends on factors such as the hardness of the polymer, molecular structure, glass transition temperature, polymer crystallinity, surface roughness of the counterface and the chemical / electrostatic interactions between the counterface and the polymer [226].

2.5.1.1 Transfer film mechanism

The growth of the transfer layer is key to its lubricant effect, there are three principal factors which contribute to transfer

- The deformation of the surface under load
- The cracking of the material
- The transfer of polymer on the antagonist surface

At low temperature and load, particles are too small and are not sufficiently adhered to allow creation of a transfer layer. Indeed, the above points are the reasons which could contribute to transfer. Deformation and cracking are controlled by stress state and contact zone, which depends on the normal load, on the type of contact (a plane contact) and on the CoF. Figure 2.12 [229] shows the different stages of the transfer film [229].

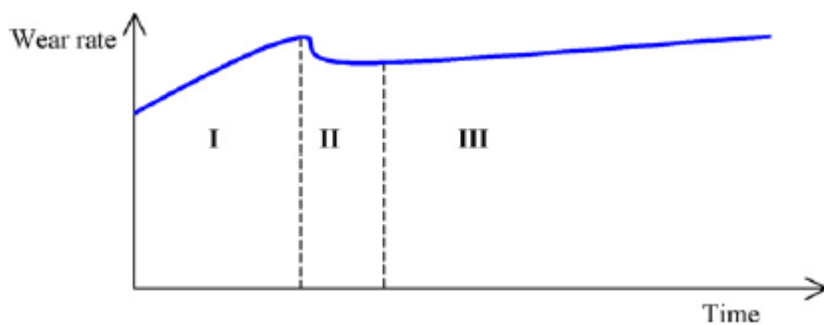


Figure 2.12: Variation of wear according to time. zone I: Formation of transfer film, zone II: Existence of transfer film, zone III: Degradation of transfer film [229]

Understanding the mechanism of transfer film formation on the metal counterface will facilitate design of better coating systems for improved

tribological performance. In general, material transfer of soft polymeric coatings to metal counterface (pin surface) could be associated to the conjugate effects of (a) chemical (adhesion) and (b) mechanical interaction between the two surfaces. In polymer-to-metal contacts, there is a natural susceptibility for polymer materials to be adhered to metallic counterfaces, which can be the basis for transfer film formation. There are different mechanisms for film adhesion, those are Coulomb electrostatic forces, Van der Waals forces, and bonding from chemical reactions [230].

Bahadur et al. studied PTFE-based coatings rubbed against the pin surface. They thought, adhesive junctions were developed due to cohesive bonding between the PTFE-end caps or other free radicals, and the metallic surface [230]. For the soft coating, the mechanical transfer of materials to the counterface is initiated at the beginning stages of sliding. Bahadur et al. showed the polymer fragments are sheared by sharp metal asperities of the counterface and interlocked into the grooves and valleys of the pin surface [231]. The transfer film mechanism can be seen in the x1500 SEM image of the pin surface (6.3 mm) tested with PTFE/Pyrrolidone under dry conditions Figure 2.13 [232].

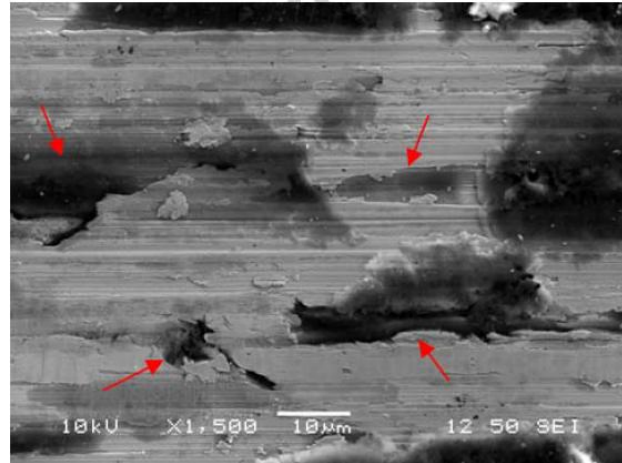


Figure 2.13 SEM image of counterface (6.3 mm pin surface) tested in contact with PTFE/Pyrrolidone coating under dry condition showing the initial formation of transfer film [232]

It clearly shows that the pits, holes and crevices of the surface are filled with darker polymer material (also marked with arrows). These small chunk of polymer material that initially form on the counterface, agglomerate with repetitive sliding, due to cohesion between mutually compatible polymer fragments, producing large transfer films [232]. With increasing number of fretting cycles, the whole surface becomes covered by transfer film, and protects the polymer film from any sharp damage and hard metal asperities, therefore the transfer film acts as a lubricious film at the contact interface [232].

Yeo et al. [232] showed higher COF and significant wear are usually observed for the PTFE/ pyrrolidone coating wear track after 20 min of testing using the 3.2 mm diameter pins shown in Figure 2.14 [232].

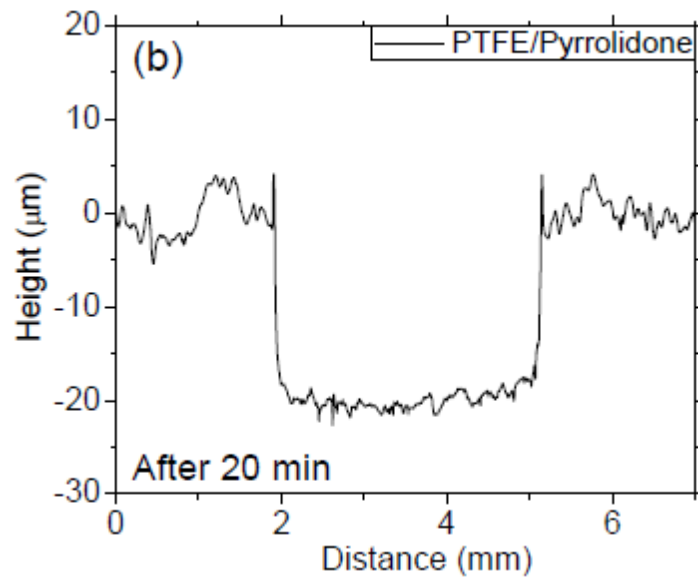


Figure 2.14 Typical profilometric cross-section wear tracks of PTFE/ Pyrrolidone coating after 20 min of fretting experiments with the 3.2 mm pin [232]

The probable explanation is, the process of transfer film formation starts at the initial stage in polymer-metal sliding. Therefore, the majority of material removes at the beginning of the test thus shows initial higher friction coefficient and wear rate, at the same time the transfer films are formed on the metal counterface. Initial transient period could be different depending on the roughness of the counterface, because it takes more time to fill the rougher surface with a polymer material [233]. Once a continuous and stable transfer film is formed on the counterface, it protects the hard asperities; material removal by mechanical interlocking is significantly reduced, thus exhibiting steady-state frictional behaviour for the rest of the test duration.

Increasing sliding, the transfer film continuity and ductility gradually improved, and the transfer film became smoother. Once the transfer film is definitely formed on the counterface, it behave as another hard coating

layer lubricating at the interface, which results in the so-called "self-lubricating" property of polymer materials. This is the reason that the PTFE/ pyrrolidone coating did not show any catastrophic failure even after the coating was completely penetrated with the reduced diameter pin [232].

Yeo et al. summarised the polymer-to-metal sliding in two steps: (1) flattening of the rough metal surface by transferred material during the transient period, and then (2) self-lubricating effect of transfer film during steady-state sliding [232]. Kowandy et al. used cylinders of 8 mm in diameter to study the tribological properties of polymer like PTFE and their composites sliding against a metal under dry friction conditions. They found their results were strongly influenced by their ability to form transfer film on the counterface [229].

2.5.1.2 Dissipated energy approach for coating lifetime prediction

To analyse lifetime of the coating, a dissipated energy approach is useful [234]. A local description of the dissipated energy is introduced by quantification of the maximum wear depth. Integrating the local energy along the axis in the sliding direction (axial axis) and perpendicularly (lateral axis) permits direct relation of linear dissipated energy with the corresponding surface of the wear scar section obtained from axial and cross profiles [43].

Mindlin [235, 236] found that the sphere/plane contact, partial slip corresponds to a composite contact where a central stick domain is

surrounded by a pulsing sliding annular domain. The contact behaviour is then defined by a coupled elastic-sliding response inducing a hysteresis tangential force $Q(t)$ vs. displacement $\delta(t)$ loop evolution [235, 236].

When gross slip occurs, the initial partial slip evolution is followed by a full sliding period. During this stage, the tangential force $Q(t)$ vs. displacement $\delta(t)$, loop presents a quadratic shape. The different domains of the sliding conditions are identified according to the normal force and the displacements through the plotting of the sliding condition fretting map Figure 2.15 [38].

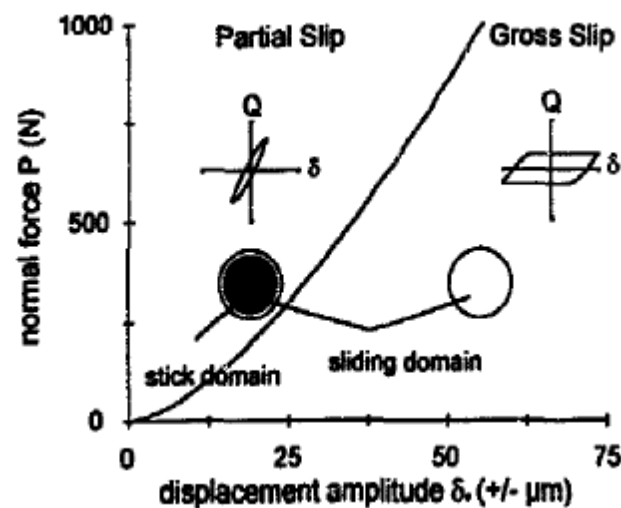


Figure 2.15 Identification of fretting conditions through the sliding condition fretting map [38]

The Archard model [237] is the most common wear model proposed in tribology. This relates the wear volume to the product of sliding distance

with the normal force. A wear coefficient (K) is usually obtained from the following relationship (Equation 2.1):

$$K = \frac{V}{PS} \quad [\text{Equation 2.1}]$$

Where K, is the wear coefficient, V, is the wear volume, S, is the sliding distance, and P, is the normal force.

A recent energy approach linking the total wear volume with the total dissipated energy [238, 239] shows higher stability [43, 240]. When the substrate is reached, the tribosystem is fully changed and catastrophic failure can be observed. Therefore to evaluate the coating wear resistance, it is also interesting to consider the wear depth evolution. The maximum depth h_w observed in the whole wear scar surface was compared by Fouvry et al. [43] with the maximum local cumulated interfacial shear work.

This energy approach permits an intrinsic correlation of a single variable 'energy' and of main parameters such as the normal force, the friction coefficient and relative displacement. It can also be expressed through more useful and industrial relevant variables, such as shear and pressure distribution or as relative sliding. The energy dissipation approach can be useful for non-homogeneous materials such as a coated system. According to Fouvry et al. [43] quantitative analysis showed plain materials and coatings can be quantitatively compared by introducing an energy wear coefficient (K_E) defined by an universal variable (Equation 2.2):

$$K_E = \frac{\text{volume (m}^3\text{)}}{\text{energy (J)}} \quad [\text{Equation 2.2}]$$

As an example, they showed that steel-alumina contacts present a wear volume coefficient still eight times larger than for the TiN coating. In addition the beneficial effect of TiN coating is emphasised by a lower friction coefficient, which reduces the dissipated energy and permits higher pressure loading or equivalent sliding distance. Therefore, similar normal force and displacement amplitude results in the same wear volume after test duration up to 16 times greater than the high speed steel (the TiN friction coefficient corresponds to half of the steel value). This local approach was extended to determine the maximum local dissipated energy, theoretically observed at the centre of the contact and to compare it with the maximum depth of the whole wear scar. A large scatter is observed with poor linearity [43].

A wear ratio of 6.4 was considered a poor correlation and can be found from the evolution of profile under fretting condition. They showed in Figure 2.16 [43], even under gross slip condition the wear scar presents maximum wear on the contact borders and a minimum at the centre. This tendency leading to a typical 'W' - shape scar decreased with number of cycles or displacement increase. For displacement values near to reciprocating conditions, the wear scar presents a characteristic U shape. The 'W' shaped contact structure is related to a modification of the surface geometry induced by the redistribution of the third body in the contact.

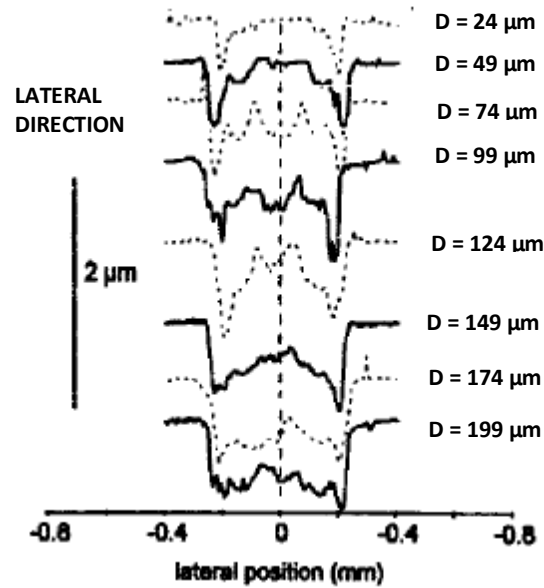


Figure 2.16 Wear scar profiles: TiN vs, alumina as a function of the sliding amplitude ($P=50$ N, 2000 Cycles) [43].

Fouvry et al.[43] choose tangential loading rather than the normal component for the wear quantification. Considering that pressure remains perpendicular to the sliding direction, the work of the normal force is equal to zero whereas the corresponding tangential force work is a scalar product different from zero. Fouvry et al. [43] also showed that the total wear volume is linearly related to the total cumulated energy dissipated in the whole fretted surface.

The fretting scar expands mainly in the lateral direction. Measurement of the amount of materials lost from the surface is the volumetric wear. Mohrbucher et al. [238], studied and used TiN coating on steel substrate. They did several interrupted tests to produce a series of profiles showed in Figure 2.17 [238]. Once the coating has been perforated, the volumetric wear represents the combined loss of TiN and steel.

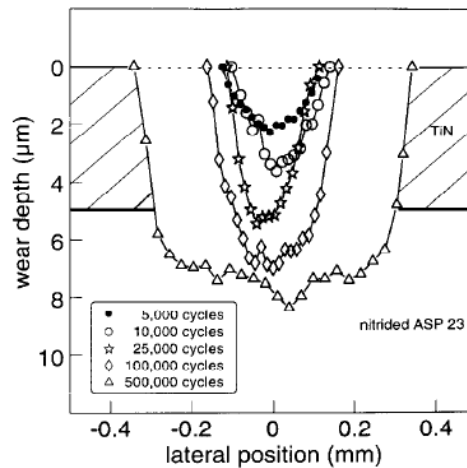


Figure 2.17 Progress of fretting damage on TiN coatings on steel [238]

The evaluation of wear volume over the test duration is fitted by two lines with different slopes as shown in Figure 2.18 [238]. When the coating layer has been perforated, the slope is 3 times less steep than when the coating still exists. A larger lateral expansion is more pronounced at the coating – substrate interface and as a consequence, the wear volume of the substrate increased after coating perforation.

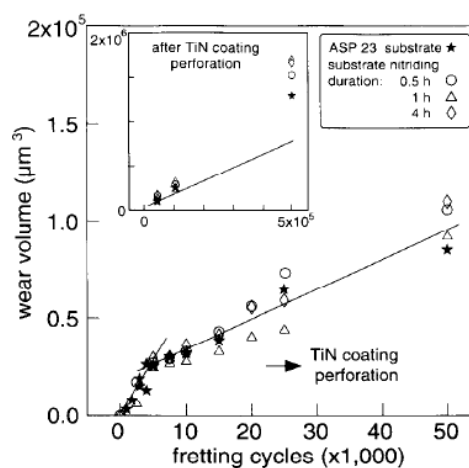


Figure 2.18 The evolution of volumetric fretting wear on TiN coated on steel [238]

The amount of coating being worn in the fretting contact is determined by the friction energy dissipated during each fretting cycle. The dissipated energy is directly proportional to the coefficient friction under the present gross slip conditions [238]. The volumetric wear being the sum of damage generated during each fretting cycle is therefore expected to correlate with the cumulative friction energy. The value of the cumulative friction energy is obtained by summing up the energies dissipated in each cycle over the test duration. For non-homogeneous material dissipated energy approach does not seem to work well.

Mohrbucher et al. showed in Figure 2.19 [238], linear increase in wear volume on the TiN coatings with the cumulative friction energy. The direct proportionality is maintained during the high as well as low friction phase which implies the same wear mechanism is operative during both phases. Thus this analysis is useful to predict the mechanism of the wear during the experiment.

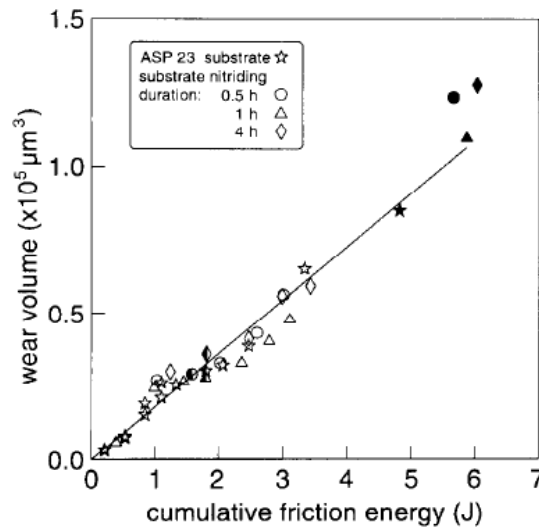


Figure 2.19 Evaluation of the measured wear volume on TiN coatings as a function of the cumulative friction energy [238]

2.6 Summary

Lubrication is one of the important methods of preventing fretting damage by reducing coefficient of friction remarkably. This literature review attempts to bring the facts concerning the lubrication in fretting situations. The review is combination of results obtained from literature. This focused on fretting wear of Ti6Al4V. Fretting of Ti alloys in industrial sector is a concern. Different methods of prevention of fretting wear have been adopted, which has been discussed in literature and then mitigating methods to prevent fretting, where dry solid lubricant has been highlighted along with the synergistic performance of the different solid lubricant additives.

A review of the influence of contact geometry, effect of coating thickness and dissipated energy approach have also been included to highlight the understanding of the ability of laboratory based experiments.

This literature review summarised various research that shows the effects of composite DFL on fretting behaviour and its lifetime. Some general features have been found although the majority of experimental data was obtained under quite differing conditions. Representative lubricants, oil, grease, polymeric film and molybdenum disulphide (MoS_2) with different physical states were discussed to prevent fretting wear.

A number of investigations have been carried out to examine both the sliding and the fretting behaviour of MoS_2 -loaded polymeric films mainly on ball and flat or pin on disk configurations. Few works have been done on cylinder on flat configurations. This thesis presents a systematic experimental investigation of evolution of coefficient of friction vs lifetime. There are few studies in literature, where Cu-Ni-In has been used as an underlayer followed by MoS_2 or other lubricants on different substrate. This thesis also made an attempt to understand the effect of Cu-Ni-In on Ti6Al4V.

In literature, many studies are available where, more than one solid lubricant added together to improve the performance of coatings. In this thesis different additives also have been added to the MoS_2 dry film lubricant and investigated their performance.

There is a lack of current overall understanding of the DFL lifetime. This thesis will investigate the behaviour of polymer bonded DFLs under a range of geometries, thicknesses in order to better understand polymer bonded DFL lifetimes so that their use can be optimised.

Chapter 3. Experimental Methodology

3.1 Materials

All samples were manufactured from a 500 X 500 X 1 cm³ sheet from Smith Metal Ltd. Ti6Al4V. It has a nominal chemical composition of 10 wt. % aluminium, 2 wt.% vanadium, with the remainder being titanium. Table 3.1 shows the composition obtained from EDX analysis of the material used in this thesis. This is consistent with the expected composition [23].

Table 3.1 Chemical composition of Ti6Al4V

Al	V	Fe	N	O	C	Ti
10	1.87	0.09	0.01	0.05	0.04	Balance

A dry-film MoS₂ lubricant, trade name PL237-R2 (Appendix B) has been procured from Indestructible Paint, Birmingham, UK. This MoS₂ containing

as received dry-film lubricant will be referred to as DFL throughout the thesis.

10% & 5% PTFE and 5% graphite were chosen as the additives to mix with the DFL. PTFE (1 μm) (Appendix D) and graphite (1-<10 μm) (Appendix E) were acquired as free flow powder from Sigma Aldrich tabulated in Table 3.2.

Table 3.2 Raw material supplier and specification

Materials	Form	Specifications	Supplier
Ti6Al4V	Sheet	500 X 500 X 1 cm ³	Smith Metal Ltd.
PL237-R2	Paint	Lubricant	Indestructible paint Ltd.
PTFE	Powder	1 μm	Sigma Aldrich
Graphite	Powder	1-<10 μm	Sigma Aldrich

A set of Ti6Al4V specimens coated with an average 150 μm thick Cu-Ni-In (METCO 58) metallic layer by thermal spray coating were received from Rolls-Royce. Ti6Al4V specimens and METCO coated Ti6Al4V specimens were coated with the DFL paint as tabulated in Table 3.4. The measured thicknesses quoted in Table 3.4 indicate the paint thickness, not the METCO layer thickness. The MoS₂ based DFL will be referred as DFL or paint in this thesis.

Table 3.3 List of test details conducted

DFL type	Geometry (mm)	Coating Thickness (μm) ± 5	Coating on Round	Load (N)
PL237-R2	15	50	PL237-R2	575
PL237-METCO	15	50	PL237-R2	575
Tests with different geometries				
PL237-R2	15	12	PL237-R2	575
PL237-R2	80	12	PL237-R2	575
PL237-R2	160	12	PL237-R2	575
PL237-R2	15	25	PL237-R2	575
PL237-R2	15	25	PL237-R2	2000
PL237-R2	80	25	PL237-R2	575
PL237-R2	160	25	PL237-R2	575
PL237-R2	15	62	PL237-R2	575
PL237-R2	80	62	PL237-R2	575
PL237-R2	160	62	PL237-R2	575
PL237-R2	15	86	PL237-R2	575
PL237-R2	15	86	PL237-R2	2000
PL237-R2	80	86	PL237-R2	575
PL237-R2	160	86	PL237-R2	575
Tests with additives				
PTFE-DFL	15	50	PL237-R2	575
Graphite-DFL	15	50	PL237-R2	575
Graphite-DFL	15	50	PL237-R2	2000

3.2 Spray painting

3.2.1 Establishing in-house painting

Both specimens making up the fretting couple were grit blasted with aluminium oxide grit (Airblast, UK, grade NK36), grit size 0.5-0.59 mm yielding surfaces with a roughness (R_a) of around 2.6 μm . Immediately

following grit blasting, the coating was applied using a spray deposition technique. The painting procedure developed is in line with the RR standard (Appendix A: Paint Spray Data Card). The painting facility in the Department of Built Environment is being used and illustrated in Figure 3.1.

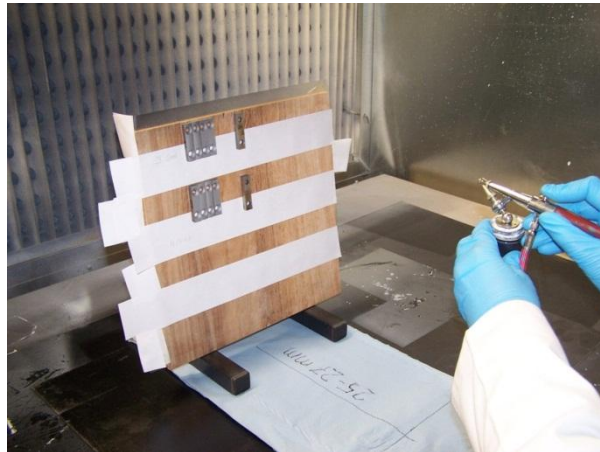


Figure 3.1 painting of the Ti6Al4V specimen with DFL

Temperature inside the paint booth was always monitored and was within 15 – 30 °C. Pressure of the spray was maintained at 2-3 bar. Surfaces of the samples were swabbed with solvent, IP 9151 (Appendix C), to clean the surface of the sample and then dried in air. The paint was mixed by stirring with glass rod and shaking thoroughly for at least 15-20 minutes before use. In addition, paint was sieved through a fine mesh filter (typically 180 micrometers) immediately prior to pouring into spray gun. Ti6Al4V specimens were fixed on a wooden board with the help of double sided tape which is then fixed in position. The wooden board was placed on to a solid slab to control the standoff distance, which was always maintained $\sim 30 \pm 1$ cm. Spraying was done by hand, moving left to right

horizontally and ~ 10 mm vertical movement to cover the whole surface once per coat. After each coat, the wooden board is moved and placed horizontally to allow the specimen to dry after painting. Initially for first 2 to 3 coats, wooden board movement was not necessary as the thickness of the coating is not high and dries easily. Paint was allowed to dry for a minimum of 10 minutes at room temperature after each coat. The repetition of the process continued as required until desired paint thickness achieved. This process produces $\sim 25 \mu\text{m}$ after 5 coats and reached approximately $50 \mu\text{m}$ with 11 coats. Thicknesses have been measured by the eddy technique after curing of initial painting trials. The normal target thickness was $50 \mu\text{m}$. Once desired thickness was achieved, paint was stoved in a circulatory air oven. Components are placed in the oven at 100°C and the oven brought up to a temperature of 190°C . It takes 1 hour to reach 190°C . The specimen is then cured at this temperature for 2 hours. Specimens were removed from the oven once cooled to room temperature. Thicknesses measurements were done for DFL thickness using eddy current thickness measurement gauge in non-ferrous mode.

The painting was done in batches to complete one set of samples for each set tests planned. The painting facility enables to paint 12 sets of flat and cylinder specimen together at a same time. This batch painting ensures the coating thickness and the quality of the paint consistency. All coatings of certain type were painted at the same time.

3.2.2 Additive mixing procedure

Powders (Graphite, PTFE) were placed inside fume hood in the in plastic containers they were supplied in. The paint was mixed thoroughly for half an hour to ensure proper mixing by glass rod and manual shaking. Each time approximately 100 ml DFL was weighed in a 250 ml glass beaker. The paint was sieved through 180 μm sieve before pour in beaker. According to the weight of the paint, the weight equal to 10% PTFE, 5% PTFE and 5% graphite was calculated and weighed powder then carefully placed into the measured DFL. For example, to prepare 10% PTFE additive paint, initially 100 ml of DFL has been taken.

Weight of 100 ml PL237-R2 = 55.33 g
10% of 55.33 g PL237-R2 = 5.53 g PTFE
Total weight = (55.33 + 5.53) = 60.86 g paint
Final % of additive (PTFE) = $[(5.53/60.86) \times 100] = 9.08 \%$ PTFE

Therefore 5.53 g of PTFE has been measured accurately and powder added slowly in small quantity (1-2g) each time into the 100 ml measured paint beaker and the paint was stirred well with an ultrasonic immersion vibrator. Few seconds pause was required after each 20-30 seconds mixing to avoid heat generation within the mixed paint. Once all powder was transferred and it was mixed well using Ultrasonic immersion vibrator until the paint was homogeneous. Finally 9.08 wt. % PTFE-DFL paint has been produced. 5 % Gr also has been added in similar fashion and final percentage of graphite is 4.76 wt. % of graphite. Approximately 10-12 minutes was taken all together to ensure good mixing. Mixed paint was then transferred into the clean glass bottle and securely sealed and used for spray. Once the mixing procedure is done, the paint can be used within 2-3 weeks time before the solid gets settled down. All safety measures

(gloves, face mask, Lab coat, Lab shoes and safety glass) have been used to have secure handling. The entire procedure below is to take place within a fume hood to avoid carcinogenic effect. 9.08 wt. % PTFE and 4.76 wt. % Gr addition will be mentioned hereafter in this thesis.

Once the additive paint was prepared, it was used for a complete set of experiments planned. The paint produced with different additives is used in paint booth with the normal procedure used in section 3.2.1 including the mixing, shaking immediately prior to use. A summary of all additives incorporated into the DFL is given in Table 3.4.

Table 3.4 summary of all additives into DFL

Paint	Percentage added to initial DFL	Final percentage after mixing
PTFE	5 wt. %	4.77 wt. %
PTFE	10 wt. %	9.08 wt. %
Graphite	5 wt. %	4.76 wt. %

3.3 Specimens

3.3.1 Fretting Test Methodology

All the tests were conducted using a crossed cylinder-on-flat arrangement shown in Figure 3.2. The cylinder-on-flat arrangement produces a 10 mm line contact on both cylinder and flat surface.

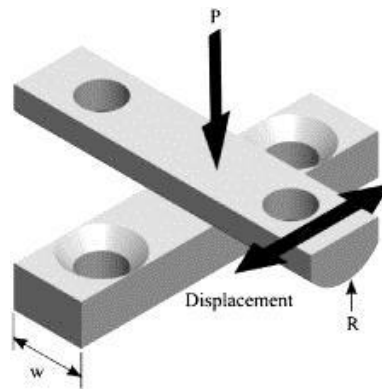


Figure 3.2 Cylinder-on-flat specimen setup for the fretting test [236], where $w = 10$ mm, $R = 15$ mm and $P = 575$ N.

The flat and cylinder specimens were firstly cut from the Ti6Al4V sheet in a computer controlled EDM machine (Electrical Discharge Machine). The machine cuts the material by means of passing an electrical charge through a thin wire, usually around 0.3mm Thick in diameter. The shape is programmed into the machine and then the material is submerged in water shown in Figure 3.3, where it is cut to the desired profile. In this thesis, three different cylindrical diameters have been used. They are 15 mm, 80 mm and 160 mm (Appendix F).

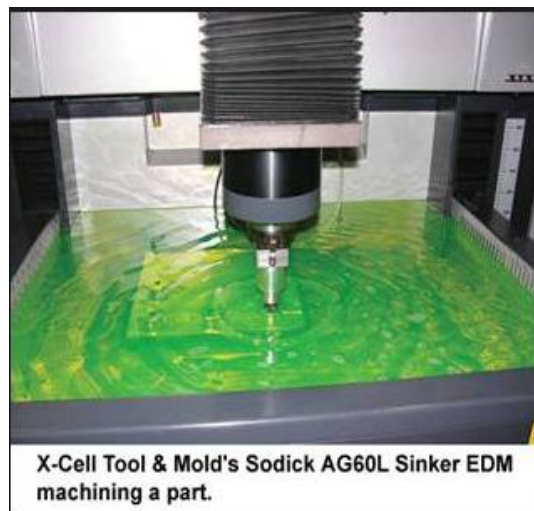


Figure 3.3 component submerged in fluid tank during the cutting cycle.

Next the securing holes are drilled in position using a CNC Milling Machine shown in Figure 3.4.



Figure 3.4 CNC Milling Machine

A schematic diagram of the test rig is given in Figure 3.5. The flat specimen was attached to the stationary Lower Specimen Mounting Block (LSMB) and the cylindrical specimen to the moving Upper Specimen Mounting Block (USMB). Prior to testing, the specimen holders were degreased and cleaned with industrial methylated spirit (IMS) solvent and allowed to dry in air. Care needs to be taken to ensure that the surface of cylindrical specimens was kept perpendicular to the flat specimen, so that the cylindrical specimen mounted perpendicular to the direction of the vibration, as misalignment between the cylinder and flat specimens will distort the 10 mm line contact. Once the coupling between LSMB and the load cell was tightened, a load of 115 N was put on the mass hanger. Then the coupling screws were loosened half way and then tightened back completely to ensure parallel surfaces of the specimens touch each other.

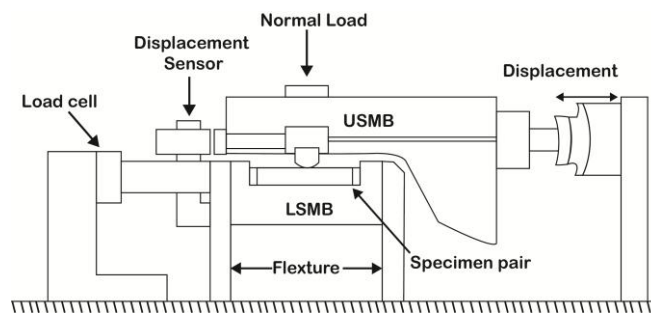


Figure 3.5 A schematic diagram of the fretting rig

An oscillatory displacement, 300 μm , and a fixed frequency of 2.5 Hz were applied to the USMB of the Electro Magnetic Vibrator (EMV). A linear variable displacement transducer (LVDT) mounted to the base of the test rig is used to measure the applied displacement continuously. The armature of the LVDT is in contact with the USMB and the voltage signal (sinusoidal waveform) produced by LVDT is fed through a signal conditioning unit through the data acquisition system. For a single fretting cycle generated, the total sliding distance travelled between the USMB and LSMB is equivalent to 4 times the applied displacement or twice the applied stroke.

A constant normal load, P , was applied to the USMB through a dead weight and a balanced lever arm, with a 5:1 ratio to the actual load. For the majority of the work a 115N weight was used to apply a 575 N load to the sample. Some higher load tests were done by applying 2000 N, for those a 400N weight was used. The tangential traction forces were measured using a piezoelectric load cell between the EMV and the USMB.

Fretting tests were conducted at ambient temperature with a fixed normal load, a summary is given in Table 3.5. Humidity percentage was measured.

Table 3.5 A summary of the range of the test conditions used in this work

Normal Load (P) / N	575, 2000
Applied Displacement δ / μm	300
Frequency (f) / Hz	2.5
Temperature (T) / $^{\circ}\text{C}$	14-25
Humidity %	29-35

3.3.2 Data acquisition and processing

The data acquisition system, that has been used in this rig permits real-time monitoring and recording of the tangential force and applied displacement using a program that was developed in the LabView software package. The fretting rig measures the tangential force and the relative remote specimen displacement which is fed into a data acquisition system in order to control the test. After a fretting test run, the rig will produce a data file. This file contains all the relevant data for the test. For visualising the data and initial data processing, NI DIAdem (National Instruments), commercially available data post-processing software was used.

During the fretting tests, the tractional force and applied displacement were recorded at a rate of 200 samples per fretting cycle, and were plotted to form fretting loops, a schematic diagram of a typical fretting loop is presented in Figure 3.6 [241].

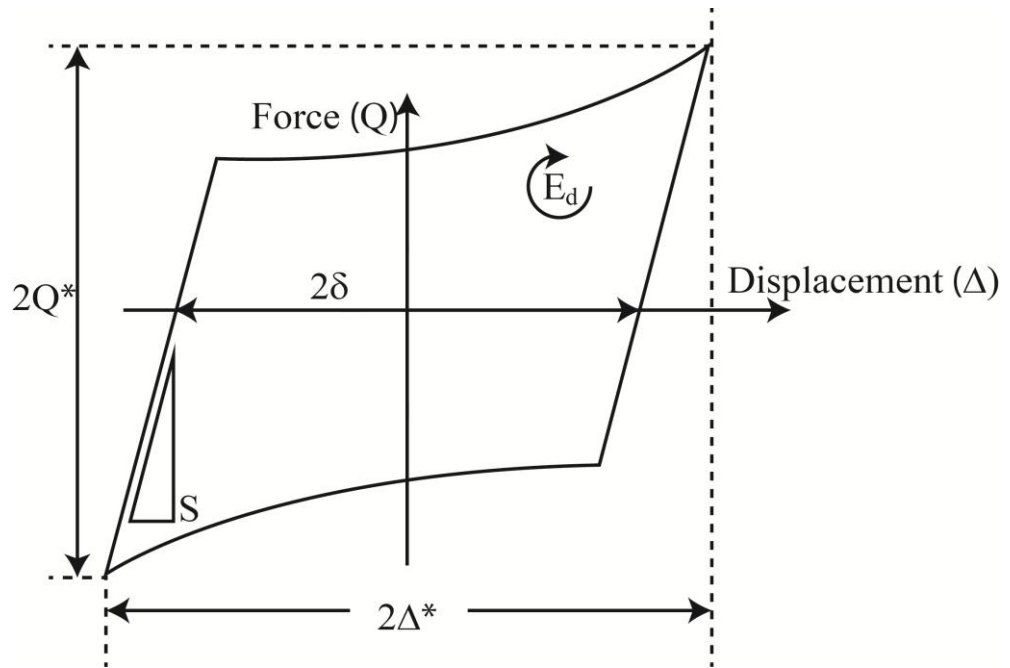


Figure 3.6 Schematic diagram of a fretting loop showing increase in tractional force Q as slip proceeds [241]

During a fretting cycle, the relationship between the tangential force, $Q(t)$, and the relative specimen displacement, $\delta(t)$, is important in identifying the contact response during the fretting process.

A number of parameters are derived from the raw data, such as, sliding amplitude, dissipated energy, coefficient of friction (CoF), energy coefficient of friction (ECoF), stiffness etc. Once these parameters are calculated, the derived parameters were incorporated into a life with the raw data so they could be easily and quickly loaded for analysis and plotting. The voltage output were fed through analogue-to-digital converters which converted the signals from the force and displacement transducers into Q and δ data.

Figure 3.6 shows a loop typical of those observed in this work where there were significant variations in the tractional force across the period of slip within each loop. The coefficient of friction (CoF) in each cycle was defined as follows in equation 3.1:

$$\mathbf{CoF} = \frac{Q^*}{P} \quad \text{Equation [3.1]}$$

It is recognized that the definition of the CoF (using the maximum tractional force) is strongly influenced by effects at the end of the traverse (such as build-up of ploughed material), another commonly used measure is that known as the energy coefficient of friction (ECoF) [86] which is based on the dissipated energy per cycle as described in Figure 3.6 and defined in equation 3.2,

$$\mathbf{ECoF} = \frac{E_d}{4 P \delta} \quad \text{Equation [3.2]}$$

with E_d being the frictional energy dissipation per cycle, and δ being the slip amplitude (distinct from the applied displacement amplitude, Δ^*). Although the ECoF was generally employed to describe the evolution of the coefficient of friction, the evolution of both CoF and ECoF are presented for a single test so that the differences between these two measures can be understood, also, as previously stated, the in-test control system which was used to terminate tests was based upon the CoF rather than the ECoF. Throughout the thesis ECoF has been used to show the evolution of CoF and the analysis. The contact 'S' stiffness has been calculated from the slope of the Y-axis from the fretting loop shown in Figure 3.6. The

dissipated energy of a particular cycle can be calculated from the rig data after processing the raw file obtained during the experiment.

For each condition examined, tests were terminated when the CoF reached a value of 0.7 (this value was chosen as it was the value observed after a low number (~ 6000) of cycles for fretting of uncoated Ti6Al4V samples in this configuration), these are termed completed tests. It was deemed that coating failure had taken place when the CoF reached 0.7, with the number of cycles to failure under those test conditions being termed the coating durability. Subsequently, separate tests were run and stopped at numbers of cycles lower than the coating durability (these are termed interrupted tests), the point of interruption was selected to allow the nature of the coating to be examined before the coating had failed, more specifically, the point of interruption was selected to be somewhere in region where the ECoF was at its lowest point in the test.

The data files are binary files in the ".tdms" file format proprietary to LabView. Additionally, each second, the average mean and amplitude of both signals are calculated and recorded. These are very important in providing information of on fretting test stability. For a 100,000 fretting cycle test results, the data file size is around 80 Mb with $\sim 10 \times 10^6$ data points.

The amplitude of oscillation, and consequently slip, are produced by a proportional integral differential (PID) control loop which acts on the difference between the desired slip amplitude and the measured amplitude. Digital filtering was applied to the data within the software to remove all

the constant background noise picked up during the data logging and also to centralise the $Q(t)$ and $\delta(t)$ waveforms to be symmetric across the time axis. These data points were then used to plot Q and δ hysteresis loops for specific fretting cycles.

Files obtained from the rig contain very basic information such as displacement, force, displacement amplitude, force amplitude and temperature as well as meta data such as filename and test conditions. Files received from the rig were processed by the script using the LabView software. There are two different scripts which were used in this case to process the files, (a) Batch process script (b) Get data script. Batch process script is used to expand the displacement and force values into CoF, dissipated energy etc. this is a temporary filter which is applied to a temporary force group to determine the cycle count. This helps to remove drift and noise from the force signal so that cycle can be determined. The get data scripts select data after fixed number of data points from the large files and create a manageable file to plot it by plotting softwares. These scripts determine the samples fretting loops, coefficient of friction, energy coefficient of friction, filter cycle, temperature, displacement and force data and decimate them. The process is illustrated by the flow diagram in Figure 3.7.

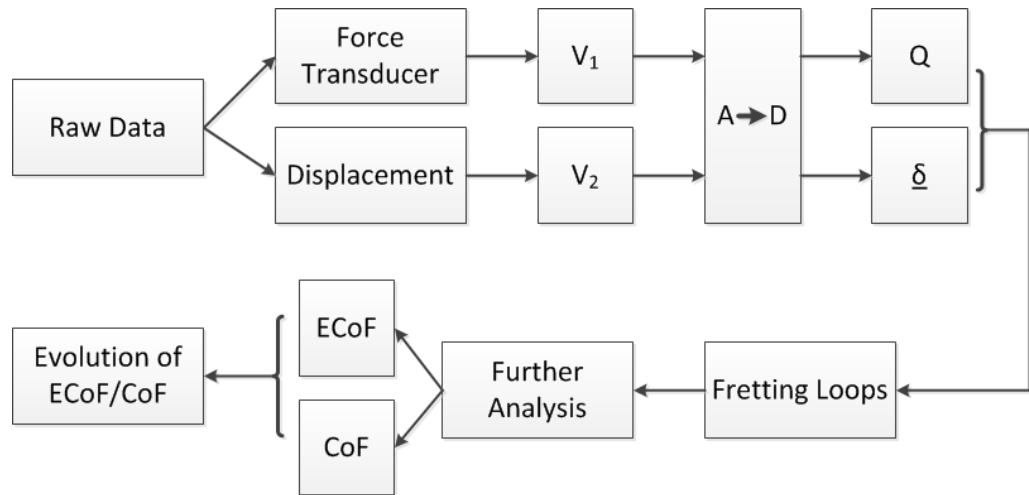


Figure 3.7 The flow chart diagram for the data process to evaluate ECoF/ CoF.

3.4 Fretting wear scars assessment

3.4.1 Surface profilometry

In this thesis, only flat specimen surface topography has been considered. To evaluate the surface topography of the flat specimens surfaces were scanned using one of two different profilometers. Early research in the thesis used Taylor-Hobson Talysurf CLI 1000, a tactile profilometer. However, during the project a Bruker Contour GT-I white light interferometer was acquired and was used for the rest of the research programme as it was faster to use and had higher resolution. A comparison of the profilometers is given in Austin Warmuth's work [242]. It was found that for 5 and 200 Hz wear scars, same general morphology is being captured by both profilometers, but more detail is seen on the scans using the Bruker equipment.

Talysurf

To evaluate the surface profile of the worn surface, unworn as produced specimens were used to compare the details of the wear scar. The talysurf profilometer uses a fine diamond stylus (90° , $2\text{ }\mu\text{m}$ radius) and has a vertical resolution of 2- 40 nm [243]. The wear scar extends across the full width of the flat specimens. An 8 mm length of the central area was profiled with 0.25 mm spacing between profiles. Measurements were taken at $1\text{ }\mu\text{m}$ intervals along each line. The width of the scar includes a few millimetres of reference surface at both ends of the scar. The width of the scar depends on the number of cycles as width increases with the increased cycles. The software allows levelling up of each scan and extraction of a mean profile to give a better representation of the wear scar shape.

Figure 3.8 Schematic diagram illustrating the profiling details of the flat fretting specimens.

The scan time is proportional to the number of profiles and not the number of points per profile, so to achieve a uniform mesh would increase the scan time by a factor of 250.

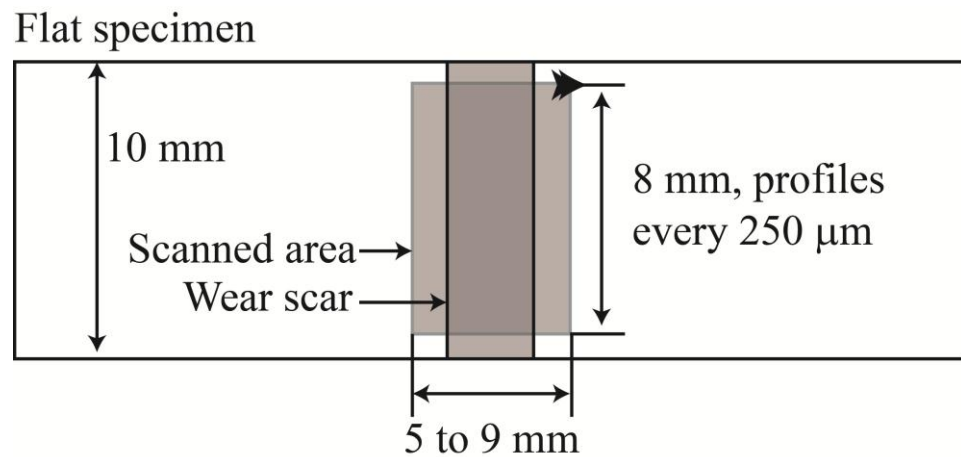


Figure 3.8 Schematic diagram illustrating the profiling details of the flat fretting specimens.

The average profile was determined and then smoothed using a 2nd order polynomial fit shown in Figure 3.9. Any material build up above the reference surface is considered to be transferred material or debris. The severity of the wear was defined from the depth of the wear scar, which was evaluated by calculating the worn area from the average wear profile.

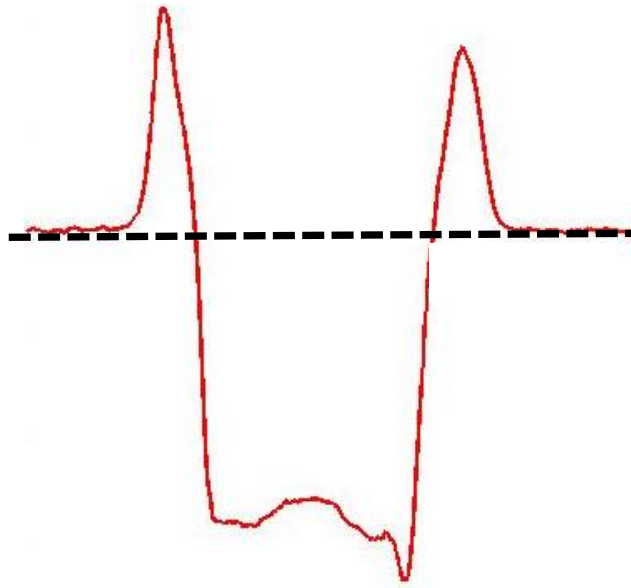


Figure 3.9 Schematic profile diagram of the wear scar with the reference surface

The software supplied with the profilometer was unable to provide the required functionality, specifically the form removal. Consequently, custom software (previously in-house in Matlab™) was used to process all of the profilometry data and also to calculate the wear volume. The software provides the GUI tool to enable the user to define the wear scar and limit the volume integral to that region. This interface also helps to centre the wear scar for later graphical presentation.

Bruker

Profilometry using the Bruker Contour GT-I was conducted using the 2.5 x objective lens, at this magnification, the vertical resolution was ~ 0.15 nm and had a lateral resolution in both directions of $4\text{ }\mu\text{m}$. Similar to the Talysurf, a few millimetre unworn surface were secured outside the wear scar to ensure the reference surface.

3.4.2 Scanning electron microscopy and energy Dispersive X-ray (EDX) analysis

SEM was used to examine both plan view of wear scars for which no sample preparation was needful, and also cross sections of same samples. EDM cutting machine was used to section some worn specimens. The newly cut specimens were mounted in WINTERCRYL RAPID POWDER (cadmium free), and WINTERCRYL RAPID REPIRE LIQUID, which is a cold mount and suitable for microscopic examination. The traditional hot mounting procedure was not taken to avoid any changes on the surface due to heat. After mounting the surface of interest was ground using different grades of silicon-carbide grinding paper, ranging from P600 to P12000 grit (15.3 μm) followed by the 0.1 μm cloth polishing by an MD-CHEM Colloidal silica disc (Struers) with SiO_2 final polishing suspension.

A Philip XL30, scanning electron microscope, fitted with a Lanthanum Hexaboride (LaB_6) filament, was used for SEM. The resin moulded samples were not conductive and a conductive coating was needed, such as, carbon coating. To conduct SEM on these samples, no carbon coating was done, rather the specimen and the mount was linked with carbon tape so that conducting issue can be avoided. The SEM was typically operated with an acceleration voltage of 20 keV, but occasionally 15 keV was used when there were charging issues. The working distance was always kept at 10 mm. Images were taken using both secondary electron (SE) and back scattered electron (BSE) mode. SE images gave the information about the surface topography, scar orientation, wear scar direction, presence of debris or any presence of layer structure, whereas, the BSE images provide

information on element distribution. BSE images are of particular interest as it shows the contrast between phases present and their distribution on the surface. The differences in the mean atomic number of elements in a phase produce these contrast variations in the BSE image, which allows a clear distinction between substrate and wear debris and between material types.

Further chemical characterisation was conducted using energy dispersive X-ray (EDX) analysis was used with a 10 keV beam acceleration voltage. An EDAXTMCDU LEAP detector was used attached with SEM to give the elemental wt. percentage analysis of the desired area on the specimen. The digitised data from the spectrum was displayed using this EDAX software.

3.4.3 XPS analysis

X-ray photoelectron spectroscopy is a surface analysis technique that measures the elemental composition and the chemical state of the elements in a material. It is also known by the alternative acronym, ESCA (Electron Spectroscopy for Chemical Analysis). The sample is exposed during analysis to X-ray bombardment. Photons are absorbed by elements on the surface region of the sample leading to ionisation and the emission of core (inner shell) electrons. The kinetic energy distribution of the emitted photoelectrons is measured in the spectrometer and the electron binding energies are determined. For every element, there will be a characteristic binding energy associated with each core atomic orbital and

therefore any given element produces its own characteristic peak 'fingerprint' in the photoelectron spectrum. The peak intensities can be related to the concentration of the given element within the sampled region. Therefore, XPS can provide a quantitative analysis of the surface composition. Changes in oxidation state or chemical environment give rise to small variations in binding energy which in turn lead to small changes in the peak positions. These shifts are known as chemical shifts. The ability to discriminate different oxidation states and chemical environments is a big advantage of the XPS technique. XPS is not sensitive to H and He, but can detect all other elements.

Samples were analysed using the Kratos AXIS ULTRA with a monochromated Al *ka* X-ray source (1486.6eV) operated at 10 mA emission current and 12 kV anode potential (120 W.). The ULTRA was used in FAT (fixed analyser transmission) mode, with pass energy of 80eV for wide scans and pass energy 20 eV for high resolution scans. The magnetic immersion lens system allows the area of analysis for to be defined by apertures, a 'slot' aperture of 300 x 700 μm for wide/survey scans and high resolution scans. The take-off angle for the photoelectron analyser is 90° and acceptance angle of 9° for hybrid lens mode utilised. Charge neutralisation was used to prevent the sample surface charging as it was mounted on a non-conducting tape and also had a fairly thick anodised oxide surface.

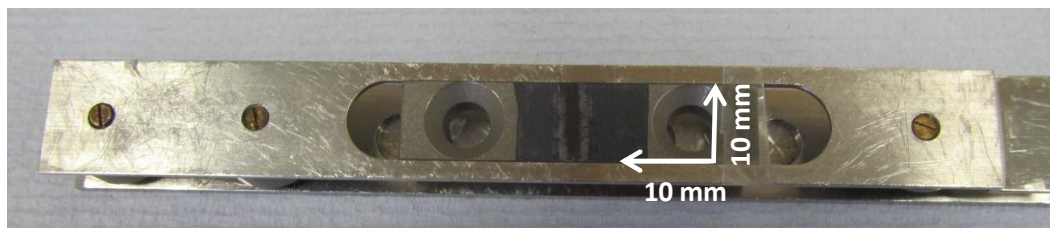


Figure 3.10 XPS sample bar with typical sample having flat specimen wear scar mounted ready for analysis.

Because the sample chemistry appeared to change across the wear scar the flat samples were analysed at points 0.5 mm apart stepping across the wear scar shown in Figure 3.11. This is close up of Figure 3.10 with similar scale.

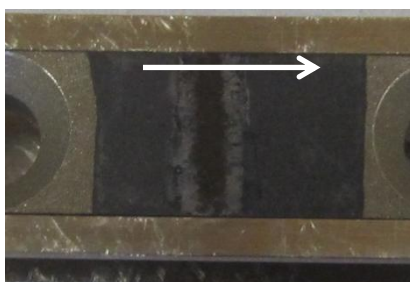


Figure 3.11 stepped analysis points indicated by the arrow, across the wear scar for sample

The analysis chamber pressure was better than 5×10^{-9} Torr. Wide scans were run for 10 or 20 minutes each. There were run at Pass energy 80 eV with a step size of 0.5 eV. (The resolution at this pass energy corresponds to a FWHM on Ag 3d peak of 1.1eV) The high resolution scans were run for 5 minutes each, with pass energy 20 eV and step size of 0.1eV.

The energy range of the XPS was calibrated using Cu, Ag and Au samples. The resolution for the photoelectron detector was based on Ag 3d_{5/2} peak

FWHM of less than 0.55 eV at PE 20 in hybrid slot mode. The transmission function of the instrument was calibrated using a clean gold sample for all lens modes and pass energies.

Data processing was carried out using CASAXPS software with Kratos sensitivity factors (RSFs) to determine atomic % values from the peak areas. The high resolution scans were charge corrected to C 1s at 285 eV and the quantifications were performed with Kratos sensitivity factor library.

3.4.4 Micro Hardness Analysis

Buehler Micro hardness was used to measure the hardness of substrate Ti6Al4V and the metallic layer Cu-Ni-In. The resin moulded cross section samples prepared for SEM were used to find the hardness of the substrate and coating.

Indentations were done on the surface of interest. The difference in length of both diagonals was taken. The HV number is then determined by the ratio of F/A , where F is the force applied to the diamond in kilograms-force and A is the surface area of the resulting indentation in square millimetres. 200 g load was used and 5 values were taken to get the average values of hardness.

Chapter 4. Evolution of damage in MoS₂-based dry film lubricants (DFLs) in fretting wear and the effect of DFL thickness and contact geometry

This chapter presents an investigation of the fretting wear behaviour of as received dry film lubricant containing MoS₂. ECoF evolution of the coefficient of friction is determined by fretting tests with a cylinder-on flat contact geometry and fretting amplitude of 300 µm. This work also investigates the effects of DFL thickness and contact geometry. Cylinders with radii of 15 mm, 80 mm and 160 mm along with DFL thicknesses between 12 µm and 86 µm were utilized. In each case examined, the DFL thickness was the same on both the flat and cylindrical specimens in the fretting couple.

The data obtained from the experimental tests along with the results from the profilometer, SEM, EDX, XPS and the cross section analysis of the wear scar are brought together in an attempt to understand the mechanism of the wear and failure of the existing coating system.

4.1 Results

4.1.1 Evolution of coefficient of friction and damage processes for DFL coated substrates in fretting

Figure 4.1 shows the cross section of the as-cured MoS₂ DFL coating with an average thickness of 50 µm on a Ti6Al4V substrate. Figure 4.2 shows the development of the coefficient of friction with increasing cycles from a single test, illustrating the difference between the CoF and the ECoF. The general form of the evolution in frictional behaviour is described equally well by the ECoF and the CoF, but the ECoF is generally lower than the CoF since it represents the average behaviour across the loop, as opposed to the CoF which utilises the maximum tractional force recorded within the loop. The ECoF is thus less sensitive than the CoF to the influences of geometrical changes in the wear scar which can cause end-peaks in fretting loops [241], and thus the ECoF is used in this thesis.

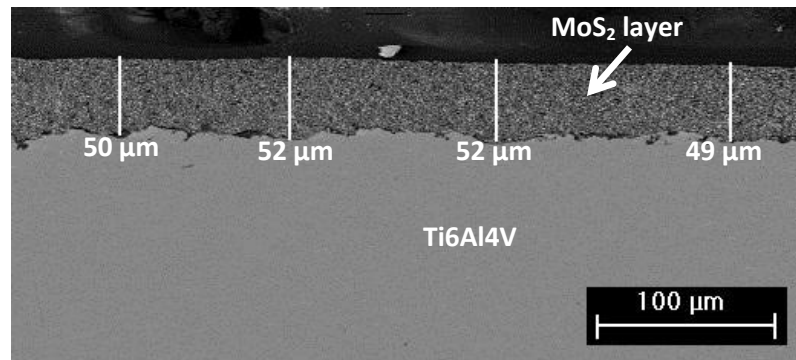


Figure 4.1 Cross section of the as-cured MoS_2 DFL paint coating shows average $50 \pm 5\ \mu\text{m}$ coating layer thickness

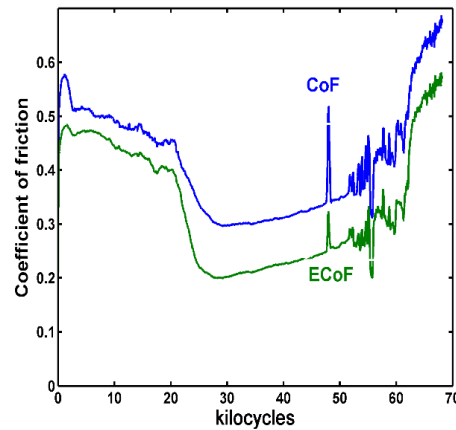


Figure 4.2 Evolution of both CoF and ECoF from the same test ($R = 15\ \text{mm}$, $t = 50\ \mu\text{m}$) which was run until coating failure.

Figure 4.3 shows the development of the ECoF with number of cycles for three DFL thicknesses (t) across the range examined on contact pairs with $R = 15\ \text{mm}$, in each case, the development of ECoF in two individual tests is presented to illustrate the repeatability of the evolution of frictional behaviour. For each thickness, three stages in the evolution of frictional behaviour are seen

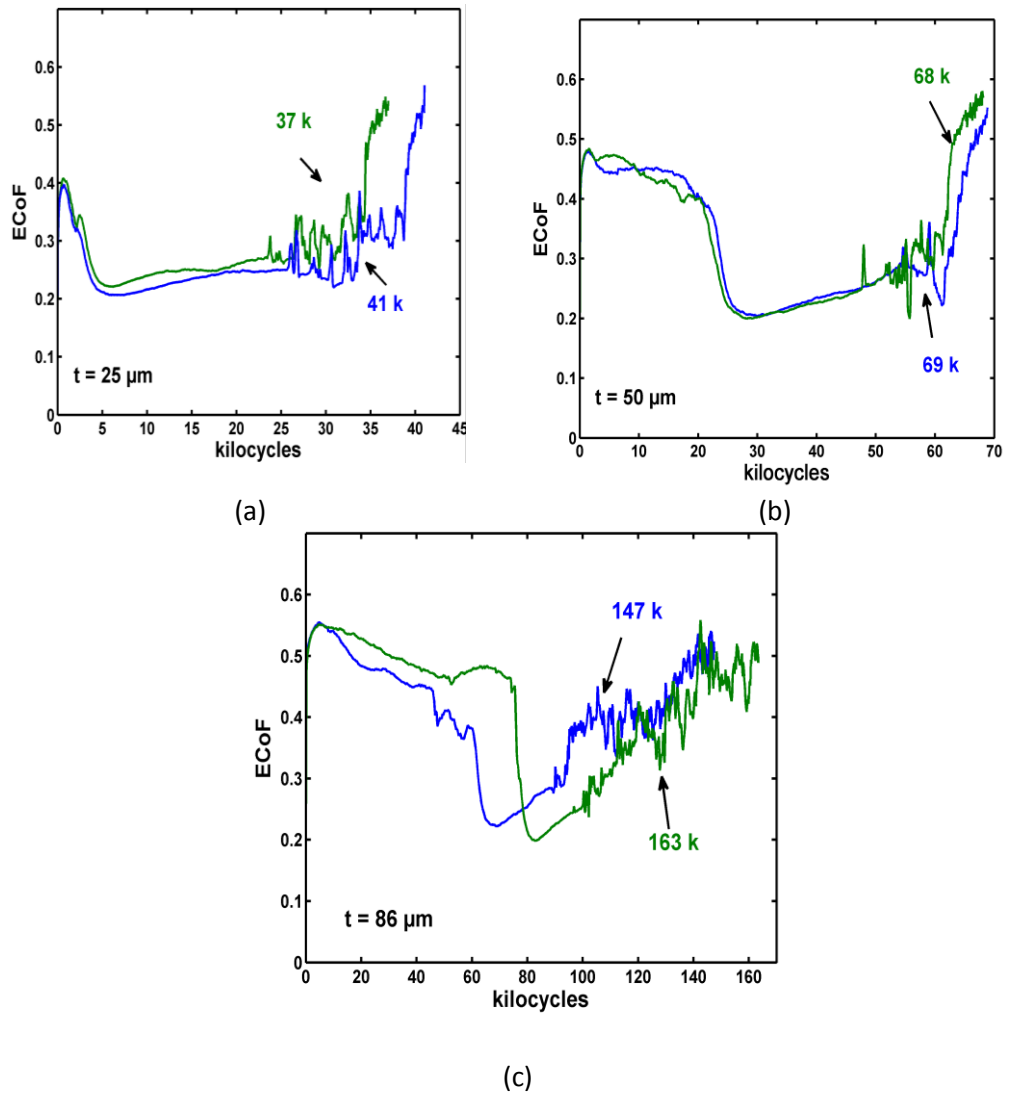


Figure 4.3 Repeatability of the evolution of ECoF with number of cycles for tests with $R = 15 \text{ mm}$ across the range of DFL thicknesses, (a) $t = 25 \mu\text{m}$, (b) $t = 50 \mu\text{m}$, (c) $t = 86 \mu\text{m}$.

An example of the ECoF evolution with number of cycles is presented in Figure 4.4 along with a categorization into three stages as follows: in Stage I, the coefficient of friction at first rises, and then slowly falls or remains approximately constant. At the start of Stage II, the coefficient of friction falls, this happens generally quite rapidly until a minimum point is reached, the ECoF then rises slowly and steadily from this minimum point until it starts to exhibit short term instability, this is defined as the end of

Stage II. In Stage III, the coefficient of friction continues to exhibit short term instability, and continues to rise until the test is terminated. The total number of cycles in each stage is thus defined as N_I , N_{II} and N_{III} , where the subscript refers to the appropriate stage.

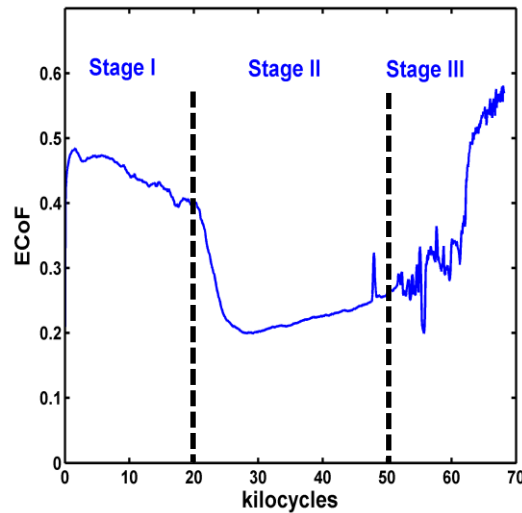


Figure 4.4 Evolution of ECoF with number of cycles ($R = 15$ mm, $t = 50$ μ m) along with categorization into stages of behaviour.

4.1.1.1 Damage mechanisms throughout the system lifetime

In order to understand the nature of the evolution of the damage which corresponds to the changes in ECoF with number of cycles, a number of interrupted tests were conducted with the same geometry and DFL thickness. Figure 4.5a replots the results shown in Figure 4.4 together with two interrupted tests, 5 kilocycles and 36 kilocycles for same conditions. A high level of reproducibility in the development of the ECoF in the three tests can be observed.

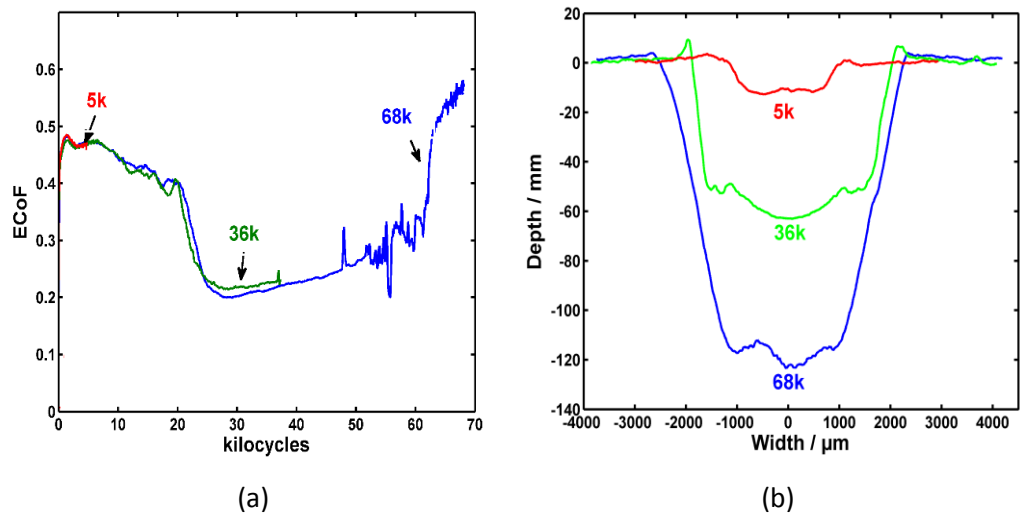


Figure 4.5 (a) Evolution of ECoF with number of cycles ($R = 15 \text{ mm}$, $t = 50 \text{ μm}$) for both completed and interrupted tests (indicating the number of cycles at interruption or completion), (b) average depth profiles across the corresponding wear scars.

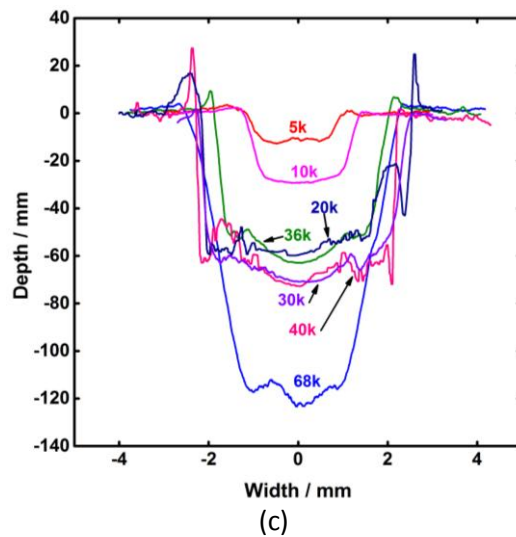


Figure 4.6 Comparison of average depth profiles across the wear scars for 5k, 10k, 20k, 30k, 36k, 40k and 68k cycles.

Figure 4.5b shows representative profiles across example wear scars, with the maximum depth of the wear scar as a function of number of cycles for all the tests conducted being presented in Table 4.1. Systematic tests have been done for 10k, 20k, 30k, 40k cycles on the same samples. Figure 4.6 shows profiles across the wear scar for each sample.

Table 4.1 Analysis from surface of wear scars ($R = 15 \text{ mm}$, $t = 50 \text{ }\mu\text{m}$) for tests interrupted at various points. The point of interruption is described by position in stage (defined by numbers of cycles). EDX analysis of titanium and molybdenum representing the substrate and DFL respectively.

N / kilocycles	Stage position	Ti / wt. %	Mo / wt. %	Depth of scar / μm
5	24% through Stage I	0	38	14
10	49% through Stage I	0	30	29
20	98% through Stage I	0	26	61
30	31% through Stage II	17	25	65
36	50% through Stage II	9	28	64
40	63% through Stage II	41	9	66
68	100% through Stage III	49	0	125

It can be seen that in stage I, the wear scar gets deeper, and is approximately as thick as the DFL layer itself at the end of Stage I. Throughout Stage II, the scar depth is just a little deeper than the original DFL thickness, whilst by the end of Stage III, the scar is much deeper than the original DFL thickness.

The distorted low magnification SEM images presented in Figure 4.7 show cross-sections through the wear scar at three points within the scar evolution which correspond to the profiles presented in Figure 4.5b. These micrographs are presented in a form where the vertical magnification is ten times that of the horizontal magnification since this provides a clearer visualisation of the damage incurred. It can be seen that after 5k cycles in Figure 4.7a, a significant wear of the DFL has occurred to approximately a third of the DFL thickness. Following 36k cycles Figure 4.7c, the coating has been largely removed from the centre region of the scar, but with areas towards both edges of the scar where a small quantity of the DFL can be seen which appears to be retained by the surface roughness of the substrate. Following 68k cycles Figure 4.7e, significant damage and material removal from the substrate can be seen.

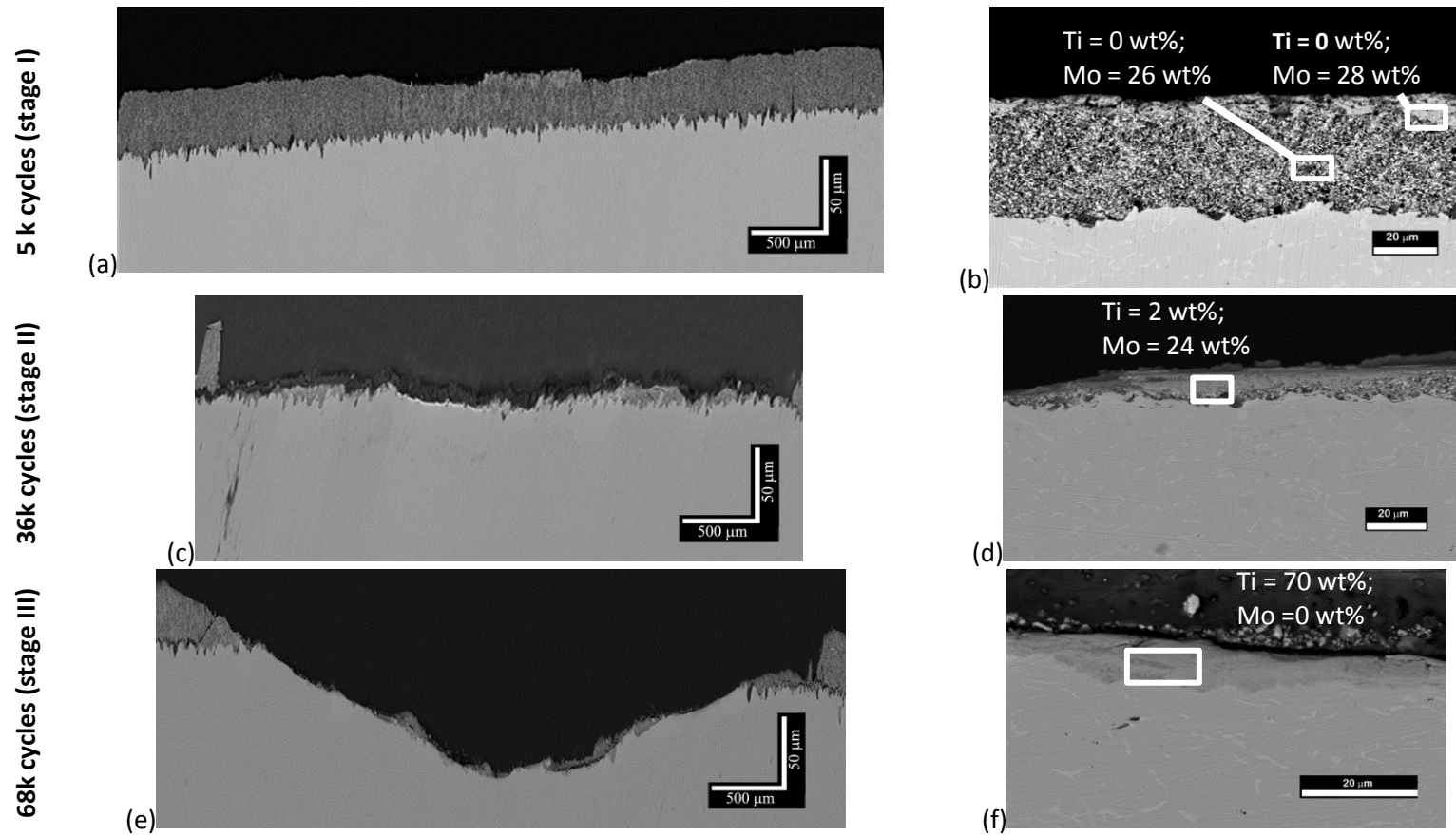


Figure 4.7 BSE micrographs of wear scar cross-sections ($R = 15 \text{ mm}$, $t = 50 \text{ }\mu\text{m}$) as a function of number of cycles corresponding to the tests described in Figure 4.5. (a), (c) and (e) are a low magnification images with a distorted aspect ratio (vertical magnification being ten times the horizontal magnification), (b), (d) and (f) are high magnification images of representative sections of the corresponding scar surface along with EDX data (elements included in the analysis: Ti, Al, V, Mo, S, C, O) representing the titanium and molybdenum contents of the areas indicated.

Figure 4.7 also shows higher magnification images of cross-sections through the wear scars, it can be seen that after 5k cycles shown in Figure 4.7b, the outer surface of the DFL has been modified, but that these changes are quite subtle and only affect a layer about 2 μm in thickness. The EDX results from the bulk and surface regions of the DFL indicate very little change in chemistry at the surface and that there is no evidence of any elements from the substrate at the wear surface by this stage. After 36k cycles shown in Figure 4.7d, there is evidence of some remnants of the DFL remaining on the surface, but it can be seen that this layer exhibits a generally homogeneous brightness in contrast to the cross-section shown in Figure 4.7b where the binder and MoS_2 can be clearly distinguished due to difference in brightness in BSE imaging. EDX analysis shows that this surface is chemically not very different from the original DFL. In Figure 4.7f, it can be seen that no traces of the DFL exist, a fact which is confirmed by the results of the EDX analysis.

EDX results in Table 4.2 are from analysis of the top surfaces of the centre of the relevant wear scars. It should be noted that Al, Ti and V can be regarded as marker elements for the Ti6Al4V substrate, whereas S and Mo are regarded as marker elements for the DFL. It is recognized that there will be significant errors associated with the absolute values quoted due to the measurement errors associated with carbon and oxygen. However, it is still clear that as the number of cycles increases, there is evidence of substrate exposure, which then increases in magnitude by 68k cycles. In contrast, there is evidence of MoS_2 until 36k cycles, which is then significantly reduced for 40k and 68k cycles. The decrease in C with increasing cycle is consistent throughout. The carbon level falling off as the

DFL layer is removed, the carbon being associated primarily with the polymeric binder phase. The oxygen level is associated with the formation of an oxide debris layer as the titanium alloy substrate begins to fret.

Table 4.2 Area analysis EDX results for 5k, 10k, 20k, 30k, 36k, 40k and 68k cycles wear scar

	At 5k cycles	At 10k cycles	At 20k cycles	At 30k cycles	At 36k cycles	At 40k cycles	At 68k cycles
Element	Weight %	Weight %	Weight %	Weight %	Weight %	Weight %	Weight %
C K	27	44	52	23	21	8	6
O K	10	7	6	15	23	30	35
Al K	0	0	0	3	2	5	3
Ti K	0	0	0	17	9	41	49
V K	0	0	0	0	0	2	2
S K	25	19	16	16	16	4	0
Mo L	38	30	26	25	28	9	0

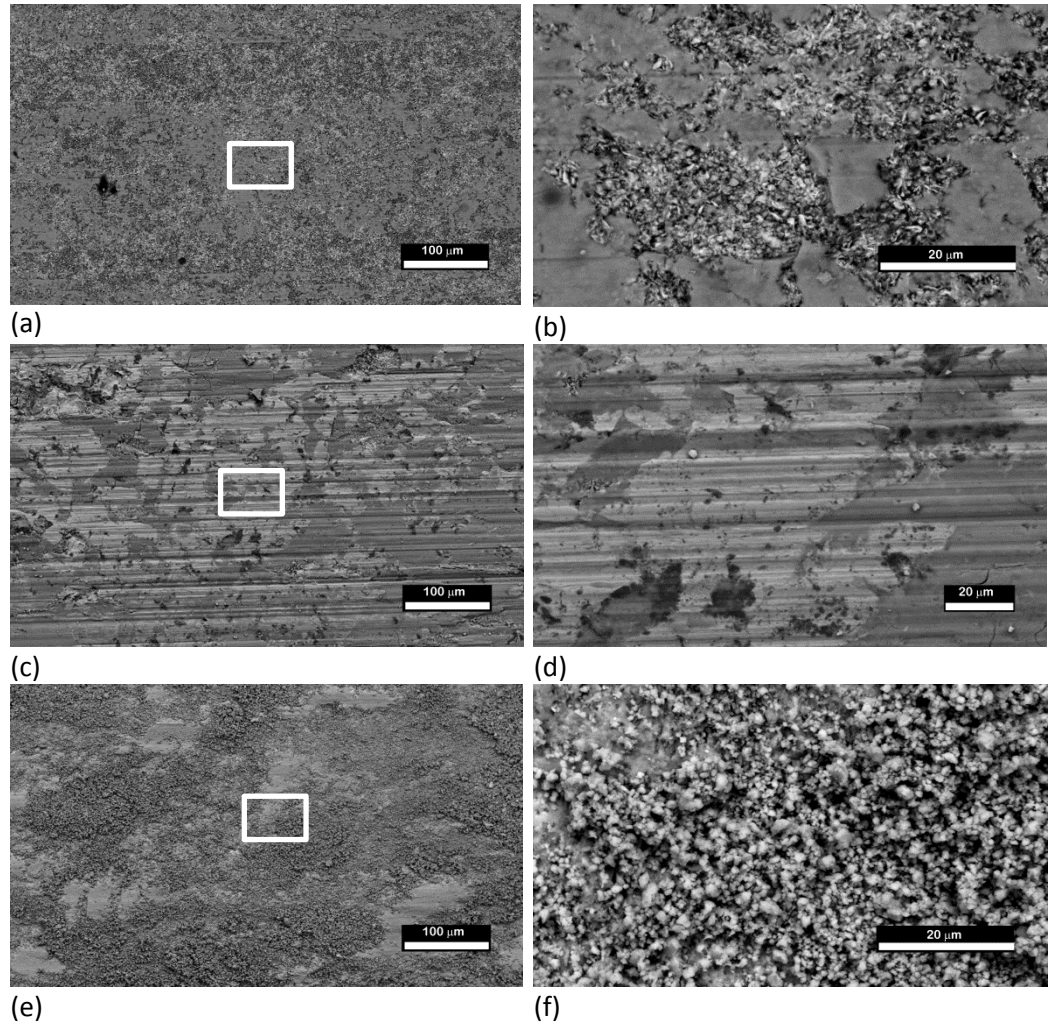


Figure 4.8 BSE plan view micrographs of wear scars ($R = 15 \text{ mm}$, $t = 50 \text{ μm}$) as a function of number of cycles corresponding to the tests described in Figure 4.5. (a), (c) and (e) are a low magnification images, (b), (d) and (f) are corresponding high magnification images from the regions indicated. (a) and (b) following 5 k cycles (stage I), (c) and (d) following 36k cycles (stage II), (e) and (f) following 68k cycles (stage III).

Figure 4.8 shows plan view images of the wear scars following the tests indicated in Figure 4.7a, with Table 4.2 detailing results from large-area EDX analyses of the same wear scars. It can be seen that there is no evidence that the substrate has been exposed within Stage I, but that by 31% through stage II, there is clear exposure of the substrate, the ratio of titanium to molybdenum tends to increase with number of cycles through Stage II, i.e. the DFL fraction reduced and the substrate fraction increased,

by the end of Stage III, all evidence of the molybdenum-containing DFL has been removed.

After 5k cycles, Figure 4.5b and Figure 4.7a indicate that there has been no penetration of the DFL to the substrate. Accordingly, it is clear that Figure 4.8a and Figure 4.8b show the worn surface of the DFL itself, some regions of which exhibit a smooth surface associated with the rubbing action of the fretting process which is linked to the subtle modification of the surface region observed in Figure 4.7b, whereas other regions exhibit a much rougher surface.

After 36k cycles, Figure 4.5b and Figure 4.7c indicate that the DFL has been penetrated. In addition, data in Table 4.2 indicates that after this number of cycles the surface is still dominated by the DFL. In this area a large fraction of molybdenum is still present, similar to that measured in the unworn DFL, but there is also evidence of a small fraction of titanium alloy in the surface material. The measured titanium content via EDX analysis in this area is ~ 9 wt.%, which equivalent to ~ 4.5 at%. The micrographs in Figure 4.8c and Figure 4.8d also indicate that the surface is made up of different regions. EDX of lower brightness regions still have evidence of DFL being present, whereas those with a higher brightness are regions where the DFL has been removed, just leaving substrate exposed. Ploughing marks can be seen running across the surface, but the surface is generally quite smooth indicating that wear has been mild at this point. However, the XPS data (Figure 4.9) show a much lower titanium (~ 1 at%) content across the surface, which indicates that the surface material which appears titanium-rich via BSE imaging and EDX analysis is in fact covered

by a layer which is rich in carbon, oxygen, molybdenum and sulphur, but that this layer is thin enough that it is detected by XPS analysis but not by EDX analysis and BSE imaging. Moreover, the XPS trace across the wear scar Figure 4.9 indicates a substantial reduction in carbon in the wear scar with an increase in molybdenum and sulphur, indicating that the surface of the wear scar is preferentially enriched in MoS_2 by the wear process itself.

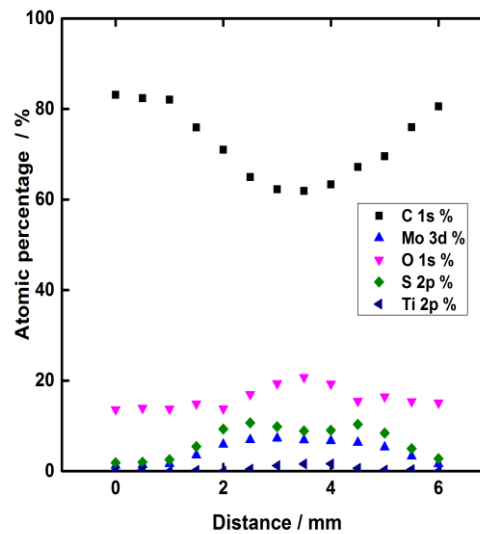


Figure 4.9 XPS analysis across the interrupted test wear scar ($R = 15 \text{ mm}$, $t = 50 \text{ }\mu\text{m}$) following 36k cycles (stage II), showing the atomic percentage of elements across the wear scar. Positionally, 0 mm and 6 mm are outside the scar, with the scar existing between these lateral positions.

After 68k cycles, Figure 4.5b and Figure 4.7e indicate that the DFL has been entirely removed, with wear to a depth twice that of the original DFL coating thickness. In addition, Table 4.2 indicates that there is a complete absence of molybdenum from the EDX analysis. The micrographs in Figure 4.8e and Figure 4.8f indicate significant surface disruption, as is commonly observed in the fretting of titanium alloys [68].

4.1.1.2 The effect of DFL thickness and fretting pair geometry

The same general trends in the evolution of frictional behaviour are also observed for the other contact geometries ($R = 80$ mm and $R = 160$ mm) across the range of DFL thicknesses shown in Figure 4.10. Overall, the durability of the system coating increased with increasing coating thickness as mentioned by Kim et al. [244]. Only in the test conducted with a DFL of thickness of $62\text{ }\mu\text{m}$ on a 160 mm radius cylinder was it difficult to identify the boundary between Stages II and III, since Stage III appeared to begin before Stage II had fully developed.

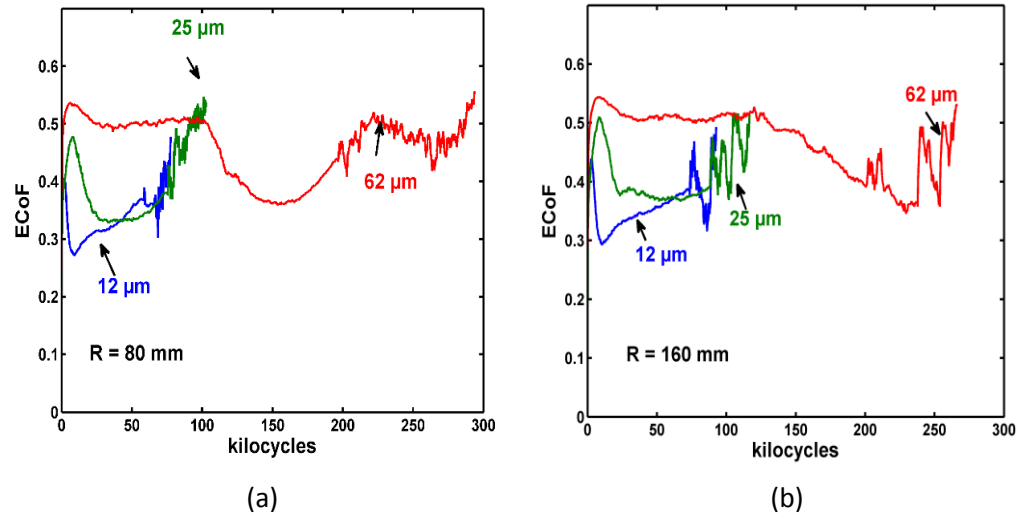


Figure 4.10 Evolution of ECoF with number of cycles as a function of DFL thickness ($t = 12\text{ }\mu\text{m}$, $25\text{ }\mu\text{m}$ and $62\text{ }\mu\text{m}$) for contacts with (a) $R = 80$ mm and (b) $R = 160$ mm.

Results reported in Section 4.1.1.1 relating to the smaller radius cylindrical samples in the fretting pairs ($R = 15$ mm) indicate that Stage II is associated with a period where the DFL has been largely removed with some exposure of titanium alloy substrate, which increases as stage II develops. To confirm that this conclusion was valid for other thicknesses of DFL and other contact radii, tests interrupted towards the start of Stage II

were conducted as indicated in Figure 4.12 ($R = 80 \text{ mm}$, $t = 12 \text{ }\mu\text{m}$ and $62 \text{ }\mu\text{m}$). In both cases, the evolution of the ECoF was very similar for the completed and interrupted tests, again indicating a high level of reproducibility of behaviour of ECoF evolution. Depth profiles of the wear scars resulting from these interrupted tests shown in Figure 4.13 show that in both cases, the wear scar depth in Stage II was slightly larger than the original DFL thickness. However, it is within the variability of the depth due to variation caused by surface roughness of the substrate. EDX analyses of the worn surfaces from the integrated, stage II samples, again reveal their mixed substrate/ DFL makeup, with Ti at 20 wt% and Mo at 21 wt.% for $12 \text{ }\mu\text{m}$ thickness and Ti at 27 wt% and Mo at 27 wt% for $62 \text{ }\mu\text{m}$ thickness. These observations are consistent with the general identification of Stage II with a period where the surface in contact is a combination of the DFL and the metallic substrate.

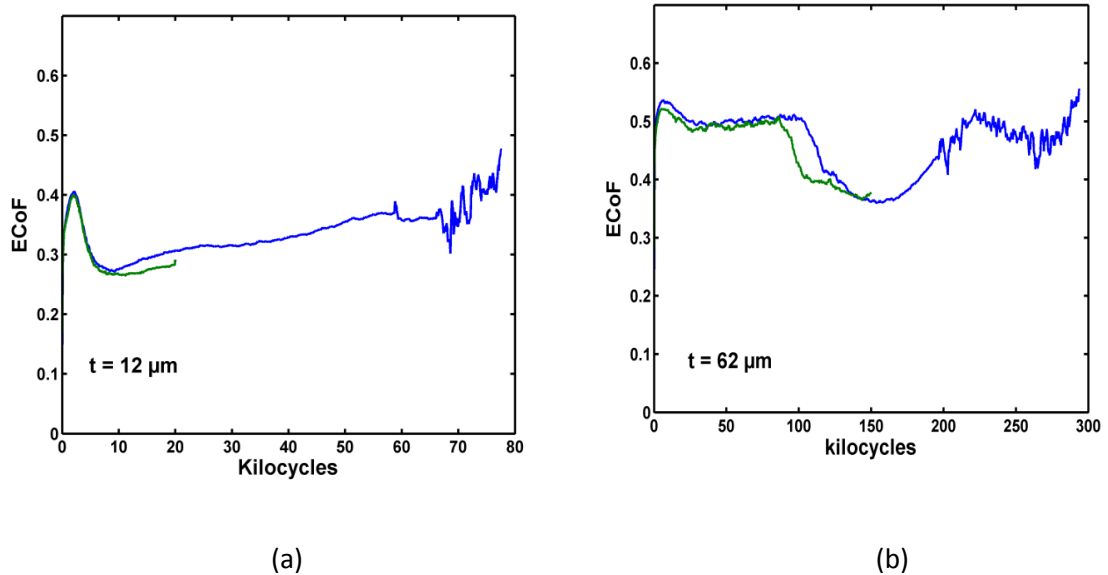


Figure 4.11 Evolution of ECoF with number of cycles for both a full and an interrupted test for both a thin and thick DFL film, (a) $t = 12 \text{ }\mu\text{m}$, $R = 80 \text{ mm}$, (b) $t = 62 \text{ }\mu\text{m}$, $R = 80 \text{ mm}$.

A range of combinations of DFL thickness and contact geometry have been examined with a constant load of 575 N. Two additional tests were conducted under the higher load of 2000 N, both with $R = 15$ mm but towards the extremes of the thicknesses considered are $25\text{ }\mu\text{m}$ and $86\text{ }\mu\text{m}$. The same sliding distance of $300\text{ }\mu\text{m}$ and the frequency of 2.5 Hz was used for the higher load tests. Figure 4.12 shows the comparison evolution of coefficient of friction under two different loads on two different thicknesses of as-received DFL. In both thicknesses, Figure 4.12 shows that applying increased load decrease the life of the coating significantly and also the overall coefficient of friction value decreases throughout the evolution. The important thing to notice that, during higher load experiments the ECoF evolution shows significant decrease in number of cycles but all the three stages can be observed.

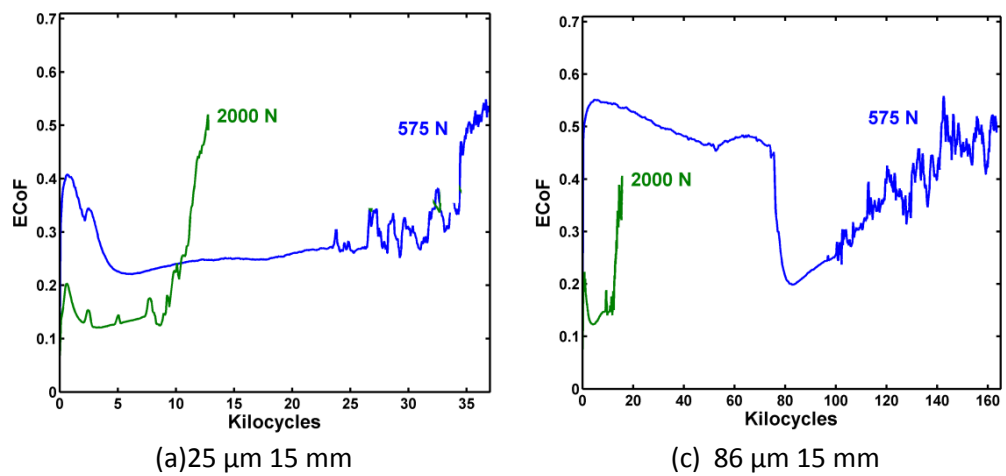


Figure 4.12 the comparison of evolution of coefficient of friction under two different loads, i.e. 575 N and 2000 N (a) $25\text{ }\mu\text{m}$ 15 mm (b) $86\text{ }\mu\text{m}$ 15 mm.

Table 4.3 Durations of Stages I, II and III in reciprocating sliding tests as a function of R, t and P

R / mm	t / μm	P / N	N _I / 1000	N _{II} / 1000	N _{III} / 1000
15	12	575	0.5	33.1	14.8
15	25	575	1.7	21.8	14.5
15	33	575	0.9	38.5	18.7
15	50	575	20.5	31.0	16.5
15	62	575	23.4	33.6	21.7
15	86	575	65.2	34.2	64.2
80	12	575	2.1	55.9	19.5
80	25	575	8.7	66.2	27.8
80	62	575	102.0	93.0	99.0
160	12	575	3.1	69.8	19.8
160	25	575	8.4	79.6	29.0
160	62	575	127.0	73.0	66.2
160	86	575	190.0	148.0	48.8
15	25	2000	0.7	7.8	4.2
15	86	2000	0.9	9.7	4.9

The full experimental programme is summarised in Table 4.3 along with the durations of the three stages for each of the tests. The durations for tests conducted with an applied load of 575 N are also presented in Figure 4.14. From examination of these data, the following general observations can be made:

- (i) For each contact radius, R, the total test duration is dominated by Stage II and III at low values of t, but Stage I becomes a very significant fraction of the total lifetime for larger values of t;

- (ii) the duration of Stage I increases both with increasing t and increasing R , although the dependence upon t is much more significant than that upon R ;
- (iii) the duration of Stage II increases slowly with R , but at each contact radius, it exhibits no clear dependence upon t ;
- (iv) at the start of stage II, a significant decrease in the ECoF is observed until a minimum is reached, the rate of this reduction decreases significantly for 62 μm thickness for the two larger values of contact radius, R (Figure 4.10);
- (v) for each contact radius, R , the duration of Stage III shows a large increase at a specific value of t , below this value of t , the duration of Stage III is broadly independent of t ;
- (vi) the minimum value of ECoF in stage II is higher for the two larger values of R than it is for 15 mm radius. At the two larger radii, the minimum value of ECoF also increases as t increases;
- (vii) the higher applied load of 2000 N resulted in a significant reduction in the duration of all three stages when compared to equivalent tests conducted with an applied load of 575 N;

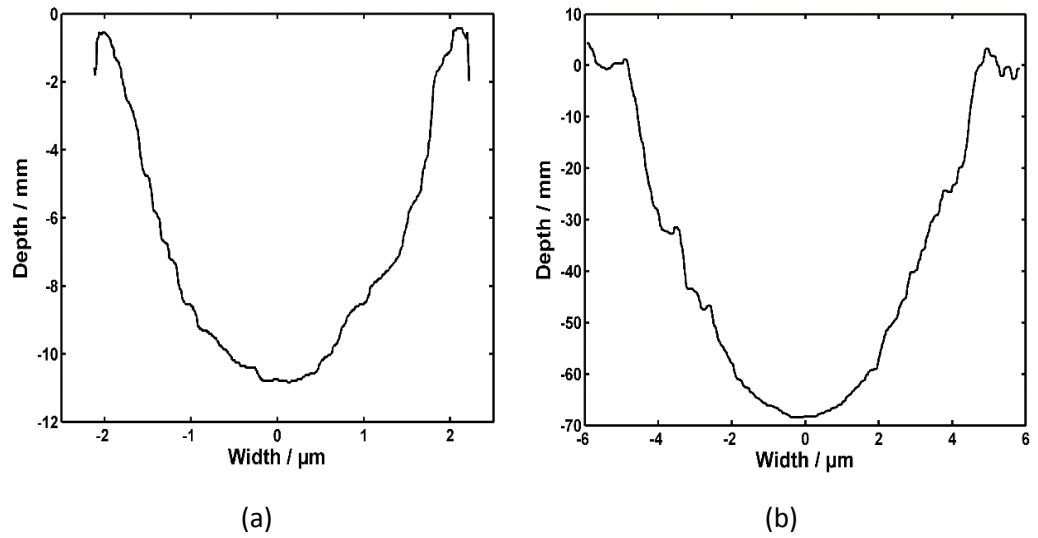


Figure 4.13 Profilometry traces showing the wear scar dimensions at the end of the interrupted tests referred to in Figure 4.11, (a) $t = 12 \mu\text{m}$, $R = 80 \text{ mm}$, (b) $t = 62 \mu\text{m}$, $R = 80 \text{ mm}$.

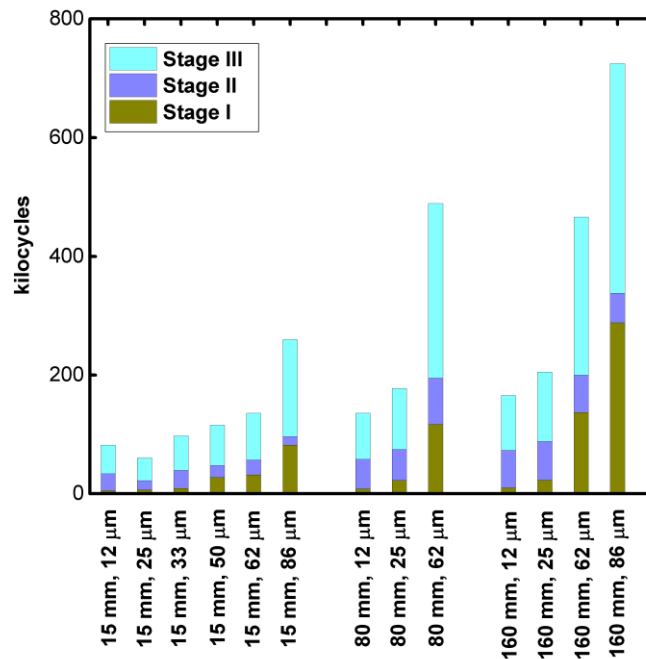


Figure 4.14 Histogram showing the numbers of cycles in each stage for each test configuration (cylinder radius, R and DFL thickness, t).

4.2 Discussion

4.2.1 Durability of surface engineered systems

Recently, there has been great interest in being able to link fretting wear damage in homogeneous materials with the energy dissipated in the contact, where the wear volume is measured following testing, and the energy dissipated is derived from the fretting loops [178]. In homogeneous materials, the behaviour and failure of the system and the mechanisms of damage accumulation do not depend strongly upon the depth to which material has been removed, and so such methodologies have generally been observed to work well.

However, the methodologies are not straight forward to apply to non-homogeneous materials such as coated or surface engineered systems. This is because the behaviour and failure of these systems, along with mechanisms of damage, depend upon the depth of material removal. Failure is often associated with complete removal of a surface engineered layer; therefore, the wear volume does not uniquely define whether failure has occurred. This means that, system failure cannot be simply linked to the frictional energy dissipated. A revised model is needed to address this problem. Fouvry and co-workers have proposed such a model [43] which has been used to determine coating lifetime in terms of the maximum frictional power density dissipated in the contact [126, 245]. The model is complex, partly because it does not specifically address the various

physical stages in the lifetime of the DFL system. In the current work, the durations of the various stages will be considered separately.

4.2.2 Duration of Stage I

It has been shown that in Stage I, the DFL is being worn away and that by the end of Stage I, the DFL has been removed and exposure of the metallic substrate starts. A basic geometrical model of this situation is presented in Figure 4.15a, which shows a coated cylinder of radius R in contact with a coated flat, with the coatings on both being of thickness t . For the substrates of the cylinder and flat to come into contact requires removal of coating from both the cylinder and flat, as shown in Figure 4.15b.

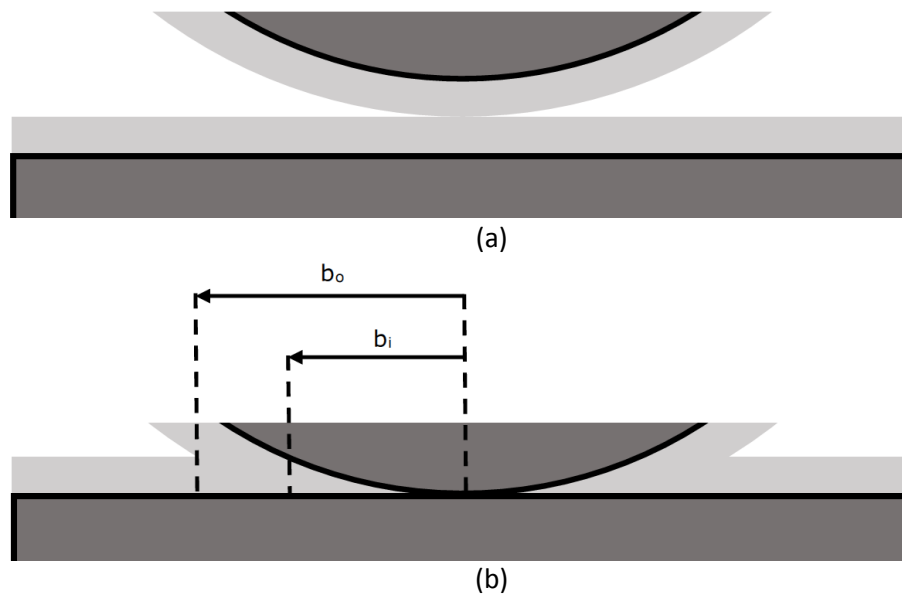


Figure 4.15 schematic diagram of geometrical changes take place in Stage I of the DFL wear process.

The contact semi-width observed on the flat sample will lie somewhere between b_i and b_o (shown in Figure 4.15b), depending upon exactly where the wear has occurred. These two are given by the following equations:

$$b_i = \sqrt{R^2 - (R - t)^2} = \sqrt{2 R t - t^2} \quad \text{Equation [4.1]}$$

$$b_o = \sqrt{(R + t)^2 - R^2} = \sqrt{2 R t + t^2} \quad \text{Equation [4.2]}$$

For the range of values of R and t employed in this work, the difference between b_i and b_o is never more than 0.2%, and accordingly, the total wear scar width observed on the flat specimen, where δ is slip amplitude and B_s can be approximated by:

$$B_s = b_i + b_o + 2 \delta \quad \text{Equation [4.3]}$$

The widths of wear scars on a range of flat samples where the tests had been terminated soon after the beginning of Stage II were measured. To test the hypothesis that Figure 4.15b is representative of this situation, the measured scar width was plotted against the idealized scar width, B_s (from Equation 4.3), Figure 4.16 shows the correlation between the measured and idealized scar widths. Finding the R-squared value to measure how close the data are to the fitted regression line. The R^2 value is 0.89, which depicts 89 % of the variation of the obtained data is explained by the above plot. This shows the model is close to the unity. Since there is such a good correlation between the measured and theoretical scar width, which further adds to the evidence that Stage I of the failure process is defined by the almost complete removal of the DFL by wear. However, the

correlation appears to be best for smaller wear scars, i.e. to get worse as wear progresses.

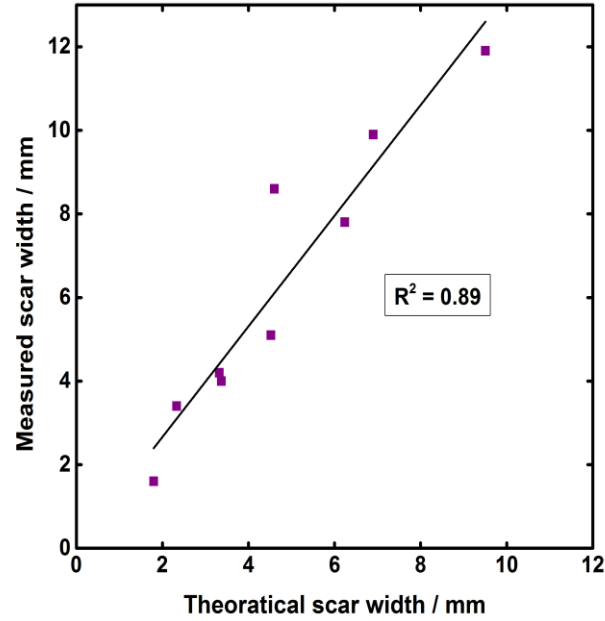


Figure 4.16 Comparison of theoretical and measured scar widths for tests interrupted at the end of Stage I from nine combinations of R (15, 80 and 160 mm) and t (12, 25 and 62 μm).

As the idealized model has been shown to be relevant to the data, it will be used for further analysis of Stage I. According to the model shown in Figure 4.15, the combined cross-sectional area of DFL which needs to be removed to allow the substrate of the two bodies to come into contact is given by the chordal area of a cylindered circle of radius R and depth 2 t. This chordal area, A_I , is related to these two parameters by the following equation:

$$A_I = R^2 \cos^{-1} \left(\frac{R-2t}{R} \right) - (R-2t) \sqrt{R^2 - (R-2t)^2} \quad \text{Equation [4.4]}$$

Since the slip amplitude is δ , then the total volume of DFL which will be removed, V_I , is given by:

$$V_I = (A_I + 2 \delta t) w \quad \text{Equation [4.5]}$$

Where, w is the contact line length shown in Figure 3.2.

If it is assumed that the volume of DFL removal in Stage I is proportional to the number of cycles and the applied load, then the following equation will apply:

$$V_I = v^2 = k_I N_I P \quad \text{Equation [4.6]}$$

To test this equation, V_I is plotted against N_I for all the tests conducted under a load of 575 N as shown in Figure 4.17. Data obtained were fitted linearly. It can be seen that the correlation is reasonable across the range of values of R and t . Fitting the line gives 98 % variation and data's were explained by the equation and hence it showed a high correlation. Fitting these data by linear fit method, results in the following relationship for Stage I:

$$k_I = 0.15 \times 10^{-6} \text{ mm}^3 \text{ cycle}^{-1} \text{ N}^{-1} \quad \text{Equation [4.7]}$$

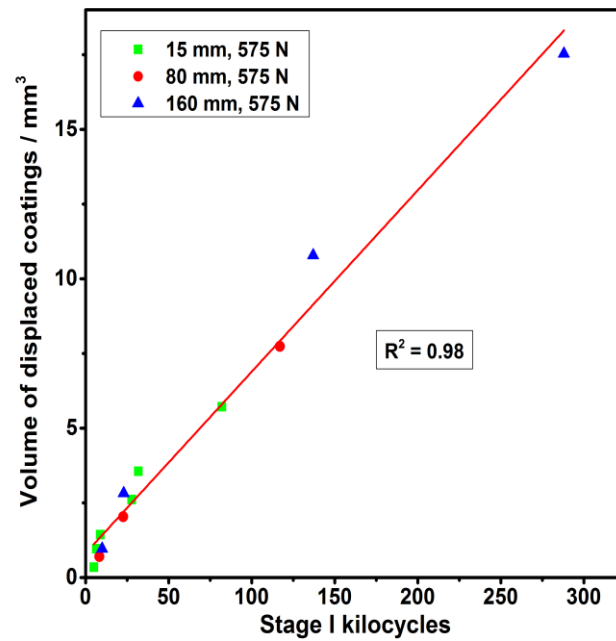


Figure 4.17 Volume removed in Stage I versus Stage I cycles

To enable this to be presented as an energy wear coefficient requires the relationship between the cumulative energy dissipated in Stage I and duration of Stage I to be known. The total dissipated energy in a stage is simply the sum of the energy dissipated in the individual cycles in that stage, E_d , shown in Figure 3.6. These data are available for all the tests conducted. Analysis of this data revealed the best fit obtained to be highly significant under the test conditions selected, which is shown in Figure 4.18. The volumetric wear coefficient for Stage I can therefore be determined as follows:

$$k_f^E = 3.9 \text{ kJ mm}^{-3} \quad \text{Equation [4.8]}$$

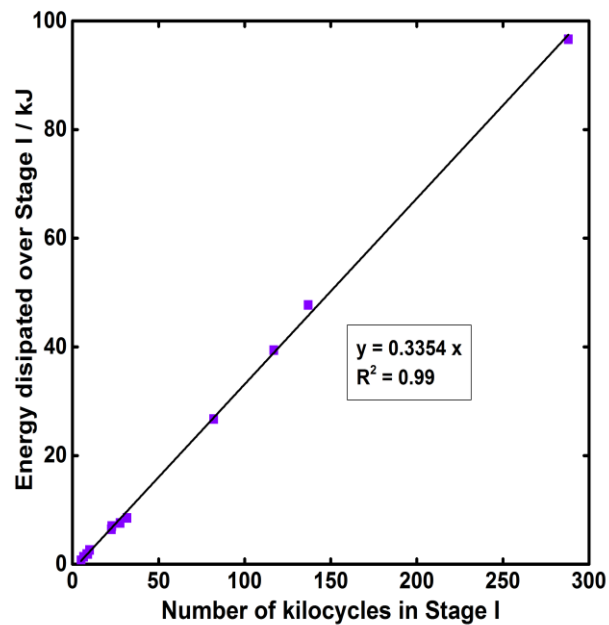


Figure 4.18 Total energy dissipated versus number of cycles in Stage I, for all test conditions examined

4.2.3 Duration of Stage II

Results indicate that the majority of the thickness of the DFL has been removed by the start of Stage II. Whilst EDX analysis of the wear scar surface at the start of Stage II shown in Table 4.1 indicates that elements from both the titanium alloy substrate and the DFL are detected, the XPS data indicate that there is a thin surface layer rich in carbon, molybdenum and sulphur, which results in the low coefficient of friction which characterizes Stage II. It is clear from the ECoF that significant direct contact between the titanium alloy substrates in the contact pair is not occurring. Such contact is typically associated with values of ECoF of > 0.7 .

It is clear that this low friction is only achieved with a layer which has some metallic content, and is not a feature of the DFL itself.

It is proposed that the nature of the surface in Stage II will be independent of the thickness of the DFL originally applied, since it has been removed by the start of this stage. However, degradation of this surface clearly occurs, and eventually, direct contact between the titanium alloy substrates takes place, with the associated high coefficient of friction which defines the end of the stage. The usual Archard wear equation indicates that wear volume is proportional to applied load. This can be rewritten in terms of material removal depth and contact pressure, with this being more appropriate for surface engineered systems when failure is often associated with removal of material to a certain critical depth. It is therefore proposed that the duration of Stage II (N_{II}) will be inversely proportional to the contact pressure, p , as follows:

$$N_{II} = \frac{c}{p} \quad \text{Equation [4.9]}$$

where c is a constant. Given that it has been shown that the majority of the DFL has been removed by the time Stage II commences, it is also proposed that the mean Hertzian contact pressure between the substrates, which depends on upon both the contact geometry and the applied load, is the appropriate pressure to use. In this contact pressure calculation, only the substrates are considered, since it is assumed that the DFL is largely absent in Stage II.

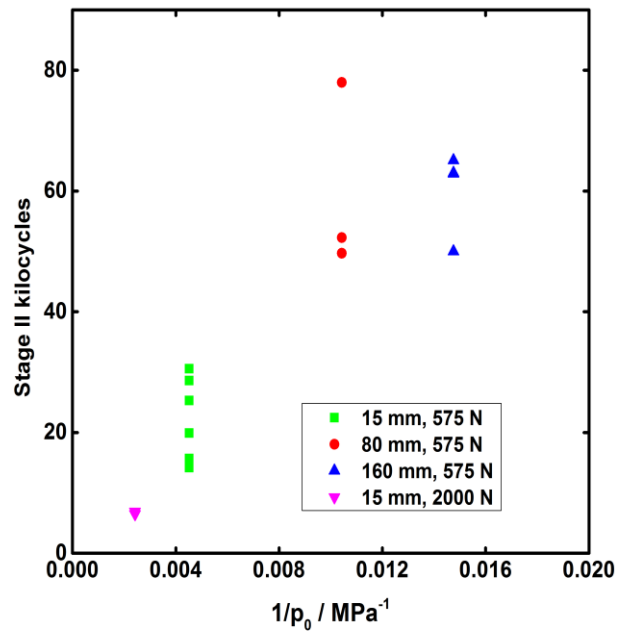


Figure 4.19 Stage II cycles as a function of the reciprocal of the contact pressure, p_0 . Individual points represent tests with different initial DFL thicknesses.

In Figure 4.19, the duration of Stage II (N_{II}) is plotted against the reciprocal of the mean Hertzian contact pressure. Although there is considerable spread in the values of N_{II} at each contact pressure examined, the general concept of the proportionality in Eq. 4.9 is supported, the two higher pressure cases ($R = 15 \text{ mm}$ and $P = 2000 \text{ N}$, $R = 15 \text{ mm}$ and $P = 575 \text{ N}$) exhibit much shorter Stage II durations than the two lower pressure cases ($R = 80 \text{ mm}$ and $P = 575 \text{ N}$, $R = 160 \text{ mm}$ and $P = 575 \text{ N}$). Using these data, the following value of c can be determined $c = 6.5 \times 10^6$ cycle MPa. However, it must be noted that although there is broad correlation, the correlation is not strong. At the two lower pressures, there is a significant range of values of N_{II} , with one value much higher than the

rest in each case. These observations indicate that there are other factors which influence N_{II} which are not addressed in this analysis, and have (as yet) not been identified.

4.2.4 Duration of Stage III

At the beginning of Stage III, the low-friction surface which characterizes Stage II is beginning to fail, with some substrate-substrate contact occurring. This removal of the low friction Stage II surface continues through Stage III until enough has been removed that the CoF reaches the value of 0.7, and the test was terminated. At the end of Stage III, the depth of the wear scar is much larger than the original DFL thickness. EDX analysis of such surfaces provides no evidence for the presence of any elements associated with the DFL shown in Table 4.1. Inspection of the values of N_{III} , which presented in Table 4.3, indicates a wide variation of durations across the tests conducted. As previously noted in the summary of observations at the end of section 4.1.1.2, at each contact radius, the duration of Stage III shows a large increase at a specific value of t , indicating that N_{III} has a dependency upon the thickness of the DFL, despite the DFL having been largely removed by the end of Stage I. Currently this dependence of N_{III} upon t is not understood. However, it should also be noted that below the critical value of t where the significant increase in N_{III} is observed, then N_{III} is broadly independent of t .

Given the discussion regarding the duration of Stage II, it might be expected that N_{III} would be expected to again be proportional to the reciprocal of the contact pressure. However, Figure 4.20 shows that, whilst

there is some evidence that N_{III} decreases as the contact pressure increases, the correlation proposed is not supported by the data.

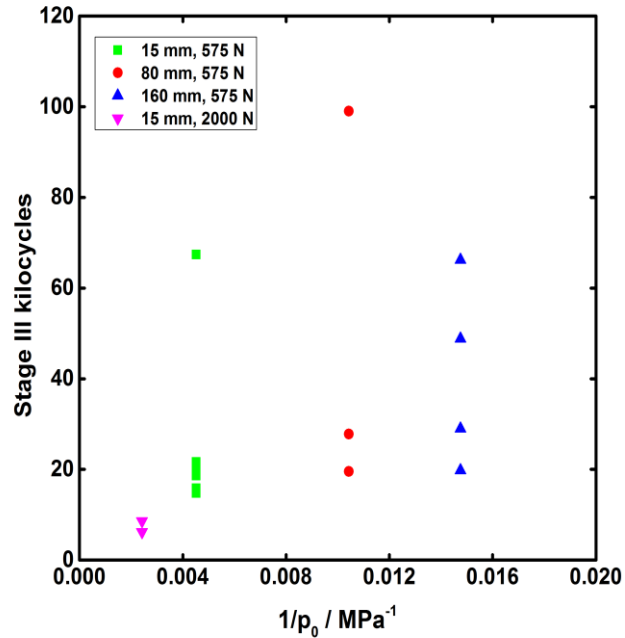


Figure 4.20 Stage III cycles as a function of the reciprocal of the contact pressure, p_0 . Individual points represent tests with different initial DFL thicknesses.

4.2.5 Lifetime of DFL system

DFLs are typically applied to components in service to reduce the coefficient of friction and as a means to avoid substrate damage. In a service environment where DFLs such as these are used, a DFL should be replaced before the end of Stage II so that significant damage to the substrate does not result. In this work, it has been shown in Equation 4.8 that the duration of Stage I is proportional to the volume of DFL that needs to be worn away before substrate-substrate contact occurs. This volume can be readily calculated if the DFL thickness and contact geometry are

known. The duration of Stage I can be calculated using the wear coefficient from Equation 4.8. This is followed by Stage II where a complex metal-DFL surface results in very low coefficients of friction. The duration of Stage II can now be predicted by Equation 4.9, noting that it is inversely proportional to the contact pressure. It is noted that in Stage III, substrate damage happens rapidly and the coefficient of friction is rising and varies in a chaotic manner. In service use of a DFL in this region should be avoided. Overall, Equation 4.8 and Equation 4.9 can be used together to determine coating lifetime.

4.2.6 Comparison with previous quantitative work

There are few studies in the literature where attempts to quantify wear coefficients to provide a basis for predictions of lifetimes of such DFL systems have been attempted. However, recently Fouvry and Paulin [178] presented data regarding a 30 μm thick polymer bonded MoS_2 DFL fretting against Ti6Al4V under a wide variety of geometries, normal loads and fretting amplitudes. In the system that they examined, the DFL was deposited onto a 150 μm thick Cu-Ni-In sublayer, which was deposited onto a titanium alloy substrate. They derived a volumetric fretting energy parameter of $\sim 66 \text{ kJ mm}^{-3}$ for the system, but this was derived from energy per unit area and an assumption that this could be converted to energy per unit volume for removal of the MoS_2 -containing DFL simply by dividing through by the DFL thickness. In addition, it is clear that the evolution of the coefficient of friction was very different from that seen in this work. For contact pressures below 500 MPa (applicable to the tests carried out in this work), the behaviour associated with Stages I to III was

not observed in the same form, with instead a gradual increase in friction being observed until the surface concentration of Cu-Ni-In reached around 55%, whereupon the coefficient of friction increased more rapidly. As such, it is clear that before to this point being reached, the surface layer was composed of a mixture of the MoS₂-containing polymer and the Cu-Ni-In, with the Cu-Ni-In clearly being observed to make up part of the surface at relatively small fractions of the number of cycles required to reach the critical point.

Fouvry and Paulin derived an energy-based wear coefficient valued 66 kJ mm⁻³ for the degradation of the system. This can be compared with the value of 3.9 kJ mm⁻³ derived in the current work which relates only to Stage I, i.e. the removal of the bulk of the DFL. The significant differences can be accounted for by the fact that the work of Fouvry and Paulin considers a system with a sprayed C-Ni-In underlayer, and that the value of wear coefficient in that work is a convolution of all aspects of wear, whereas these have been separated into stages in the current work.

4.3 Conclusions

The degradation of a MoS₂-based DFL on a titanium alloy substrate has been shown to take place in three distinct stages. In the first stage, the polymer-based DFL wears away until the substrate starts to come into contact, during this stage the coefficient of friction falls slowly. In the second stage, there is initially a significant reduction in the coefficient of friction, this is linked to the formation of a surface made up of features both of the metallic substrate and the DFL. There is an enhanced level of

MoS₂ on the surface with very little metallic material is present at the very surface, However the low friction material which covers the metallic substrate is very thin. After a number of cycles, this protective low friction material is no longer effective, and true metal-to-metal contact begins to take place with a commensurate increase in the coefficient of friction, this is the stage III. In the first stage, the volume of coating removed is observed to be proportional to the number of cycles, therefore, the duration of this stage can be estimated based upon the geometry of the contact and the DFL thickness. The duration of the second stage was seen to be inversely proportional to the contact pressure, this can therefore be estimated based upon a knowledge of the geometry of the contact. The start of stage three indicates the start of the end of the coating working lifetime.

Chapter 5. The role of thermally sprayed Cu-Ni-In underlayer in the durability of a dry-film lubricant system in fretting in light of microstructural study

This chapter presents an investigation of the effect of a Cu-Ni-In underlayer on the fretting. Three stages in the evolution of the coefficient of friction were identified and these were linked to the damage observed. The behaviour was examined in terms of coefficient of friction and system lifetime (durability) under fretting. The lifetimes of the systems are understood in terms of the detailed microstructural analysis of the damage and key stages in the lifetime are established and explained.

Cylinders-on flat fretting tests are carried out using 15 mm radius cylinders. The Cu-Ni-In underlayer, with a nominal thickness of 150 μm

and Ra of 16.6 μm has applied to the flat samples only. A DFL thickness of 50 μm was used on both parts of the wear couple.

5.1 Results

It should be noted that a number of results from Chapter 4 are represented here in order to allow comparison of behaviour with and without the Cu-Ni-In layer.

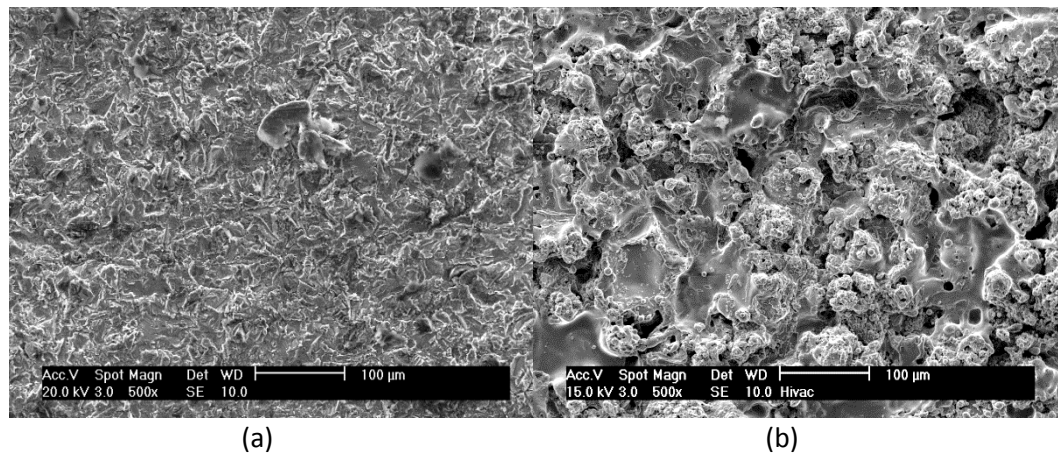


Figure 5.1 SE-SEM images of the surfaces prior to DFL application, (a) grit-blasted Ti6Al4V, (b) plasma-sprayed Cu-Ni-In

Figure 5.1 shows the surfaces to which the DFL paints were applied. The roughnesses were 2.6 μm and 16.57 μm for the grit-blasted Ti6Al4V surface and the Cu-Ni-In surface respectively.

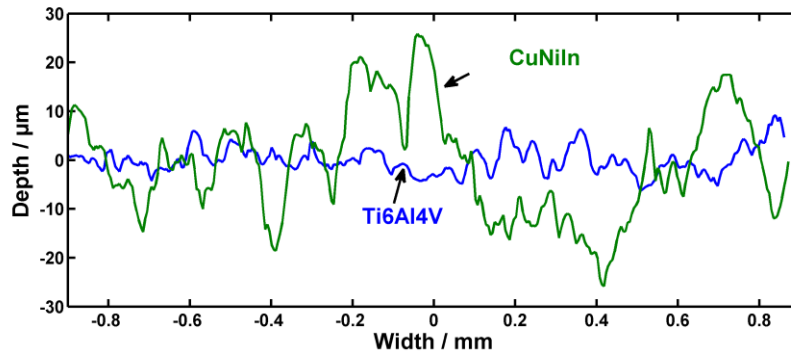


Figure 5.2 Surface profile of the two surface types prior to application of the DFL

Figure 5.2 shows line surface profiles on the two surfaces before application of the DFL paint. Both long-range and short-range differences in surface profile can be seen, with the Cu-Ni-In surface displaying a peak-to-trough variation of more than 40 μm. The micro hardness measured of the Ti6Al4V substrate was 287 ± 10 HV and that of the Cu-Ni-In interlayer was 177 ± 20 HV. Figure 5.3 shows plan-view SEM images of the as-cured DFL coating deposited on the titanium alloy substrate, where it can be seen that the film is a bonded agglomerate of individual MoS₂ particles, the appearance of this surface was very similar when the DFL coating was applied on top of the plasma-sprayed Cu-Ni-In, although some increase in roughness was evident.

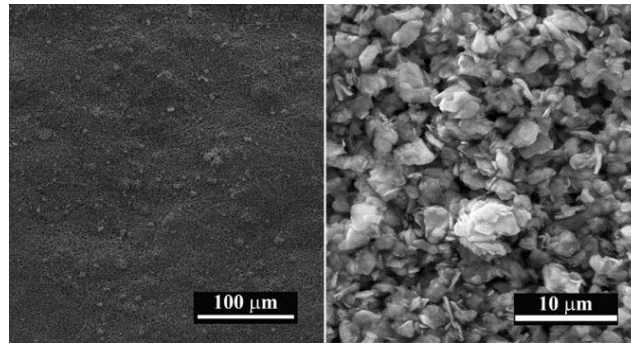


Figure 5.3 Low magnification (left) and high magnification (right) SEM micrograph of the surface of the as-cured DFL paint coating MoS_2

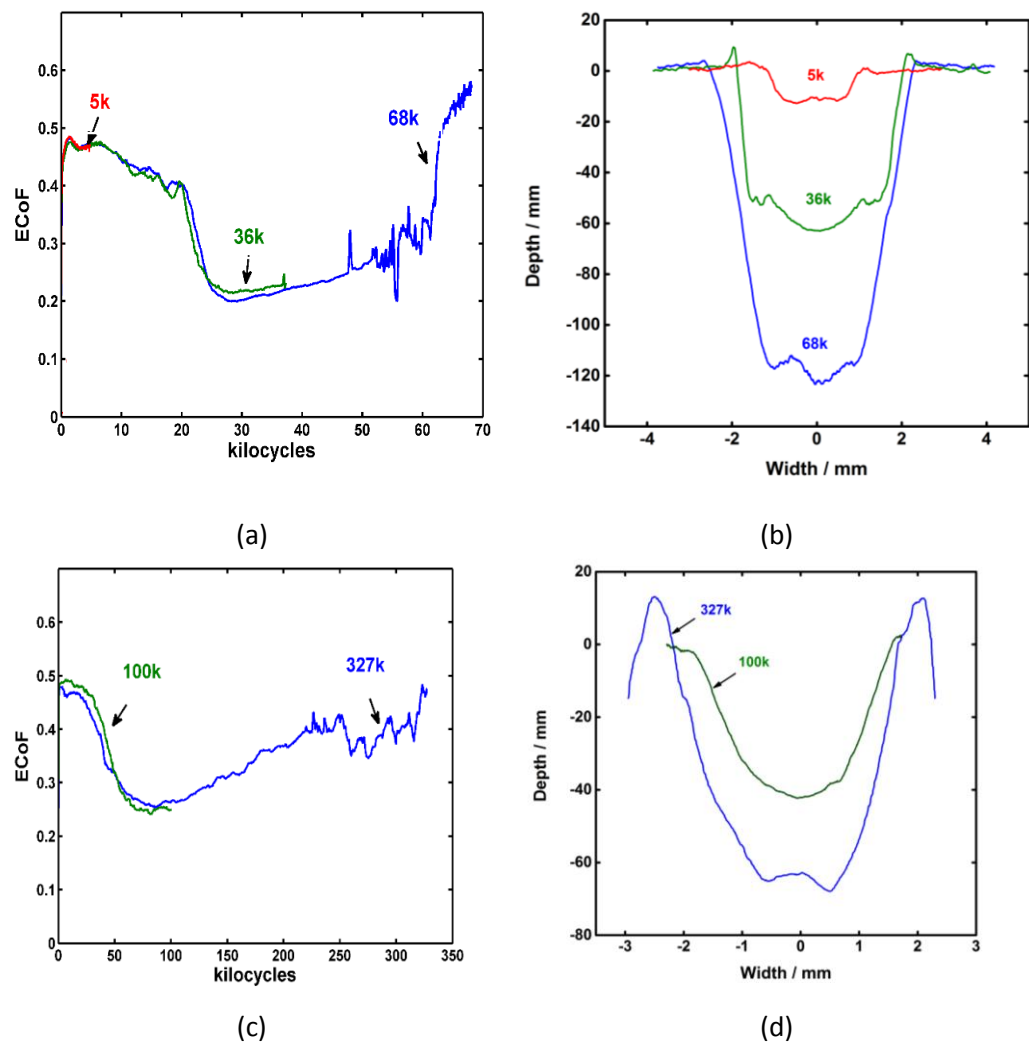
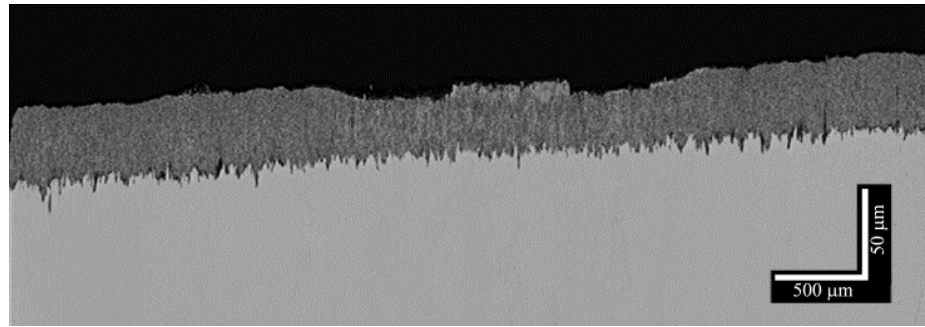


Figure 5.4 Evolution of ECoF with number of cycles for both completed and interrupted tests (indicating the number of cycles at interruption or completion), along with average depth profiles across the corresponding wear scars, (a), (b) DFL-Ti6Al4V system, (c), (d) DFL-CuNiIn-Ti6Al4V system

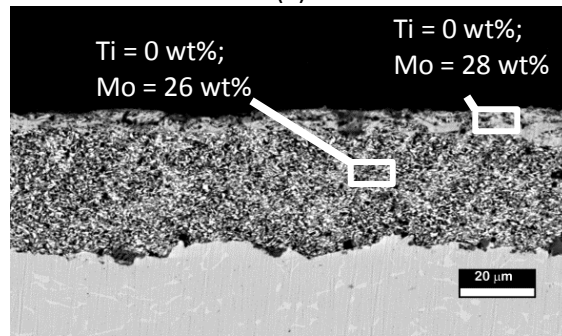
Figure 5.4 shows the development of ECoF for both interrupted and completed tests for the two sample types, the corresponding depth profiles across the wear scar at each point are presented alongside. It should be noted that for the two graphs showing evolution of the ECoF, the horizontal scales are different, and that the duration of the test for the DFL-Cu-Ni-In-Ti6Al4V samples is more than four times longer than that for the DFL-Ti6Al4V samples. The working lifetimes which were defined in the end of Chapter 4, as being the end of Stage II are in a similar ratio of 48 kilocycles and 237 kilocycles for the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V samples respectively. The initial contact between the DFLs on the two specimens in the pair results in values of ECoF of just under 0.5 for both sample types, in the DFL-Ti6Al4V samples; this is followed by a rapid decrease in the ECoF in the period just after 20 kilocycles. As shown in Chapter 4, the start of this steep drop is identified with the point where the DFL has been removed to a depth where the underlying substrate begins to feature in the contact, and the rapid fall in ECoF is related to the rapid increase in the width of the contact over which the DFL has been removed and thus the substrate is featuring. The behaviour with the DFL-Cu-Ni-In-Ti6Al4V sample is somewhat different. The development of the ECoF is initially very similar. This is the region where the behaviour is controlled by the DFL itself and is not affected by underlying material, so this similarity is to be expected. A similar drop in the ECoF is observed, however, the rate at which it falls is much slower, with the minimum coefficient of friction only being reached after around 80 kilocycles. The depth profile across the wear scar shown in Figure 5.4d indicates that after 100 kilocycles, the penetration is only 40 μm , which is less than the full thickness of the DFL. The ECoF then rose slowly after 100 kilocycles, and showed signs of

instability after about 220 kilocycles. After 327 kilocycles, the depth profile shown in Figure 5.4d indicates that the DFL has been fully penetrated. Examination of the fretting loops indicates that the Stage I contact stiffness, explained in Section 3.3.2, was around 65 MN m^{-1} and 50 MN m^{-1} for the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V samples respectively.

To accompany the profilometry, Figure 5.5 (Stage I), Figure 5.6 (Stage II) and Figure 5.7 (Stage III) show low magnification cross-sections of the wear scars following the tests indicated in Figure 5.4, again, these micrographs are distorted and are presented in a form where the vertical magnification is ten times that of the horizontal magnification since this provides a clearer presentation of the damage incurred. In Figure 5.5, it can be seen that in Stage I (after 5 kilocycles with the DFL-Ti6Al4V samples), the DFL layer is intact. It can be seen that after 5 kilocycles shown in Figure 5.5b, the outer surface of the DFL has been modified, but that these changes are quite subtle and only affect a layer about $2 \mu\text{m}$ in thickness. The EDX results from the bulk and surface regions of the DFL shown in Figure 5.5b indicate very little change in chemistry at the surface, and that there is no evidence of any elements associated with the substrate at the wearing surface by this stage.



(a)



(b)

Figure 5.5 BSE micrographs of a wear scar cross-section for DFL-Ti6Al4V in stage I (after 5 k cycles). (a) low magnification image with a distorted aspect ratio (vertical magnification being ten times the horizontal magnification), (b) high magnification image of representative sections along with EDX data (elements included in the analysis: Ti, Al, V, Mo, S, C, O) representing the titanium and molybdenum contents of the areas indicated.

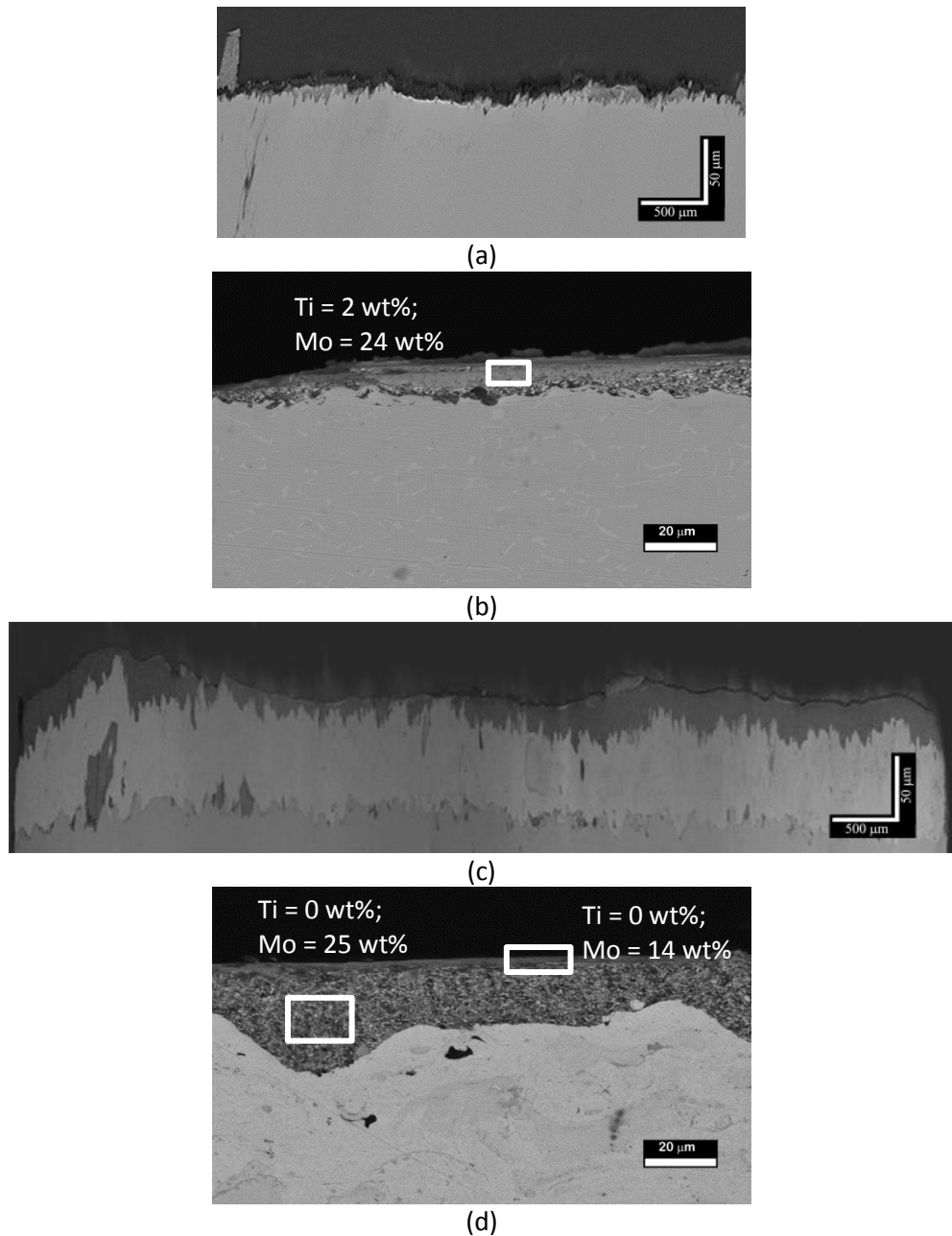


Figure 5.6 BSE of wear scar cross-sections for both DFL-Ti6Al4V and DFL-Cu-Ni-In-Ti6Al4V in Stage II corresponding to the tests described in Figure 9. (a) and (c) are a low magnification images with a distorted aspect ratio (vertical magnification being ten times the horizontal magnification), (b) and (d) are high magnification images of representative sections of the corresponding scar surface along with EDX data (elements included in the analysis: Ti, Al, V, Mo, S, C, O, Cu, Ni, In) representing the titanium and molybdenum contents of the areas indicated. (a) and (b) MoS₂-Ti6Al4V, following 36 kilocycles (c) and (d) DFL-Cu-Ni-In-Ti6Al4V following 100 kilocycles.

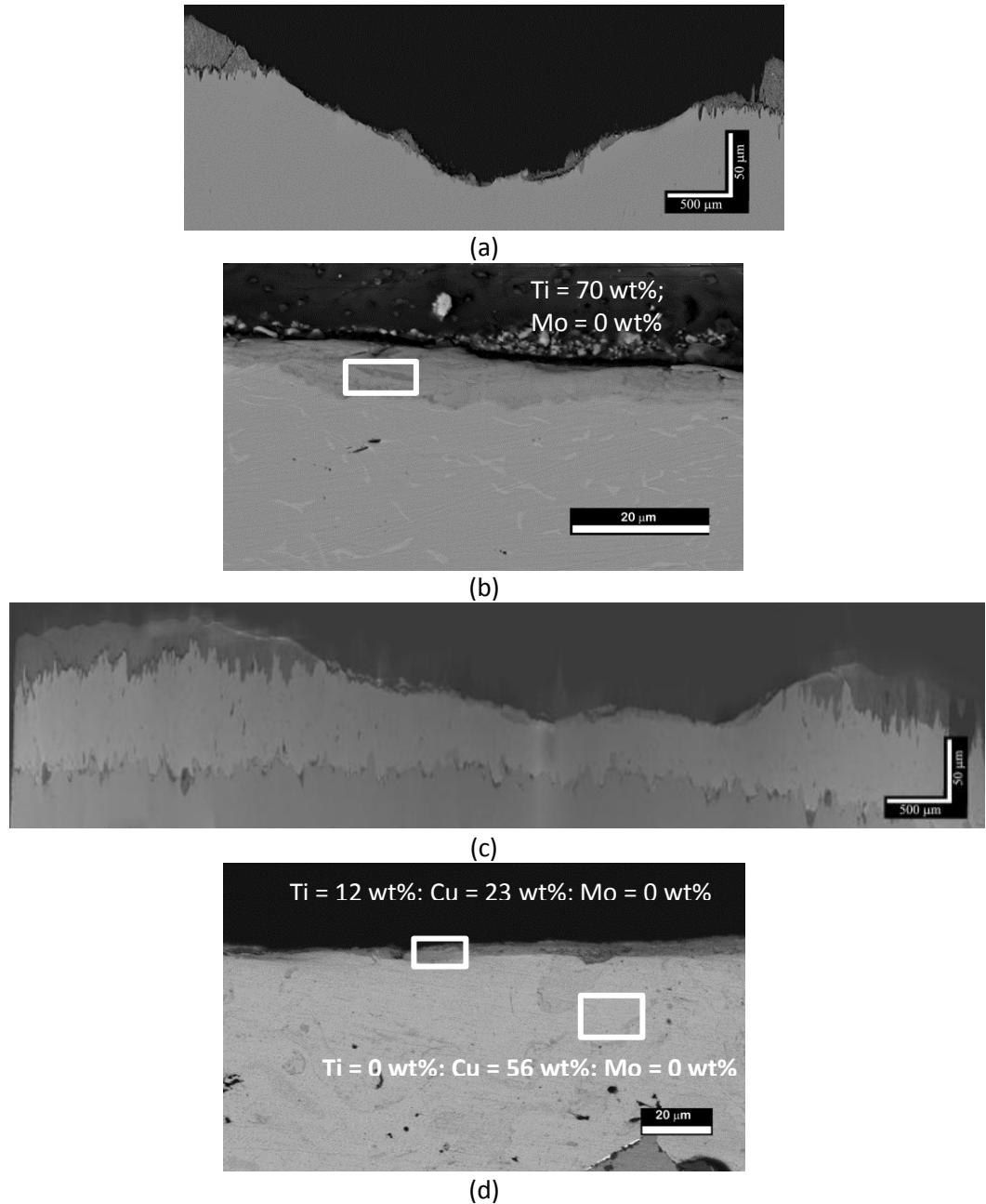


Figure 5.7 BSE of wear scar cross-sections for both DFL-Ti6Al4V and DFL-Cu-Ni-In-Ti6Al4V in Stage III corresponding to the tests described in Figure 9. (a) and (c) are a low magnification images with a distorted aspect ratio (vertical magnification being ten times the horizontal magnification), (b) and (d) are high magnification images of representative sections of the corresponding scar surface along with EDX data (elements included in the analysis: Ti, Al, V, Mo, S, C, O, Cu, Ni, In) representing the titanium, copper and molybdenum contents of the areas indicated. (a) and (b) DFL-Ti6Al4V following 68 kilocycles (c) and (d) DFL-Cu-Ni-In-Ti6Al4V following 327 kilocycles.

The following discussion includes some points already made in Chapter 4 to enable a clear comparison of behaviour with and without Cu-Ni-In. Figure 5.6a and Figure 5.6b confirm the removal of the bulk of the DFL to the substrate interface in Stage II for the DFL-Ti6Al4V sample after 36 kilocycles. Towards the edges of the wear scar, where the DFL has been largely removed, it is clear that there has been no disruption of the initial surface roughness of the Ti6Al4V substrate into which the DFL is keyed. There is evidence of some remnants of the Figure 5.6b, but it can be seen that this layer exhibits a generally homogeneous brightness in contrast to the cross-section shown in Figure 5.5b where the binder and MoS₂ in the DFL can be clearly distinguished from each other due to differences in brightness in BSE imaging. EDX analysis shows that this surface is chemically not very different from the original DFL, however, there is some evidence of titanium in the surface material shown in Figure 5.6b. In contrast, for the DFL-Cu-Ni-In-Ti6Al4V sample in Stage II, Figure 5.6c and Figure 5.6d indicate that after 100 kilocycles, the DFL has been removed to a thickness whereby the Cu-Ni-In underlayer is only in contact with the counterbody at a few selected points, i.e. the majority of the contact surface area is still made up of DFL, also, it can be seen that despite the removal of the DFL, the surface profile of the Cu-Ni-In is the same both inside and outside the wear scar, indicating that there has been no plastic deformation of the Cu-Ni-In associated with the fretting removal of the DFL. EDX analysis from the higher magnification image shown in Figure 5.6d indicates that the worn DFL surface shows no evidence of any material from either the Cu-Ni-In or the substrate at this stage.

The extent of damage in the two coating systems at the end of Stage III is indicated in Figure 5.7. In accord with the depth profile shown in Figure 5.4, it is clear that for the DFL-Ti6Al4V sample, material removal from the substrate has occurred to significant depths across the majority of the wear scar shown in Figure 5.7a. The higher magnification image indicates that no traces of the DFL exist, a fact which is confirmed by the results of the EDX analysis presented alongside shown in Figure 5.7b and supported by the large-area plan view EDX data of the same surface presented in Table 5.1. In contrast, for the DFL-Cu-Ni-In-Ti6Al4V sample shown in Figure 5.7c, it can be seen that the Cu-Ni-In layer is still intact, and although it has been penetrated to a significant depth across its whole surface, there is no exposure of the underlying substrate at this stage. The original rough surface of the Cu-Ni-In onto which the DFL was painted has been completely removed. However, the higher magnification image shown in Figure 5.7d indicates that a thin surface layer exists in this region which has evidence of titanium from the substrate of the counter body which did not have the Cu-Ni-In layer applied. There is no molybdenum present, indicating complete removal of the DFL material. This is consistent with the large area plan view EDX data of the same surface presented in Table 5.1, where titanium and copper are the main elements detected.

Figure 5.8 shows plan view images of the wear scars following the tests interrupted in Stage II for both tests, 36 kilocycles and 100 kilocycles for the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V samples respectively, large-area EDX analyses of the same wear scars are presented in Table 5.1.

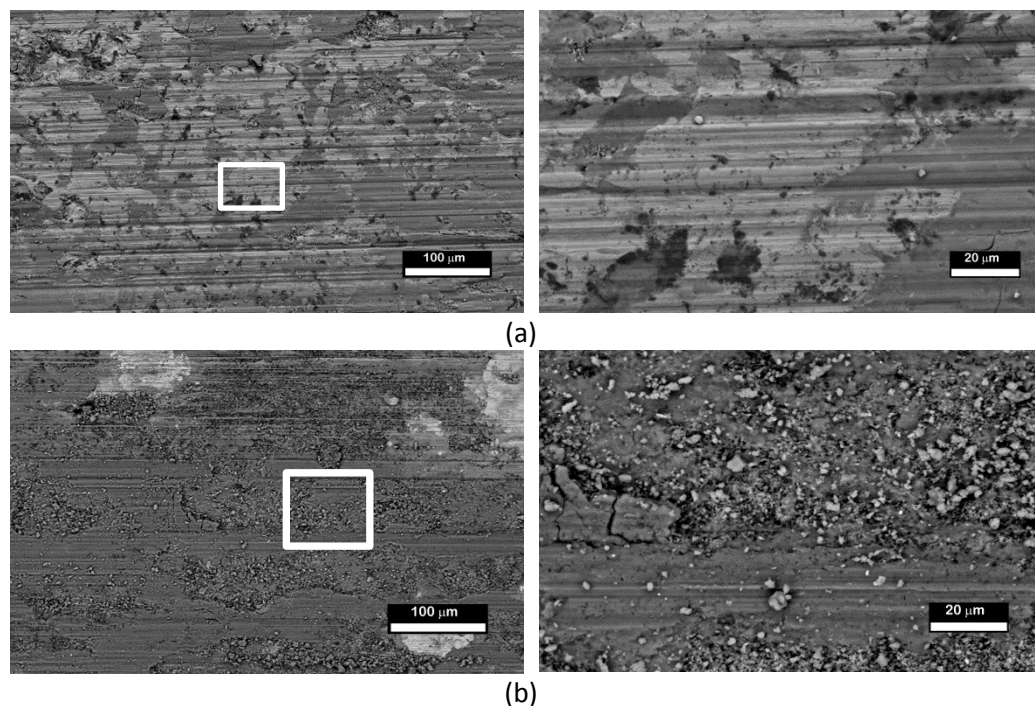


Figure 5.8 BSE plan view micrographs of wear scars for both the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V systems following interruption in Stage II at both low (left) and high (right) magnification (the high magnification image is of the region shown in the white box in the low magnification image), (a) DFL-Ti6Al4V following 36 kilocycles, (b) DFL-Cu-Ni-In-Ti6Al4V following 100 kilocycles.

Table 5.1 Analysis from surface of wear scars for tests interrupted at various points. EDX analysis of titanium, molybdenum and copper representing the substrate, DFL and Cu-Ni-In materials respectively (elements included in the EDX analysis: Ti, Al, V, Mo, S, C, O, Cu, Ni, In in the case of the DFL-Ti6Al4V DFL-Cu-Ni-In-Ti6Al4V sample). The maximum depth of wear scar in each case is also presented.

System	N / kilocycles	Stage	Ti / wt%	Mo / wt%	Cu / wt%	Depth of scar / μm
DFL-Ti6Al4V	36	Stage II	9	28	-	64
DFL-Ti6Al4V	68	Stage III	49	0	-	122
DFL-Cu-Ni-In-Ti6Al4V	100	Stage II	0	30	3	42
DFL-Cu-Ni-In-Ti6Al4V	327	Stage III	13	1	29	63

In addition, Figure 5.9 provides elemental line profiles across the same wear scars generated via the more surface-sensitive XPS analysis technique. For the DFL-Ti6Al4V interrupted in Stage II shown in Figure 5.8a, it can be seen that the surface is made up of different regions, those

with a lower brightness still have evidence of DFL being present, whereas those with a higher brightness are regions where the DFL has been removed, leaving the substrate exposed. Ploughing marks can be seen running across the surface, but the surface is generally quite smooth indicating that wear has been mild at this point. EDX analysis indicates that the surface is still dominated by the DFL, but there is also evidence of the titanium alloy substrate as part of the surface material. The measured titanium content via EDX analysis is ~ 9 wt%, equivalent to ~ 4.5 at%. However, the XPS data shown in Figure 5.9a shows a much lower titanium content, approximately 1 at%, across the surface, which indicates that the surface material, which appears titanium-rich via BSE imaging and EDX analysis, is in fact covered by a layer which is rich in carbon, oxygen, molybdenum and sulphur. This layer is thin enough that it is only detected by XPS analysis but not by EDX analysis and BSE imaging. XPS trace across the wear scar also indicates a significant reduction in carbon in the wear scar with an increase in molybdenum and sulphur. This shows that for both sample types the surface of the wear scar is preferentially enriched in MoS_2 by the wear process itself at the expense of the epoxy binder.

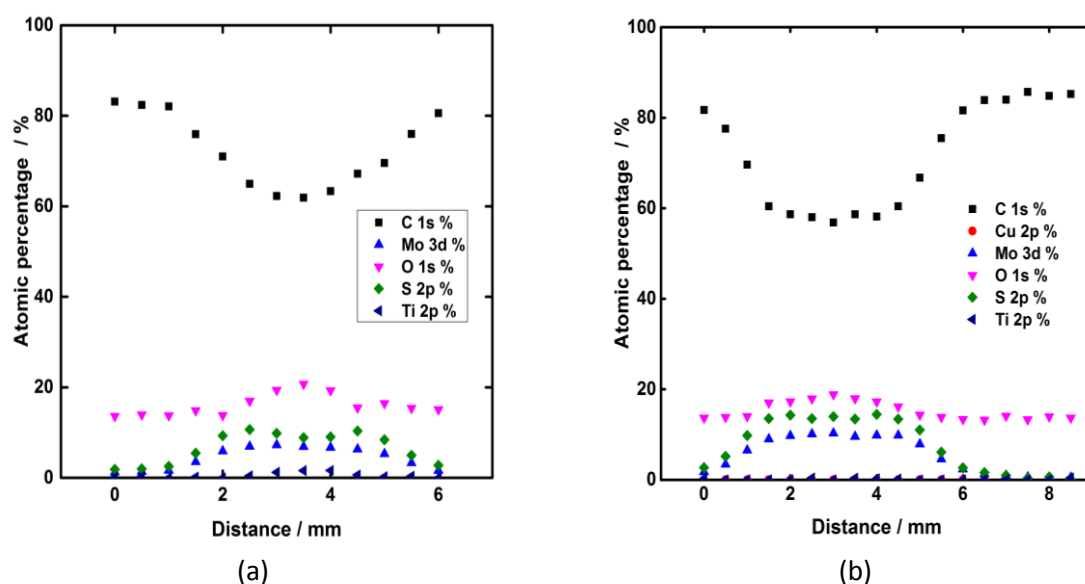


Figure 5.9 XPS analysis across the wear scars for both the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V systems following interruption in Stage II showing the atomic percentage of elements across the wear scar., (a) DFL-Ti6Al4V following 36 kilocycles (positionally, 0 mm and 6 mm are outside the scar, with the scar existing between these lateral positions), (b) DFL-Cu-Ni-In-Ti6Al4V following 100 kilocycles (positionally, 0 mm and 8 mm are outside the scar, with the scar existing between these lateral positions).

For the DFL-Cu-Ni-In-Ti6Al4V sample interrupted in Stage II shown in Figure 5.8b, it can be seen that the surface is broadly covered with the darker contrast DFL, with only very small patches of the higher contrast Cu-Ni-In visible. This is supported by the large-area EDX analysis shown in Table 5.1 which indicates a copper content of only 3 wt%. The DFL surface is rough, and indicates that material is being removed by delamination. The XPS trace across the wear scar shown in Figure 5.9b indicates that no titanium substrate or copper, which is representative of Cu-Ni-In layer, can be detected at this stage. This is in contrast to the data in Figure 5.9a where a small amount of titanium is detected. A substantial reduction in carbon in the wear scar is seen again, along with an increase in molybdenum and sulfur, indicating that the surface of the wear scar is preferentially enriched in MoS_2 by the wear process itself.

5.2 Discussion

In Chapter 4, it has been shown that for the DFL-Ti6Al4V sample, Stage I ends when the wear scar has penetrated to the substrate interface, but that during Stage II, a low friction surface material is formed and exists until it too is degraded / removed, whereupon the coefficient of friction begins to become unstable due to true substrate-substrate contact. The lifetime of Stage II is a significant portion of the overall lifetime of the system, and the duration of this stage is inversely proportional to the contact pressure. The metal – DFL surface formed in stage II has a high durability, it is of limited thickness, and yet the duration of Stage II (31 kilocycles) is longer than that of Stage I (20 kilocycles).

The role of the Cu-Ni-In in the lifetime of such systems has been discussed in previous work. It has been suggested that the low hardness and stiffness of the Cu-Ni-In may result in deformation, both elastic and plastic, which reduces the severity of the contact and therefore increase the lifetime [27, 127]. Others have attributed the benefits of the Cu-Ni-In in these systems to its high roughness which promotes retention of the DFL layer [126]. In the current work, where systems with and without the Cu-Ni-In layer are directly compared, it is observed that the addition of a plasma-sprayed Cu-Ni-In layer before addition of the DFL significantly extends the lifetime of the system. It is shown that Stage I, where the DFL is removed until the underlying metal begins to be exposed is of approximately the same duration for both the DFL-Ti6Al4V and the DFL-Cu-Ni-In-Ti6Al4V samples, and that differences in system lifetimes are mainly associated with the evolution of the ECoF in Stage II. No evidence of plastic

deformation of the Cu-Ni-In below the contact is observed when the DFL layer is still largely intact, even when the Cu-Ni-In is very close to the wearing surface shown in Figure 5.6c. Also, despite differences in the contact stiffness for the two coating systems, the elastic displacement in both cases is a very small fraction of the overall displacement amplitude, i.e. in both cases, the displacement amplitude of 300 μm is still dominated by contact slip.

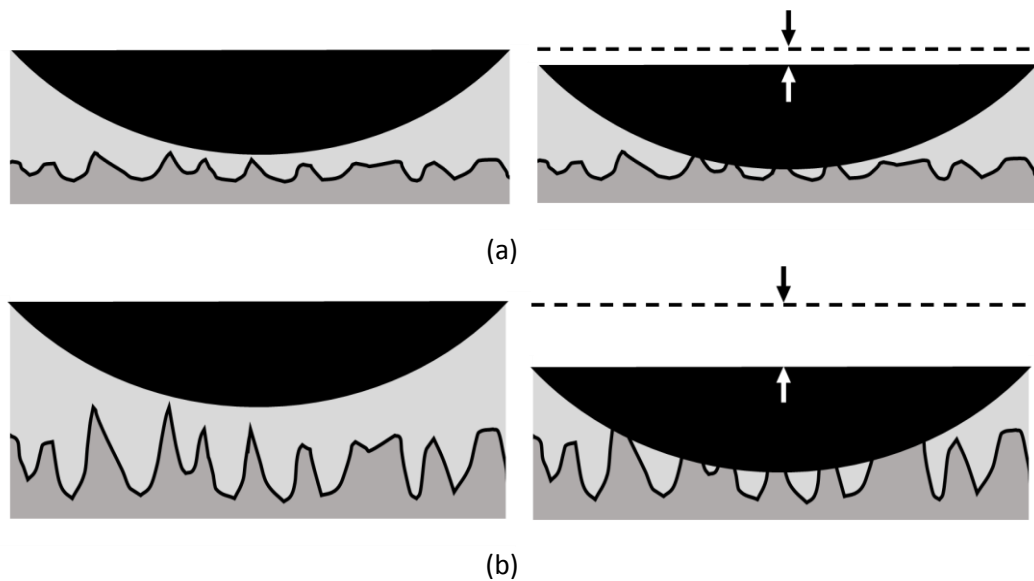


Figure 5.10 Schematic diagram of penetration of cylindrical body through an interface of different roughnesses, with penetration increasing from left to right, (a) low roughness interface, (b) high roughness interface. The differences in penetration depth are indicated in the right hand side of each part.

Instead, it is suggested that it is primarily the surface roughness of the Cu-Ni-In underlayer which results in the significant lifetime increase in this system. This is in line with the observations of Fridrici et al. [126]. The work on the DFL-Ti6Al4V coating system shows that Stage II, where the wearing surface consists of both metal and DFL provides a low coefficient of friction and exhibits high durability, i.e. high resistance to wear. The high surface roughness of the metal – DFL interface in the DFL-Cu-Ni-In-

Ti6Al4V system means that the fraction of metal in the wearing contact increases more gradually with depth of wear as it passes through this rough interface, compared to the smoother interface in the DFL-Ti6Al4V system. The number of cycles over which this transition occurs in the DFL-Cu-Ni-In-Ti6Al4V system will be further extended by the fact that the surfaces that consist of both metal and DFL exhibit very low rates of wear, and so are penetrated more slowly. This is illustrated schematically in Figure 5.10. For the low roughness interface between the DFL and the underlying metal in the DFL-Ti6Al4V system it can be seen that rate of change of the nature of the interface in terms of fractions of metal and DFL with depth of wear is high shown in Figure 5.10. This results in the rapid reduction in ECoF following initial DFL penetration, which is just after 20 kilocycles with this sample shown in Figure 5.4a. In contrast, for the high roughness interface between the DFL and the underlying metal in the DFL-Cu-Ni-In-Ti6Al4V samples shown in Figure 5.10b, it can be seen that the rate of change of the nature of the interface in terms of fractions of metal and DFL with depth of wear is much lower. This results in the much more gradual reduction in ECoF following initial DFL penetration with this coating system shown in Figure 5.4b.

Also, given that it has been shown that the mixed metal-DFL interfaces exhibit high durability, i.e. low rates of wear, then the extended number of cycles until the onset of Stage III, where metal-metal contact with no influence of the DFL first dominates with the higher roughness interface can also be rationalised. It should be noted that an assumption in this discussion is that the DFL-metal material always has low friction and high durability. There will clearly be both physical and chemical interactions

between the metal and DFL, and therefore the characteristics of this metal-DFL surface will depend upon both the metal type and the DFL type as well as the complex interactions between them.

From the results presented here and in Chapter 4, it is clear that the wear of the DFL alone is generally quite rapid and makes up a small fraction of the total system lifetime. The wear of the mixed DFL-metallic surface material is much less rapid and therefore makes up a large fraction of the total system lifetime. This suggests that the system lifetime will be very sensitive to the profile (roughness) of the metal – DFL interface, but much less sensitive to variations in the precise thickness of the DFL. As such, in terms of extending lifetime of such systems, a DFL-metal interface with high roughness is desirable. To reduce variability in system lifetime, the variations in the roughness of the metal onto which the DFL is to be sprayed needs to be controlled.

5.3 Conclusions

The behaviour of an epoxy-bonded DFL sprayed directly onto a grit-blasted titanium alloy has been compared with that of the same DFL sprayed onto a Cu-Ni-In interlayer which had been plasma sprayed onto the titanium alloy. The behaviour was examined in terms of coefficient of friction and system lifetime (durability) under fretting. The lifetimes of the systems have been understood and explained by sub-dividing the evolution of the behaviour into two stages. A third stage was identified, but failure of the system was linked with entry into this stage. In both systems, the first stage involves wear of the DFL, the influence of the metal onto which the

DFL had been deposited was small, and thus the behaviour in this stage was very similar for both systems. The behaviour in the second stage is controlled by the characteristics of the material at the interface which is made up of both metal and DFL. This material has low friction and high wear resistance. The changes in the makeup of the interface are very sensitive to the profile (roughness) of the interface between the metal and the DFL. Higher roughness results in reduced rates of change in behaviour and a significant extension of the duration over which the surface material is made up of a mixture of DFL and metal. The high durability of the system with the Cu-Ni-In underlayer is therefore mainly attributed to the high roughness of the as-sprayed underlayer onto which the DFL was deposited.

Chapter 6. Effect of different additives

This chapter presents an investigation of the fretting wear behaviour of different additives added into MoS₂ dry film lubricant. PTFE, Graphite powder has been considered as additives, added in commercially available MoS₂-based polymeric DFL and used as paint. Main aim of the current work is to understand the behaviour of individual additives, compare different additives. Experiments focused on evolution of the coefficient of friction of additive paints on Ti6Al4V and Cu-Ni-In and characterise the wear surface in great detail. Cylinder-on-flat fretting tests were run using 15 mm radius cylinders. The additive modified DFL was applied to the flat samples, with un-modified DFL being used for the cylindrical samples in each case. All coatings were 50 µm±5.

The data obtained from the experimental tests along with the results from the profilometer, SEM, EDX, XPS and the cross section analysis of the wear

scar are brought together in an attempt to understand the mechanism of the wear and failure of the different systems.

6.1 Results for additives on Ti6Al4V

6.1.1 Effect of PTFE addition on evolution of CoF

Experiments were done with 4.77 wt. % and 9.08 wt. % PTFE additions to as received MoS₂. The addition of PTFE was restricted after 9.08 wt. % since the paint become highly viscous. In literature, there is an indication of additive used within the range of 4-12 % [204] [203, 246, 247] of PTFE or other fillers. Figure 6.1a shows the comparison of evolution of coefficient of friction between 0%, 4.77% and 9.08% addition of PTFE in DFL. It should be noted that the 0% PTFE results are the same experiment as these shown in Figure 5.4a, with a life of 68k cycles. Addition of higher percentage of PTFE shows increasing life of the coating system. 4.77% PTFE increased the life to 108k cycles, 9.08 wt. % PTFE additions shows even more life of 275k cycles. The evolution of ECoF for 0% DFL-PTFE and 4.77% DFL-PTFE are shown in Figure 6.1b and Figure 6.1c respectively for clear view.

The stages in the evolution of frictional behaviour are shown in Figure 6.2, using the same definition of stages as has in Chapter 4 and Chapter 5. The evolution of ECoF of PTFE-DFL can be broken down into three different stages. Figure 6.2a shows different stage of evolution of ECoF vs. cycles of 0 wt. % PTFE where in stage I coefficient of friction rises first, then slowly

falls and remains constant in stage II while maintaining low ECoF at this stage, in stage III ECoF rises slowly and steadily showing short term instability.

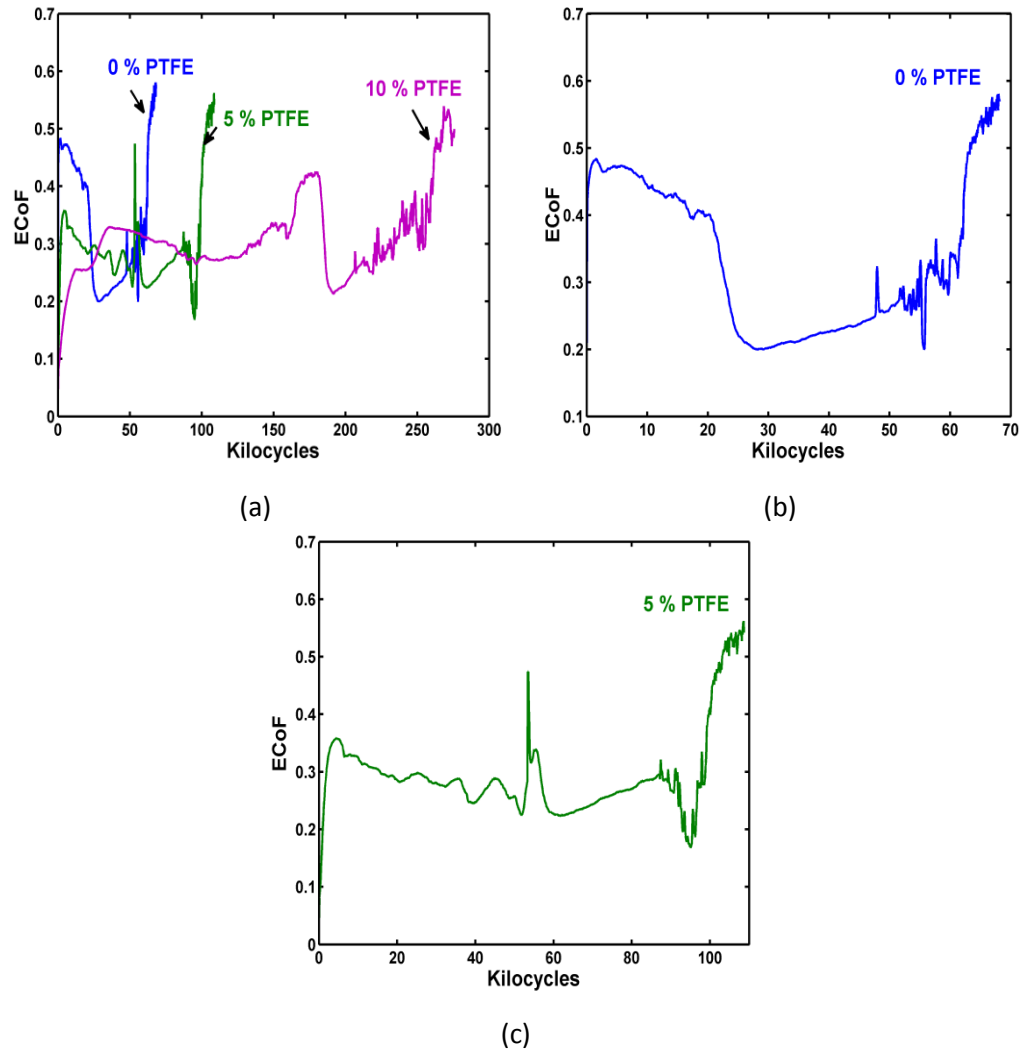


Figure 6.1 Evolution of ECoF with number of cycles comparison between 0%, 4.77% and 9.08% addition of 50 μm PTFE-DLF on Ti6Al4V.

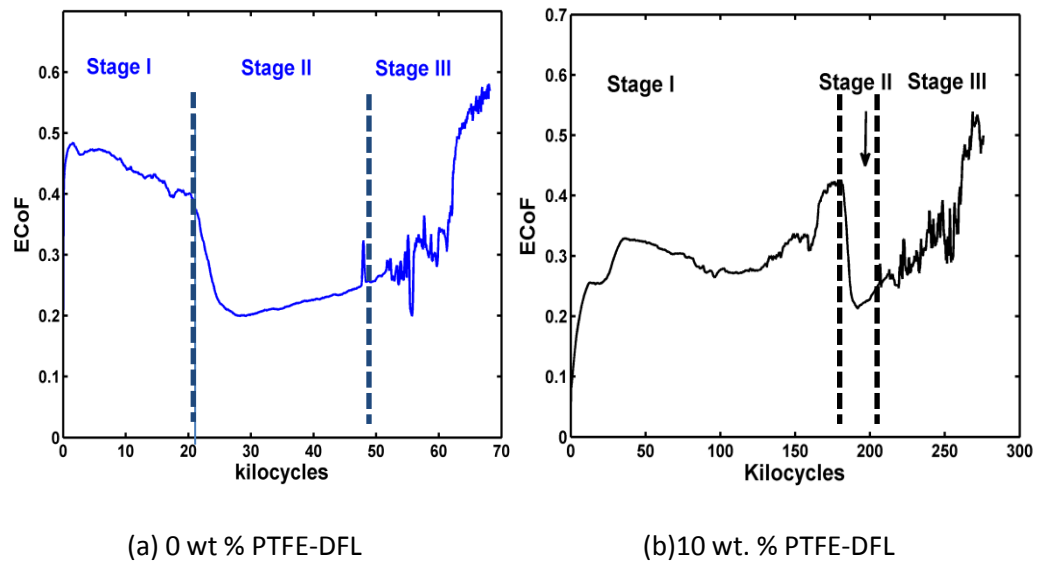


Figure 6.2 Stage wise evaluation of ECoF with number of cycles for (a) 0 wt. % PTFE-DFL system (b) 9.08 wt. % PTFE-DFL system on 15 mm 50 μ m Ti6Al4V

In contrast, Figure 6.2b shows different stages of evolution of ECoF vs. cycles for 9.08 wt. % PTFE addition. In this case, stage I has the initial rise of ECoF first, then doesn't show any steep fall but maintains the ECoF for number of cycles and then in stage III ECoF rises slowly and steadily, showing continuous instability towards the end of the DFL life.

6.1.1.1 Damage mechanisms throughout the system lifetime

In order to understand the nature of the evolution of the damage which corresponds to the changes in ECoF with number of cycles, a number of interrupted tests were conducted with the same geometry and PTFE-DFL thickness as described in Figure 6.2b. The evolution of ECoF with cycles is presented in Figure 6.3 for the same test shown in Figure 6.2b as well as four of the interrupted tests, following 13k, 27k, 55k, 115k cycles. These tests are interrupted tests and each test used a different specimen. The

combined plot also shows the high level of reproducibility in the development of the ECoF over the 5 tests observed in Figure 6.3. In this case, initially the coefficient of friction at first rises, maintains a constant ECoF range of 0.25 to 0.35 over a period of 150k cycles (denote as Stage I), and then, the coefficient of friction falls quite rapidly maintaining a ECoF of 0.2 for very small number of cycles 30k cycles (Stage II). The ECoF then rise slowly and steadily from this minimum point until it starts to exhibit short term instability, where the coefficient of friction is very high but also continues to rise and completes stage III.

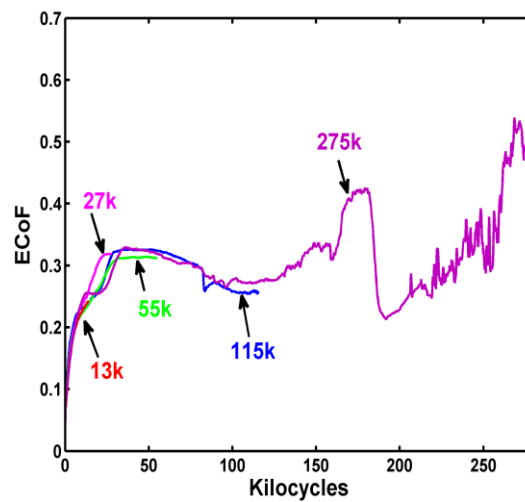


Figure 6.3 Evolution of ECoF with number of cycles for the combined graph for 9.08 wt. % PTFE-DfL-Ti6Al4V at different intermediate stages

Table 6.1 Analysis from surface of wear scars ($R = 15 \text{ mm}$, $t = 50 \text{ }\mu\text{m}$) for tests interrupted at various points. The point of interruption is described by position in stage (defined by numbers of cycles). EDX analysis of titanium and molybdenum representing the substrate and DFL respectively (elements included in the EDX analysis: Ti, Al, V, Mo, S, C, O). The maximum depth of wear scar is also presented.

N / kcycles	Stage position	Ti / wt%	Mo / wt%	Depth of scar / μm
13	15% through DFL	0	23	7.5
27	32% through DFL	0	23	16
55	52% through DFL	0	25	26
115	80% through DFL	0	25	40
275	330% through Stage III	57	0	165

Figure 6.4 shows the combined profiles across the wear scars, with the maximum depth of wear scar as a function of number of cycles for all the tests conducted being presented in Table 6.1. The original thickness of the coating is $50 \pm 5 \text{ }\mu\text{m}$. From the wear scar it can be seen that 13k, 27k, 55k, 115k cycles wear depth penetrates $40 \text{ }\mu\text{m}$ after 115k cycles, which is well within the original PTFE-DFL thickness, which indicates wear scars exist within stage I. 275k cycles shows wear depth of $165 \text{ }\mu\text{m}$, which indicates the DFL has worn away completely and the wear scar definitely penetrates the metallic substrate as the wear depth is $105 \text{ }\mu\text{m}$ and ECoF is 0.7, indicating metal-metal contact.

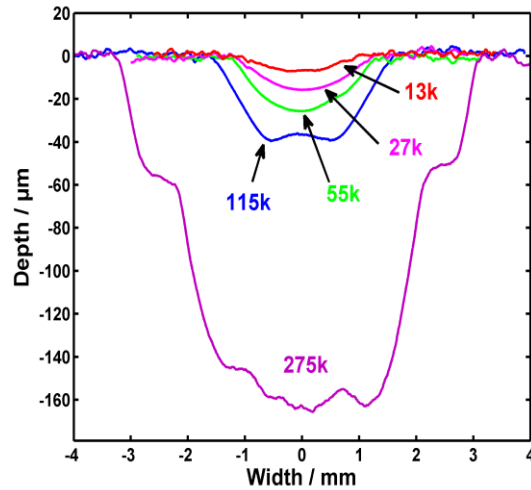


Figure 6.4 Profilometry of wear scars on the flat specimens from the (a) completed test profile at 275k cycles (stage III) (b) interrupted tests for the PTFE-DFL-Ti6Al4V system (indicating the number of cycles at interruption or completion).

Chemical analysis of the wear scar surfaces by energy-dispersive X-ray analysis (EDX) indicated in Table 6.2, that no elements associated with the metallic substrate could be detected in Stage I (13k, 27k, 55k and 115k cycles), while showing high amount of carbon with low oxygen. No evidence of DFL was present on the surface of stage III, metallic surface has been exposed as high Ti level were found in the wear track with a high amount of oxygen. As mentioned earlier, the accuracy of the EDX data (given that the analysis includes carbon and oxygen) means that this observation needs to be treated with some caution. However, It can be recognised that F indicates the presence of PTFE and C is associated with the paint binder and O is associated with the metal debris. The EDX results therefore consistent with the measured wear scar depths.

Table 6.2 Chemical analysis of the wear scar surfaces of 9.08 wt. % PTFE-DFL at 13k, 27k, 55k, 115k (stage I) and 275k (stage III)cycles by (EDX)

Element	13k area analysis / wt%	27k area analysis / wt%	55k area analysis / wt%	115k area analysis / wt%	275k area analysis / wt%
Ti	0	0	0	0	57
Al	0	0	0	0	3
V	0	0	0	0	2
Mo	23	23	25	25	0
S	14	14	14	15	0
F	14	14	15	11	0
C	43	43	39	43	2
O	6	7	6	6	32

To understand the effect of PTFE on the friction wear behaviour of the PTFE-DFL coating, the worn surface was studied under SEM and XPS. Figure 6.5 shows the scanning electron micrographs of the worn surfaces at various interrupted cycles mentioned earlier in Figure 6.3. Figure 6.5 (a)(b)(c)(d) are low magnification BSE images (left) and high magnification BSE images (right) of 13k, 27k, 55k, 115k and 275k cycles accordingly of the same worn surfaces associated with stage I. Low magnification BSE images in Figure 6.5 (a) (b) (c) (d) shows the ploughing marks across the wear surface and the high magnification image in Figure 6.5a shows the PTFE-DFL. At Stage III, 275 cycles, surfaces are full of discrete particles along with a bright metallic surface which indicates presence of Ti.

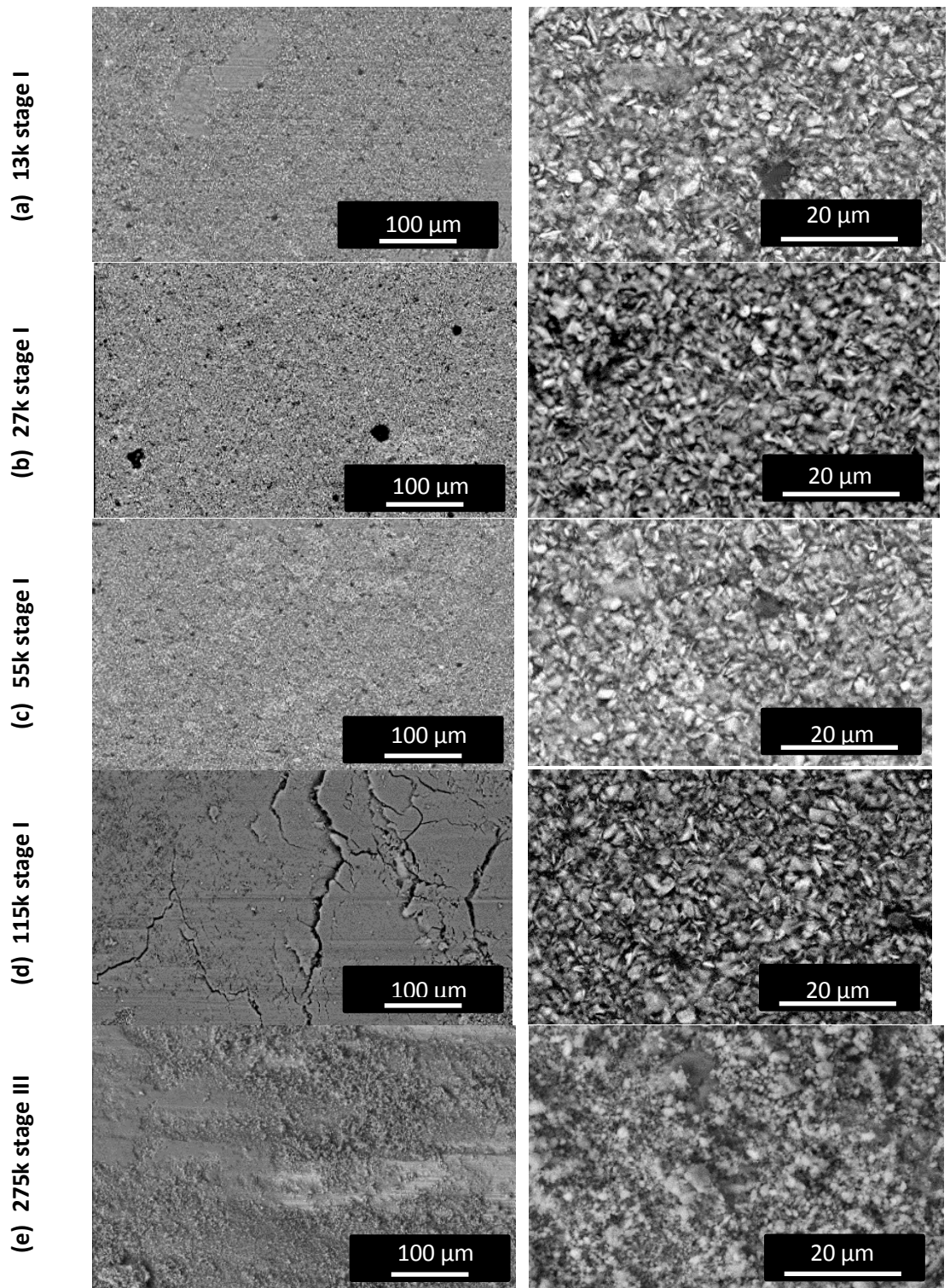


Figure 6.5 BSE plan view micrographs of wear scars for the PTFE-MoS₂-Ti6Al4V system for both completed and interrupted tests at both low (left) and high (right) magnification (the high magnification image is of the region shown in white box in the low magnification image), (a) following 13k cycles (b) following 27k cycles (c) following 55k cycles (d) following 115k cycles (e) following 275k cycles

It can be seen that after 13k cycles, the outer surface of the DFL has been modified (shown in 6.5a), but the changes are quite subtle and only affect 7.5 μm in thickness (Table 6.1), which is only 15 % of the total DFL thickness. The EDX results from the bulk shown in Table 6.2 and surface regions of the DFL indicate very little change in chemistry at the surface and there is no evidence of any elements from the substrate at the wear surface by this stage. After 27k cycles, 55k cycles and 115k cycles (Figure 6.5 (b) (c) (d)), the wear depth reached was 16 μm , 26 μm and 40 μm corresponding to 32 %, 52 % and 80 % of the total coating thickness respectively. EDX analysis shows that after 115k cycles the surface is chemically not very different from the original DFL. Profilometry results show that 20% of the DFL remains shown in Table 6.1. Following 275 kilocycles, which is at completion of the test, the wear depth (Figure 6.4) of 165 μm is 3 times greater than (Table 6.1) the original coating thickness. Significant damage and material removal from the substrate can be seen at this stage shown in Figure 6.5e.

Ploughing marks can be seen running across the surface, and the surface is generally quite smooth in the (Figure 6.5d) low magnification BSE image (left) but in high magnification image shown in Figure 6.5d (right), the surface shows the existence of DFL chemistry in Figure 6.5d. The XPS data shown in Figure 6.6 shows that the F content goes down (<10 at%) at the middle of the wear scar, indicating PTFE quantity decreased while S content increases. Moreover, the XPS trace across the wear scar (Figure 6.6) indicates a substantial increase in carbon in the wear scar with an increase in molybdenum and sulphur, indicating that the surface of the wear scar is preferentially enriched in MoS_2 by the wear process itself.

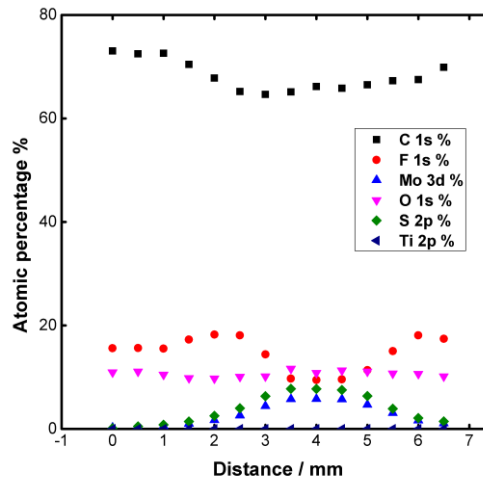


Figure 6.6 XPS analysis across the interrupted test wear scar on the PTFE-MoS₂-Ti6Al4V system following 115k cycles (stage II), showing the atomic percentage of elements across the wear scar. 0 mm and 6.5 mm are outside the wear scar, with the scar existing between these lateral positions.

6.1.2 Effect of evolution of coefficient of friction of Graphite on Ti6Al4V wear surface

The evolution of coefficient of friction of 4.76 wt. % Gr-DFL paint shown in Figure 6.7, where the load used is 575 N. The evolution shows an initial significant rise in coefficient of friction to 0.42, which is considered as stage I. Then the coefficient of friction falls slowly and steadily to ECoF 0.23 and is maintains until the experiment stopped unexpectedly at 658k cycles, ECoF 0.29.

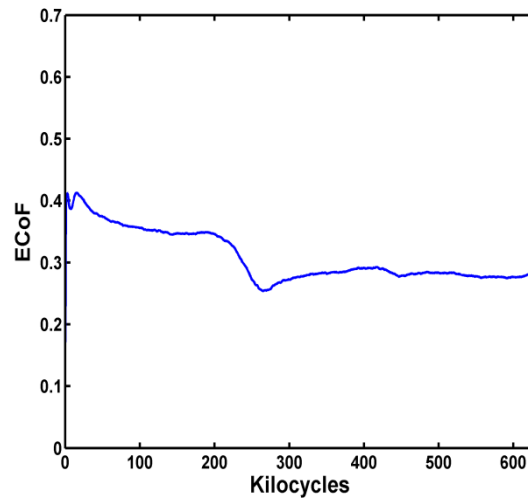


Figure 6.7 Evaluation of ECoF with number of cycles of 4.76 wt. % Gr-DLF system on 15 mm 50 µm on Ti6Al4V.

To accelerate the rate of wear in order to accelerate final failure a higher load of 2000 N was applied.

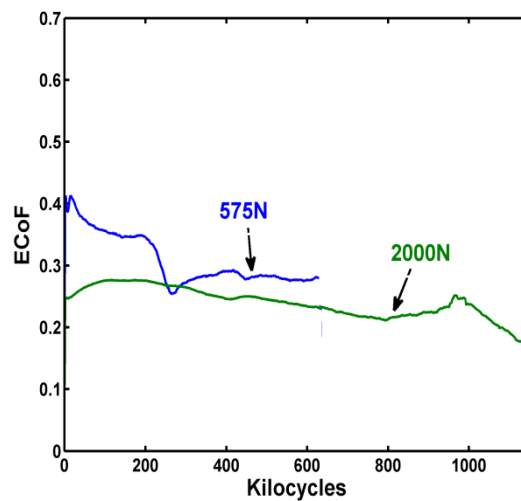


Figure 6.8 Comparison of Evaluation of ECoF with number of cycles of 4.76 wt. % Gr-DLF system on 15 mm 50 µm on Ti6Al4V for 575N (blue) and 2000 N (green).

The initial rise of ECoF was until 0.25 at stage I, then the coefficient of friction is maintained within a narrow range of 0.2 to 0.25 upto 1000 kilocycles. There is no evidence of raising the coefficient of friction

towards failure. Figure 6.8 shows the comparison of evolution of coefficient of friction for two different loads of 575 N and 2000 N. The initial level of ECoF has decreased; the coating then maintains its low ECoF region for long time showing no indication of entering stage III, before the end of the test. Figure 6.9 shows profiles across the wear scar following the two tests, the maximum depth of wear scar at 575 N load shown in Figure 6.9 and 2000 N load shown in Figure 6.9 was 60 μm and 100 μm respectively.

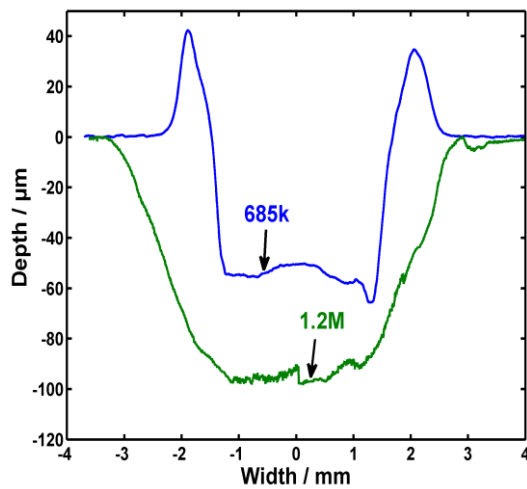


Figure 6.9 Profilometry of the wear scars on the flat specimens from the (a) 658 kilocycles under 575 N (a) profile at 1.2 million cycles under 2000N tests for the $50 \pm 5 \mu\text{m}$ thickness 4.76 wt. % Gr-DfL-Ti6Al4V system (indicating the number of cycles at interruption)

After 658 cycles, DFL has been removed completely to a thickness greater than its original thickness, which is $50 \pm 5 \mu\text{m}$, indicating that there has been substantial removal of material from the titanium alloy substrate. However, in Figure 6.10a which shows low and high magnification BSE images after 658k cycles where the ploughing effect on the surface from left to right is observed, there is no indication of exposure of the metallic surface on the wear scar. At 2000 N after 1.2M cycles, the material removal is even higher. The low magnification image shown in

Figure 6.10a, shows there is severe wear in the rough areas but the higher magnification image clearly shows there is not much debris formed on the surface, despite Figure 6.9 showing a wear depth of 100 μm . To accompany the profilometry, Figure 6.11 shows low magnification cross section of the full wear scar following profilometry indicated in Figure 6.9. This micrograph is presented, where the vertical magnification is ten times that of the horizontal magnification to have a clear view of damage. Clear evidence of complete removal of DFL can be seen in Figure 6.10b, bright metallic surface has been exposed but no debris found while maintaining low ECoF of <0.2 .

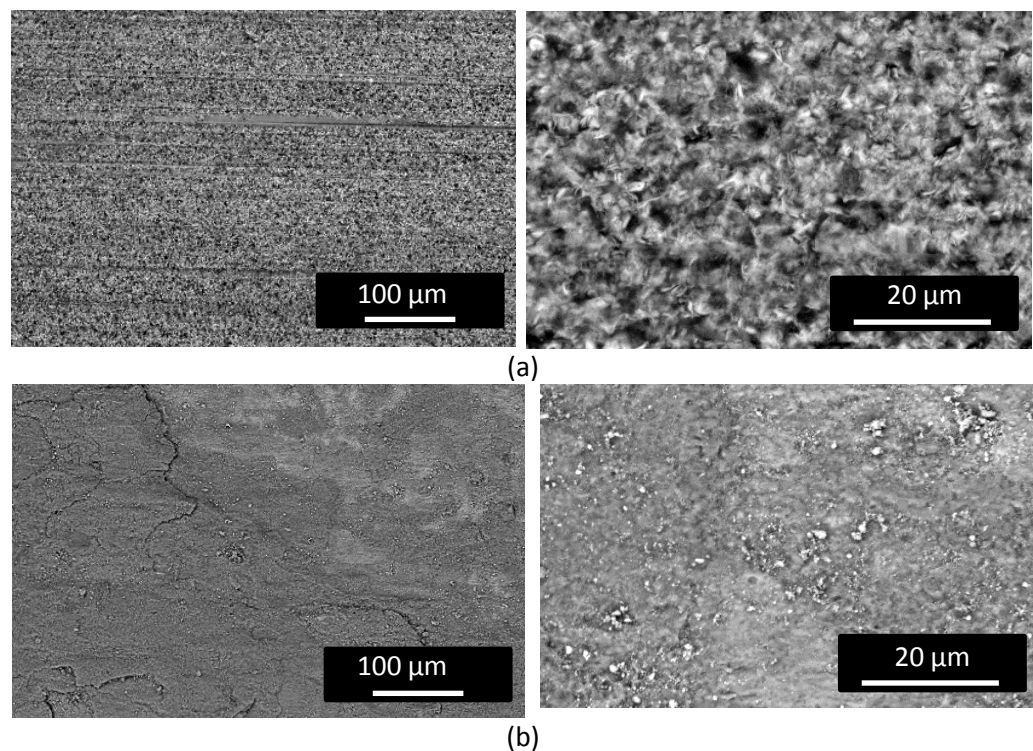


Figure 6.10 BSE plan view micrographs of wear scars for the 4.76 wt. % Gr-DfL-Ti6Al4V system for both interrupted tests at both low (left) and high (right) magnification, (a) 658 kilocycles (b) 1.2million cycles

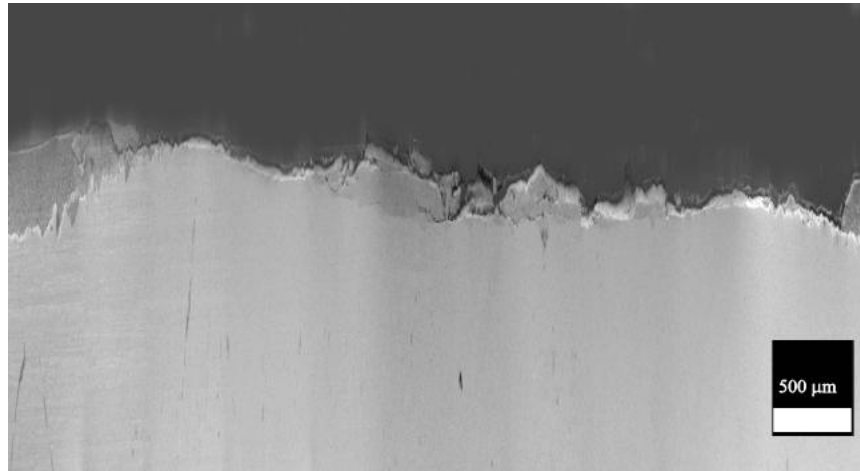


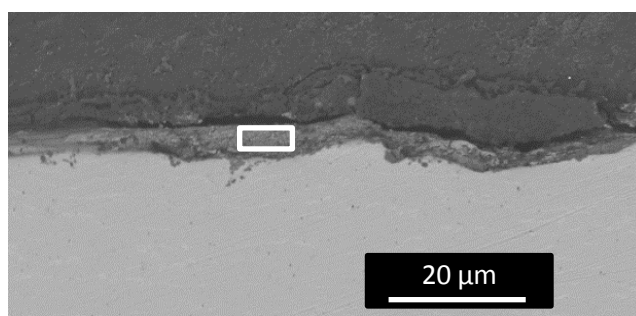
Figure 6.11 BSE micrographs of wear scar cross-sections ($R = 15 \text{ mm}$, $t = 50 \text{ μm}$) as a function of number of cycles corresponding to the tests described in Figure 6.12. This is a low magnification images with a distorted aspect ratio (vertical magnification being ten times the horizontal magnification) under 2000N load.

The EDX result after 658k cycles from the bulk and surface regions of the DFL (as indicated) in Table 6.3 indicate a high amount of carbon, with low oxygen and DFL is still present without showing any presence of Ti on the surface. After 1.2M cycles, the amount of carbon, molybdenum decrease significantly which indicates loss of DFL completely with an increase of oxygen and shows the presence of high Ti. However, it is recognised that the accuracy of the EDX data (given that the analysis includes carbon and oxygen) means that this observation needs to be treated with some caution, while it is important to mention C and O are associated with DFL.

Table 6.3 Large area EDX analysis from the surface of wear scars for 4.76 wt. % Gr-DFL-Ti6Al4V systems following 658 kilocycles and 1.2 million cycles under two different load 575N and 2000N respectively.

	After 685k cycles	After 1.25M cycles
C K	51.24	1.92
O K	9.24	35.13
Al K	0.00	3.25
S K	15.43	0.14
Ti K	0.14	51.23
V K	0.00	2.35
Mo	23.95	0.25

Previously, low magnification image in Figure 6.11 showed the full length wear scar of 1.2 million cycles surface. A part of the full wear scar in higher magnification shown in Figure 6.12, where a thin layer can be seen rich in titanium with no evidence of the DFL present on the surface.



Element	C K	O K	Al K	S K	Ti K	V K	Mo L
Weight%	5.20	9.68	5.48	0.28	73.16	6.20	0.00

Figure 6.12 BSE micrographs of wear scars cross section for the 4.76 wt. % Gr-DFL-Ti6Al4V system for 1.2 million cycles interrupted test under 2000N. Below table shows elemental analysis by EDX method shown in white box.

In addition, Figure 6.13 provides XPS elemental line profiles across the wear scar following 658k cycles and 1.2M cycles. The XPS data shown in Figure 6.13a shows a substantial decrease in C content, which is associated with both graphite and the polymeric binder, in the wear scar along with an increased Mo content within the wear scar, indicating that the surface of

wear scar in preferentially enriched in DFL by the wear process itself. The XPS data shown in Figure 6.10b shows the elemental line profiles across the wear scar following 1.2M cycles. A significant decrease in carbon content in the wear scar is seen. Significant increase in oxygen and Ti content can also be seen in the wear scar.

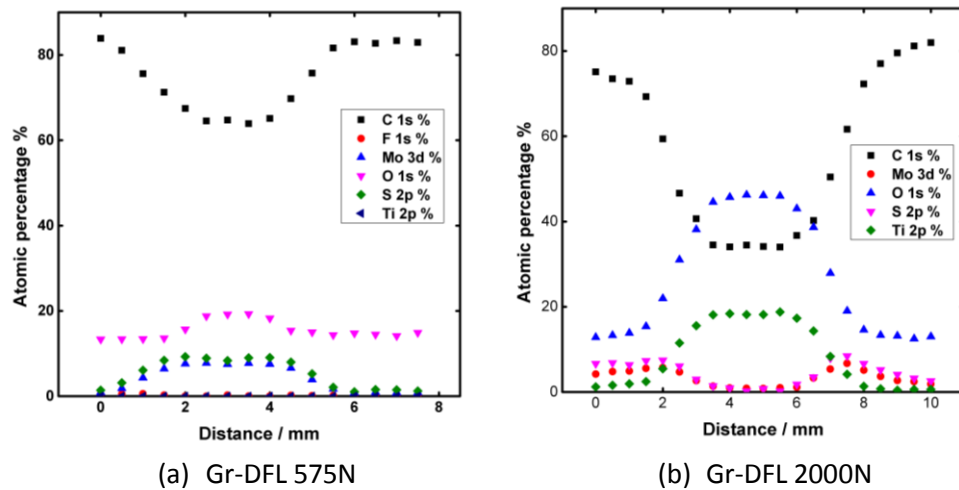


Figure 6.13 XPS analysis across the wear scars for both the interrupted tests for 4.76 wt. % Gr-DFL-Ti6Al4Vsystem (a) 658 kilocycles under 575 N (positionally, 0 and 6 mm are outside the scar, with the scar existing between these lateral positions), (b) 1.2 million cycles under 2000N (positionally, 2 mm and 7 mm are outside the scar, with the scar existing between these lateral positions), showing the atomic percentage of elements across the wear scar.

6.2 Discussion

It is observed that the addition of PTFE and Graphite both extends the lifetime of the system.

6.2.1 Effect of PTFE addition on durability of DFL

The PTFE has modified the evolution of ECoF. Analysis of the behaviour is done using the same three stage approach developed in Chapter 4 and Chapter 5. The overall system durability, i.e. lifetime, is significantly extended by the presence of PTFE. This is seen to be done to the extension of stage I, which continues to 180 kilocycles shown in Figure 6.2b.

The initial pattern of ECoF evolution in Figure 6.2b shows a decrease in ECoF near 100 kilocycles but it is not significant enough to be regarded as the start of stage II. The interrupted run for 115 kilocycles lies in the initial low ECoF region shown in Figure 6.3. The measured depth of the wear scar shows that only 80% of the total DFL thickness has been worn through shown in Table 6.1. The corresponding large area EDX analysis in Table 6.2 shows, the presence of significant amounts of molybdenum (25 wt. %) and fluorine (11 wt. %), very similar to results from 134 kilocycles (molybdenum content (23 wt. %) and fluorine (14 wt. %)) when 15 % of the coating was worn through. The fluorine content seems a little lower at 115 kilocycles than after 13 kilocycles but DFL presence is obvious. The XPS analysis, shown in Figure 6.6 shows decreased F content in the wear scar Mo and S levels increase in the wear scar. These results are similar to these seen in Chapter 4 for unmodified DFL.

The low ECoF region seen after 180 kilocycles is considered as stage II shown in Figure 6.2a and has a similar number of cycles (31 kilocycles) as the 0 wt. % PTFE addition sample (DFL-Ti6Al4V system).

Low magnification BSE image shown in Figure 6.5 a, b, c and d shows the ploughing marks across the image and shows that the PTFE-DFL and DFL contacts are still smoothly sliding until 115k cycles. The high magnification BSE images shown in Figure 6.5 a, b, c and d shows the chemistry of DFL is intact and no disruption or appearance of bright metallic surface which is evident the wear is well within the DFL. At 275 kilocycles, DFL penetration is evident in Figure 6.5d where the discrete particles are observed with the bright metallic surface in between and Figure 6.4 shows the wear penetrates through 3 times of original DFL thickness shown in Table 6.1. Large area EDX analysis in Table 6.2 confirms the presence of high amount of titanium and no DFL left at this stage.

It is also important to note that, the wear depth appears to increase proportionally as number of cycles increases. The wear profile shown in Figure 6.4 across the wear scar has the 'U' shape until 55 kilocycles and after 115 kilocycles, the wear profile converts into 'W' shape. As explained by Fouvry et al. [43] in Figure 2.16, for 13k, 27k, 55k cycles, when the U shape indicates that the displacement values are near to reciprocating conditions. The 'W' shaped contact structure is related to a modification of the surface geometry induced by the redistribution of the third body in the contact.

In presence of PTFE, the system shows high durability in stage I where no metal-DFL layer formed and the PTFE itself helps the DFL towards long life. The ECoF is maintained in the range of 0.25 – 0.32 for PTFE – DFL system where the ECoF for DFL alone was around 0.2 during the long life shown in Figure 6.2a. The XPS results show the same Mo and S evident in the wear

scar that was noted in Chapter 4 for the un-modified DFL. This implies that the mechanism of wear in the scar is unchanged, albeit that the PTFE has extended stage I.

6.2.2 Effect of graphite addition on durability of DFL

Graphite has been successfully used as a solid lubricant [139, 182, 184]. 4.76 wt. % addition of graphite showed a great improvement in overall durability. In Figure 6.7, the evolution of ECoF of Gr-DFL-Ti6Al4V system has been shown. It is observed that the addition of 4.76 wt. % graphite into DFL significantly extends the lifetime of the system. The ECoF initially rises above ECoF 0.4, from there ECoF decreases gradually for 200 kilocycles. An ECoF of 0.23 found near 280 kilocycles and the ECoF is maintained below 0.3 until the experiment need to be stopped after 658 kilocycles. Figure 6.9 shows a wear depth of 59 μm , which indicates the entire DFL thickness, has just been removed. The profile of wear scar shows the 'W' shape, indicates, according to Fouvry et al. [43], that severe wear might start at any point after 658 kilocycles. Low magnification BSE image in Figure 6.10 clearly shows ploughing marks running from left to right through the wear scar and the high magnification BSE image in Figure 6.10 indicates the DFL is still present on the wear surface. EDX analysis in Table 6.3 shows no evidence of titanium on the wear surface. XPS elemental analysis shown in Figure 6.13a confirm the fact that metal surface is still not exposed.

The higher load shows initial rise of ECoF 0.25 and then gradually slowed down until 990 kilocycles and then after little rise it continuously falls into

low ECoF. The experiment was stopped 1.2 million cycles, before the point of final failure. At this stage, Figure 6.9 shows higher wear depth (90 μm), which is far greater than the original Gr-DfL thickness. Table 6.3 confirms the presence of 51 wt. % titanium and a reduction in C (~ 2 wt. %) was observed, where C is associated with both graphite and the polymer binder. This concludes the underlying metal has been exposed. Figure 6.10b shows the plan view of the wear surface, which shows the bright metallic surface however little debris was found in comparison to the PTFE-DfL-Ti6Al4V system (Figure 6.5e) or DfL-Ti6Al4V system (Figure 4.8f). The low magnification cross section image of the full wear scar apparently shows damage on the wear scar with no DfL left but the high magnification BSE image of the cross section shown in Figure 6.12 shows a titanium rich thin layer with 5 wt. % C and 10 wt. % O left. The elemental line scan from XPS (Figure 6.13b) shows significant reduction in C and Mo, and a graphite and DfL accordingly with significant increase in Ti and O content, which is associated with the metallic contact and oxide debris. This is different to all other samples, where Mo and S enrich near scar.

6.3 Conclusion

Addition of 4.77 wt. %, 9.08 wt. % PTFE and 4.76 wt. % graphite, all increase DfL coating lifetime. The 4.76 wt. % graphite produced such a dramatic increased lifetime that it was not possible to run any samples long enough to run to failure. Somewhat different pattern of evolution was observed than seen for Chapter 4 and Chapter 5.

The behaviour of an epoxy-bonded DFL added with different additive, such as, PTFE, graphite sprayed directly onto a grit-blasted titanium alloy has been developed and compared with the same DFL sprayed onto a grit-blasted titanium alloy. The behaviour was examined in terms of coefficient of friction and system lifetime under fretting; using the three stage concept developed in Chapter 4 and Chapter 5. In the case of PTFE, different stages have been found and the extension of stage I was found to be expanded for the longer lifetime compared both DFL-Ti6Al4V system. Stage II was found to be unchanged.

In graphite-DFL, stages could not be differentiated as such it maintains the low coefficient of friction in all stages and showed the maximum durability of the system among all system used in this thesis. There is different mechanism underlying behind it. Low ECoF behaviour maintained despite wear depth significantly exceeds original coating thickness and barely any debris found on the surface, which is completely different than other system showed in Chapter 4 and Chapter 5.

Chapter 7. Summary and Conclusions

Throughout this thesis, comparison of interrupted and completed tests has demonstrated high reproducibility of the results. This thesis has established a phenomenological model of the lifetime of polymer bonded DFLs which can be applied regardless of contact geometry, thickness and load. It states the common classification that held for all experiments.

Experiments carried out on different DFL thickness and geometries revealed that the evolution of ECoF was a 3 stage process. The degradation of a MoS₂-based DFL on a titanium alloy substrate has been shown to take place in three distinct stages. In the first stage, the polymer-based DFL wears away until the substrate starts to come into contact, during this stage the coefficient of friction falls slowly. In the second stage, there is initially a significant reduction in the coefficient of friction, this is linked to the formation of a surface made up of features both of the metallic substrate and the DFL. There is an enhanced level of MoS₂ on the surface

with very little metallic material is present at the very surface, However the low friction material which covers the metallic substrate is very thin. After a number of cycles, this protective low friction material is no longer effective, and true metal-to-metal contact begins to take place with a commensurate increase in the coefficient of friction, this is the stage III. In the first stage, the volume of coating removed is observed to be proportional to the number of cycles, therefore, the duration of this stage can be estimated based upon the geometry of the contact and the DFL thickness. The duration of the second stage was seen to be inversely proportional to the contact pressure, this can therefore be estimated based upon a knowledge of the geometry of the contact. The start of stage three indicates the start of the end of the coating working lifetime.

Chapter 5 demonstrated that the 3 stage phenomenological model of Chapter 4 could be modified to explain the effect of a Cu-Ni-In underlayer. The behaviour of an epoxy-bonded DFL sprayed directly onto a grit-blasted titanium alloy has been compared with that of the same DFL sprayed onto a Cu-Ni-In interlayer which had been plasma sprayed onto the titanium alloy. The behaviour was examined in terms of coefficient of friction and system lifetime (durability) under fretting. The lifetimes of the systems have been understood and explained by sub-dividing the evolution of the behaviour into two stages. A third stage was identified, but failure of the system was linked with entry into this stage. In both systems, the first stage involves wear of the DFL, the influence of the metal onto which the DFL had been deposited was small, and thus the behaviour in this stage was very similar for both systems. The behaviour in the second stage is controlled by the characteristics of the material at the interface which is

made up of both metal and DFL. This material has low friction and high wear resistance. The changes in the makeup of the interface are very sensitive to the profile (roughness) of the interface between the metal and the DFL. Higher roughness results in reduced rates of change in behaviour and a significant extension of the duration over which the surface material is made up of a mixture of DFL and metal. The high durability of the system with the Cu-Ni-In underlayer is therefore mainly attributed to the high roughness of the as-sprayed underlayer onto which the DFL was deposited.

It has been demonstrated that DFL dramatically can be improved by the use of additives. The behaviour of an epoxy-bonded DFL added with different additive, such as, PTFE, graphite sprayed directly onto a grit-blasted titanium alloy has been developed and compared with the same DFL sprayed onto a grit-blasted titanium alloy. The behaviour was examined in terms of coefficient of friction and system lifetime under fretting. The lifetimes of the systems have been understood and the trend of different stage has been identified according to the evolution of the coefficient of friction, which was attempt to link with the failure of DFL. In case of PTFE, different stages have been found and the initial stage I was found to be associated for the longer lifetime than in DFL-Ti6Al4V system. Stage II found to be almost similar duration and then leads to failure, which is stage III. The behaviour of the stage II in DFL seems to be controlled by the characteristic mixed-metal layer but in PTFE-DFL system, the stage I was dominated to increase the lifetime of the system. In graphite-DFL, stages could not be differentiated as such it maintains the

low coefficient of friction in all stages and showed the maximum durability of the system among all system used in this thesis.

The work presented here presents increased understanding of the behaviour of polymer bonded DFL and should be useful in optimising the use of such systems.

Chapter 8. Future work

This thesis has demonstrated the three stage mechanism through the evolution of coefficient of friction of the fretting wear behaviour to understand the mechanism lying behind it. The following section will describe the author's opinion regarding the direction of the most useful future research in this area.

In Chapter 4, three different stages have been identified in DFL coating lifetime. Stage II was associated with mixed metal-DFL layer which leads to a lower coefficient of friction zone, where the thin layer helps to lubricate the surface enough to maintain the lower ECoF. However, the role of debris formation which represents the mixed metal-DFL layer was not investigated. As this lower coefficient of friction is dependent on entrapment of debris, it would be of benefit to understand if and how the contact conformity or the particle size of the debris influence the dependence of fretting wear behaviour in ambient temperature in dry sliding conditions. All the experiments were done on cylinder on flat

geometry. Extension of model to other geometries would be an interesting work, e.g. flat on flat.

In Chapter 1, the effect of evolution of coefficient of friction shown with or without Cu-Ni-In, where it can be seen the underlying layer of Cu-Ni-In improves the lifetime of MoS₂ based polymer lubricant. In Chapter 6, effect of PTFE-DfL and graphite-DfL has been studied without Cu-Ni-In underlayer. Investigation for an effect of Cu-Ni-In underlayer for different additives-DfL should be studied. Experiments with different Cu-Ni-In surface roughness would be another aspect for research.

Due to limits of experimental capability, the tests presented in Chapter 6 for graphite-DfL-Ti6Al4V against DfL-Ti6Al4V were incomplete. This would be a great interest to finish this long experiment to conclude its extreme point. More interrupted experiments would be useful in every case to conclude more accurately and find out in depth mechanism of different system.

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Appendices

Appendix A: Paint Spray Data Card

Title Paint Spray Data Card		Document ref. DKK 103	Issue 12
		Controlling Specification: RPS 661/9	
Additional keywords DKK 200, MSRR 9274		Date: 23 rd March 2009	
Material Code and Spec No: Various titanium alloys		Reason for Re-issue: New paint shaker in use.	
Material Condition: Superpolished & degreased			
Op. Description: Apply dry film lubricant			
NOT SEALED		SUBJECT TO JES 125 CONTROL	
NOT SENSITIVE		CRITICAL	
Paint thickness as per component drawing/manufacturing instructions			Air Pressure: 30 - 40 psi
Apply MSRR 9274 to RPS661/9			
Viscosity: N/A - use as supplied but paint should be filtered see op 4) below.			
Thinners: Use Indestructible IP9151 thinners.			
Prior to paint spraying, check that the paint is the correct specification, is batched and within the expiry date - if it is not, notify laboratory. Ensure that this information is legible and clean off any excess from the outside of the tin after use. 1) All areas requiring masking and painting are outlined in the relevant component drawing. 2) Check the surface condition of the component, where paint is to be applied the components should be in a clean, dry condition. Swab with an approved solvent as required. 3) Mask all areas not requiring paint application using paper tapes to CSS13 and polyethene bag/sheet. See the standard operating procedure (SOP) for details. 4) Thoroughly mix paint (on vibro shaker) for at least 15 minutes before use. In addition, the paint should be sieved through a fine mesh filter (typically 200 micron) prior to pouring into spray gun. 5) Apply one coat of paint to the specified area of the component(s). 6) Allow to dry for a minimum of 10 minutes at room temperature. 7) Repeat ops 5) & 6) until the desired paint thickness has been achieved. See sheet 2. 8) Carefully remove all masking materials and polyethene from the component(s). 9) Stove the paint in an air circulatory oven. Components may be placed in the oven at 100°C and the oven brought up to temperature. This will take approximately ½ - 1 hour. Stove at 190 ± 5°C for 2 hours. 10) Allow to cool to room temperature.			

Paint Thickness Control & Monitoring

Paint thickness on the component is controlled by the number of coats applied. This is detailed in the following chart: -

Number Of Coats	Total Coating Thickness (mm)
1	0,008 – 0.022
2	0,024 – 0,037
3	0,033 – 0,050
4	0,043 – 0,065

In addition, the paint thickness is monitored using a calibrated coating thickness measuring device. Normally, one blade is checked per batch of blades sprayed. The results are recorded in the SPC file held in the department.

Paint Batch No. Record

To enable traceability of the paint batch used on the blades, the relevant R-R batch no. of the paint must be recorded on the route card at the paint op).

Temperature & Humidity Checks

Temperature of paint shop shall be 15 – 30°C.

Temperature and humidity shall be continually monitored with a suitable calibrated gauge/meter kept in the paint shop.

Appendix B : Material Safety Data Sheet

for PL237-R2 (as received Mo based DFL)

Report Date : 24/01/2011
REVISION DATE: 24/01/2011

REV. NO./REPL. SDS GENERATED : 2



SAFETY DATA SHEET MOLY-DISULPHIDE DRY FILM LUBRICANT

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

PRODUCT NAME MOLY-DISULPHIDE DRY FILM LUBRICANT
PRODUCT NO. PL237-R2
SUPPLIER INDESTRUCTIBLE PAINT LTD
19-25 Pentos Drive
Sparkhill
Birmingham
England
B11 3TA
Tel +44(0)121 702 2485
Fax +44(0)121 778 4338
sales@indestructible.co.uk
EMERGENCY TELEPHONE +44 (0) 121 244 5671

2 HAZARDS IDENTIFICATION

Flammable. Irritating to eyes and skin. May cause sensitisation by skin contact. Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
CLASSIFICATION (1999/45) Xi;R36/38. R43. R10, R52/53.

3 COMPOSITION/INFORMATION ON INGREDIENTS

Name	EC No.	CAS-No.	Content	Classification (67/548)
1-METHOXY-2-PROPANOL	203-539-1	107-98-2	5-10%	R10
4-HYDROXY-4-METHYLPENTAN-2-ONE	204-626-7	123-42-2	< 1%	Xi;R36
BUTANOL-norm	200-751-6	71-36-3	< 1%	R10 Xn;R22 Xi;R37/38,R41 R67
BUTYL ACETATE -norm	204-658-1	123-86-4	5-10%	R10 R66 R67
CRESOL -ortho	202-423-8	95-48-7	< 1%	T;R24/25 C;R34
DIACETONE ALCOHOL		123-42-2	10-30%	Xi;R36.
EPOXY RESIN (Number average MW <= 700)	500-033-5	25068-38-6	10-30%	R43 Xi;R36/38 N;R51/53
FORMALDEHYDE ...%	200-001-8	50-00-0	< 1%	Carc. Cat. 3;R40 T;R23/24/25 C;R34 R43
METHYL ISO AMYL KETONE		110-12-3	5-10%	Xn;R20. R10.
METHYL N.AMYL KETONE		110-43-0	5-10%	Xn;R20,R22. R10.
PHENOL	203-632-7	108-95-2	< 1%	Muta. Cat. 3;R68 T;R23/24/25 C;R34 Xn;R48/20/21/22

The Full Text for all R-Phrases are Displayed in Section 16

COMPOSITION COMMENTS

The Data Shown is in accordance with the latest EC Directives.

4 FIRST-AID MEASURES

INHALATION

Move the exposed person to fresh air at once. Get medical attention if any discomfort continues.

MOLY-DISULPHIDE DRY FILM LUBRICANT

INGESTION

Immediately rinse mouth and provide fresh air. DO NOT induce vomiting. Get medical attention immediately. Do not induce vomiting. If vomiting occurs, the head should be kept low so that stomach vomit doesn't enter the lungs.

SKIN CONTACT

Immediately remove contaminated clothing. Wash off promptly and flush contaminated skin with water. Promptly remove clothing if soaked through and flush skin with water. Get medical attention if any discomfort continues.

EYE CONTACT

Make sure to remove any contact lenses from the eyes before rinsing. Promptly wash eyes with plenty of water while lifting the eye lids. Get medical attention promptly if symptoms occur after washing.

5 FIRE-FIGHTING MEASURES

EXTINGUISHING MEDIA

Fire can be extinguished using: Foam, carbon dioxide or dry powder. Dry chemicals, sand, dolomite etc.

SPECIAL FIRE FIGHTING PROCEDURES

Use pressurised air mask if product is involved in a fire. Cool containers exposed to flames with water until well after the fire is out.

SPECIFIC HAZARDS

When heated and in case of fire, irritating vapours/gases may be formed. In case of fire, toxic gases may be formed (COx, NOx).

PROTECTIVE MEASURES IN FIRE

Self contained breathing apparatus and full protective clothing must be worn in case of fire.

6 ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS

Wear protective clothing as described in Section 8 of this safety data sheet.

ENVIRONMENTAL PRECAUTIONS

Spillages or uncontrolled discharges into watercourses must be IMMEDIATELY alerted to the Environmental Agency or other appropriate regulatory body.

SPILL CLEAN UP METHODS

Keep combustibles away from spilled material. Extinguish all ignition sources. Avoid sparks, flames, heat and smoking. Ventilate. Absorb in vermiculite, dry sand or earth and place into containers.

7 HANDLING AND STORAGE

USAGE PRECAUTIONS

Keep away from heat, sparks and open flame. Avoid spilling, skin and eye contact. Ventilate well, avoid breathing vapours. Use approved respirator if air contamination is above accepted level.

STORAGE PRECAUTIONS

Flammable/combustible - Keep away from oxidisers, heat and flames. Store in tightly closed original container in a dry, cool and well-ventilated place. Keep in original container. Avoid contact with oxidising agents. Store in closed original container at temperatures between 5°C and 25°C.

STORAGE CLASS

Flammable liquid storage.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

MOLY-DISULPHIDE DRY FILM LUBRICANT

Name	Std	TWA - 8 hrs		STEL - 15 min		Notes
1-METHOXY-2-PROPANOL	WEL	100 ppm	375 mg/m3	150 ppm	560 mg/m3	Sk
4-HYDROXY-4-METHYLPENTAN-2-ONE	WEL	50 ppm	241 mg/m3	75 ppm	362 mg/m3	
BUTANOL-norm	WEL			50 ppm	154 mg/m3	Sk
BUTYL ACETATE -norm	WEL	150 ppm	724 mg/m3	200 ppm	966 mg/m3	
FORMALDEHYDE ...%	WEL	2 ppm	2.5 mg/m3	2 ppm	2.5 mg/m3	
PHENOL	WEL	2 ppm(Sk)				

WEL = Workplace Exposure Limit.
 Sk = Can be absorbed through skin.

PROTECTIVE EQUIPMENT



PROCESS CONDITIONS

Provide eyewash station.

ENGINEERING MEASURES

Provide adequate ventilation, including appropriate local extraction, to ensure that the defined occupational exposure limit is not exceeded. All handling to take place in well-ventilated area.

RESPIRATORY EQUIPMENT

Wear mask supplied with: Gas cartridge suitable for organic substances.

HAND PROTECTION

Use protective gloves made of: Neoprene. Nitrile. Rubber (natural, latex).

EYE PROTECTION

Wear splash-proof eye goggles to prevent any possibility of eye contact.

OTHER PROTECTION

Wear appropriate clothing to prevent any possibility of skin contact.

HYGIENE MEASURES

DO NOT SMOKE IN WORK AREA! Wash at the end of each work shift and before eating, smoking and using the toilet. Promptly remove any clothing that becomes contaminated. Use appropriate skin cream to prevent drying of skin. When using do not eat, drink or smoke.

9 PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE	Coloured liquid		
COLOUR	Brown		
ODOUR	Characteristic		
BOILING POINT (°C)	119-122 760 mm Hg	RELATIVE DENSITY	1.22
FLASH POINT (°C)	27 CC (Closed cup).	FLAMMABILITY LIMIT - LOWER(%)	0.8
VOLATILE ORGANIC COMPOUND (VOC)	690 g/litre		

10 STABILITY AND REACTIVITY

STABILITY

No particular stability concerns.

CONDITIONS TO AVOID

Avoid heat, flames and other sources of ignition. Avoid contact with strong oxidisers.

MOLY-DISULPHIDE DRY FILM LUBRICANT

HAZARDOUS DECOMPOSITION PRODUCTS

Thermal decomposition or combustion may liberate carbon oxides and other toxic gases or vapours.

11 TOXICOLOGICAL INFORMATION

GENERAL INFORMATION

Prolonged and repeated contact with solvents over a long period may lead to permanent health problems.

INHALATION

In high concentrations, vapours may irritate throat and respiratory system and cause coughing. Harmful by inhalation.

INGESTION

Gastrointestinal symptoms, including upset stomach.

SKIN CONTACT

Harmful in contact with skin. Irritating to skin.

EYE CONTACT

Irritating and may cause redness and pain.

12 ECOLOGICAL INFORMATION

ECOTOXICITY

The product is not expected to be hazardous to the environment.

13 DISPOSAL CONSIDERATIONS

GENERAL INFORMATION

Waste to be treated as controlled waste. Disposal to licensed waste disposal site in accordance with local Waste Disposal Authority.

14 TRANSPORT INFORMATION



UK ROAD CLASS	3	UK ROAD PACK GR.	III
PROPER SHIPPING NAME	PAINT	ADR CLASS	Class 3: Flammable liquids.
UN NO. ROAD	1263	TUNNEL RESTRICTION CODE	(D/E)
ADR CLASS NO.	3	ADR LABEL NO.	3
ADR PACK GROUP	III	CEPIC TEC(R) NO.	30GF1-III, 30GF1-sp
HAZARD No. (ADR)	30	RID PACK GROUP	III
HAZCHEM CODE	*3YE	IMDG CLASS	3
RID CLASS NO.	3	EMS	F-E, S-E
UN NO. SEA	1263	AIR CLASS	3
IMDG PACK GR.	III		
UN NO. AIR	1263		
AIR PACK GR.	III		

15 REGULATORY INFORMATION

LABELLING

MOLY-DISULPHIDE DRY FILM LUBRICANT



Irritant

CONTAINS EPOXY RESIN (Number average MW <= 700)

RISK PHRASES

R10 Flammable.
R36/38 Irritating to eyes and skin.
R43 May cause sensitisation by skin contact.
R52/53 Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

SAFETY PHRASES

S24/25 Avoid contact with skin and eyes.
S37 Wear suitable gloves.
S60 This material and its container must be disposed of as hazardous waste.
P5 Contains epoxy constituents. See information supplied by the manufacturer.

EU DIRECTIVES

Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, including amendments.

16 OTHER INFORMATION

REVISION DATE 24/01/2011

REV. NO./REPL. SDS GENERATED 2

RISK PHRASES IN FULL

R34 Causes burns.
R10 Flammable.
R20 Harmful by inhalation.
R22 Harmful if swallowed.
R48/20/21/22 Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R36/38 Irritating to eyes and skin.
R36 Irritating to eyes.
R37/38 Irritating to respiratory system and skin.
R37 Irritating to respiratory system.
R40 Limited evidence of a carcinogenic effect.
R43 May cause sensitisation by skin contact.
R68 Possible risk of irreversible effects.
R66 Repeated exposure may cause skin dryness or cracking.
R41 Risk of serious damage to eyes.
R23/24/25 Toxic by inhalation, in contact with skin and if swallowed.
R24/25 Toxic in contact with skin and if swallowed.
R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R67 Vapours may cause drowsiness and dizziness.

DISCLAIMER

This information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process. Such information is, to the best of the company's knowledge and belief, accurate and reliable as of the date indicated. However, no warranty guarantee or representation is made to its accuracy, reliability or completeness. It is the user's responsibility to satisfy himself as to the suitability of such information for his own particular use.

Appendix C: Material Safety Data Card for thinner (IP 9151)



SAFETY DATA SHEET
Thinner

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

PRODUCT NAME Thinner
PRODUCT NO. IP9151
SUPPLIER INDESTRUCTIBLE PAINT LTD
19-25 Pentos Drive
Sparkhill
Birmingham
England
B11 3TA
Tel +44(0)121 702 2485
Fax +44(0)121 778 4338
sales@indestructible.co.uk
EMERGENCY TELEPHONE +44 (0) 121 244 5671

2 HAZARDS IDENTIFICATION

Flammable. Harmful by inhalation, in contact with skin and if swallowed. Irritating to eyes and respiratory system. Limited evidence of a carcinogenic effect.

CLASSIFICATION (1999/45) Xn;R20/21/22. Carc. Cat. 3;R40. Xi;R36/37. R10.

3 COMPOSITION/INFORMATION ON INGREDIENTS

Name	EC No.	CAS-No.	Content	Classification (67/548)
CYCLOHEXANONE		108-94-1	60-100%	Xn;R20. R10.
ISOPHORONE		78-59-1	30-60%	Xn;R21/22. Carc. Cat. 3;R40. Xi;R36/37.

The Full Text for all R-Phrases are Displayed in Section 16

COMPOSITION COMMENTS

The Data Shown is in accordance with the latest EC Directives.

4 FIRST-AID MEASURES

INHALATION

Move the exposed person to fresh air at once. Get medical attention if any discomfort continues.

INGESTION

Immediately rinse mouth and provide fresh air. Do not induce vomiting. If vomiting occurs, the head should be kept low so that stomach vomit doesn't enter the lungs. Get medical attention immediately!

SKIN CONTACT

Immediately remove contaminated clothing. Wash off promptly and flush contaminated skin with water. Promptly remove clothing if soaked through and flush skin with water. Get medical attention if any discomfort continues.

EYE CONTACT

Make sure to remove any contact lenses from the eyes before rinsing. Promptly wash eyes with plenty of water while lifting the eye lids. Get medical attention promptly if symptoms occur after washing.

5 FIRE-FIGHTING MEASURES

EXTINGUISHING MEDIA

Fire can be extinguished using: Foam, carbon dioxide or dry powder. Dry chemicals, sand, dolomite etc.

SPECIAL FIRE FIGHTING PROCEDURES

Use pressurised air mask if product is involved in a fire. Cool containers exposed to flames with water until well after the fire is out.

Thinner

SPECIFIC HAZARDS

When heated and in case of fire, irritating vapours/gases may be formed. In case of fire, toxic gases may be formed (COx, NOx).

PROTECTIVE MEASURES IN FIRE

Self contained breathing apparatus and full protective clothing must be worn in case of fire.

6 ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS

Wear protective clothing as described in Section 8 of this safety data sheet.

ENVIRONMENTAL PRECAUTIONS

Spillages or uncontrolled discharges into watercourses must be IMMEDIATELY alerted to the Environmental Agency or other appropriate regulatory body.

SPILL CLEAN UP METHODS

Keep combustibles away from spilled material. Extinguish all ignition sources. Avoid sparks, flames, heat and smoking. Ventilate. Absorb in vermiculite, dry sand or earth and place into containers.

7 HANDLING AND STORAGE

USAGE PRECAUTIONS

Keep away from heat, sparks and open flame. Avoid spilling, skin and eye contact. Ventilate well, avoid breathing vapours. Use approved respirator if air contamination is above accepted level.

STORAGE PRECAUTIONS

Flammable/combustible - Keep away from oxidisers, heat and flames. Store in tightly closed original container in a dry, cool and well-ventilated place. Keep in original container. Avoid contact with oxidising agents. Store in closed original container at temperatures between 5°C and 25°C.

STORAGE CLASS

Flammable liquid storage.

8 EXPOSURE CONTROLS/PERSONAL PROTECTION

PROTECTIVE EQUIPMENT



PROCESS CONDITIONS

Provide eyewash station.

ENGINEERING MEASURES

Provide adequate ventilation, including appropriate local extraction, to ensure that the defined occupational exposure limit is not exceeded. All handling to take place in well-ventilated area.

RESPIRATORY EQUIPMENT

Wear mask supplied with: Gas cartridge suitable for organic substances.

HAND PROTECTION

Use protective gloves made of: Neoprene. Nitrile. Rubber (natural, latex).

EYE PROTECTION

Wear splash-proof eye goggles to prevent any possibility of eye contact.

OTHER PROTECTION

Wear appropriate clothing to prevent any possibility of skin contact.

HYGIENE MEASURES

DO NOT SMOKE IN WORK AREA! Wash at the end of each work shift and before eating, smoking and using the toilet. Promptly remove any clothing that becomes contaminated. Use appropriate skin cream to prevent drying of skin. When using do not eat, drink or smoke.

9 PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE	Clear liquid		
COLOUR	Colourless		
ODOUR	Characteristic		
RELATIVE DENSITY	0.94	VOLATILE BY VOL. (%)	100
FLASH POINT (°C)	40-44 CC (Closed cup).	FLAMMABILITY LIMIT - LOWER(%)	0.8

Thinner

VOLATILE ORGANIC COMPOUND 940 g/litre
(VOC)

10 STABILITY AND REACTIVITY

STABILITY

No particular stability concerns.

CONDITIONS TO AVOID

Avoid heat, flames and other sources of ignition. Avoid contact with strong oxidisers.

HAZARDOUS DECOMPOSITION PRODUCTS

Thermal decomposition or combustion may liberate carbon oxides and other toxic gases or vapours.

11 TOXICOLOGICAL INFORMATION

GENERAL INFORMATION

Prolonged and repeated contact with solvents over a long period may lead to permanent health problems.

INHALATION

In high concentrations, vapours may irritate throat and respiratory system and cause coughing. Harmful by inhalation.

INGESTION

Gastrointestinal symptoms, including upset stomach.

SKIN CONTACT

Harmful in contact with skin. Irritating to skin.

EYE CONTACT

Irritating and may cause redness and pain.

12 ECOLOGICAL INFORMATION

ECOTOXICITY

The product is not expected to be hazardous to the environment.

13 DISPOSAL CONSIDERATIONS

GENERAL INFORMATION

Waste to be treated as controlled waste. Disposal to licensed waste disposal site in accordance with local Waste Disposal Authority.

14 TRANSPORT INFORMATION



UK ROAD CLASS	3		
PROPER SHIPPING NAME	PAINT RELATED MATERIAL		
UN NO. ROAD	1263	UK ROAD PACK GR.	III
ADR CLASS NO.	3	ADR CLASS	Class 3: Flammable liquids.
ADR PACK GROUP	III	TUNNEL RESTRICTION CODE	(D/E)
HAZARD No. (ADR)	30	ADR LABEL NO.	3
HAZCHEM CODE	*3YE	CEPIC TEC(R) NO.	30GF1-III, 30GF1-sp
RID CLASS NO.	3	RID PACK GROUP	III
UN NO. SEA	1263	IMDG CLASS	3
IMDG PACK GR.	III	EMS	F-E, S-E
UN NO. AIR	1263	AIR CLASS	3
AIR PACK GR.	III		

15 REGULATORY INFORMATION

Thinner

LABELLING



Harmful

CONTAINS

CYCLOHEXANONE
ISOPHORONE

RISK PHRASES

R10	Flammable.
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
R36/37	Irritating to eyes and respiratory system.
R40	Limited evidence of a carcinogenic effect.

SAFETY PHRASES

S25	Avoid contact with eyes.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37	Wear suitable protective clothing and gloves.
S51	Use only in well-ventilated areas.
S60	This material and its container must be disposed of as hazardous waste.

EU DIRECTIVES

Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, including amendments.

16 OTHER INFORMATION

REVISION DATE 19/12/2009

REV. NO./REPL. SDS GENERATED 1

RISK PHRASES IN FULL

R10	Flammable.
R20	Harmful by inhalation.
R21/22	Harmful in contact with skin and if swallowed.
R36/37	Irritating to eyes and respiratory system.
R40	Limited evidence of a carcinogenic effect.

DISCLAIMER

is information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in y process. Such information is, to the best of the company's knowledge and belief, accurate and reliable as of the date indicated. However, no rranty guarantee or representation is made to its accuracy, reliability or completeness. It is the user's responsibility to satisfy himself as to the tability of such information for his own particular use.

Appendix D: Material Safety Data Card for PTFE powder

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 5.0 Revision Date 12.11.2012
Print Date 04.03.2013

1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name : Poly(tetrafluoroethylene)

Product Number : 430935
Brand : Aldrich
CAS-No. : 9002-84-0

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Company Ltd.
The Old Brickyard
NEW ROAD, GILLINGHAM
Dorset
SP8 4XT
UNITED KINGDOM

Telephone : +44 (0)1747 833000
Fax : +44 (0)1747 833313
E-mail address : eurtechserv@sial.com

1.4 Emergency telephone number

Emergency Phone # : +44 (0)1747 833100

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Not a hazardous substance or mixture according to Regulation (EC) No. 1272/2008.
This substance is not classified as dangerous according to Directive 67/548/EEC.

2.2 Label elements

The product does not need to be labelled in accordance with EC directives or respective national laws.

2.3 Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Synonyms : PTFE

Formula : (CF₂CF₂)_n

4. FIRST AID MEASURES

4.1 Description of first aid measures

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration.

In case of skin contact

Wash off with soap and plenty of water.

In case of eye contact

Flush eyes with water as a precaution.

If swallowed

Never give anything by mouth to an unconscious person. Rinse mouth with water.

4.2 Most important symptoms and effects, both acute and delayed

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

4.3 Indication of any immediate medical attention and special treatment needed

no data available

5. FIREFIGHTING MEASURES**5.1 Extinguishing media****Suitable extinguishing media**

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture

Carbon oxides, Hydrogen fluoride

5.3 Advice for firefighters

Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information

no data available

6. ACCIDENTAL RELEASE MEASURES**6.1 Personal precautions, protective equipment and emergency procedures**

Avoid dust formation. Avoid breathing vapors, mist or gas.

6.2 Environmental precautions

Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Sweep up and shovel. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

For disposal see section 13.

7. HANDLING AND STORAGE**7.1 Precautions for safe handling**

Provide appropriate exhaust ventilation at places where dust is formed.

7.2 Conditions for safe storage, including any incompatibilities

Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

7.3 Specific end uses

no data available

8. EXPOSURE CONTROLS/PERSONAL PROTECTION**8.1 Control parameters****Components with workplace control parameters**

Contains no substances with occupational exposure limit values.

8.2 Exposure controls**Appropriate engineering controls**

General industrial hygiene practice.

Personal protective equipment**Eye/face protection**

Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Aldrich - 430935

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Delivery 0430819872-000020 Purchase Order S030835_20156264

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Body Protection

Choose body protection in relation to its type, to the concentration and amount of dangerous substances, and to the specific work-place. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection

Respiratory protection is not required. Where protection from nuisance levels of dusts are desired, use type N95 (US) or type P1 (EN 143) dust masks. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

9. PHYSICAL AND CHEMICAL PROPERTIES**9.1 Information on basic physical and chemical properties**

a) Appearance	Form: powder Colour: white
b) Odour	no data available
c) Odour Threshold	no data available
d) pH	no data available
e) Melting point/freezing point	Melting point/range: 321 °C
f) Initial boiling point and boiling range	no data available
g) Flash point	no data available
h) Evaporation rate	no data available
i) Flammability (solid, gas)	no data available
j) Upper/lower flammability or explosive limits	no data available
k) Vapour pressure	no data available
l) Vapour density	no data available
m) Relative density	2.15 g/mL at 25 °C
n) Water solubility	no data available
o) Partition coefficient: n-octanol/water	no data available
p) Autoignition temperature	no data available
q) Decomposition temperature	no data available
r) Viscosity	no data available
s) Explosive properties	no data available
t) Oxidizing properties	no data available

9.2 Other safety information

no data available

Aldrich - 430935

Delivery 0430819872-000020 Purchase Order S030835_20156264

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10. STABILITY AND REACTIVITY

- 10.1 Reactivity**
no data available
- 10.2 Chemical stability**
no data available
- 10.3 Possibility of hazardous reactions**
no data available
- 10.4 Conditions to avoid**
no data available
- 10.5 Incompatible materials**
Strong oxidizing agents
- 10.6 Hazardous decomposition products**
Other decomposition products - no data available
-

11. TOXICOLOGICAL INFORMATION**11.1 Information on toxicological effects**

Acute toxicity
no data available

Skin corrosion/irritation
no data available

Serious eye damage/eye irritation
no data available

Respiratory or skin sensitization
no data available

Germ cell mutagenicity
no data available

Carcinogenicity

Carcinogenicity - rat - Implant

Tumorigenic: Equivocal tumorigenic agent by RTECS criteria. Tumorigenic: Tumors at site or application.

Carcinogenicity - mouse - Implant

Tumorigenic: Equivocal tumorigenic agent by RTECS criteria. Tumorigenic: Tumors at site or application.

IARC: 3 - Group 3: Not classifiable as to its carcinogenicity to humans (Ethene, 1,1,2,2-tetrafluoro-, homopolymer)

Reproductive toxicity
no data available

Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects

Inhalation	May be harmful if inhaled. May cause respiratory tract irritation.
Ingestion	May be harmful if swallowed.
Skin	May be harmful if absorbed through skin. May cause skin irritation.
Eyes	May cause eye irritation.

Signs and Symptoms of Exposure

To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information

RTECS: KX4025000

12. ECOLOGICAL INFORMATION**12.1 Toxicity**

no data available

12.2 Persistence and degradability

no data available

12.3 Bioaccumulative potential

no data available

12.4 Mobility in soil

no data available

12.5 Results of PBT and vPvB assessment

no data available

12.6 Other adverse effects

no data available

13. DISPOSAL CONSIDERATIONS**13.1 Waste treatment methods****Product**

Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION**14.1 UN number**

ADR/RID: -

IMDG: -

IATA: -

14.2 UN proper shipping name

ADR/RID: Not dangerous goods

IMDG: Not dangerous goods

IATA: Not dangerous goods

14.3 Transport hazard class(es)

ADR/RID: -

IMDG: -

IATA: -

14.4 Packaging group

ADR/RID: -

IMDG: -

IATA: -

14.5 Environmental hazards

ADR/RID: no

IMDG Marine pollutant: no

IATA: no

14.6 Special precautions for user

no data available

15. REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

no data available

15.2 Chemical Safety Assessment

no data available

16. OTHER INFORMATION

Further information

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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

Appendix E: Material Safety Data Sheet

for Graphite powder

EC safety data sheet



Trade name: TIMREX synthetic Graphite

Current version : 1.8.0, issued: 23.04.2012

Replaced version: 1.7.0, issued: 20.12.2011

Region: GB

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Trade name

TIMREX synthetic Graphite

Substance name Graphite
REACH registration no. 01-2119486977-12-0011

Identification numbers

CAS no. 7782-42-5
EC no. 231-955-3

1.2 Relevant identified uses of the substance or mixture and uses advised against

Relevant identified uses of the substance or mixture

Electrical and thermal conductive additive
Friction modifier
Carbon carrier
Lubricant
Refractory

1.3 Details of the supplier of the safety data sheet

Address

TIMCAL AG

-

CH-6743 Bodio (Switzerland)

Telephone no. +41 91 873 20 10

Fax no. +41 91 873 20 19

Information provided by / telephone

Technological Development

Advice on Safety Data Sheet

sdb_info@umco.de

1.4 Emergency telephone number

+41 91 873 20 10

Monday - friday: 7.30 - 12.00, 13.15 - 17.15 h

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification information

This product does not meet the classification and labelling criteria given in the Regulation (EC) No 1272/2008 (CLP).

This product does not meet the classification and labelling criteria given in the Dangerous Preparations Directive 67/548/EC (DSD)

2.2 Label elements

Not relevant

2.3 Other hazards

No data available.

SECTION 3: Composition/Information on Ingredients

3.1 Substances

Chemical characterization

Substance name Graphite (> 95 %)
Formula C1
Molecular weight 12,01

EC safety data sheet



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Region: GB

Identification numbers

CAS no. 7782-42-5
EC no. 231-955-3

3.2 Mixtures

Not applicable. The product is not a mixture.

SECTION 4: First aid measures

4.1 Description of first aid measures

General information

In case of persisting adverse effects, consult a physician. Remove contaminated clothing and shoes immediately, and launder thoroughly before reusing.

After inhalation

Remove affected person from the immediate area. Ensure supply of fresh air.

After skin contact

Wash off immediately with soap and water.

After eye contact

Separate eyelids, wash the eyes thoroughly with water (15 min.).

After ingestion

Rinse mouth thoroughly with water. Seek medical advice immediately. Never give anything by mouth to an unconscious person.

4.2 Most important symptoms and effects, both acute and delayed

No data available.

4.3 Indication of any immediate medical attention and special treatment needed

No data available.

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media

Graphite is difficult to combust. Extinguishing measures to suit surroundings.

Unsuitable extinguishing media

No data available.

5.2 Special hazards arising from the substance or mixture

In the event of fire, the following can be released: Carbon monoxide (CO); Carbon dioxide (CO₂)

5.3 Advice for firefighters

Use self-contained breathing apparatus. Wear protective clothing.

SECTION 6: Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures

For non-emergency personnel

Refer to protective measures listed in sections 7 and 8. Avoid contact with skin, eyes and clothing. Ensure adequate ventilation. Avoid dust formation. High risk of slipping due to leakage/spillage of product.

For emergency responders

No data available. Personal protective equipment (PPE) - see Section 8.

6.2 Environmental precautions

Do not discharge into the drains/surface waters/groundwater.

6.3 Methods and material for containment and cleaning up

Take up mechanically. When picked up, treat material as prescribed under heading "Disposal considerations".

6.4 Reference to other sections

No data available.

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SECTION 7: Handling and storage

7.1 Precautions for safe handling

Advice on safe handling

Provide good ventilation of working area (local exhaust ventilation, if necessary). If workplace exposure limits are exceeded, respiratory protection approved for this particular job must be worn.

General protective and hygiene measures

Do not eat, drink or smoke during work time. Keep away from foodstuffs and beverages. Avoid contact with eyes and skin. Remove soiled or soaked clothing immediately. Wash hands before breaks and after work. Do not inhale dust. Provide eye wash fountain in work area.

Advice on protection against fire and explosion

Dust can form an explosive mixture with air. Take precautionary measures against static charges. Keep away from sources of heat and ignition.

7.2 Conditions for safe storage, including any incompatibilities

Technical measures and storage conditions

Keep container tightly closed and dry.

Requirements for storage rooms and vessels

Containers which are opened must be carefully resealed and kept upright to prevent leakage. Always keep in containers of same material as the original one.

Advice on storage assembly

None known

7.3 Specific end use(s)

No data available.

SECTION 8: Exposure controls/personal protection

8.1 Control parameters

Occupational exposure limit values

No	Substance name	CAS no.	EC no.
1	DUST		
	List of approved workplace exposure limits (WELs) / EH40		
	total inhalable dust		
	TWA	10	mg/m ³
	List of approved workplace exposure limits (WELs) / EH40		
	respirable dust		
	TWA	4	mg/m ³

8.2 Exposure controls

Appropriate engineering controls

No data available.

Personal protective equipment

Respiratory protection

If workplace exposure limits are exceeded, a respiration protection approved for this particular job must be worn. In case of dust formation, take appropriate measures for breathing protection in the event workplace threshold values are not specified. Dust mask

Respirator FFP2SL (EN 149)

Eye / face protection

Safety glasses with side protection shield (EN 166)

Hand protection

Sufficient protection is given wearing suitable protective gloves checked according to i.e. EN 374, in the event of risk of skin contact with the product. Before use, the protective gloves should be tested in any case for its specific work-station suitability (i.e. mechanical resistance, product compatibility and antistatic properties). Adhere to the manufacturer's instructions and information relating to the use, storage, care and replacement of protective gloves. Protective gloves shall be replaced immediately when physically damaged or worn. Design operations thus to avoid permanent use of protective gloves.

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Appropriate Material rubber

Other

Normal chemical work clothing.

Environmental exposure controls

No data available.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

Form/Colour			
Powder			
grey to black			
Odour			
odourless			
Odour threshold			
No data available			
pH value			
No data available			
Boiling point / boiling range			
No data available			
Melting point / melting range			
Value	appr.	3500	°C
Decomposition point / decomposition range			
No data available			
Flash point			
Not applicable			
Ignition temperature			
Value	>	570 - 740	°C
Reference substance	dispersed dust cloud		
Value	>	365	°C
Reference substance	deposited dust		
Auto-ignition temperature			
No data available			
Oxidising properties			
No data available			
Explosive properties			
No data available			
Flammability (solid, gas)			
The product is NOT highly flammable according to Regulation (EG) Nr. 440/2008 , method EC A.10 (flammability, solids)			
Lower flammability or explosive limits			
No data available			
Upper flammability or explosive limits			
No data available			
Vapour pressure			
Value	<	0,01	mbar
Reference temperature		20	°C

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Vapour density			
No data available			
Evaporation rate			
No data available			
Relative density			
No data available			
Density			
Value	2,08	- 2,30	g/cm ³
Reference temperature		25	°C
Bulk density			
Value	70	- 720	kg/m ³
Solubility in water			
Value	<	0,001	g/l
Solubility(ies)			
No data available			
Partition coefficient: n-octanol/water			
No data available			
Viscosity			
No data available			

9.2 Other information

Other information			
Flammability BZ1: not burning (100 °C), source of ignition: glowing platinum wire, 1000 °C approx.			
Impact sensitivity: not impact sensitive			

SECTION 10: Stability and reactivity

10.1 Reactivity

No data available.

10.2 Chemical stability

No data available.

10.3 Possibility of hazardous reactions

No data available.

10.4 Conditions to avoid

No data available.

10.5 Incompatible materials

Fluorine; Chlorine trifluoride

10.6 Hazardous decomposition products

No hazardous decomposition products known.

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute oral toxicity			
LD50	>	2000	mg/kg
Species	rat		
Method	OECD 401		

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Acute dermal toxicity	
No data available	
Acute inhalational toxicity	
No data available	
Skin corrosion/irritation	
Duration of exposure	4 h
Species	rabbit
Method	OECD 404
Evaluation	non-irritant
Serious eye damage/irritation	
Species	rabbit
Method	OECD 405
Evaluation	slightly irritant
Respiratory or skin sensitisation	
No data available	
Germ cell mutagenicity	
No data available	
Reproduction toxicity	
No data available	
Carcinogenicity	
No data available	
STOT-single exposure	
No data available	
STOT-repeated exposure	
No data available	
Aspiration hazard	
No data available	
Delayed and immediate effects as well as chronic effects from short and long-term exposure	
Contact with the skin and eyes may cause mechanical irritation. Inhalation of dusts may irritate the respiratory tract.	

SECTION 12: Ecological information

12.1 Toxicity

Fish toxicity	
No data available	
Daphnia toxicity	
No data available	
Algae toxicity	
No data available	
Bacteria toxicity	
No data available	

12.2 Persistence and degradability

Biodegradability	
Evaluation	not degradable

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12.3 Bioaccumulative potential

No data available.

12.4 Mobility in soil

No data available.

12.5 Results of PBT and vPvB assessment

No data available.

12.6 Other adverse effects

No data available.

12.7 Other information

Other information

Do not discharge product unmonitored into the environment.

SECTION 13: Disposal considerations

13.1 Waste treatment methods

Product

Allocation of a waste code number, according to the European Waste Catalogue, should be carried out in agreement with the regional waste disposal company.

Packaging

Residuals must be removed from packaging and when emptied completely disposed of in accordance with the regulations for waste removal. Incompletely emptied packaging must be disposed of in the form of disposal specified by the regional disposer.

SECTION 14: Transport information

14.1 Transport ADR/RID/ADN

The product is not subject to ADR/RID/ADN regulations.

14.2 Transport IMDG

The product is not subject to IMDG regulations.

14.3 Transport ICAO-TI / IATA

The product is not subject to ICAO-TI / IATA regulations.

14.4 Other information

The product is NOT highly flammable according to Regulation (EG) Nr. 440/2008 , method EC A.10 (flammability, solids)

14.6 Special precautions for user

No data available.

14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code

Not relevant

SECTION 15: Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

EU regulations

Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances

Remarks

Annex I, part 1 + 2: not mentioned. With regard to possibly appropriate decomposition products see Chapter 10.

National regulations

National chemical inventories

EINECS/ELINCS (European Community)	listed	
TSCA (USA)	listed	
DSL/NDL (Canada)	DSL listed	
MITI/ENCS (Japan)	listed	
ECL (Corea)	listed	KE-18101
AICS (Australia)	listed	
IECSC / NEPA (China)	listed	
PICCS (Philippines)	listed	
NZIoC (New Zealand)	New Zealand: not subject to the provisions of the HSNO Act.	

15.2 Chemical safety assessment

No data available.

SECTION 16: Other information

Sources of key data used to compile the data sheet:

EC Directive 67/548/EC resp. 99/45/EC as amended in each case.

Regulation (EC) No 1907/2006 (REACH), 1272/2008 (CLP) as amended in each case.

EC Directives 2000/39/EC, 2006/15/EC, 2009/161/EC

National Threshold Limit Values of the corresponding countries as amended in each case.

Transport regulations according to ADR, RID, IMDG, IATA as amended in each case.

The data sources used to determine physical, toxic and ecotoxic data, are indicated directly in the corresponding chapter.

Department issuing safety data sheet

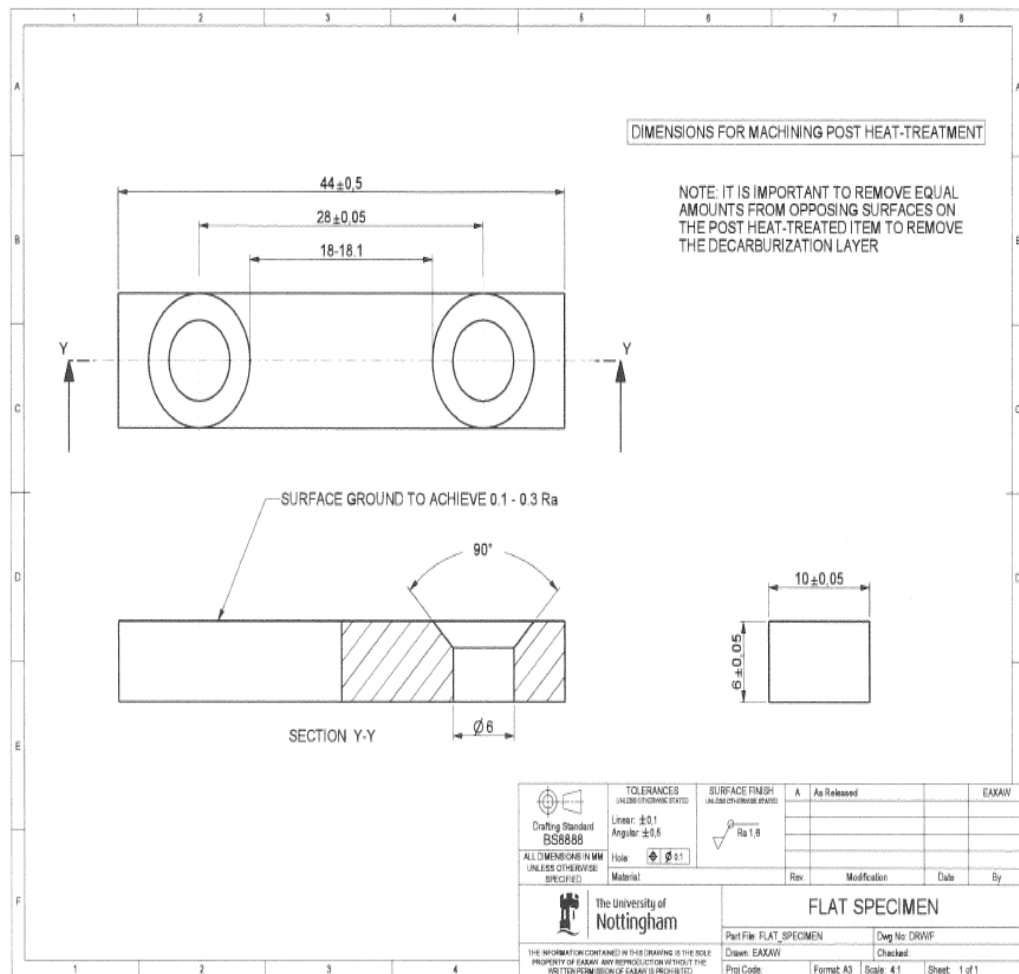
UMCO Umwelt Consult GmbH

Georg-Wilhelm-Str. 183, D-21107 Hamburg

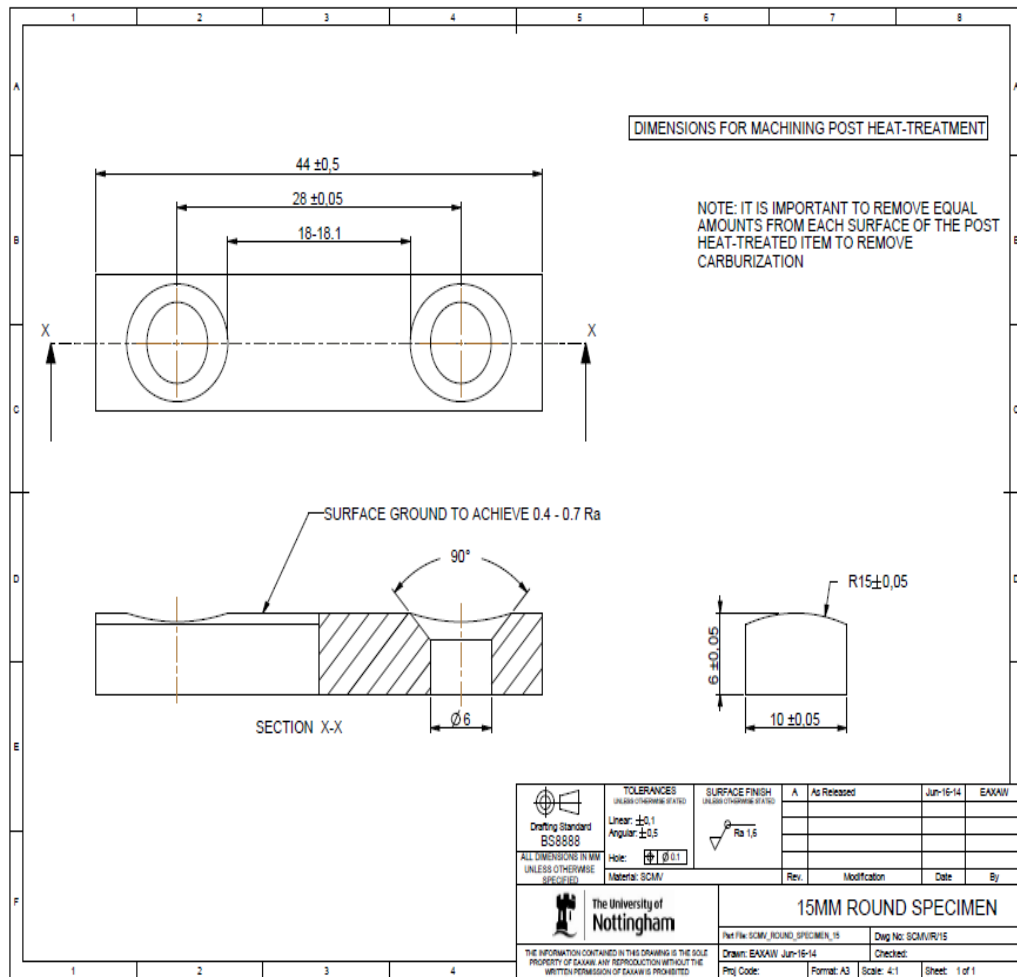
Tel.: +49 40 / 79 02 36 300 Fax: +49 40 / 79 02 36 357 e-mail: umco@umco.de

This information is based on our present state of knowledge. However, it should not constitute a guarantee for any specific product properties and shall not establish a legally valid relationship.

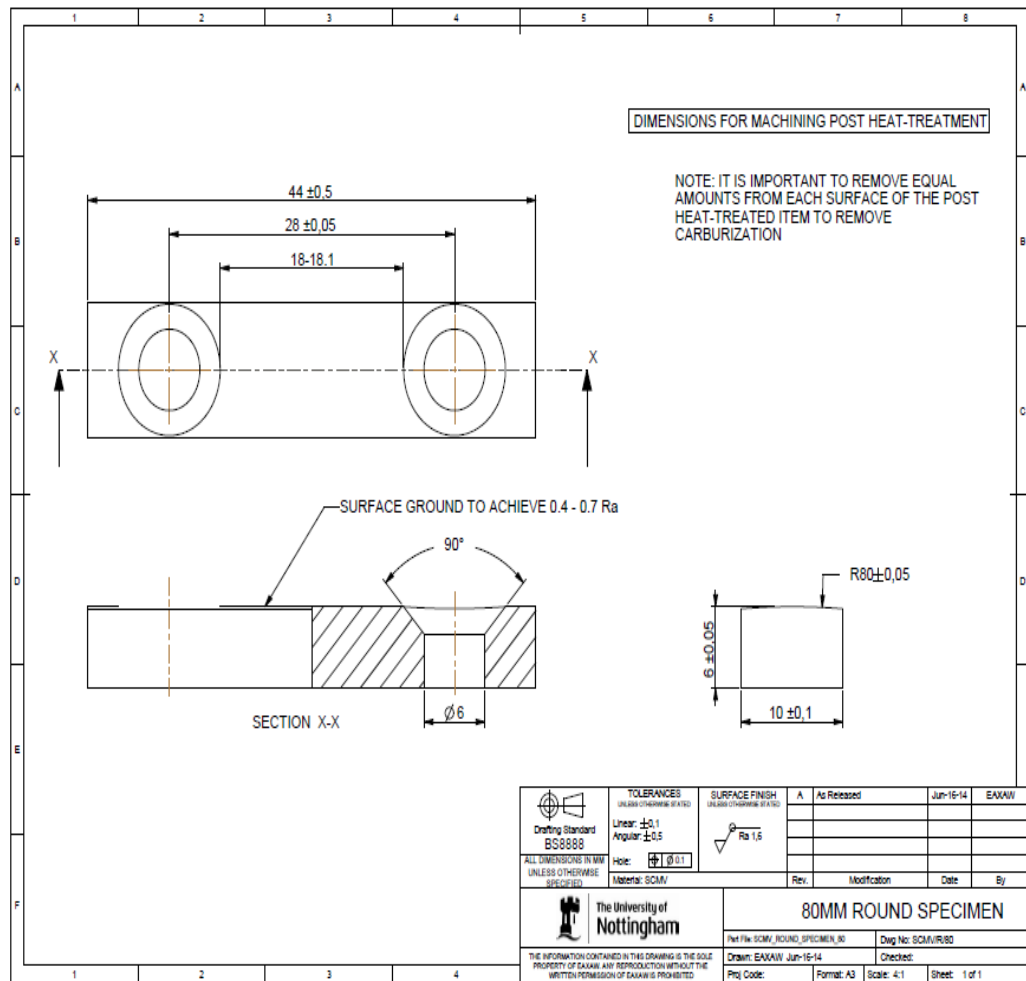
Appendix F : Specimen Drawing



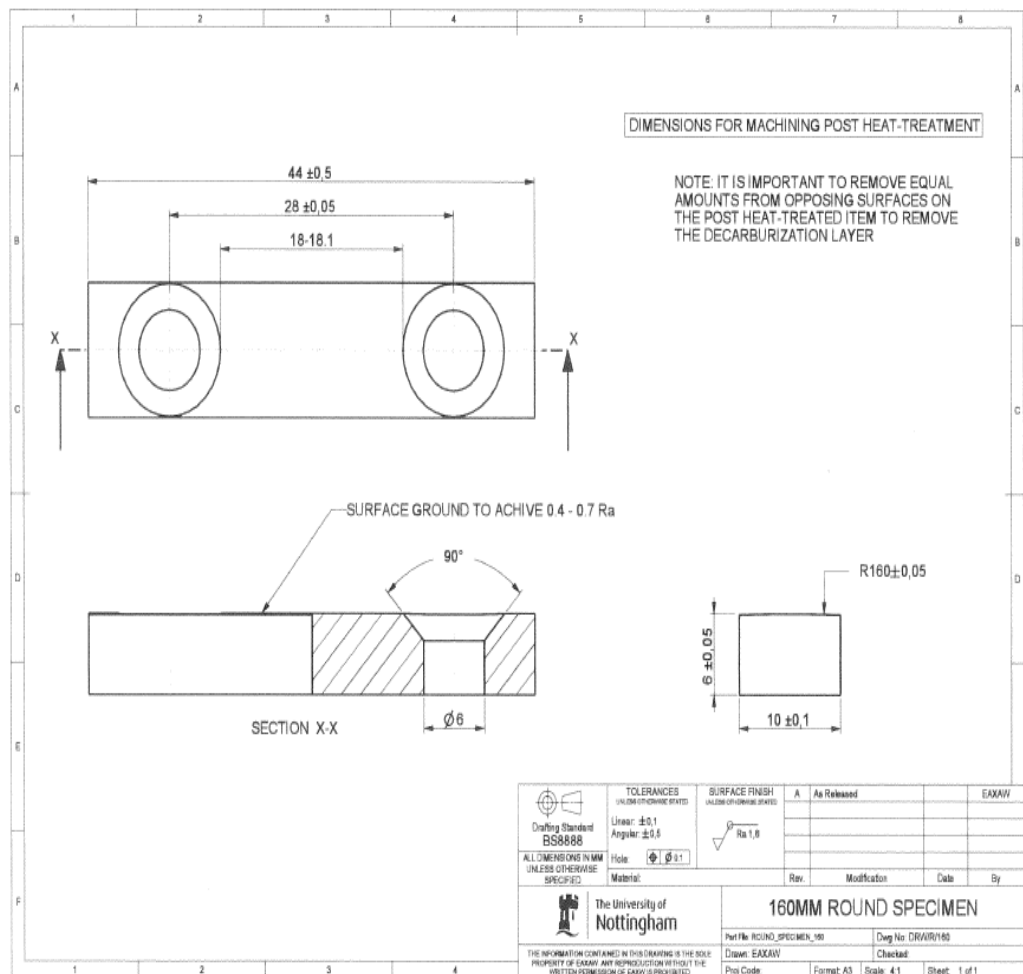
(a) Flat specimen



(c) 15 mm cylinder specimen



(d) 80 mm cylinder specimen



(e) 160 mm cylinder specimen