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**Fabrication, Characterisation and Oxidation
Behaviour of Pt-Based Bond Coats for High
Temperature Applications**

By

Lingyi Qian, MSc

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

2016

Abstract

Over the years, platinum modified aluminide (PtAl) bond coats have been used in high temperature protection systems for commercial aircraft engines to protect turbine blades from high temperature oxidation and corrosion. In the process of operation, the oxidation and rumpling behaviours of the bond coats are the key factors in determining the lifetime of the thermal barrier coating. The latest development in aircraft engines has given rise to the need for bond coats with better oxidation and rumpling resistance at high temperature.

This investigation aims to improve the oxidation and rumpling resistances of general PtAl bond coats by introducing ZrO₂ nanoparticles, Ir and Pd additions: ZrO₂ nanoparticles were incorporated into PtAl bond coats by co-electrodeposition in an attempt to enhance their performance by exploiting the effect of reactive element (Hf, Zr, etc.) oxides. PtAl coatings with and without ZrO₂ nanoparticles were deposited onto three commercially available Ni-based superalloys, namely, Mar-M-247, Mar-M-246 and Inconel 718. Thermal cycling oxidation tests were performed to evaluate the influence of ZrO₂ addition and substrate composition. The addition of ZrO₂ particles to PtAl coatings on Mar-M-246 and Inconel 718 appeared to accelerate the growth of thermally grown oxide and reduced the rumpling of thermally grown oxide. However, when depositing PtAl coatings with ZrO₂ nanoparticles on Mar-M-247, there was no changes, as mentioned above, in thermally grown oxide. Through the analysis of the coatings on different substrates, the interactions among Hf, Al and ZrO₂ have been revealed and clarified,

which offers a better understanding of the reactions of ZrO_2 and the influence of substrate composition on bond coats.

Ir and Pd coatings were deposited by means of electroplating and electroless plating respectively to explore the effects of other platinum group metals. Ir-modified PtAl coatings were investigated on Mar-M-246 with different vacuum annealing durations before the cyclic thermal test, which presented a significant reduction in growth rate of TGO and inward diffusion of Al in the oxidation test. Instead of oxygen diffusion barrier, Ir exhibited a diffusion barrier to Al possibly by forming a high temperature solid solution with Al, which has a higher melting point than general $\beta\text{-NiAl}$ phase. As a result, it restrained the inward diffusion of Al and slowed down the outward diffusion of Al, thus improving the oxidation resistance. In addition, Ir concentration produced an effect on the diffusion barrier of Ir. When it is reduced lower than 15 wt.%, the barrier effect of Ir begins to degrade, which provides a better comprehension of the diffusion barrier effect of Ir. However, Pd-modified PtAl coating did not strengthen oxidation resistance, which may be caused by the phosphorus precipitates generated from the electroless plating process.

ZrO_2 and Pd-modified PtAl bond coats were further investigated with 8 wt.% yttria stabilised zirconia top coat. Comparison between conventional PtAl and high velocity oxygen fuel sprayed NiCoCrAlY bond coats was made as well. Isothermal and cyclic thermal oxidation tests were carried out to evaluate the prepared bond coats. ZrO_2 modified PtAl coating showed the best oxidation and rumpling resistance in cyclic thermal oxidation, while Pd-modified PtAl coating was worse than conventional PtAl coating and better than the

NiCoCrAlY coating. It has been observed that ZrO₂- and Pd-modified PtAl bond coats are affected by different methods of oxidation test. Isothermal oxidation has a greater impact on ZrO₂- and Pd-modified PtAl bond coats. The difference is considered to be a consequence of long term annealing in isothermal oxidation, which leads to a fast grain boundary diffusion of Al.

Publications

1. Lingyi Qian, Fang Xu, K.T. Voisey, Vahid Nekouie, Zhaoxia Zhou, Vadim V. Silberschmidt, Xianghui Hou, "Incorporation and Evolution of ZrO₂ Nanoparticles in Pt-modified Aluminide Coating for High Temperature Applications", Surface and Coating Technologies, Accepted.
2. Lingyi Qian, Fang Xu, K.T. Voisey, Vahid Nekouie, Zhaoxia Zhou, Vadim V. Silberschmidt, Xianghui Hou, "Influence of Iridium on the Oxidation Resistance of Pt-modified Aluminide Coating", Surface and Coating Technologies, In preparation.

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Acknowledgements

I wish to express my deepest gratitude to Dr. Xianghui Hou and Dr. Katy Voisey for their supervision and support throughout my PhD studies. I would like to thank the staff and technicians in the Wolfson Building. Special thanks to Mr Rory Screaton for sample preparations. I would like to thank Dr Fang Xu, Dr Nigel Neate, Mr Martin Roe, Dr Li Guan and Dr Deen Zhang for their kind help in XRD and SEM training and results discussion, and all others who have helped me throughout my study in Nottingham.

A special thank goes to Steven Ding for his time and help and all other friends and colleagues in the Wolfson Building who have made my life in Nottingham enjoyable and unforgettable.

I would also like to take this opportunity to thank the joint PhD studentship between The University of Nottingham and AVIC Commercial Aircraft Engine Co., Ltd. (China) for the research grant and provision of a PhD studentship.

List of Abbreviations

8YSZ	8 wt.% Ytria stabilised zirconia
APS	Air Plasma Spray
BSE	Backscattered electron
CGDS	Columnar grain directionally solidified
CMAS	Calcium–Magnesium–Alumino–Silicates
CTE	Thermal expansion coefficient
CVD	Chemical vapour deposition
DBTT	Ductile to brittle transition temperature
DTS	Desktop spallation
EB-PVD	Electron beam physical vapour deposition
EDX	Energy dispersive X-ray spectroscopy
FIB	Focused Ion Beam
FOD	Foreign object damage
HVOF	High Velocity Oxygen Fuel
IDZ	Inter-diffusion zone
In718	Inconel 718
Ir-PtAl	Iridium modified platinum aluminide
LPPS	Low pressure plasma spray
M247	Mar-M-247
M246	Mar-M-246
MCrAlX	(Nickel, Cobalt, Iron)-Chromium-Aluminium-(Yttrium, Hafnium, Tantalum)
MIDS	Moisture induced delayed spallation

ODB	Oxygen diffusion barrier
OEM	Original equipment manufacturer
PC	Polycrystalline
Pd-PtAl	Palladium modified platinum aluminide
PGMs	Platinum group metals
psi	Pounds per square inch
PtAl	Platinum aluminide or Pt modified aluminide
PTFE	Polytetrafluoroethylene
Pt-ZrAl	Platinum modified zirconium aluminide
REs	Reactive elements
SCDS	Single crystal directionally solidified
SEM	Scanning electron microscope
slpm	Standard litre per minute
SRZ	Secondary reaction zone
TBC	Thermal barrier coating
TEM	Transmission Electron Microscopy
TGA	Thermal gravimetric analysis
TGO	Thermally grown oxide
VPS	Vacuum plasma spray
XRD	X-ray Diffraction
YSZ	Yttria stabilised zirconia
ZrAl	Zirconium aluminide or Zirconium modified aluminide

List of Symbols

ΔH	Activation energy of diffusion
Δc	Concentration change over distance
D	Diffusion coefficient
J	Diffusion flux
r'	Formed oxide density
R	Gas constant
R_p	Maximum peak height of the surface profile
R_t	Maximum height of the surface profile
R_v	Maximum valley depth of the surface profile
T	Temperature in kelvins
t	Time
x	Diffusion distance

Chapter 1 Introduction

Over the past few decades, thermal barrier coating (TBC) technology has grown to be one of the most important and efficient ways to improve the performance of gas turbine engines. The development of advanced gas turbine engines requires higher turbine inlet temperature over 1800K in aero engine applications [1]. Applying TBCs onto the surface of superalloy turbine vanes or foils can protect turbine blades from high operating temperature. Based on modern design procedure of new aero-engines, it is the degree of turbine inlet temperature that is the key to enhancing the performance of gas turbine engines, not the efficiency of aerodynamics [2]. The next generation of aero gas turbine engines will require an even higher turbine inlet temperature, which leads to further demands on innovative thermal barrier coating systems.

The state-of-the-art technologies indicate that TBCs usually consist of three layers, namely, the ceramic top coat, thermally grown oxide (TGO) and the bond coat. The top coat is usually made of ceramics with low thermal conductivities to act as the thermal insulations. The TGO is formed at the interface between the top coat and bond coat as a thin oxide layer during the operation service period. The lifetime of TBC system strongly depends on the thickness growth rate of TGO. Slower growth rate of TGO will increase the lifetime of a TBC system [3]. The bond coat plays an important role in bonding the superalloy substrate and the top coat, because the TGO layer is formed by the oxidation resistant elements in the bond coat. However, bond coat suffers from severe hot corrosion and oxidation in the process of service and usually fails in rumpling and spallation owing to the

formation of TGO in practical applications [4]. Higher turbine inlet temperature requires new TBCs with lower thermal conductivities, and bond coats with stronger oxidation and better corrosion resistance.

The nickel aluminide (NiAl) system has been investigated for many years as a candidate material to be used for bond coats in thermal barrier coating systems because of its high melting point and excellent oxidation resistance [5-7]. Besides simple binary NiAl coating, MCrAlX (M: Ni, Co and Fe. X: Y, Ta, Hf and Si) coatings are utilized to provide both oxidation and corrosion resistances, which are usually fabricated by thermal spray technologies, such as Air Plasma Spray (APS) and High Velocity Oxygen Fuel (HVOF) [8, 9]. Pt-modified aluminide (PtAl) coatings are generally manufactured by diffusion methods, and offer excellent high temperature properties which are more suitable for turbine rotational parts [10, 11].

Reactive elements (REs) and their oxides have been used in MCrAlX bond coats and are reported to improve the oxidation resistance [9]. However, there is a gap in introducing reactive elements into PtAl bond coats as a result of their manufacturing processes, which makes PtAl bond coats more reliable on substrate compositions. Moreover, investigations are only carried out on coating alloys instead of coating itself [12]. In addition, there is an interest in other platinum group metals (PGMs) being used to improve the oxidation resistance of PtAl coating [13, 14]. Ir, which is also regarded as a diffusion barrier candidate, stands out from other PGMs. However, the diffusion barrier effect of Ir has not been reported in coatings other than Ir bulk alloys [15, 16].

This project is aimed at developing Pt-based bond coats with improved oxidation resistance. The objectives of this project are listed as follows: 1) to further reduce the TGO growth rate of PtAl coating; 2) to increase the rumpling resistance of PtAl coating; 3) to investigate the affecting mechanisms of REs and PGMs in PtAl coating and 4) to study the oxidation behaviour of optimised PtAl coatings together with standard top coat (e.g. 8 wt.% Y_2O_3 stabilised ZrO_2).

The modifications of PtAl coatings are accomplished by introducing ZrO_2 nanoparticles and PGMs, such as Ir and Pd. Co-electrodeposition, electroplating and electroless plating methods are used to deposit ZrO_2 nanoparticles, Ir and Pd, respectively. The modified PtAl coatings are evaluated by isothermal and cyclic thermal oxidation tests, as well as in an APS-prepared TBC system. The TGO growth behaviour and rumpling level are calculated by converting TGO layer to pixels and calculated the length and roughness of the pixels. Effects of ZrO_2 nanoparticles and PGMs in PtAl coatings are characterised by SEM and XRD. Detailed discussion is provided to understand the influence of REs and PGMs on TGO growth.

This thesis is divided into seven chapters. The current chapter introduces the basic background, motivation and objectives of the research. Chapter 2 presents the literature review of the background, fabrication technologies, and failure mechanism as well as developments for bond coats. Detailed methodologies including substrates and coating preparations, oxidation tests and characterisations are presented in Chapter 3. Chapter 4 describes the fabrication and oxidation behaviour of ZrO_2 nanoparticle-modified PtAl coating, and discusses the development and oxidation behaviour of ZrAl coatings. The effects of Ir and Pd in general PtAl coating are

discussed in Chapter 5. Chapter 6 studies the capabilities of the prepared bond coats in TBC systems, and Chapter 7 is a summary of the conclusions and future work.

Chapter 2 Literature Review

2.1 Turbofan Aero Engines

Gas turbine engines have been widely used in aircraft, land-based and sea-based engines. In modern commercial aero engines, turbofan engines have been developed to provide the desirable thrust for large airplanes due to the high bypass ratio [17]. Figure 2.1 is a schematic of a typical turbofan engine [18]. It usually consists of four sections: fan, compressors (including low pressure compressors and high pressure compressors), combustion and turbines [17]. The turbines are driven by the exhaust hot gas coming from the combustion chamber to supply energy for the fan and compressors [17]. A typical three-stage turbine is shown in Figure 2.2. The turbine inlet temperature has increased from 1200 ~ 1300 K to 1700 ~ 1800 K in recent years [1]. Further requirements of improving the thermal efficiency of turbine engines have demanded even higher turbine inlet temperatures in the future [17]. In Figure 2.2, the colour indicates the temperature distribution of a turbine. The high pressure turbine blades have the highest temperature and rotation speed in the turbine. The temperature difference between the high pressure turbine and low pressure turbine can be over 500°C [18]. The high pressure turbine is demanded to survive after 10000 h before the first overhaul examination [1].

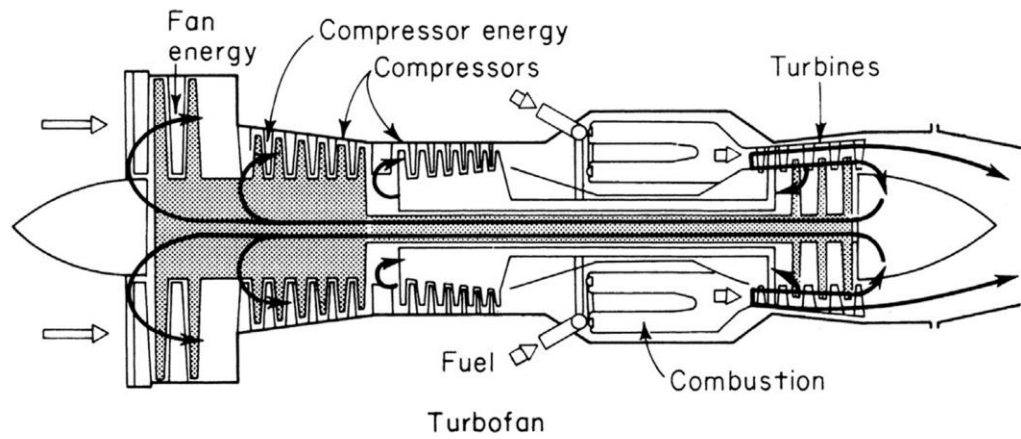


Figure 2.1 Schematic of turbopfan aircraft engine [18].

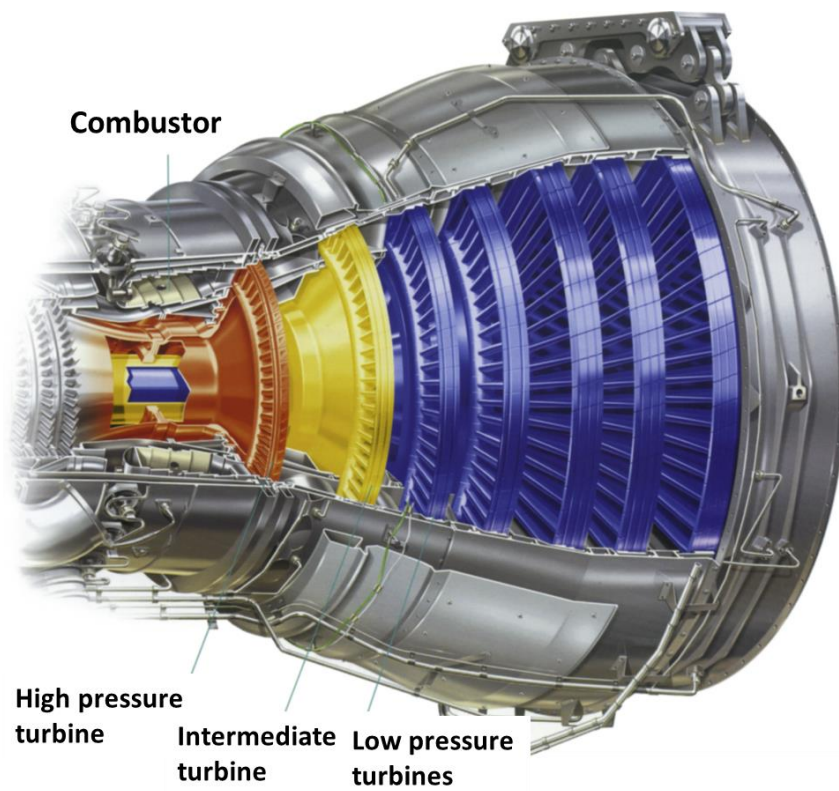


Figure 2.2 Detailed turbine module in turbopfan engine [17].

2.1.1 High Pressure Turbine Blades

The high pressure turbine contains the nozzle guide vane and turbine blade [17], as shown in Figure 2.3. The working conditions of the vane and blade are different. In general, the hot gas coming from the combustion chamber will go through the nozzle guide vane first and is then guided to the turbine blades [17]. Therefore, the vane works at high temperature and suffers from thermal stresses caused by different temperatures between the vane back and trailing edge [1]. The stress can reach $400 \sim 500$ MPa according to the modelled results [19]. The turbine blades operate at lower temperatures than the vane but they are also affected by mechanical stresses, such as tensile stresses caused by centrifugal forces (usually not higher than $200 \sim 250$ MPa) and bending stresses caused by aerodynamic forces [20-22]. Both the vane and blades are also influenced by oxidation and corrosion. In a turbine, the single crystal Ni superalloy blade, the cooling technology and the thermal barrier coating are the three key elements to consider in the design and manufacturing.

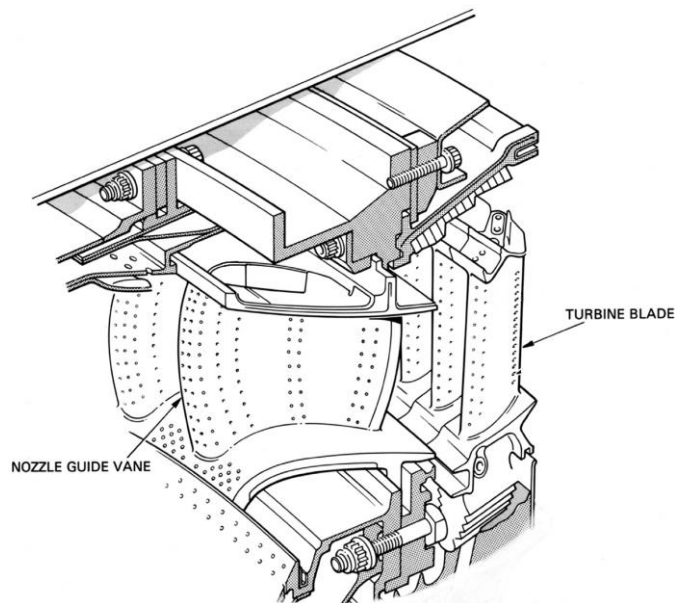


Figure 2.3 Construction of a typical high pressure turbine blade [17].

Ni superalloys are generally used in turbine engines because they can maintain high strength at high temperatures close to their melting point due to the precipitated γ' phase [23]. In practice, investment casting is successfully applied to manufacture superalloy blades [24, 25]. The high working temperature and the centrifugal forces make the creep resistance critical to blade lifetime. The development of crystal structures in cast Ni superalloy blades starts from a conventional equiaxed structure to a directionally solidified structure and then to the single crystal structures used nowadays [17]. High temperature performance of equiaxed and directionally solidified blades are both limited by the grain boundaries because of creeping. However, the blade lifetime can be significantly increased using single crystal Ni superalloy, as shown in Figure 2.4 [23].

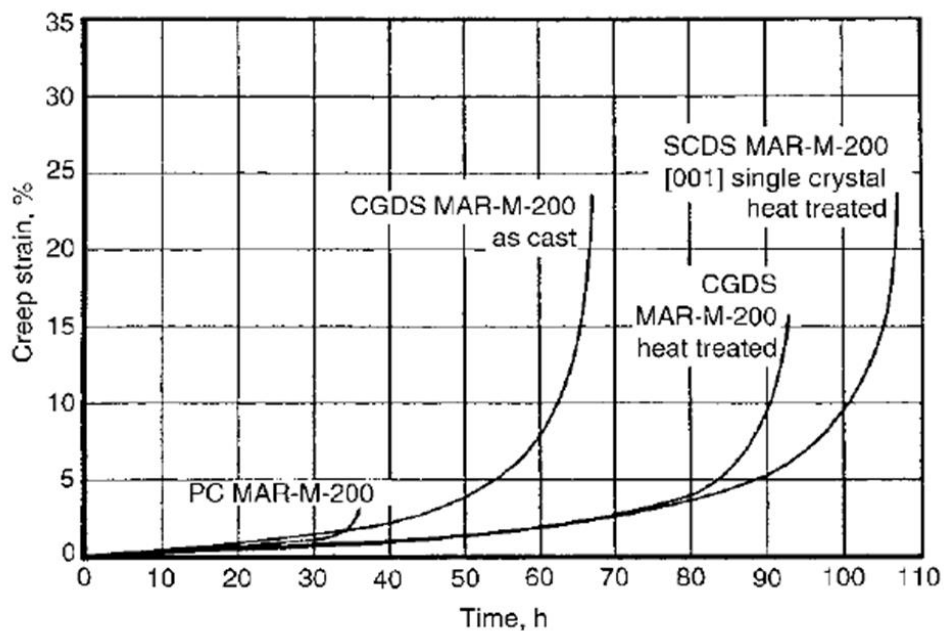


Figure 2.4 Creep behaviour of PC (polycrystalline) cast with longitudinal SCDS (Single Crystal Directionally Solidified) and CGDS (Columnar Grain) MAR-M-200 alloy at 982 °C and 207 MPa [23].

Even though the single crystal Ni superalloy is equipped with high temperature strength, the temperature of the gas entering turbine is still much higher than the allowed working temperature of the alloy, by 300 ~ 400 °C and still increasing in modern aircraft engines [26-28]. Air cooling technology makes it possible to operate the blade and vane in a high temperature environments which exceed the melting points of the turbine materials without affecting their integrity [1]. Multi-pass internal cooling tunnels, and film cooling are designed to achieve the maximum efficiency of cooling air stream in modern turbine blades (Figure 2.5 [29]). The cooling holes are usually manufactured by laser drilling as round or shaped and are carefully designed to reduce the aerodynamic losses caused by film hole injection [30].

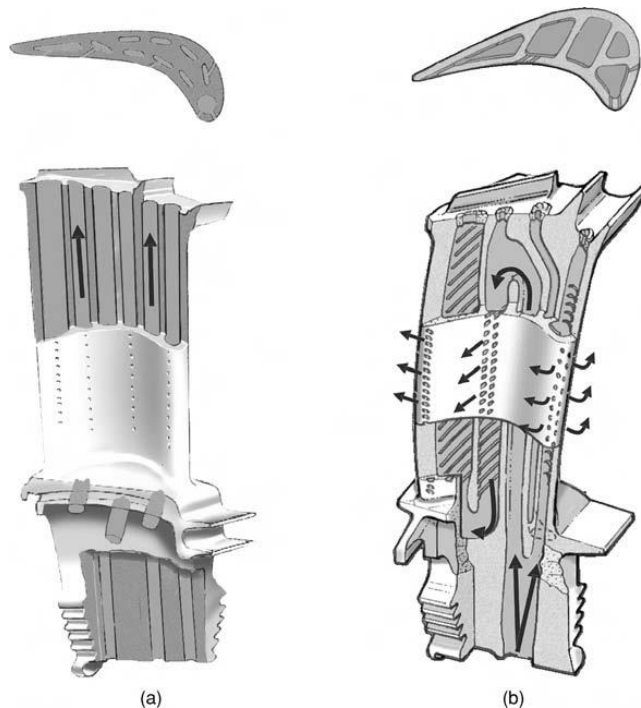


Figure 2.5 Multi-pass internal cooling tunnels and film cooling in modern turbine blades [29].

2.1.2 Thermal Barrier Coating

TBC is used to further improve the performance of turbine blades by providing a low thermal conductivity barrier between the hot gas and the alloy surface [1, 31]. The TBC allows increased turbine inlet temperature without increasing the surface temperature of the alloy [31]. A basic TBC system is shown in Figure 2.6 [31]. The TBC layer is generally deposited by an electron beam physical vapour deposition (EB-PVD) or air plasma spray (APS) [1]. The most commonly used composition of a TBC is Y_2O_3 - ZrO_2 , so called yttria-stabilised zirconia (YSZ). The doped Y_2O_3 not only stabilises the ZrO_2 but also has a similar vapour pressure to ZrO_2 which allows the uniform deposition by EB-PVD [32]. Even though the rare earth oxide doped zirconias (such as Yb_2O_3 stabilised zirconia) have been investigated for possession of lower thermal conductivity, zirconia with 6 ~ 8 wt.% Y_2O_3 is still considered as the optimum material for TBC [32-35].

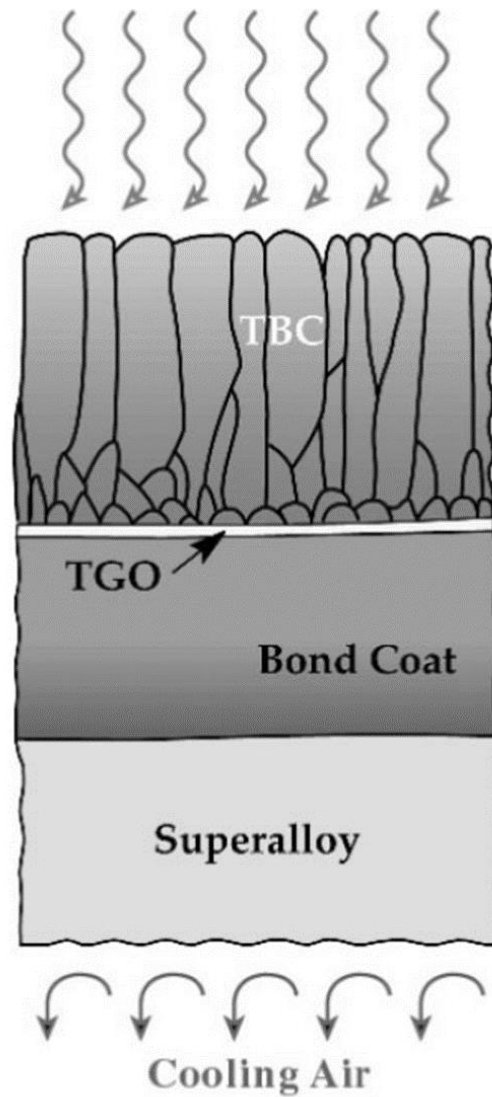


Figure 2.6 Design of thermal barrier coating system [31].

In practice, the TBC is not directly deposited on the alloy surface. A metallic layer is used to protect the turbine blades from oxidation and corrosion at high temperatures due to the high oxygen permeability of YSZ [32]. The metallic layer is called a bond coat (Figure 2.6) which is also used to bind the TBC to the alloy. It builds up a relationship with the TBC via the formation of the thermally grown oxide (TGO). TGO forms at the interface between the TBC and bond coat (as shown in Figure 2.6) during high temperature operation, and the faster growth rate of the TGO can accelerate the failure of the TBC system

[32]. Because the growth of TGO is mainly affected by the oxidation resistance of bond coats at high temperatures, the development of better oxidation resistant bond coats is needed for higher operation temperatures.

2.2 Bond Coats

Bond coats in a thermal barrier coating system should have good oxidation and hot corrosion resistances as well as high temperature stability, good adhesion and satisfactory thermal mechanical properties [36]. To achieve good oxidation and corrosion resistances, the bond coat should have the ability to form a uniform and stable protective scale at high temperatures [37]. In addition, the bond coat should have a high volume of the elements that form protective scales to avoid rapid depletion [37]. A good adhesion between the protective scale and the bond coat is also desired [37]. The bond coats are divided into two families: diffusion coatings and overlay coatings, according to their fabrication methods.

2.2.1 Diffusion Coatings

Diffusion coatings have been developed for many years to protect the alloy substrates from oxidation by enriching the alloy surface with Cr, Al or Si [37]. Chromising was popular in the early 1950s for the protection of low alloy steels [38]. In the 1960s, aluminised coatings were first used to protect turbine engine foils [39]. Siliconising was developed for improving the protection at high temperature in the early 1970s [40]. However, siliconised coatings were dismissed due to their high temperature embrittlement [37]. Diffusion coatings are still being widely applied in turbine blades due to the development of PtAl coatings [37]. These coatings have been licensed to original

equipment manufacturers (OEMs) since 1970 and developed with many variants [37]. The bonding between the diffusion coating and the alloy substrate is based on chemical bonding, usually by forming solid solutions [9]. Therefore, the processing and performance of diffusion coatings are influenced by the alloy substrates.

2.2.1.1 Conventional Aluminide Coatings

Based on the Ni-based superalloys, aluminide coatings were developed not only due to the good oxidation resistance of Al but also the specific solid solution between Al and Ni. Figure 2.7 shows the phase diagram of Ni-Al [41]. The β -NiAl (AlNi in Figure 2.7) phase exhibits the highest melting point among the different phases, which makes it suitable to withstand high temperatures and act as a reservoir of Al for oxidation resistance. The phase diagram also indicates that the β -NiAl phase reaches the highest melting point when the atomic ratio of Ni and Al is around 1:1. In practice, the detected weight percent of Ni in a β -NiAl phase may vary from 63% to 75%.

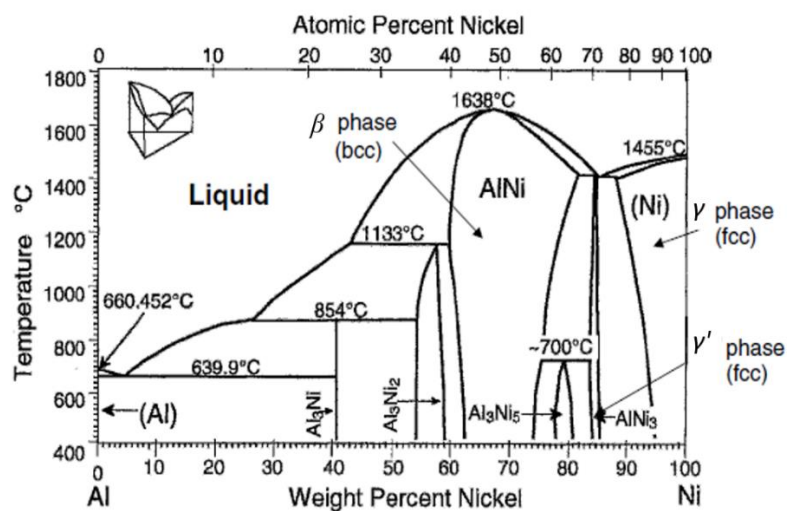


Figure 2.7 Ni-Al phase diagram [42].

Three main methods are used to apply aluminide coatings onto Ni-based superalloys. Figure 2.8 summarises the applications of the three methods, which are above-the-pack process, pack process (including slurry) and chemical vapour deposition (CVD) method [9].

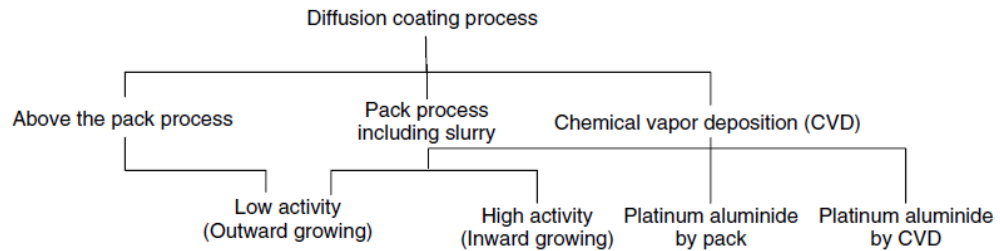


Figure 2.8 General aluminising processes [9].

Pack process is the most basic method being utilised to fabricate aluminide coatings. A typical pack diffusion setup is shown in Figure 2.9 [37]. The components are surrounded by the pack mixture and protected either by Ar or H₂ atmosphere [43]. The powder mixture is made of Al, Al₂O₃ and NH₄Cl, where Al is the element that diffuses into the matrix, Al₂O₃ acts as the stabiliser which can hold Al powder in the mixture, preventing sintering of the Al powder. Ammonia chloride acts as the activator [37, 43]. The main role of the activator is to supply HCl during high temperature decomposition. HCl will react with Al and form AlCl₃ which has a high vapour pressure. The stabiliser could then hold the AlCl₃, leading to the reaction with the Ni matrix [37, 43].

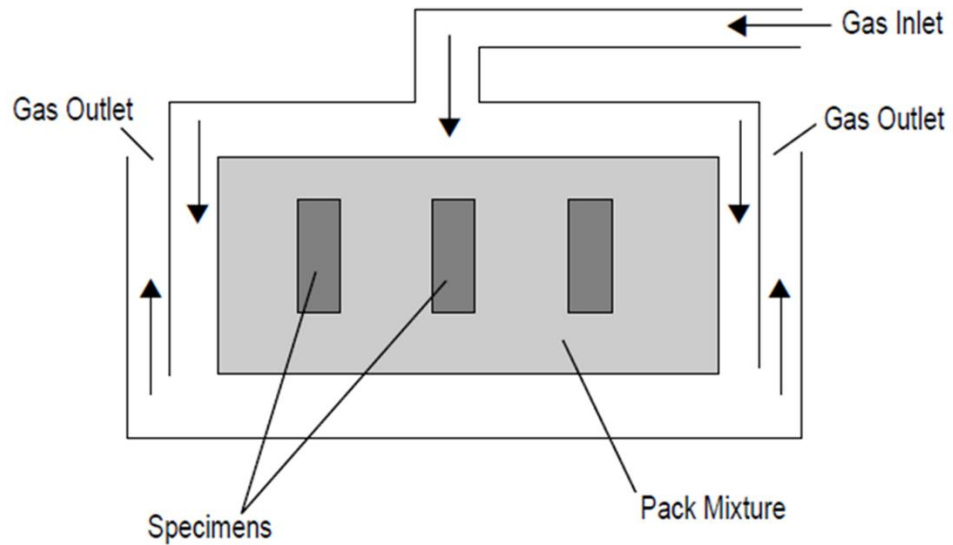


Figure 2.9 Sketch of a typical pack diffusion setup [37].

In a pack diffusion process, two types of diffusion mechanism are well established, which are the low temperature high activity and the high temperature low activity processes. It is reported that the diffusion coefficients of Ni and Al play important roles in different diffusion mechanisms [44, 45]. The prior work reveals that a low activity diffusion mechanism occurs when the diffusivity ratio between Ni and Al is about 3, i.e. $D_{\text{Ni}}/D_{\text{Al}} \approx 3$, and the phase is Ni-rich NiAl with less than 50 at.% Al content. When $D_{\text{Al}}/D_{\text{Ni}} \geq 3$, the main phase tends to be the Al-rich NiAl with around 51.5 at.% Al content [44-47]. The main reactions in the different processes are shown in Figure 2.10. The high temperature low activity aluminising, which usually occurs at $900 \sim 1050^\circ\text{C}$, can form β -NiAl during the reaction. For the low temperature high activity aluminising, because of the high activity of the Al, δ - Ni_2Al_3 phase appears after the aluminising process. The final β -NiAl phase is transformed from the δ - Ni_2Al_3 phase during a heat treatment after the pack diffusion [9]. In addition to the diffusivities of Ni and Al, aluminising temperatures also vary with different

aluminising mechanisms. The low activity aluminising is usually carried out at $900 \sim 1050^{\circ}\text{C}$, whereas the high activity aluminide is performed at $750 \sim 950^{\circ}\text{C}$ [46].

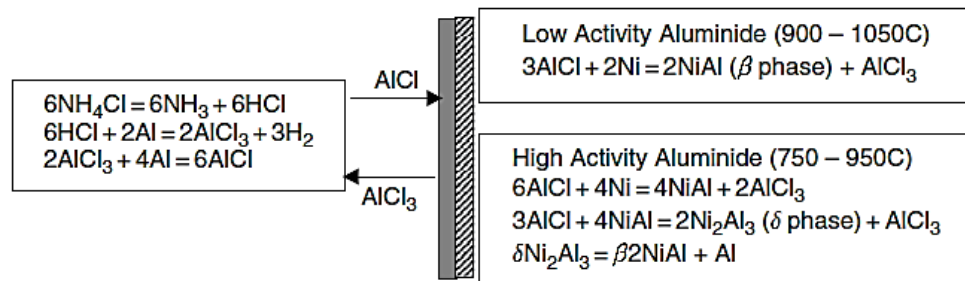
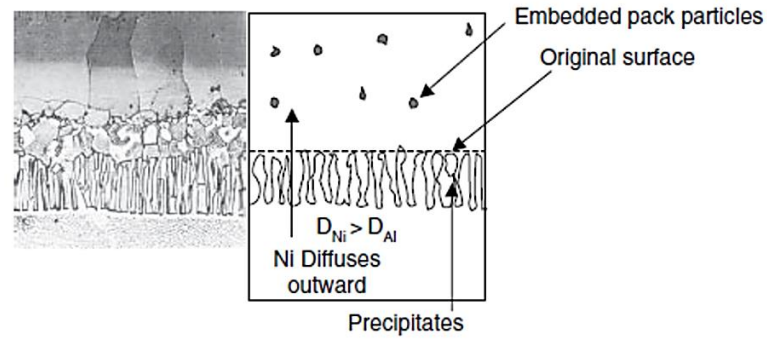
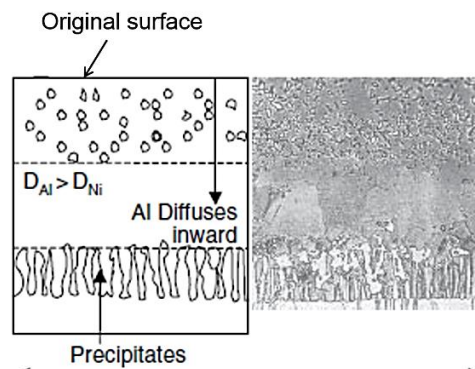


Figure 2.10 Main reactions in two different aluminising processes [9].

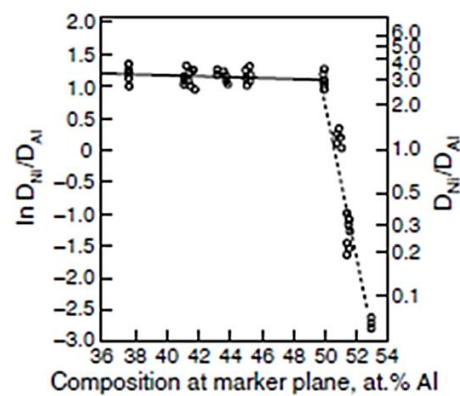
The microstructure of aluminide coatings varies in different processes. Figure 2.11 gives an overview of the low activity and high activity aluminide bond coatings [48]. In the low activity process, Ni diffuses outwards to form the NiAl phase, but Al diffuses inwards to form the same phase in the high activity condition. A new surface is formed in the low activity process by the outward diffusion of Ni, but the original surface remains intact after the high activity process, which is a clear way to distinguish the processes from each other.



(Low Activity)
Outward Diffusion Aluminide
(a)



(High Activity)
Inward Diffusion Aluminide
(b)



(c)

Figure 2.11 Microstructures of (a) the low activity and (b) the high activity aluminide bond coatings. (c) the diffusivity relationships between Ni and Al [48].

Rather than burying the components in the pack diffusion mixture, another pack diffusion process called above-the-pack method is used for aluminising engine parts. Figure 2.12 shows the above-the-pack process [49]. The parts are placed above the powder tray containing the pack diffusion mixtures. Similar to the general pack diffusion, the above-the-pack process also uses AlCl vapour carried by an inert gas to deposit and diffuse Al into the substrates [9]. In general, above-the-pack process is based on the high temperature low activity aluminising method. The main benefit of the above-the-pack process is that not only the surface of the part is aluminised, but also the internal cooling tunnels and cooling holes would also be aluminised to improve the oxidation resistance of parts such as high pressure turbine blades [9]. The surface of above-the-pack is also cleaner than that of the pack diffusion processed parts, because there is no direct contact with the aluminising mixtures [9].

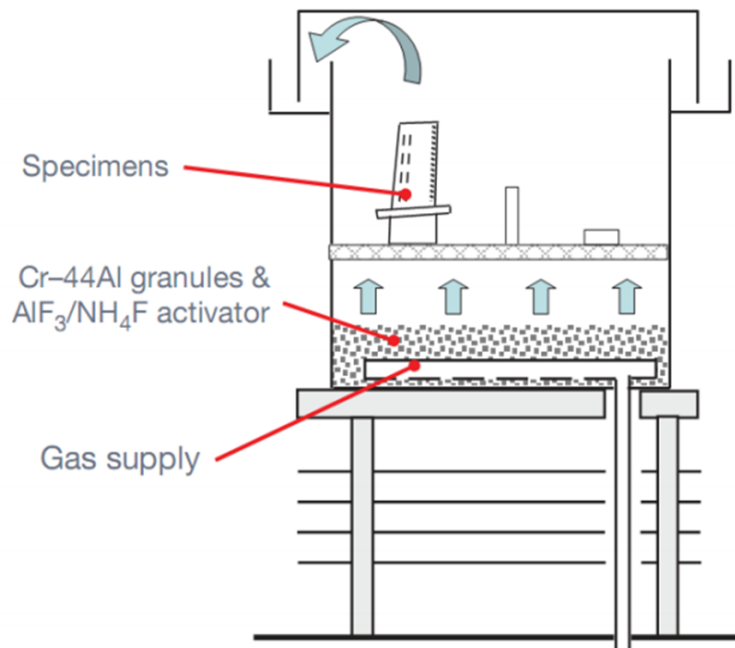


Figure 2.12 An illustration of the above-the-pack aluminising process [49].

As mentioned above, the above-the-pack aluminising process is similar to the general CVD process. However, the AlCl vapour is generated from the external process before being delivered to the reactor chamber in CVD. Figure 2.13 shows the general setup of a CVD. The reactions are shown below [50]:



When HCl or Cl₂ passing through the Al source at around 300°C, it reacts with the Al to form AlCl gas [50]. The AlCl gas is then guided through the external and internal tubes into the reactor chamber. External gases are mainly used to aluminise the outside surface of the parts and the internal gases are designed to aluminise the internal tunnels of the parts. Normally, the reactor chamber is maintained at around 1000°C ~ 1100°C [51]. The CVD process is usually characterised as a high temperature low activity process. In addition, if other elements also need to be deposited or diffused, the external gases can be modified as indicated in Figure 2.13 [51]. Not only the external gases, but also other elements sources such as Si and Hf, will go through the Al source [51]. The CVD in general can produce high quality aluminide coatings on turbine blades, but the equipment cost is higher than that of the pack diffusion process.

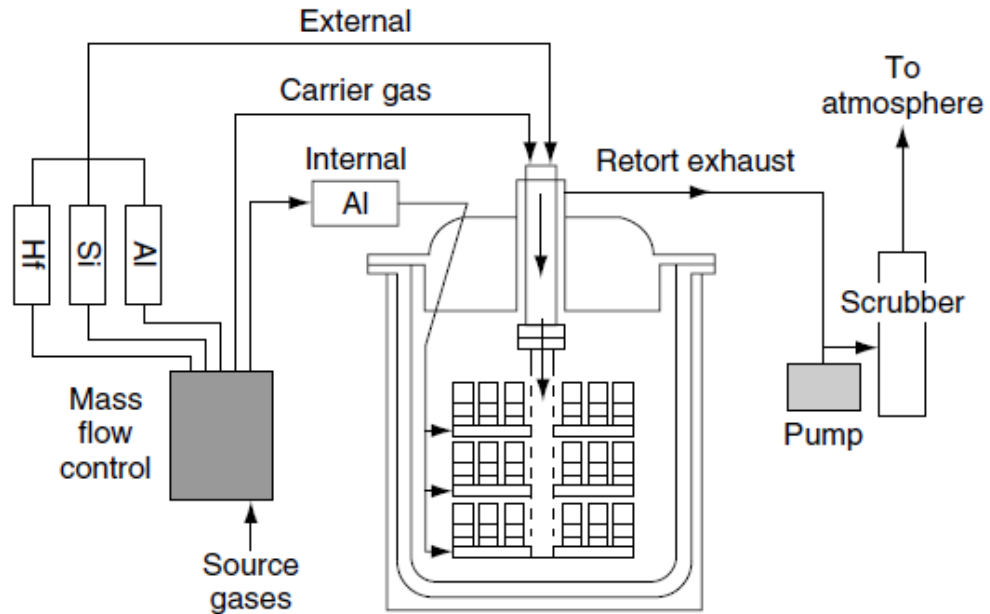


Figure 2.13 The process setup of a chemical vapour deposition [51].

2.2.1.2 Pt-Modified Aluminide Coatings

Pt-modified aluminide (PtAl) coating is widely used as a bond coat in a TBC system to fulfil the high temperature requirements for turbine engine components [52, 53]. Due to the strong chemical bond between the PtAl bond coat and the substrate, PtAl bond coats are suitable for rotating parts such as high pressure turbine blades. The nature of thermal sprayed bond coats makes the MCrAlX bond coats obsolete for this key application [54].

PtAl bond coats include the Pt-modified aluminide coating, i.e. the conventional β -(Ni, Pt)Al coats and the novel Pt-diffused $\gamma + \gamma'$ coats [55-58]. The role of Pt in the coats is mainly to promote the formation of Al_2O_3 pegs which can enhance the bonding strength between the bond coat and the substrate. Meanwhile, Pt can increase the activity of Al and accelerate the diffusion of Al from the bond coat to surface,

which results in good oxidation resistance. Furthermore, Pt can also eliminate the undesirable effects of harmful elements such as Ti, Mo, W and S [5].

In addition to the general aluminising process, the Pt coating is introduced and followed by a heat treatment to diffuse Pt into the substrate before the aluminising process [5]. The Pt coating is generally created by an electroplating method. In practice, Q salt $(\text{NH}_3)_4\text{Pt}(\text{HPO}_4)$ and P salt $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$ are widely used by different aero-engine OEMs to deposit pure Pt coatings [59-61]. Because the aluminising has two different processes (low and high Al activities), the microstructure of Pt-modified aluminide coatings is also divided into two main groups. Figure 2.14 gives an overview of the microstructures of different PtAl coatings. The low activity aluminising process will normally generate a two-layer microstructure, which contains an outer layer and inter-diffusion zone (IDZ). Meanwhile, for the high activity aluminising, an additional intermediate layer can be found between the outer layer and the IDZ.

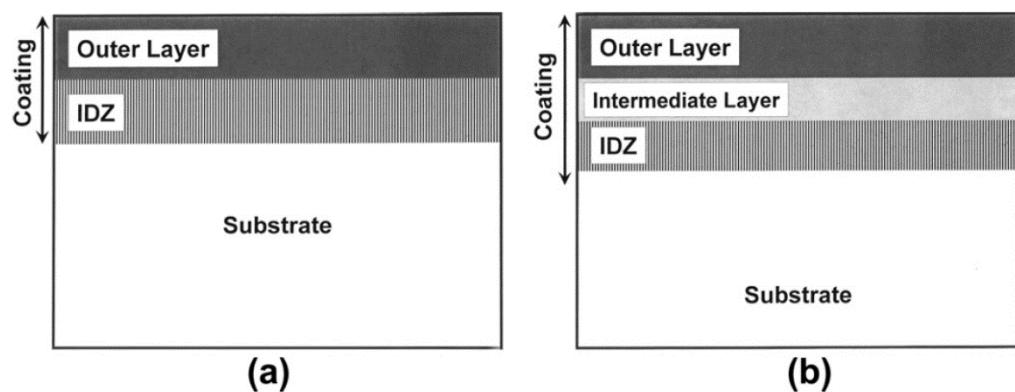


Figure 2.14 Microstructures of Pt-modified aluminide coatings for different aluminising processes: (a) the low activity aluminising process, and (b) the high activity process [62].

In detail, with different heat treatments before and after the aluminising process, the high activity aluminised PtAl coatings have varied microstructures. Figure 2.15a and 2.15d give the microstructure when the outer layer of the substrate is Pt-enriched, and the three layers are ξ -PtAl₂ (outer layer), β -(Ni, Pt)Al (intermediate layer) and IDZ layers, respectively. In addition, Figure 2.15b and 2.15e indicate the microstructure when the Pt is well diffused into the substrate and only the β phase is formed in the bond coat. However, with a moderate diffusion of Pt, i.e. the Pt concentration is slightly higher at the surface, the outer layer is formed by ξ + β phases and the intermediate layer consists of the pure β phase [5]. For the low activity aluminised samples, because the Ni is diffusing outward, the outer layer mainly consists of β phase.

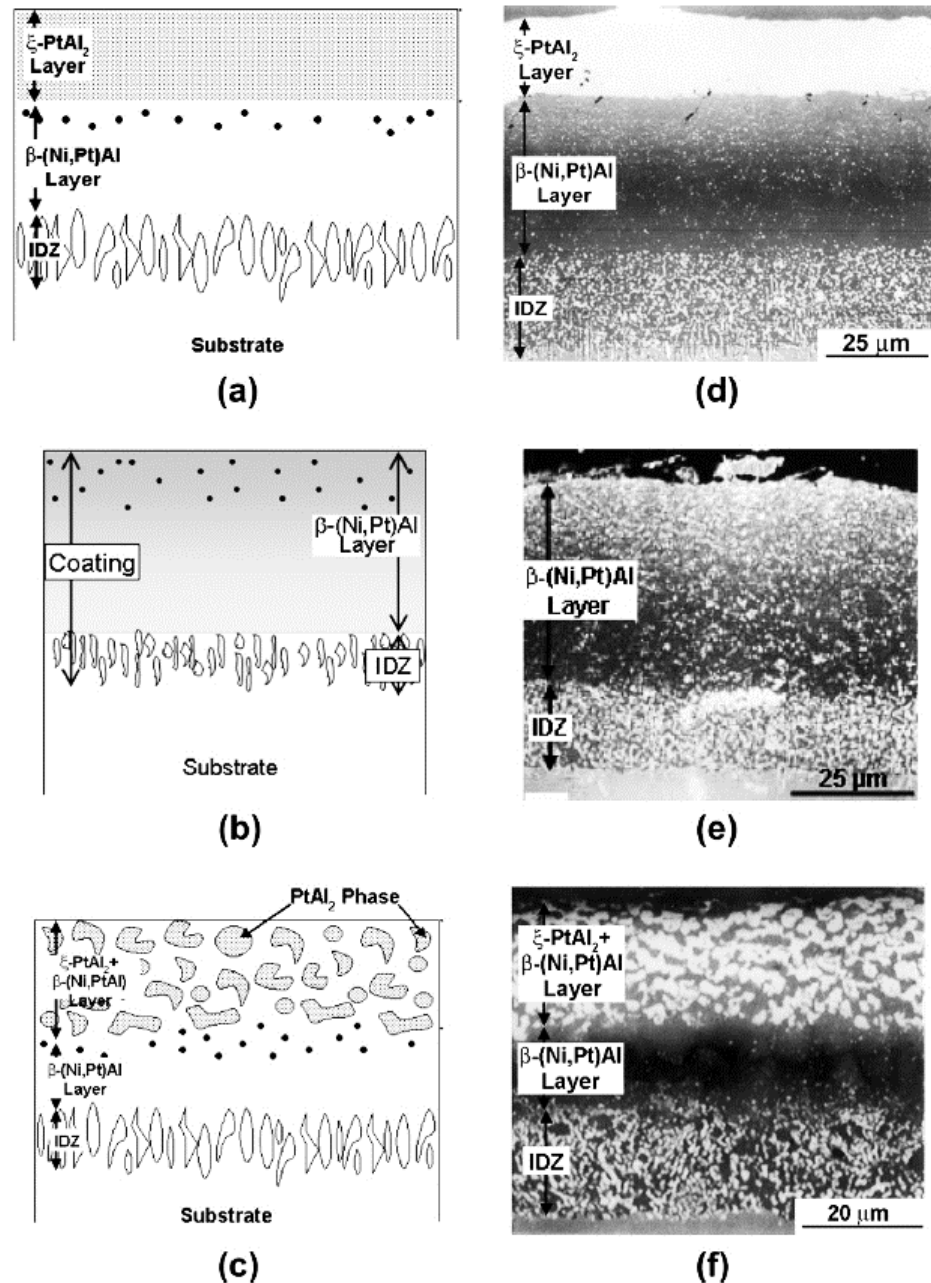


Figure 2.15 Various microstructures of Pt-modified aluminide coatings. (a) and (d) showing the three different layers caused by the high Pt content at the surface; (b) and (e) showing a two-layer structure of a uniformly distributed Pt concentration, and (c) and (f) showing the transition microstructure with a two mix-phased top layer [63-65].

Different from the general PtAl coating, Pt-diffused coating, i.e. Pt-modified $\gamma+\gamma'$ coating, only undergoes two processing steps without the post-aluminising process. The first step is to create Pt coating on

the sample surface and then a diffusion heat treatment is carried out to form the final bond coat. The aluminising process is not involved in the Pt-diffused coating not only for economic reasons but also due to the slow growth rate and uniform growth of the TGO layer [5, 66, 67].

The advantage of Pt-modified $\gamma+\gamma'$ coating is that the low concentration of Al prevents the formation of a secondary reaction zone (SRZ) which is usually caused by the high content of Al and refractory elements in the substrate [68-71]. The driving force for the formation of the SRZ is the inter-diffusion between Al and Ni. When Al is consumed by the inward diffusion, the oxidation resistance of the bond coat is reduced [62, 72]. The Pt-modified $\gamma+\gamma'$ coating is reported to have a good compatibility with the substrate. In addition, the oxidation resistance of the Pt-modified $\gamma+\gamma'$ coating is well-maintained at high temperatures compared with the PtAl coating [73, 74]. The typical microstructures of aluminide coating and the Pt-modified $\gamma+\gamma'$ coats are shown in Figure 2.16. It is clearly revealed that the SRZ has a thickness of around 50 μm in a conventionally aluminised coating (Figure 2.16a), but no SRZ is found in the Pt-modified $\gamma+\gamma'$ coating (Figure 2.16b, zone 1 represents the outer layer of the bond coat and zone 2 refers to the inter-diffusion zone).

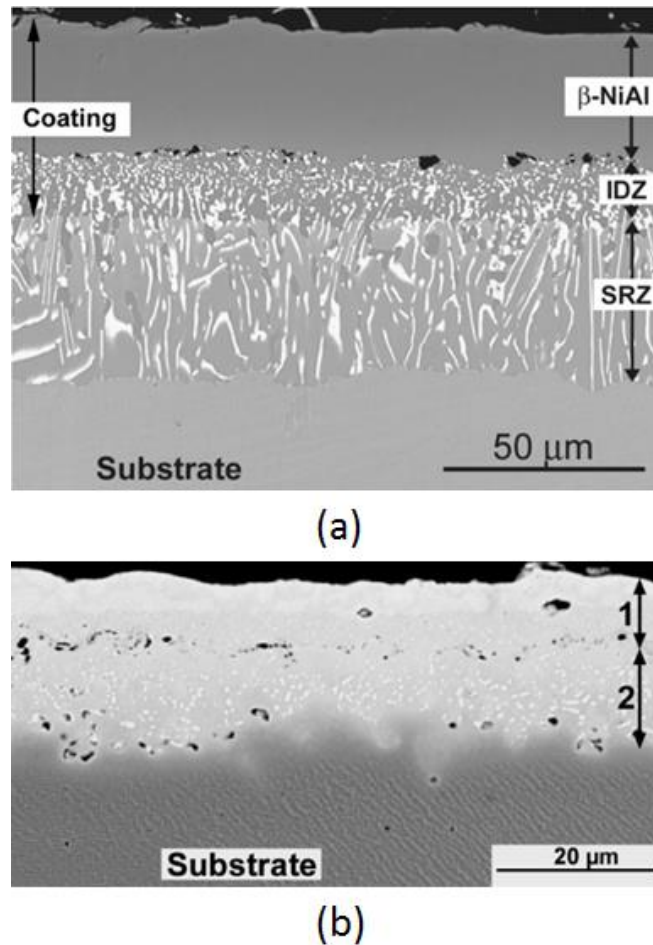


Figure 2.16 (a) The microstructure of an aluminide coating after thermal cycling showing the SRZ; (b) The microstructure of a Pt-diffused coating containing no SRZ [68, 75].

2.2.2 Overlay Coatings

Overlay coatings have been developed as a new generation bond coat to replace the early generations of aluminide bond coat [9]. The first overlay coating (Co-25Cr-14Al-0.5Y) was reported in 1970 [76]. Overlay coatings have custom compositions which are independent of the alloy substrates. This makes it possible to design overlay coatings for different applications with great flexibilities [32].

Modern overlay coatings are designed based on the MCrAlX system [37], where M is the metallic base element and X refers to other elements in the system. The composition of M varies with different superalloy substrates, but is usually selected from elements which have similar properties with the substrates. Modern superalloys are mainly Fe-based, Ni-based and Co-based [23], so these three elements are the best ones to be chosen to make up M composition. FeCrAlX bond coats can only be used under 700°C, which it is not suitable for aero engine applications [9]. NiCrAlX bond coats can be operated at temperatures above 900°C and have good hot corrosion resistance and high temperature plasticity properties. However, NiCrAlX bond coats are sensitive to sulfur corrosion which limits their applications in watercraft gas turbine engines. CoCrAlX bond coats have lower operating temperatures but good resistance to sulfur corrosion compared with the NiCrAlX bond coats. Therefore, NiCoCrAlX bond coats offer combined optimum benefits of NiCrAlX and CoCrAlX bond coats [77, 78].

The essential compositional elements in the MCrAlX system are Al and Cr, which are added to provide high temperature oxidation and hot corrosion resistance [77]. Figure 2.17 summaries the general roles of the Cr and Al contents. Cr is responsible for corrosion resistance at relatively low temperatures (650 - 900°C) and Al generally improves the high temperature (above 900°C) oxidation resistance by forming Al_2O_3 [77, 79]. Cr and Al are added together to promote the benefits of each. It has been reported that the Cr_2O_3 can help to raise the hot corrosion resistance of Al_2O_3 in bond coat [79]. Furthermore, Cr_2O_3 can increase the activity of Al and prompt the formation of Al_2O_3 at a relatively lower Al concentration levels by consuming O atoms to decrease the partial pressure of oxygen [79]. This can avoid the

brittleness of the bond coat as a consequence of high Al content. Cr can also boost the transition from θ - Al_2O_3 to α - Al_2O_3 to make the Al_2O_3 layer more stable. However, high concentrations of both Cr and Al will be harmful to the bond coat. High Cr content will lead to the precipitation of α -Cr which decreases the corrosion resistance, while high Al concentration can increase the ductile to brittle transition temperature (DBTT), which may lead to the bond coat failure in a short service period [77]. In practice, the content of Cr in MCrAlX coating is usually 15 ~ 35 wt.% and the concentration of Al is commonly controlled to less than 10 wt.% [77, 79].

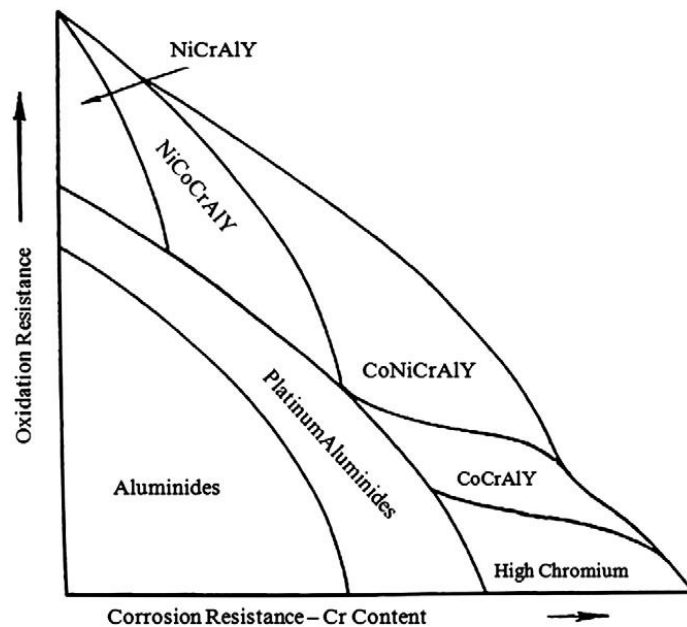


Figure 2.17 Al and Cr concentrations vs the oxidation and corrosion resistances of the alloys [80].

The X element in MCrAlX bond coats is usually chosen from Y, Hf and Ta [9]. A small amount of Y addition can improve the bonding strength of the oxide layer, which helps to prevent the spalling failure of the whole TBC system. The benefits of Y are attributed to its large atom size and high attraction to oxygen. Y acts as pegs to the oxide layer,

therefore strengthening the adhesion between the bond coat and TGO [77]. Hf has similar effects to Y, and is reported to have better properties than Y [81-84]. Ta is another choice in MCrAlX bond coats, but the benefits of Ta vary with its content [85]. Further investigations should be carried out to study the principles of Ta influences [86, 87]. Similar to Y and Hf, oxygen reactive elements such as Zr, Sc, La and Ce are also useful additive elements to MCrAlX bond coatings [9]. The oxygen reactive elements can also trap the S, which prevents the undesirable segregations at the coating interfaces and strength reduction of the bond coatings [88].

Overlay bond coats can be deposited by Electron Beam Physical Vapour Deposition (EB-PVD), Air Plasma Spray (APS), Vacuum Plasma Spray (VPS) or Low Pressure Plasma Spray (LPPS), and High Velocity Oxygen Fuel (HVOF) spray. Microstructures and properties of overlay bond coats vary with different thermal spray technologies.

2.2.2.1 Electron Beam Physical Vapour Deposition

The early overlay coatings were deposited by an electron beam physical vapour deposition (EB-PVD) [76]. Though EB-PVD plant has high capital costs, overlay coatings deposited by EBPVD are still considered as the commercial standard against other methods [37]. The typical equipment set up of EB-PVD is shown in Figure 2.18 [89]. During the operation, the electron beam will evaporate the ingot into vapour and the vapour will be deposited on the work piece surfaces. The general working pressure for depositing MCrAlY bond coats is around $10^{-2} \sim 10^{-4}$ Pa [90]. Specimens are generally preheated in a vacuum to $800 \sim 1100^{\circ}\text{C}$, and are rotated during the deposition process to achieve uniform coatings [91]. A typical EB-PVD prepared CoCrAlY coating is shown in Figure 2.19 [37]. The high deposition

temperature leads to a fast diffusion rate resulting in dense coating microstructure.

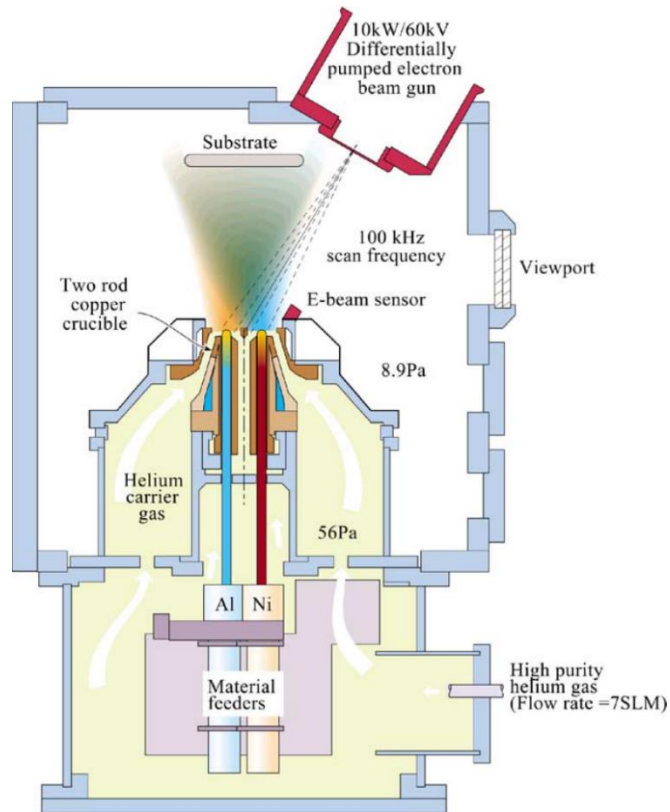


Figure 2.18 A schematic of the EB-PVD setup for overlay coatings. A single electron beam can scan across four metal sources, which are used to build up the four main compositions in the MCrAlX coating system [89].

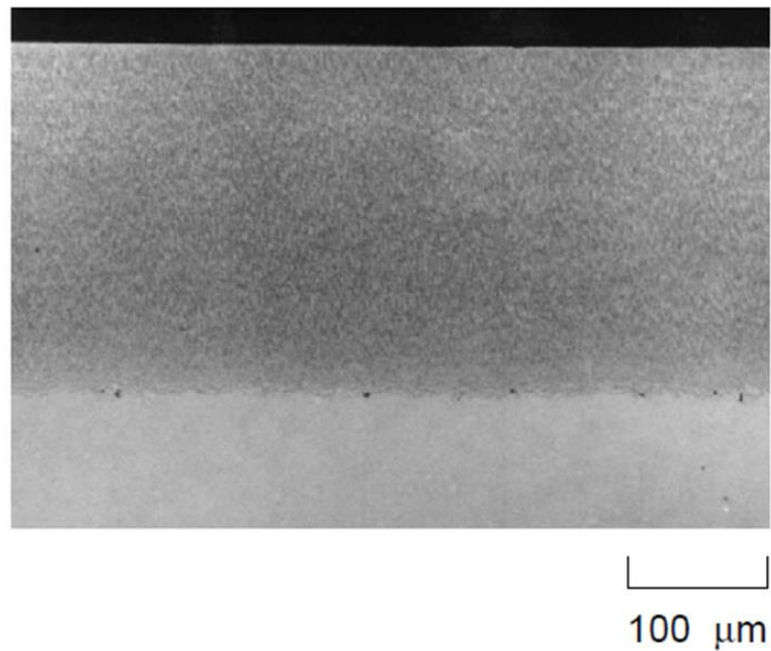


Figure 2.19 SEM image of the microstructure of an EB-PVD prepared CoCrAlY coating [37].

2.2.2.2 Air Plasma Spray

Air Plasma Spray (APS) is the most common process in thermal spray technologies. The plasma spray technology can be traced back to the 1960s, when the process of plasma spray was firstly patented in 1960 and 1962 by Giannini, Ducati and Gage et al [92]. The basic concept of plasma spray is to utilise the heat generated from the recombination of electrons and ions to melt the powders and then the melt is sprayed onto the surface of components [93]. In order to generate the electrons and ions, a strong electric field is used to ionise the gas [93]. Ar is the general gas used to generate the plasma. Other mixed gases like Ar+ H₂, Ar+ He and Ar+N₂ can also be used. Commercially, a ternary gas mixture is often used to obtain the plasma, stated as Ar+He+H₂ or Ar+He+N₂ [92].

Figure 2.20 illustrates the sketch of a plasma torch which is used to generate the plasma and spray the coating [92]. The anode is made of Cu and the cathode is made of thoriated tungsten. The cathode and anode are connected through the cooling water outlet and inlet tubes. The inlet gas is heated up through the electrical field and forms a jet through the nozzle. A normal gas flow rate is about 40 ~ 50 slpm (Standard Litre Per Minute). The coating powders are delivered by the powder feeder, melted in the gas jet and sprayed on to the substrate surface [92].

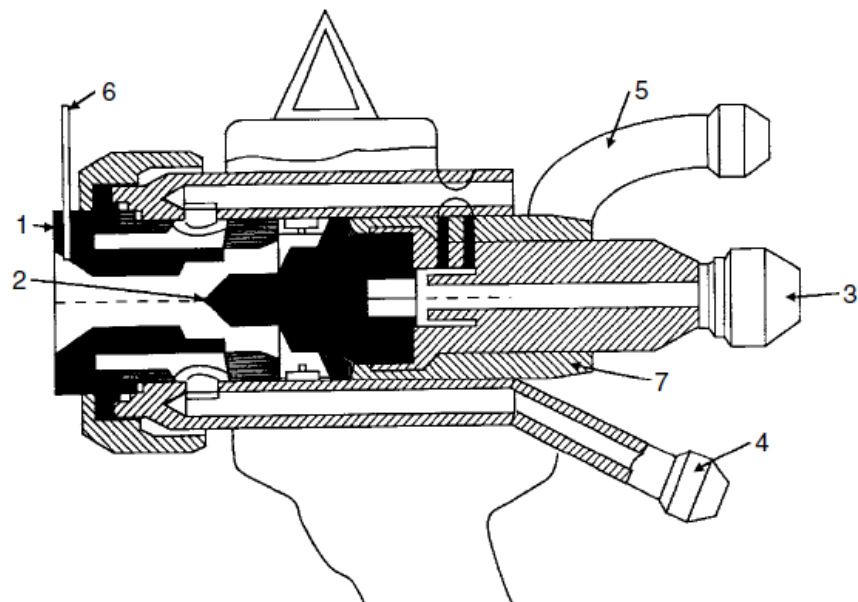


Figure 2.20 A typical plasma spray gun consists of :1) electric anode; 2) electric cathode; 3) cooling water outlet tube; 4) cooling water inlet tube; 5) work gas tube; 6) powder feeder; and 7) insulator [92].

The microstructure of an air plasma sprayed coating usually contains voids, un-melted particles and oxide inclusions. Figure 2.21 shows a typical microstructure of an APS sprayed coating, where the voids and oxides are clearly revealed inside the coating. These voids and oxide inclusions are harmful to the strength of metallic coatings working at

high temperatures [9]. Because of the defects in APS sprayed bond coats, vacuum plasma spray (VPS) or low pressure plasma spray (LPPS) is developed to optimise the coating microstructures [37].

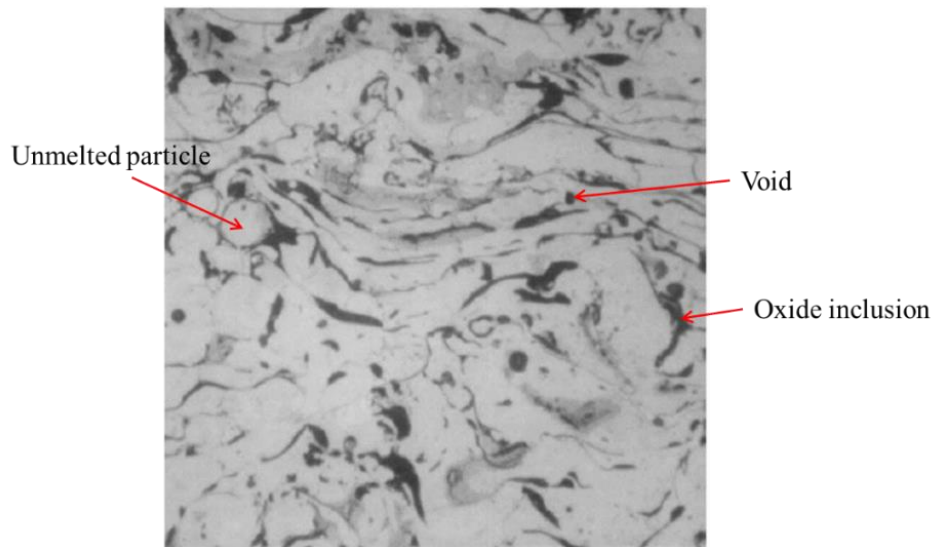


Figure 2.21 A typical microstructure of the APS sprayed NiAl coating. The un-melted particles, voids and oxide inclusion can be observed in the microstructure [93].

2.2.2.3 *Controlled Environment Plasma Spray*

To reduce and eliminate the defects in APS sprayed coatings, a controlled environment plasma spray is investigated to manufacture metallic bond coats. The basic concept of the controlled environment is to use inert gas or vacuum to protect the melted coating powders from oxidation [93].

The vacuum plasma spray (VPS) or the low pressure plasma spray (LPPS) is a method of controlled environment plasma spray, which was first reported in 1973 [9, 92]. Different from APS, the VPS process is operated in a vacuum chamber. The working pressure for VPS is generally between 0.2 and 0.5 mbar, and the low pressure on

the other hand gives a better plasma jet length [9, 94]. Figure 2.22 provides a comparison of the plasma jet length with varied pressures. With a long plasma jet length, the coating particles could be fully melted before they hit the component surfaces. In addition, the long plasma jet will boost the particles and gives them a higher velocity than that of APS. With long plasma jet, the coatings manufactured by VPS or LPPS have fewer voids, can even be porosity free, with stronger bonding strength than those applied by APS [9]. Figure 2.23 shows a typical microstructure of the vacuum plasma sprayed coating. It can be seen that the oxide inclusions and voids are significantly reduced. Even though the equipment cost is the drawback of VPS or LPPS process compared with APS, it has been used for applying bond coats on the turbine engine parts [9].

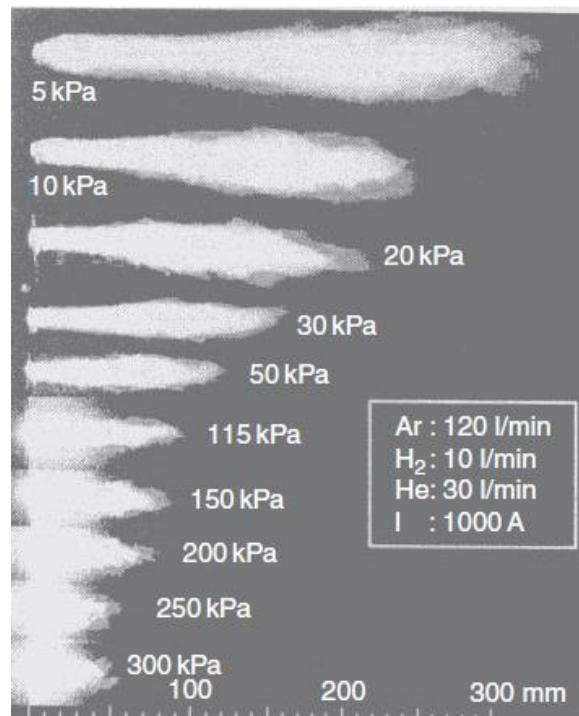


Figure 2.22 The plasma jet length varied with different pressures [94].

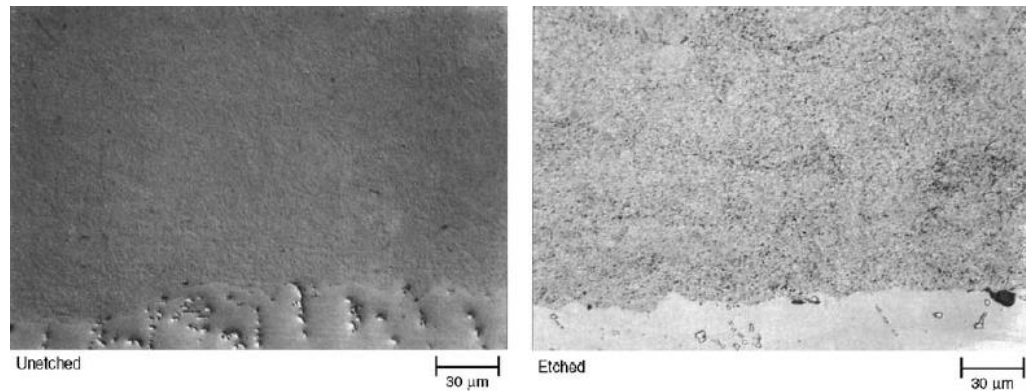


Figure 2.23 The typical microstructures of the vacuum plasma sprayed MCrAlY coating before (left) and after (right) etching [93].

2.2.2.4 High Velocity Oxygen Fuel Spray

The High Velocity Oxygen Fuel (HVOF) gun has been developed for more than 30 years since its first invention in late 1970s [92, 95]. A typical HVOF torch is shown in Figure 2.24. The fuel and oxygen are mixed in the combustion chamber, and ignited by the ignition generator. The exhaust gas is then accelerated by the nozzle flow to the barrel. The powder is fed and mixed with the exhaust gas and sprayed on the part surface [92]. Normally, the gas temperature of HVOF is lower than that of the plasma spray, around 1650 ~ 2760°C depending on the fuel [9]. The exhaust jet can reach a high speed of 2000 m/s [96]. Because the coating powders have a high speed, they will go through the flame in less time compared with APS, which means less oxidation caused by the combustion [37]. In addition, the high speed jet also provides powders with high kinetic energy, which would produce a dense coating (less porosity) during spraying [37]. Hydrocarbon gases, such as propylene (C_3H_6), and hydrocarbon liquids, such as kerosene, are usually used as fuel for HVOF [92].

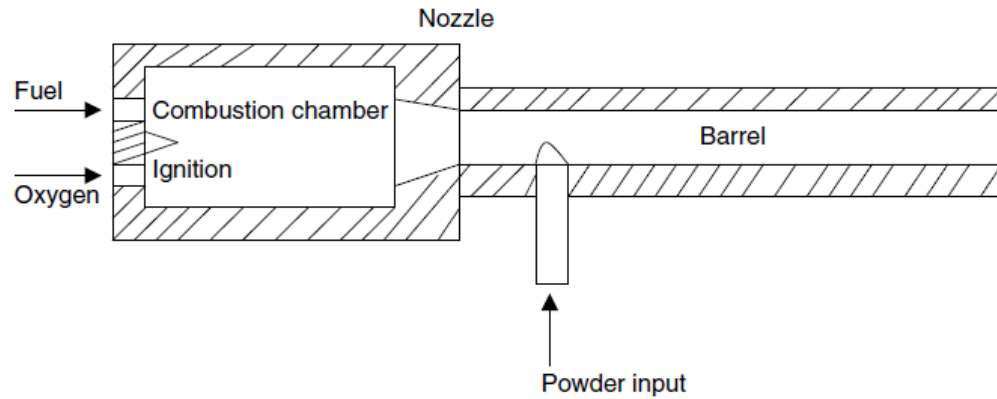


Figure 2.24 A typical structure of the HVOF torch [92].

A typical microstructure of an HVOF sprayed bond coat is shown in Figure 2.25. Both voids and oxide inclusions are reduced in the HVOF sprayed coating [97]. The HVOF can produce bond coats with low porosity ($<2\%$) and low oxide content ($<2\%$), which are closed to those of the LPPS or VPS [9], while the capital cost of HVOF is much lower than LPPS or VPS.

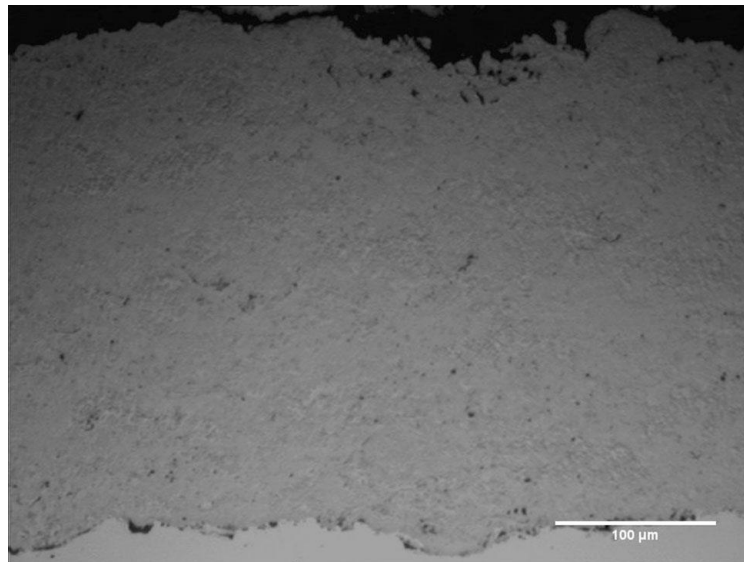


Figure 2.25 A microstructure of the HVOF sprayed NiCoCrAlY bond coat [97].

2.3 Oxidation Behaviour of Bond Coats

Investigations on the oxidation behaviour of bond coats are usually carried out by isothermal or thermal cyclic oxidation tests. The oxidation resistance of the bond coats is evaluated by the growth rate of thermally grown oxide (TGO). In practice, the growth behaviour of TGO is determined by measuring the thickness of TGO or weight changes of samples during the oxidation test [98].

During an isothermal oxidation, the oxide growth mainly depends on the diffusion of elements through the oxide scale because of the long dwell period at high temperatures [9]. Therefore, a parabolic growth behaviour of the TGO layer is derived from Fick's law $J = -D \, dc/dx$. The derived equation is described as below:

$$x^2 = 2D \, \Delta c \, t / r' \quad (2.4)$$

where x is the diffusion distance, Δc is the concentration change over distance x . t is time and r' is the formed oxide density. x can be considered as the thickness of the formed TGO. Meanwhile, the diffusivity coefficient D is influenced by the reaction temperature. The equation is given as:

$$D = D_0 \exp (-\Delta H/RT) \quad (2.5)$$

where D_0 is a constant, ΔH is the activation energy of diffusion, T is the temperature in kelvins, and R is the gas constant.

Figure 2.26 shows the parabolic growth behaviour of the MCrAlX bond coats in an isothermal oxidation [99]. However, a different growth behaviour is usually found at early stages of oxidation. At the

beginning of the oxidation, a protective oxide scale is not formed, the growth of TGO mainly depends on the reaction between oxygen and metallic elements [9]. Thus a linear growth behaviour of the TGO layer is observed. In practice, the growth behaviour of the TGO layer shows a linear behaviour at early stages of oxidation which is followed by the parabolic growth. Figure 2.27 shows a mass gain result of the HVOF sprayed bond coats obtained from the thermal gravimetric analysis (TGA) at 1000°C [98]. It is observed that when the samples are heated up to 1000°C, a dramatic growth of the TGO is observed in the first 100 min then followed by the parabolic growth.

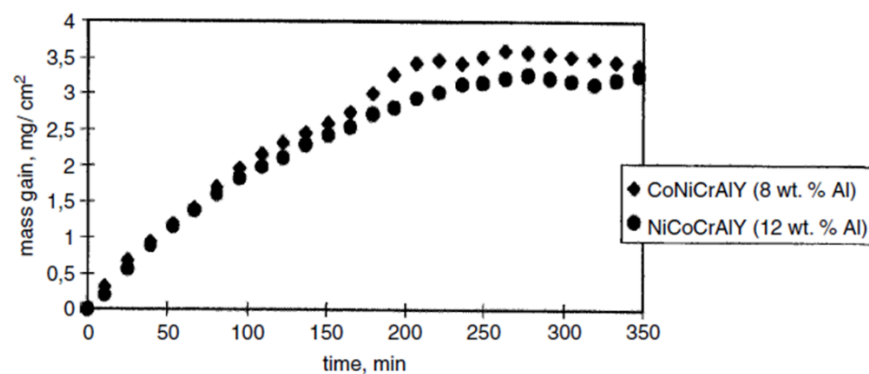


Figure 2.26 The parabolic behaviour of mass gain in an isothermal oxidation test on CoNiCrAlY and NiCoCrAlY coatings [99].

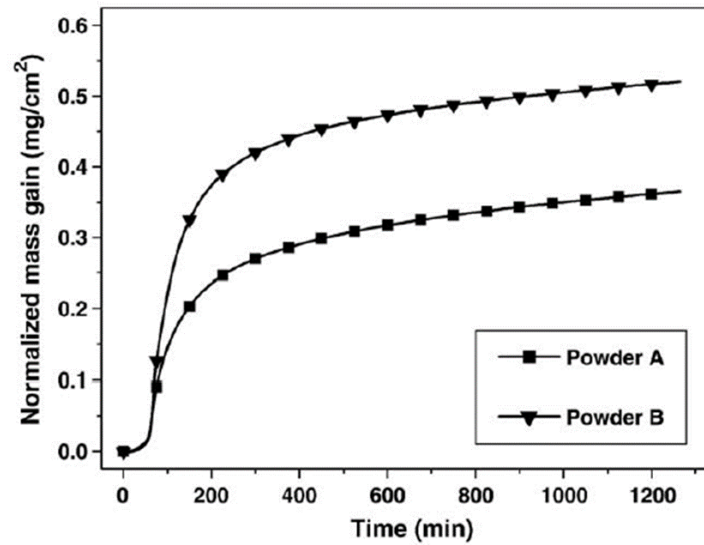


Figure 2.27 TGA mass gain results of (a) CoNiCrAlY and (b) CoNiCrAl(Y, Ca, Si) bond coats (heating up rate: 15 °C/min) [98].

Different from isothermal oxidation, the thermal cyclic oxidation is more relevant to the real aero engine operating conditions. The repeated heating up and cooling down processes can damage the formed TGO layer due to different thermal expansion coefficients (CTE) of the TGO and the bond coat, as well as the TBC [9]. The crack initiation and propagation are accelerated by the repeated fast heating and cooling, thus the breakaway of the TGO is usually observed in the thermal cyclic oxidation [9]. Figure 2.28 shows the weight change of aluminide coatings in the thermal cyclic oxidation. The weight loss can be found in the later thermal cycles [100].

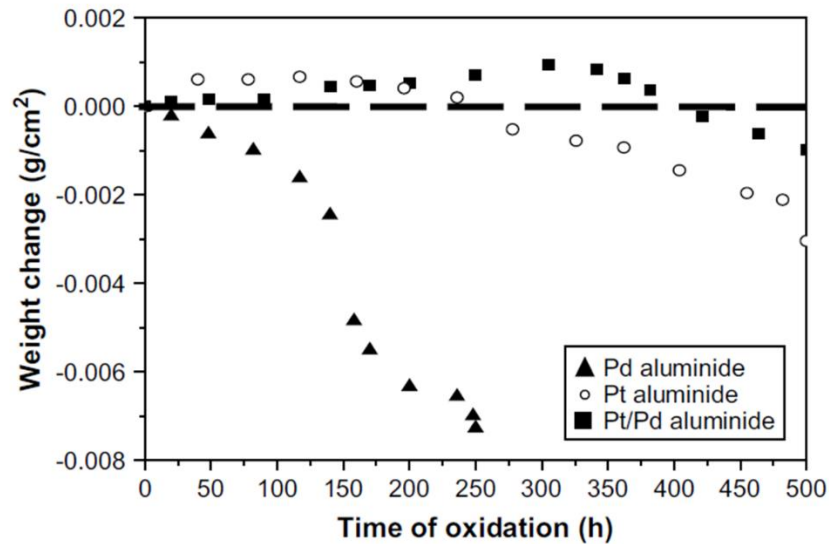


Figure 2.28 Weight change of aluminide coatings in the thermal cyclic oxidation [100].

It is suggested that the parabolic growth can be observed in the thermal cyclic oxidation if the spalled oxides are weighted together or measured in thickness [9, 101]. Figure 2.29 shows the parabolic growth of the TGO layer as well as the influences of different dwell times of the thermal cyclic tests at different temperatures. The investigation suggests that a short dwell time can shorten the lifetime of coatings, and the higher testing temperature can significantly reduce the service lifetime of coatings [101].

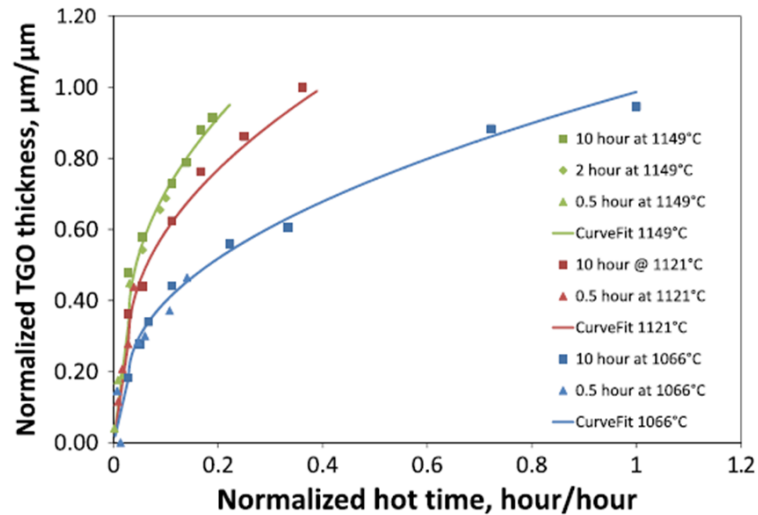


Figure 2.29 The parabolic growth of TGO layer in thermal cyclic oxidation with different dwell times and temperatures [101].

Because the oxidation rate is higher at the early stage than the later stage, a fast growth of the TGO can initiate stresses at the coating interface, and a poor adherence of the oxide scales occurs more easily at the early stages [102]. On the other hand, the growth is slower and more steady at later stages of the parabolic growth [103]. It is then reported that the pre-oxidation treatment, i.e. heat treatment of the coatings to form a very thin layer of oxide before further oxidation test, can improve the oxidation performance of the bond coat [104].

In addition to the oxidation resistance, high temperature corrosion resistance is another important property that the bond coat should possess. Hot corrosion can be found in aero gas turbine engines, but particularly in industrial and oceanic applications [105]. Two types of hot corrosion are involved during the service life of components. Type I hot corrosion usually occurs at higher temperature and Type II hot corrosion takes place at a lower operating temperature. Figure 2.30 shows the characteristics of the types of hot corrosion. Type I generally occurs at around 900°C and type II happens at about 700°C

[105]. The type I hot corrosion can lead to the dissolving of protective oxide scales. Co is added to improve the hot corrosion resistance of MCrAlX bond coatings, thus Co-containing MCrAlX bond coats have better type II corrosion resistance than the PtAl coating [106]. However, the type II corrosion is not often observed in aero-engine applications because the operating temperature is much higher than 700°C [107]. MCrAlX bond coats have better resistance than PtAl bond coats to Type I corrosion due to the high chromium content [37]. However, PtAl bond coats show better oxidation resistance than MCrAlX bond coats at high temperatures [106, 108].

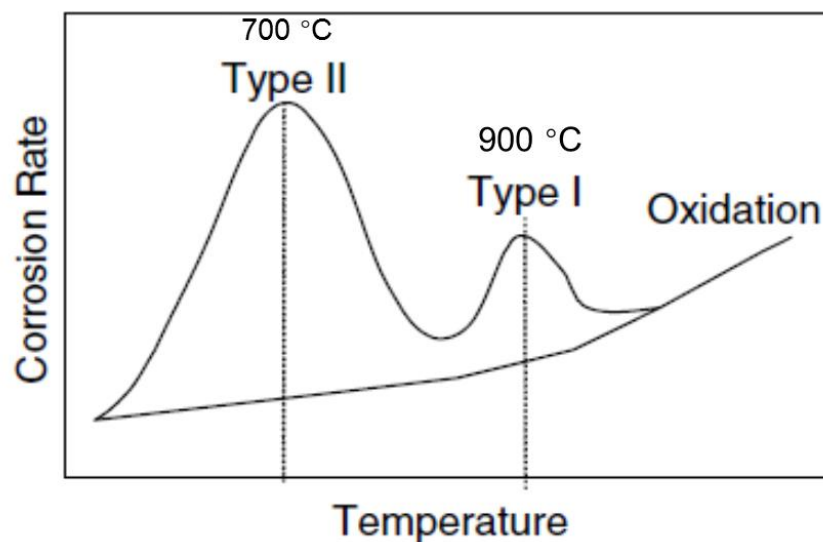


Figure 2.30 The two types of hot corrosion during different operation temperatures [109].

2.3.1 Thermally Grown Oxide

Thermally grown oxide (TGO) has a great influence on the durability of the TBC system as a consequence of oxidation. Cracks or stresses within the TGO layer will lead to delamination in the TBC system [110]. Based on the industrial and commercial experiences, the thickness of

the TGO layer could reflect the lifetime of the TBC system. It has been found that during the service period, the thickness of the TGO layer at the end of life was usually about $6 \sim 7 \mu\text{m}$ and would not exceed $10 \mu\text{m}$ [111]. Compositions of the TGO vary with different bond coats. In a simple Ni-Al alloy, when the content of Al is $< 6\%$, the outer layer is covered by NiO and Al_2O_3 with an inner layer of spinel (NiAl_2O_4). When content of Al is $6 \sim 17\%$, the outer layer is mainly Al_2O_3 . However, as the depletion of Al, the NiO can form a spinel phase. When the Al content is $> 17\%$, the oxide scale is taken over by the single Al_2O_3 phase [9]. The typical microstructure of the TGO in an overlay NiCrAlY coating is shown in Figure 2.31. The Al grains are elongated so that the O diffuses faster than Al. Y forms a garnet phase with Al to pin at the grain boundaries, which can improve the strength of the oxide avoiding spallation. In addition, the spinel is formed at the interface between the TGO and bond coat [9, 111].

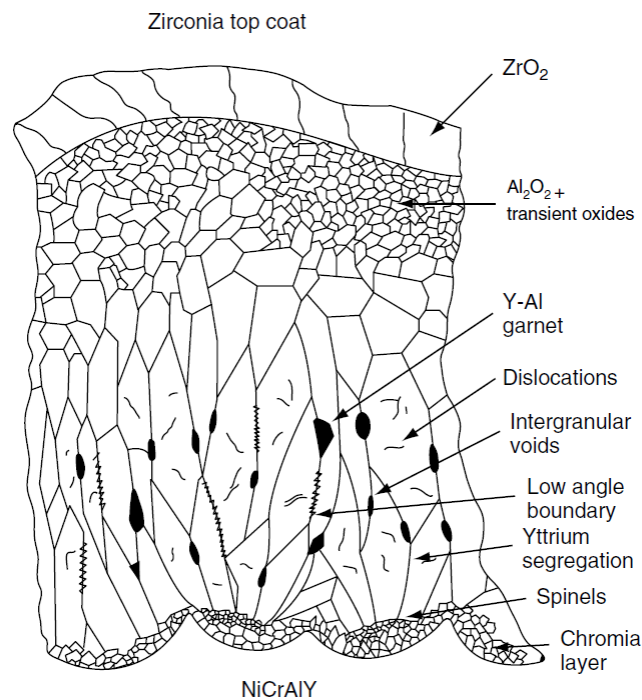


Figure 2.31 The microstructure of the TGO in a MCrAlY bond coat [111].

However, the formation of spinel is more complicated in the oxidation test. Figure 2.32 shows the microstructure of a CoNiCrAlY coating after oxidation, where the spinel forms above the Al_2O_3 layer [8]. On the other hand, spinel is also detected underneath the Al_2O_3 layer in Pt-modified $\gamma+\gamma'$ coating, as shown in Figure 2.33 [112]. Further studies need to be carried out to investigate the formation of spinel in different bond coats and conditions.

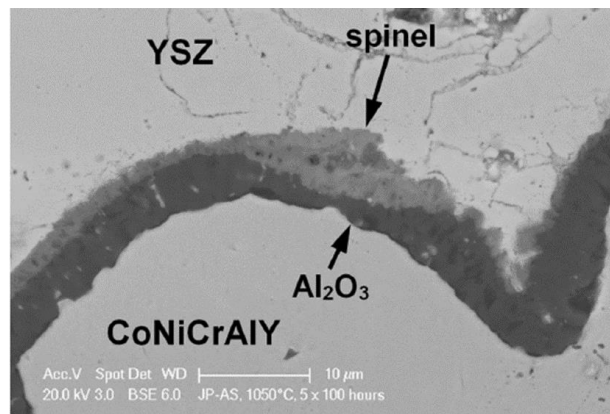


Figure 2.32 Spinel formed on the top of Al_2O_3 in a CoNiCrAlY coating [8].

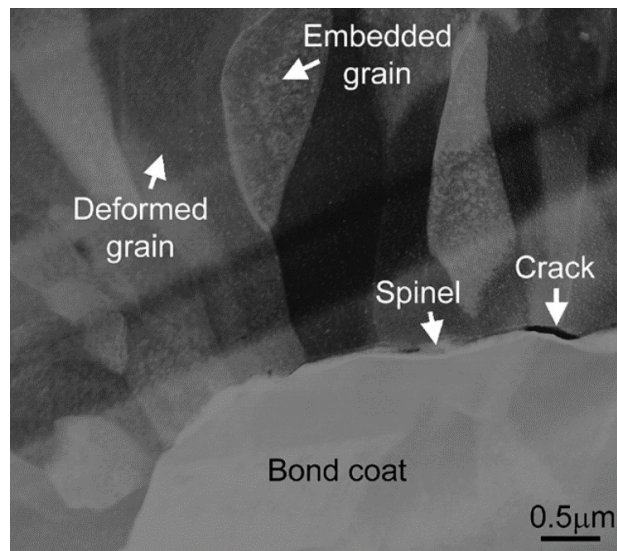


Figure 2.33 Spinel formed underneath the Al_2O_3 in a Pt-modified $\gamma+\gamma'$ coating [112].

2.3.2 Failure Mechanisms

Figure 2.34 describes five major failure modes in the TBC system, which are the Al depletion, Ni diffusion through TGO, “Planar” interface with imperfection, undulating/wrinkled interface and foreign object damage [113]. The first and second failure modes are usually caused by chemical reactions which can introduce the spinel involved failure. As mentioned in Figure 2.32 and Figure 2.33, spinel can form at both interfaces between the TBC and TGO and between the TGO and the bond coat when Al is depleted in the bond coat. The formation of spinel is thought to lead to the TBC failure because cracks may be generated across the spinel layer. However, this is not substantiated [113]. The third and fourth failure modes usually involve the thermomechanical failure, which is based on the TGO growth in the bond coat. When the TGO consists of imperfect oxides, it can form a planar interface at failure. The cracks will nucleate and propagate along the imperfect oxides [114, 115]. Figure 2.35 shows the imperfection in the TGO of a NiCoCrAlY bond coat [113]. The growth of imperfect oxides depends on the composition of bond coats. For example, the reactive elements can affect the growth of imperfect oxides in the TGO [113]. The fifth failure mode is caused by foreign object damage (FOD) and is more related to the ceramic top layer, which can be attacked by CMAS (calcium-magnesium-alumino-silicates) [116, 117].

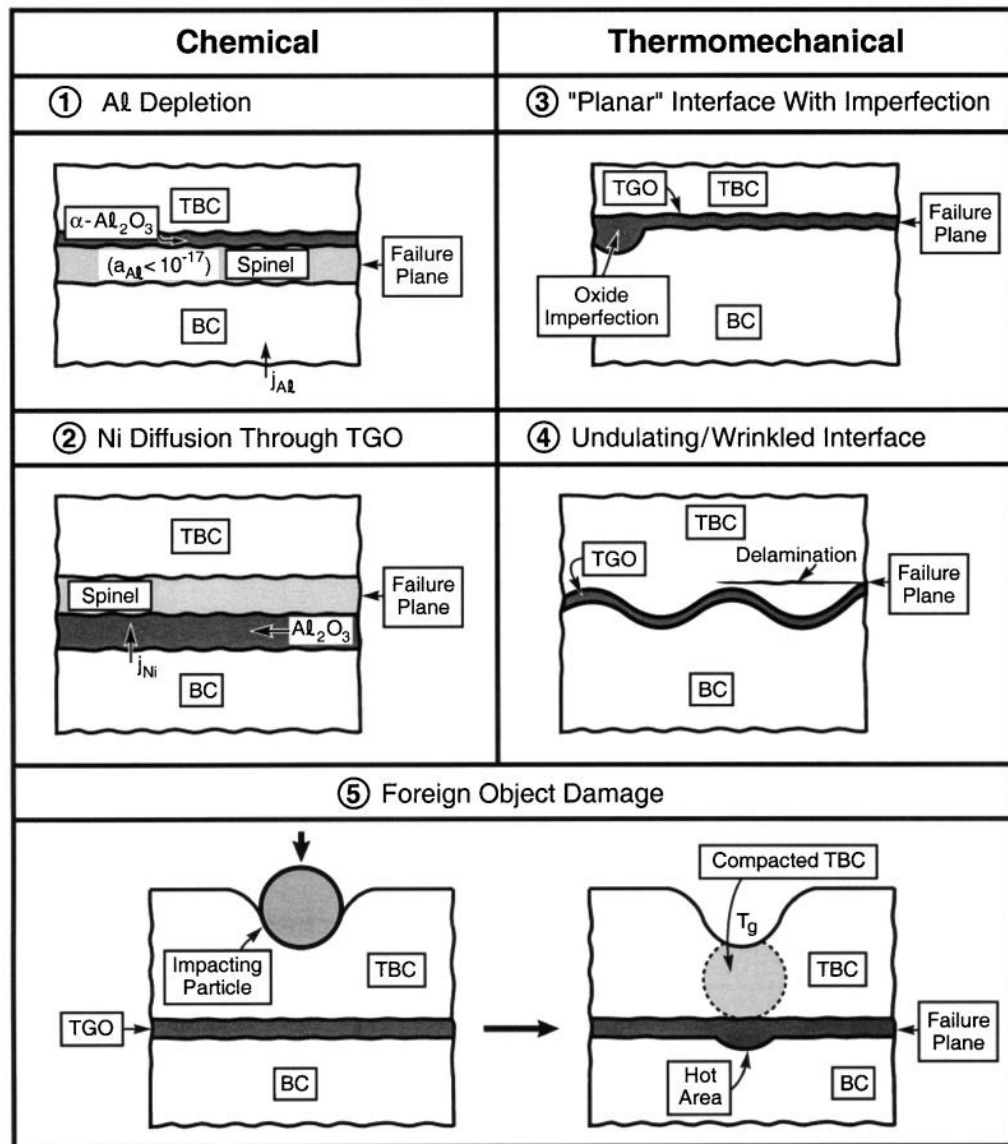


Figure 2.34 Five major failure modes of TBC system [113].

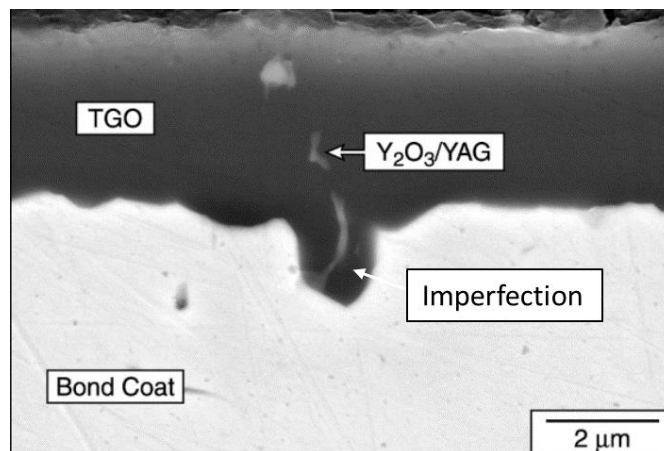


Figure 2.35 The imperfection in the TGO of a NiCoCrAlY bond coat [113].

In the fourth failure mode, rumpling of the TGO and the bond coat during cooling down and cyclic thermal oxidation plays important roles. Interfacial rumpling is the prevailing failure mechanism in a thermal barrier coating system [118]. Figure 2.36 shows the microstructure of the interfacial rumpling which occurred in the TBC system with a PtAl bond coat and an EB-PVD deposited ceramic top coat [31]. The as-deposited flat bond coat changes its surface morphology after oxidation, indicating an interface separation.

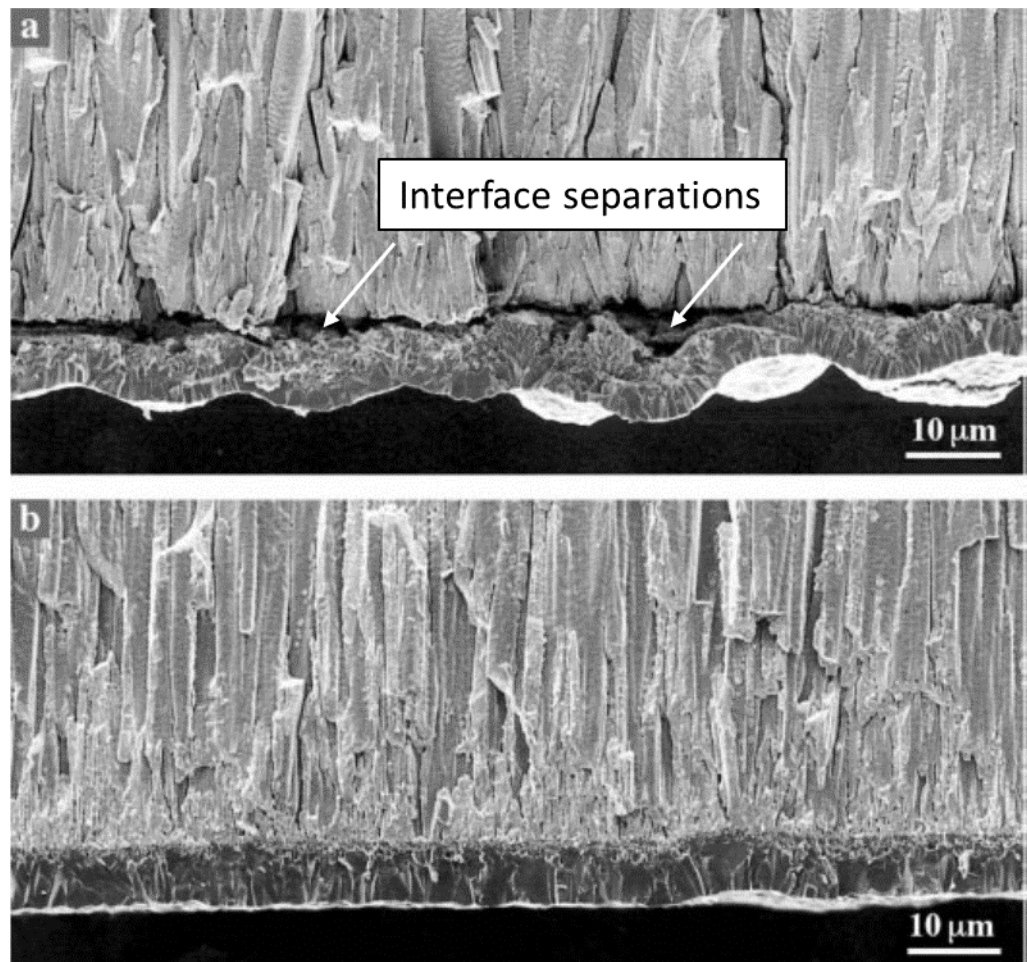


Figure 2.36 Microstructural characterisation of the interfacial rumpling of a PtAl bond coat with an EB-PVD deposited TBC, showing (a) the rumpling of bond coat after the oxidation test, and (b) the microstructure of an as-prepared TBC system [31].

Two rumpling mechanisms have been proposed. One of the most common theories is the "ratcheting" phenomenon, which is motivated by the compressive stress in TGO, introducing roughening (as shown in Figure 2.37) [113]. Compressive stresses are generated in the TGO during the oxidation, which is confirmed by measurements (Figure 2.37a) [119]. When the temperature cools down, the TGO will try to reduce the elastic strain energy [31]. This can only be achieved by undulating because the TGO is attached to the bond coat [113]. Besides, the undulating process requires the deformation of both the TGO and bond coat (Figure 2.37b) [113]. Due to the different mechanical properties between the TGO and bond coat, cracks may be initiated during the undulating process. Since the thermal cycling will continue to introduce compressive stress, the amplitude of rumpling will become greater with increased thermal cycles [31, 113]. This will lead to the interface separation if the ceramic top coat or the bond coat cannot deform to match the displacements of the TGO [31].

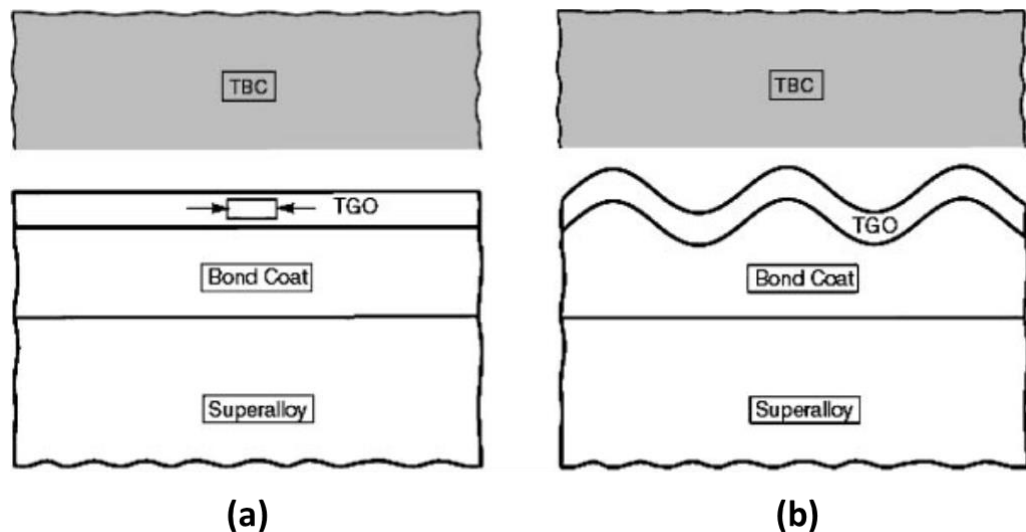


Figure 2.37 The schematic of the rumpling mechanism of the TGO and bond coat. (a) A compressive stress is generated in the TGO layer during the oxidation, and (b) the TGO layer undulates to decrease the elastic strain energy [113].

Another mechanism states that the coating undulation can be induced by the microstructural degradation of bond coats. In Figure 2.7, the β -NiAl will transform to γ' phase as the consumption of Al continues during the oxidation. The transformation from β to γ' can introduce internal stresses and cause deformation of bond coats [120].

In addition, the martensitic transformation of the β phase also occurs when it cools down to room temperature because the Al is depleted [120]. The general martensitic transformation temperature of the β phase is 300°C [121]. Alloying elements such as Pt can increase the martensitic transformation temperature to around 600°C [122]. This indicates that Pt can destabilise the β phase and promote the β to $L1_0$ martensitic transformation [123]. On the other hand, Co and Cr act as the β stabilisers which can retard the martensitic transformation [123].

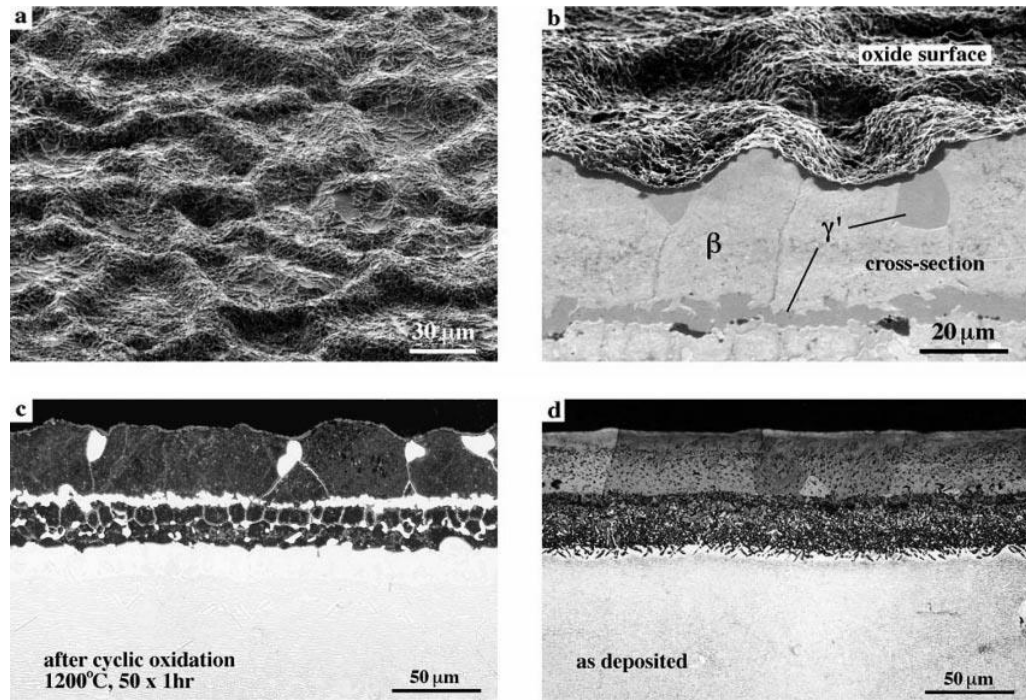


Figure 2.38 Microstructures of the PtAl bond coat after 50 1-h cycles at 1200°C: (a) surface rumpling; (b) cross-section of rumpling showing the β and γ' phases; (c) optical image of etched cross-section after cyclic oxidation and (d) optical image of etched cross-section of as-aluminised bond coat. Dark areas on the optical images correspond to the β phase, whereas the γ' phase in the coating appears white [120].

The rumpling of the TGO and bond coat can initiate coating buckling at the early stage of failure [113, 114], which could be used to examine the coating state. Figure 2.39 shows a spallation failure of the TBC after oxidation [31]. In Figure 2.39b, the surface of bond coat and TBC itself can be found after coating spallation. Because the amplitude of rumpling becomes greater with increased thermal cycles, interface roughness can be used to evaluate the performance of bond coats. Figure 2.40 shows the surface rumpling of a Pt-modified aluminide coating after the cyclic oxidation at 1100°C [124]. At the early stage (25% of maximum cycles) shown in Figure 2.40a, the PtAl coating has a relatively flat surface. When the oxidation cycles increase to the medium (50% of maximum cycles) and last stages

(maximum cycles), an increased surface roughness can be detected and is shown in Figure 2.40b and 2.40c.

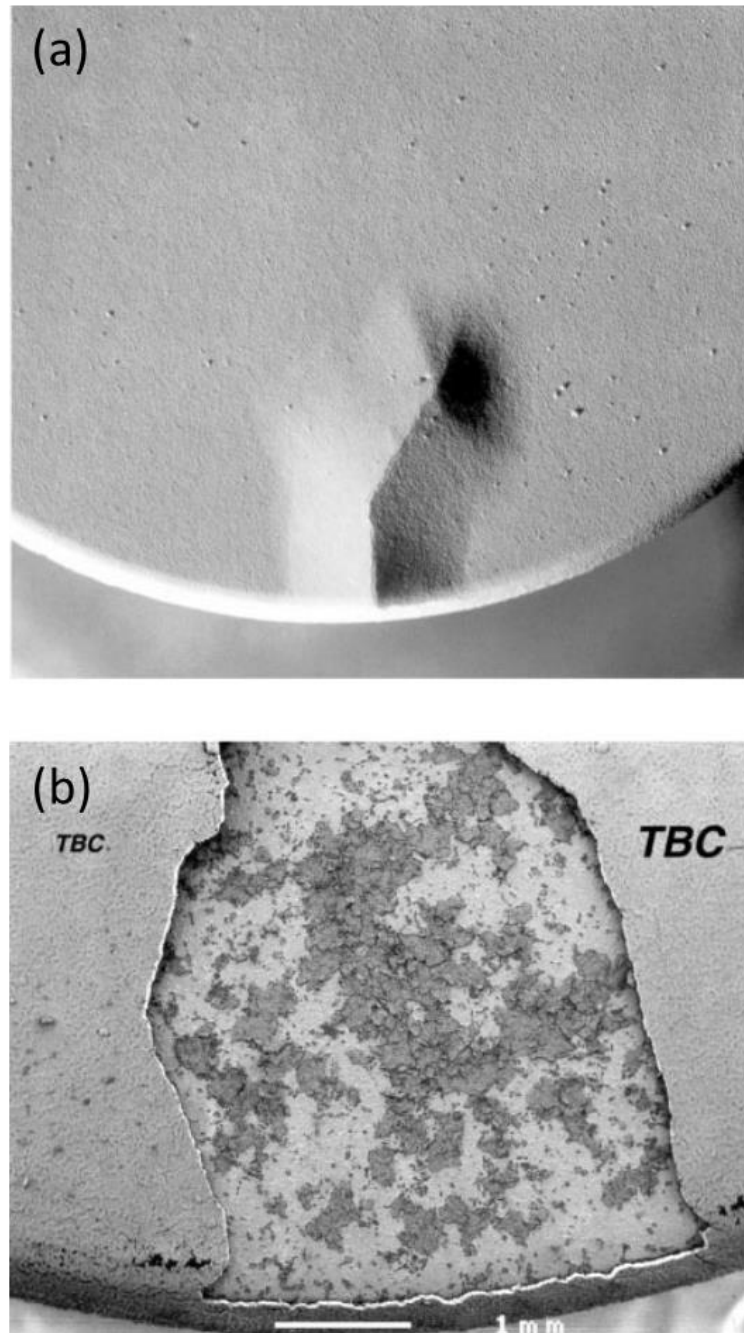


Figure 2.39 (a) Surface buckling of a TBC coating after oxidation. (b) Spallation of the TBC showing the fracture interface between the bond-coat (dark regions) and the TBC itself (light regions) [31].

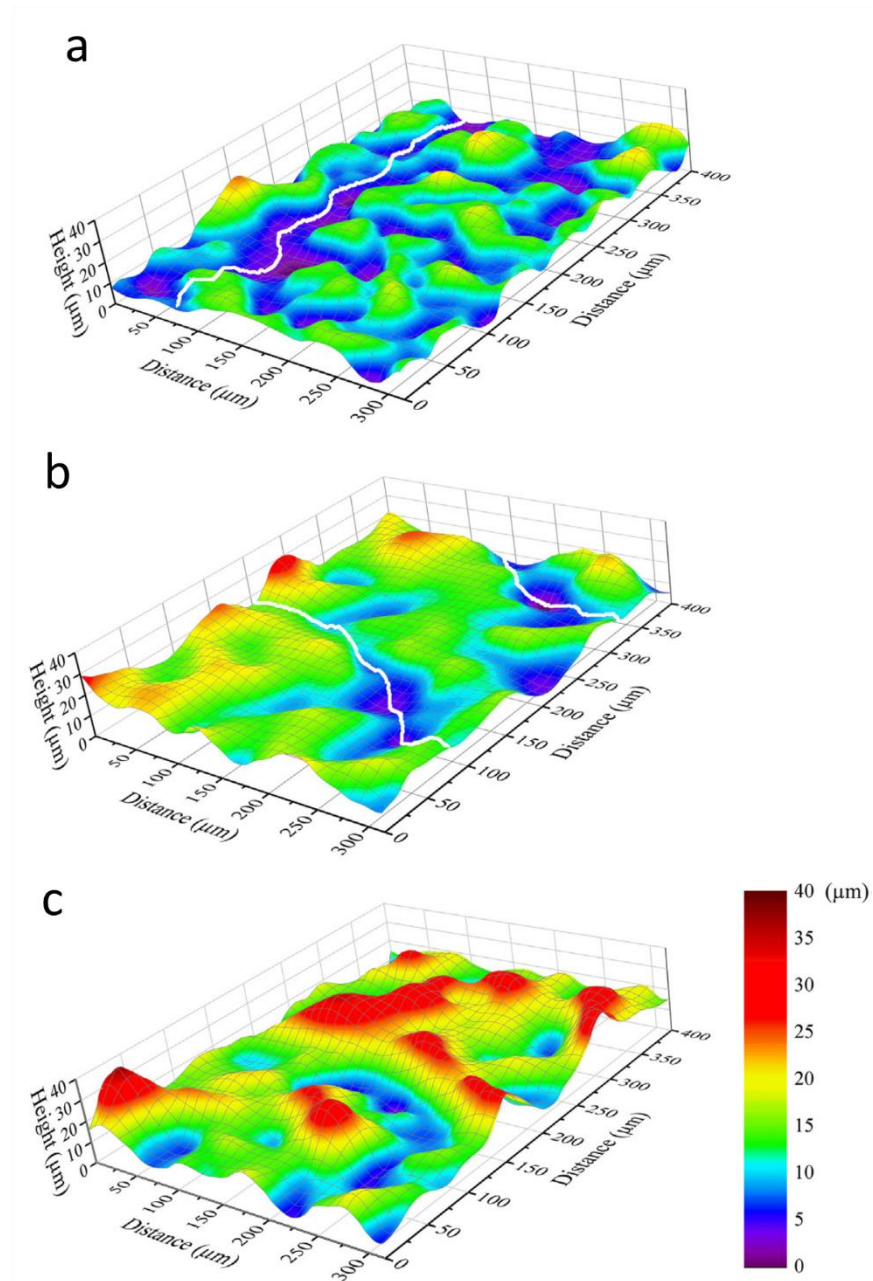


Figure 2.40 The rumpling of a Pt-modified aluminide coating after the cyclic oxidation at 1100°C when the oxidation cycles at (a) the early stage (25% of maximum cycles), (b) the medium stage (50% of maximum stage) and (c) the last stage (maximum stage). [124]. These results were obtained from a Keyence VHX 1000 optical microscope [124].

Another failure mode is also observed in laboratory scale. The moisture induced delayed spallation (MIDS) is well known in laboratory investigations [125]. Different to the spallation shown in Figure 2.39, the MIDS usually leads to a “desktop spallation” (DTS) of the TBC, as shown in Figure 2.41 [126]. Moisture caused hydrogen embrittlement due to the reaction between water and Al (in bond coat), is proposed as the fundamental mechanism for DTS [125]. In addition, the MIDS can also increase the surface rumpling level in Pt aluminide bond coats and decrease the TBC lifetime [127].

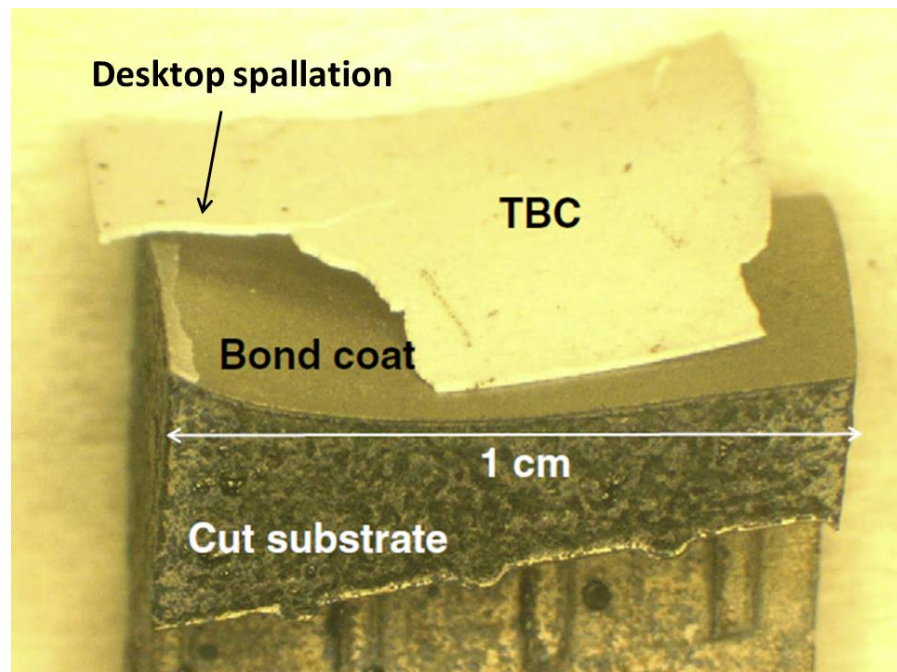


Figure 2.41 An optical image showing the “desktop spallation” caused by the moisture induced delayed spallation [126].

2.4 Development of Bond Coats

The recent development of thermal barrier coatings has required higher operating temperatures for bond coats. Because faster growth of the TGO occurs at higher temperatures, improved oxidation resistance with a slower growth rate of TGO is required for bond coats working at such a temperature [32]. In addition, the cyclic thermal oxidation resistance should be improved to reduce the rumpling amplitude.

The degradation of bond coats at high temperature also depends on the inter-diffusion between the bond coat and substrate. The inward diffusion of Al and outward diffusion of the substrate elements will form SRZ, which is detrimental to the creep and rupture properties of the substrates [128]. A diffusion barrier deposited between the bond coat and substrate can avoid the formation of the SRZ [129-131]. However, the developed diffusion barriers either have poor oxidation resistance or are unstable at high temperatures. A diffusion barrier possesses good stability and oxidation resistance has yet to be developed [32]. In addition, the development of low thermal conductivity TBCs has addressed new composition systems [32], which may challenge existing bond coat systems for new bond coat compositional design.

2.4.1 Improving Oxidation Resistance

Reactive elements (REs) have been utilised to improve the general properties of bond coating materials for many years. They can form oxide pegs between the TGO and the bond coat to increase the bonding strength of the TGO and reduce rumpling the amplitude [132]. The most widely used elements in conventional bond coatings are Y,

Hf and Ta [9, 37]. These elements can be easily added into overlay coatings but not the diffusion coatings, which are limited by the substrate compositions. However, diffusion coatings are the major candidates for bond coats in turbine blades. Improving the oxidation resistance of bond coats can increase the lifetime of the TBC system. Investigations are being carried out to modify the aluminide coatings with the REs. Most of the work is done by studying the oxidation behaviour of NiAl alloys with reactive element additions [12, 133-135].

A recent study has focused on investigating the effects of other reactive elements, such as Dy, Zr and La [136, 137]. Li et al. have completed an investigation on the cyclic oxidation properties of β -NiAl with various dopants at 1200°C [136], comparing Dy, Zr and La with the conventional Y and Hf. Figure 2.42 shows the mass gain rates for different reactive elements modified samples. Hf- and Zr-doped materials show a lower oxidation rate, whilst the Dy-doped one exhibit a better rumpling resistant ability [136]. It is suggested that co-doping Dy and Hf or Zr may give even better high temperature oxidation properties [138].

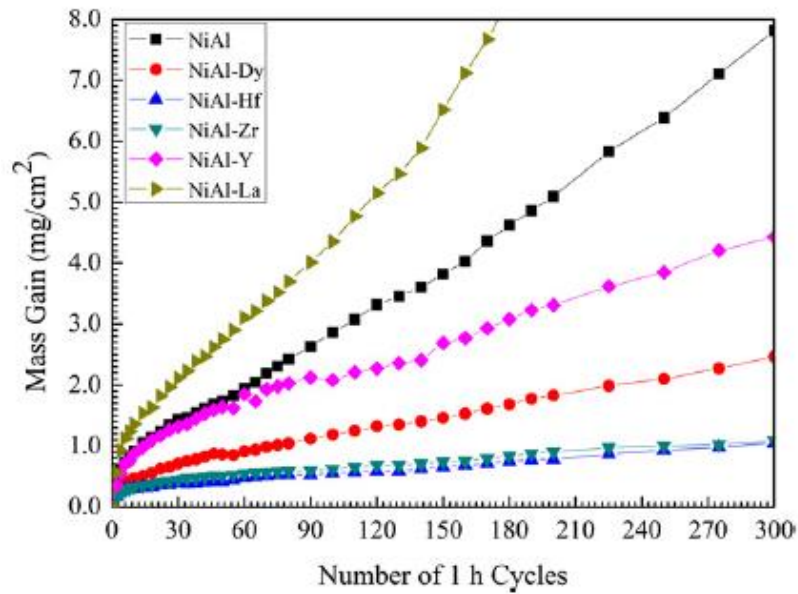


Figure 2.42 Oxidation test results of the differently modified NiAl alloys [136].

2.4.2 Oxygen Diffusion Barrier

As one of the PGMs, Ir is considered to act as an oxygen diffusion barrier, thus a reduced growth rate of the TGO is expected [139]. Most investigations are carried out on Ir-contained NiAl alloy. 60.17 Al, 34.77 Ni, and 5.07 Ir alloys were developed and investigated by F. R. Lamastra et al. [140]. It was indicated by Lamastra that this kind of alloy has the potential to make up a new bond coats [140]. In past reports, the deposited Ir layer is thin and no oxygen diffusion barrier (ODB) or Ir-rich areas have been found in the Ir-modified aluminide coatings [141-143]. Nevertheless, the ODB formation is found in the binary alloys with a high volume of Ir and a low content of Al [15].

2.4.3 Novel Compositions

Investigations on glass-ceramic type bond coat were carried out by Das et al. [144]. The procedure to fabricate the glass-ceramics bond coat is described as wet milled from enamel frit containing SiO₂

40 - 45; BaO 40 - 45; CaO 2 - 6; MgO 2 - 3; ZnO 2 - 8; MoO₃ 2 - 8 in wt.%. During the milling, other additions should be added to make the final products, such as fume silica 3.0 ~ 5.0 wt.%, washed Cr₂O₃ 4.0 ~ 5.0 wt.% and cobalt oxide 0.3 ~ 0.5 wt.%. The traditional thermal spray method can be used to fabricate glass-ceramics bond coat. The advantage of the new bond coat is its better oxidation performance over than the shortcomings of conventional bond coat, but more tests should be run to draw a conclusion [75].

2.4.4 Co-electrodeposition of Metal and Ceramic Particles

A co-electrodeposition of metal and ceramic particles can usually refer to the composite plating or the "inclusion plating" [145]. The co-depositing metal and ceramic particles is a potential method for producing metal matrix composites [146]. The history of composite plating can be traced back to 1928 when a Cu-graphite coating was studied for an automotive bearing system [147]. Since the 1960s, the development of composite plating is mainly used for wear resistant coatings in the aerospace and automotive industry [145]. Nowadays, the matrix materials are usually chosen from Cu, Ni, Ag, Zn and Co [145, 148-151]. The inclusions can be oxides, carbides, graphite, and polytetrafluoroethylene (PTFE) [152-154]. The size of inclusions also can be nano-scale [146]. Besides the wear resistant coating, solid state lubricant coatings and corrosion resistant coatings can also be produced by composite plating [145, 155].

The mechanism of a composite plating is shown in Figure 2.43 [145]. The co-deposition process of metal and particles starts from the particle charging. Ions can be absorbed by the particles which are then charged. The particles are physically transported through a convection, usually due to agitation. The particles travel across the

diffusion layer through mass transportation and are migrated via the potential gradient across an electrical double layer. When ions are reduced and deposited, the particles will be physically embedded on the cathode surface [145].

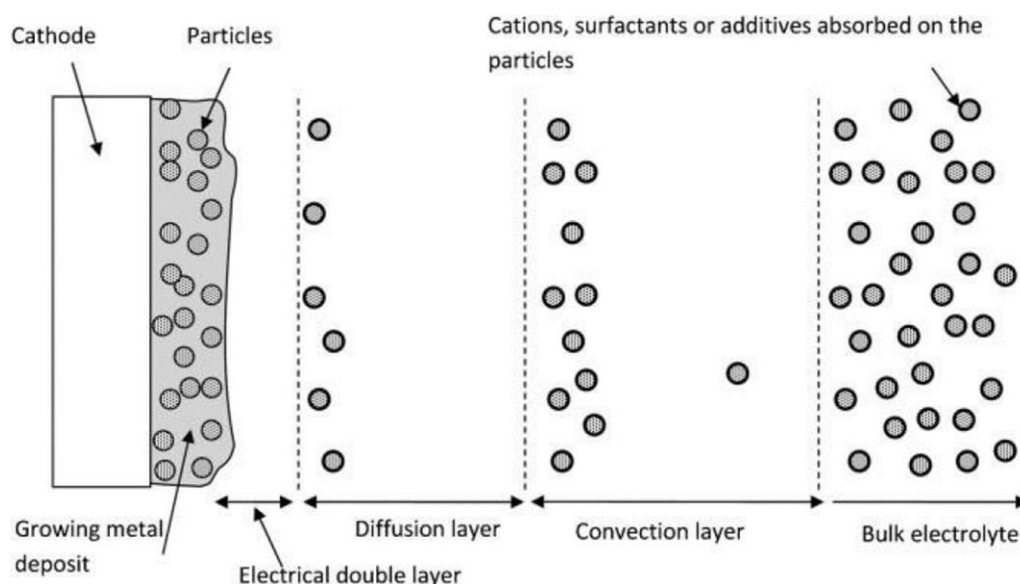


Figure 2.43 A illumination of the mechanism for composite plating [145].

A typical composite coating deposited by the composite plating is shown in Figure 2.44 [146]. The black spots in the BSE image shown in Figure 2.44 are the embedded Al_2O_3 particles. To achieve well distributed particles in the coating, the dispersion of particles in electrolyte is preferred [146]. Because there is no any report on Pt-based composite coatings deposited by composite plating, it is a good attempt to produce Pt composite coatings with specific particles. The embedded particles in Pt coating may have the potential to improve the oxidation resistance of the PtAl coating for high temperature applications.



Figure 2.44 BSE image of a typical microstructure of Ni/Al₂O₃ composite coating. The pointed locations are embedded Al₂O₃ particles [146].

2.5 Summary

In this chapter, the requirement for thermal barrier coating is reviewed in aero-engine application. The bond coat is used to provide high temperature oxidation and corrosion resistances in the TBC system. Moreover, bond coats play important roles in the failure of the TBC system at high temperature, affecting the lifetime of the TBC system.

Two groups of bond coats are developed so far and utilised in different applications. The MCrAlX-type overlay bond coats are usually deposited by thermal spray technologies, such as APS and HVOF. The diffused aluminide bond coats, on the other hand, are produced by diffusion heat treatment, which creates a higher bonding strength than the overlay bond coats.

The isothermal and thermal cyclic oxidation tests are generally used to evaluate the oxidation resistance of bond coats. A parabolic growth behaviour of thermally grown oxide is expected for good oxidation resistance. Different from isothermal oxidation, the thermal cyclic

oxidation usually causes breakaway of the formed oxides due to different CTEs of oxide and bond coat. The spallation of TBC is mainly caused by the rumpling of the TGO layer, as a consequence of the TGO growth.

Recent studies have focused on the improvement of reactive elements, such as Zr and rare earth elements. The combined effect of the REs is expected to further improve the oxidation resistance of the bond coats. The methods of introducing reactive elements to PtAl coatings are very limited. A cost effective way of introducing reactive elements to PtAl coatings has yet to be developed.

Ir has been receiving attention in the development of new bond coats, due to the ability of forming the oxygen diffusion barrier effect in IrAl alloys. Such an effect has not been observed in Ir-modified PtAl coatings, possibly due to low Ir contents. Investigations in this area are expected to clarify the role of Ir in PtAl coatings and maximize its benefits.

Chapter 3 Research Methodology

3.1 Substrate Preparation

Mar-M-247 (Advanced Alloy Services Ltd.) was used as the main coating substrates due to the similar composition to single crystal alloy CMSX-4 [156]. Mar-M-246 (Select Alloys & Materials Ltd.) was used to verify the influence of Hf on bond coat behaviours. In some cases, Inconel 718 (Goodfellow) substrates were also prepared as the reference substrates because they did not contain any Hf or Zr. The chemical compositions of the three alloys are summarised in Table 3.1.

All materials were machined into proper shape for coating deposition according to their as-received form. The Mar-M-247 (M247) was machined into 15 mm and 20 mm diameter pellets. The Mar-M-246 (M246) was cut into 20 mm diameter pellets, and Inconel 718 (In718) was cut into 20 mm × 10 mm × 2mm square plate. For both M247 and M246 pellets, 2 mm thick substrates were used for the diffusion bond coat preparation and 5 mm thick substrates were utilised for the thermal sprayed bond coats.

Table 3.1 Chemical compositions of Mar-M-247, Mar-M-246 and Inconel 718.

Elements (wt. %)	C	Cr	Ni	Co	Mo	W	Ta	Ti	Al	B	Zr	Hf	Nb	Fe
Mar-M-247	0.16	8.2	Bal.	10	0.6	10	3	1	5.5	0.015	0.05	1.5	-	-
Mar-M-246	0.15	9	Bal.	10	2.5	10	1.5	1.5	5.5	0.015	0.05	-	-	-
Inconel 718	0.05	19	52.5	-	3	-	-	0.9	0.55	0.005	-	-	5	Bal.

3.2 Preparation of Bond Coats

3.2.1 ZrO₂ Nanoparticle-modified PtAl Coating

Figure 3.1 shows the process flow chart of preparing the ZrO₂ nanoparticle-modified PtAl (ZrO₂-PtAl) coating as well as the preparation of general PtAl coatings. The substrates used for electrodeposition were sandblasted with a Guyson Formula 1200 cabinet using F220 (average size 68 µm) white alumina (Guyson). The substrates were ultrasonically washed in soapy water followed by rinsing in de-ionised water, and oven-dried prior to the electroplating process. For the ZrO₂-PtAl coating, the co-electrodeposition of ZrO₂ nanoparticles and Pt was performed after the substrate be cleaned. A vacuum heat treatment was carried out after the electrodeposition to diffuse the coating elements into the substrates. The aluminising process was performed after the diffusion heat treatment, and a post vacuum heat treatment was conducted to finalise the coating microstructures. The preparation of the general PtAl coating followed the same routine, but only a pure Pt layer was electroplated.

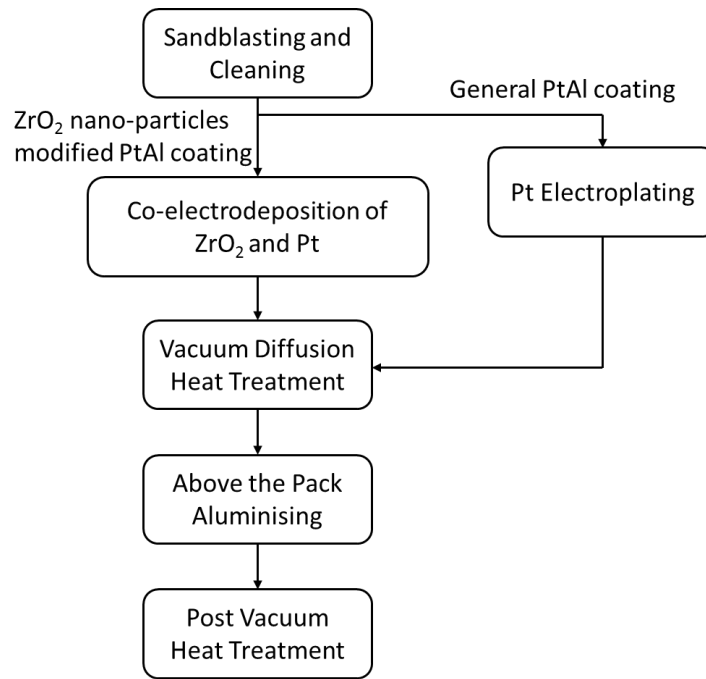


Figure 3.1 The process flow chart of the ZrO₂ nanoparticle-modified PtAl coating and the general PtAl coating.

A commercial Q salt (Johnson Matthey) was used for both the Pt electroplating and co-electrodeposition of ZrO₂ nanoparticles and Pt. The chemical composition of Q salt was (NH₃)₄Pt(HPO₄). The Q salt was diluted from 20 g/L (as received) to 5 g/L before electroplating. The plating temperature was controlled by a hot plate at around 92 ~ 93°C, and the pH value was maintained at around 10.0 ~ 10.5. The current density was kept at 5 mA/cm². The total electroplating time was 40 min. A magnet stirrer was applied for the agitation at 100 ~ 150 rpm. A sketch of the experiment setup is shown in Figure 3.2.

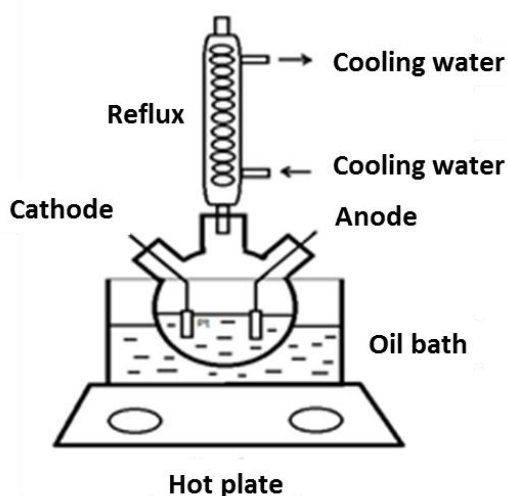


Figure 3.2 Sketch of the Pt electroplating setup.

The incorporation of ZrO_2 nanoparticles in a Pt coating was achieved by co-electrodeposition [157]. The ZrO_2 nanoparticles (TOSOH, ≤ 200 nm) were dispersed into the commercial Q salt $[(\text{NH}_3)_4\text{Pt}(\text{HPO}_4)]$, 5 g/L by an ultrasonic homogeniser (Cole-Parmer). The concentrations of ZrO_2 particles was 20 g/L. The same Q salt plating parameters were used to deposit the ZrO_2 -Pt coating. In addition to nanoparticles, ZrO_2 micro-sized particles (Sigma Aldrich) were also used to investigate the particle size effect on co-electrodeposition. Furthermore, different particle concentrations (5 g/L, 50 g/L and 100 g/L) of both the nano- and micro-particles were also prepared, to study the influence of particle concentrations. As M247, M246 and In718 had different chemical compositions, they were used to investigate the effects of the substrate compositions on the behaviour of ZrO_2 nanoparticles.

The vacuum diffusion heat treatment was carried out in order to diffuse Pt into the substrate after the electrodeposition. The diffusion heat treatment was performed in a high temperature vacuum tube furnace (Elite, TVH12/75/600). Samples were heat treated at 1100°C

for 1 h. The vacuum level during the heat treatment was maintained at around $10^{-5} \sim 10^{-6}$ mbar. The samples were firstly placed into the furnace and the heating rate was 3 °C/min. The samples were cooled inside the furnace with maintained vacuum level at a 3 °C/min cooling rate.

For the Pt-ZrO₂ coating, an additional diffusion heat treatment was carried out to verify the microstructure evolution caused by the ZrO₂ nanoparticles. One ZrO₂-Pt coated sample was vacuum heat treated at 700, 800, 900 and 1000°C. For each temperature the annealing period was kept for 1 h. After every heat treatment, one piece of the Pt-ZrO₂ specimen was cut and used for cross-sectional characterisation.

A conventional above-the-pack aluminising process was applied to diffuse Al into the substrates after diffusion heat treatment. In this study, a high temperature low activity pack mixture was used for aluminising. The pack mixture consisted of 10 wt.% pure Al powder (Alfa Aesar), 87 wt.% Al₂O₃ (Sigma-Aldrich) and 3 wt.% NH₄Cl (Sigma Aldrich). The aluminising process was carried out at 1140 °C for 1 h in a tube furnace (Carbolite STF15/450) protected by 5% H₂/95% Ar gas (BOC). The flow rate of the protection gas was 0.5 l/min. The above-the-pack setup is shown in Figure 3.3. When the aluminising process was finished, a post heat treatment was performed on the aluminised samples, to finalise the coating microstructures and properties.

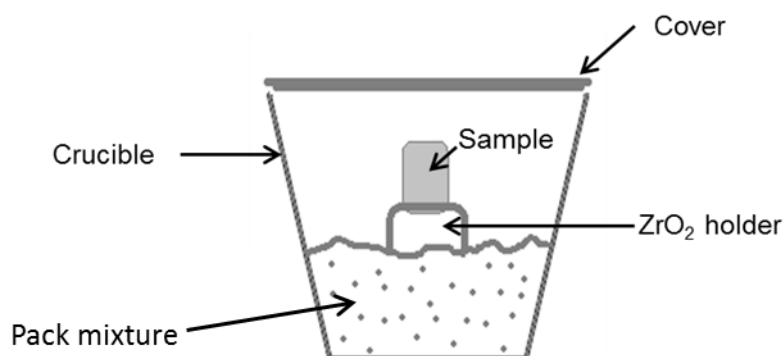


Figure 3.3 Sketch of the above-the-pack aluminising setup.

3.2.1.1 Investigation on Reactions Between Al and ZrO₂ Particles at 1100°C

The pure Al powder and ZrO₂ nanoparticles (TOSOH) were mixed and pressed into 20 mm diameter pellets using a Pellet Press (Specac, 130 MPa, as shown in Figure 3.4) to verify reactions between Al and ZrO₂. Two different heat treatments were applied to investigate the reactions under different environments which had been used to prepare bond coats: (1) pellets of 1.5 g Al and 1.5 g ZrO₂ were heat treated at 1100°C in vacuum (10^{-6} mbar); (2) pellets of 1.5 g Al and 0.5 g ZrO₂ were heat treated at 1100°C in a controlled environment (5%H₂/95%Ar). The high Al loading was deliberately chosen in order to study the effect of Al contents on the reaction products.



Figure 3.4 Image of the pellet press used to press the powder mixtures of Al and ZrO_2 into a 20 mm diameter pellet.

3.2.1.2 Pack Aluminising for Co-diffusing Zr and Al

In addition to the conventional aluminising process, a Zr-doped aluminide (ZrAl) coating was developed to investigate the influence of pure Zr addition on the oxidation resistance of PtAl coatings.

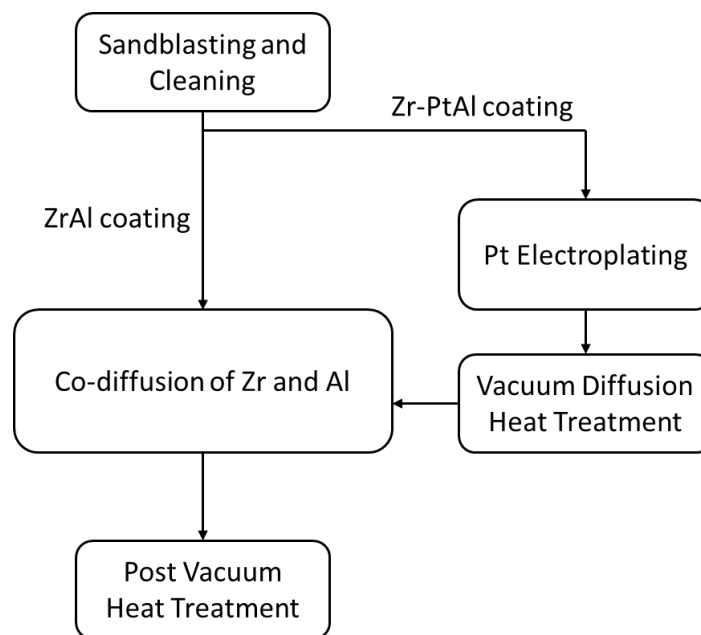


Figure 3.5 Process flow chart for the preparation of ZrAl and Zr-PtAl coatings.

Figure 3.5 shows the preparation procedure of ZrAl coatings. The substrates were treated using the same route as described in section 3.2.1. The samples were buried in a specific powder mixture to ensure a better contact for the Zr diffusion reaction. The compositions of powder mixtures used for the ZrAl coating are summarised in Table 3.2. ZrCl_4 was only added in Mixture2 to maintain ZrCl_4 vapour at high temperatures. Mixture3 and Mixture5 were carried out to verify the effects of Al and NH_4Cl additions. ZrAl coatings were named after the used powder mixtures. Mixture1 prepared ZrAl coating was called ZA1 and the others were named by this principle as shown in Table 3.2. All the samples were heated up to 1140°C and held for 1 h with the protection of 5% H_2 /95% Ar gas (BOC). The heating up and cooling down rates were $8^\circ\text{C}/\text{min}$ and $15^\circ\text{C}/\text{min}$, respectively. M247 was used as the coating substrates. Zr-modified PtAl (Zr-PtAl) coatings were prepared based on the ZA1 coating. Pt coating was electrodeposited (20 min) prior to co-diffusion for the purpose of investigating the effect of pure Zr on PtAl (Zr-PtAl) coating. A vacuum diffusion heat treatment was also carried out to diffuse Pt before the co-diffusion process.

Table 3.2 Compositions of the powder mixtures used for Zr-doped aluminide coating.

Chemicals /g	Mixture1 (ZA1)	Mixture2 (ZA2)	Mixture3 (ZA3)	Mixture4 (ZA4)	Mixture5 (ZA5)
ZrO_2	74.8	66.8	75	15	98
Al	25	25	25	15	\
NH_4Cl	0.2	0.2	\	0.2	2
ZrCl_4	\	8	\	\	\
Al_2O_3	\	\	\	69.8	\

3.2.2 PGMs Modified PtAl Coatings

The process flow chart for the preparation of Ir and Pd-modified PtAl coatings is shown in Figure 3.6. The substrates preparation followed the same route in section 3.2.1. Ir and Pd coatings were both deposited prior to Pt electroplating. The parameters of the Pt electroplating were kept to the same as those shown in section 3.2.1, except that the plating time was 20 min instead of 40 min. For the Ir-modified PtAl (Ir-PtAl) coating, different vacuum diffusion heat treatments were carried out using 1 h (Ir-PtAl-1h) or 4 h (Ir-PtAl-4h) durations. For the Pd-modified PtAl (Pd-PtAl) coating, an eletroless plating method was used to deposit the Pd coating. The vacuum diffusion treatment was carried out on the Pd-PtAl coating for only 1 h. Both coatings were aluminised and followed by a post vacuum heat treatment to optimise the coating microstructures.

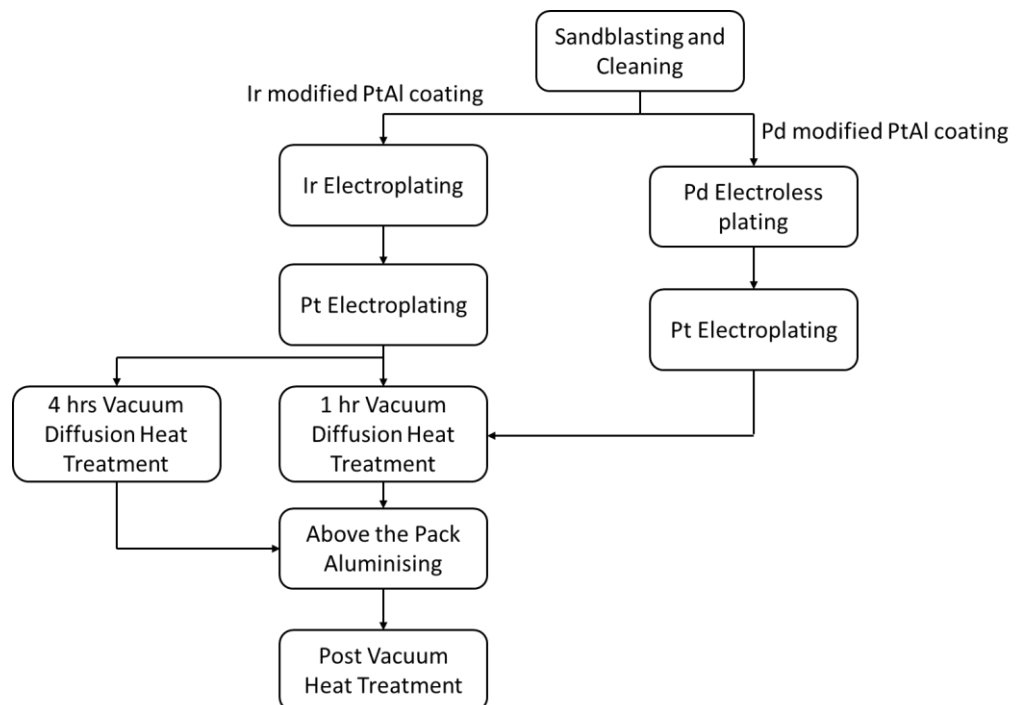


Figure 3.6 Process flow chart of preparing Ir- and Pd-modified PtAl coatings.

Even though the sputtering method is usually used to prepare Ir coating for Pt-Ir coating applications [158-160], the high cost and low deposition rate are not preferred. Only a few reports are available on the electrodeposition of Ir, and the limited reports indicated that the Ir halogens can be used to deposit very thin Ir coating ($\leq 1 \mu\text{m}$) [161, 162]. Among the Ir halogens, Ir bromide was reported to have the potential for the preparation of thick Ir coatings [162, 163]. In this study, the Ir coating was electroplated using an IrBr_3 aqueous solution.

The electrolyte solution used for Ir plating was made from Ir bromide hydrate ($\text{IrBr}_3 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) by dissolving the precursor in deionised water and adjusting the pH value to around 1.9 by 37 % HCl (Sigma Aldrich). The samples were immersed in a 0.5 wt.% PdCl_2 solution for 60 sec before electroplating. Concentration of $\text{IrBr}_3 \cdot x\text{H}_2\text{O}$ was varied from 2 g/L $\sim$ 4 g/L. The current density was set to 2 $\sim$ 3 mA/cm^2 . The electroplating temperature was maintained at 75°C and each sample was plated for 1 h using the 2 g/L solution and 2 h using the 4 g/L solution. In addition, a 5% H_2 /95% Ar mixed gas (BOC) was used to optimise the electroplating of Ir by bubbling the gas into the solution to remove dissolved oxygen. The de-oxygen process was carried out for 2 h before the Ir electroplating. The electroplated Ir coatings were mainly deposited on M246 substrates.

Different from the Ir coatings, the Pd coating was prepared by electroless plating method [164]. The solution of Pd electroless plating contained 2 g/L PdCl_2 (Sigma Aldrich), 4 mL/L 37% HCl (Sigma Aldrich) and 160 mL/L NH_4OH (Sigma Aldrich). The three chemicals were well stirred to be totally dissolved before the next step. As an activator, NH_4Cl (Sigma Aldrich) was added just before the deposition

with a concentration of 27 g/L. NaH_2PO_2 (Sigma Aldrich) was also added to the solution, which acted as a buffer reagent. The final pH value of the solution was around 7. The chemical deposition of Pd coating was carried out at 50°C for 1 ~ 2 h. A shaker was used to agitate the solution, in order to obtain homogeneous Pd coating.

3.2.3 High Velocity Oxygen Fuel Sprayed NiCoCrAlY Coating

The High Velocity Oxygen Fuel (HVOF) sprayed NiCoCrAlY coating was prepared as a benchmark. The HVOF process was carried out in a Metallisation manufactured system, and a METJET III spray gun was used to produce the NiCoCrAlY bond coats. The process flow chart is shown in Figure 3.7. The substrates used for HVOF were sandblasted by Guyson Formula 1400 using F20 (average size 1 mm) brown alumina (Guyson). Then the sandblasted substrates were cleaned by a high pressure air gun to remove the blasting media residual. The flow rates of O_2 , kerosene and N_2 were adjusted by the control unit during the spraying process. The sprayed mixed powders were placed in the powder feeder (Metallisation) and carried to the spray gun by N_2 gas flow [165]. The spray gun (METJET III) was installed in a vertical axis robot arm. A control panel attached to the robot arm can preset the move passes of the spray gun, thus controlling the thickness of sprayed coatings. The spray gun moved from the upper to the lower position and travel back is taken as one pass, i.e. samples were sprayed twice during one pass. As shown in Figure 3.8, the pellet samples were firstly attached to the sample holders and fastened to the carousel. The carousel rotated at a constant rotation speed and a compressed air jet was used to cool the substrates during the spraying process.

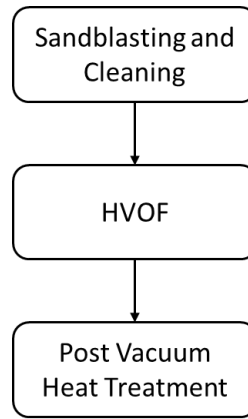


Figure 3.7 Process flow chart for the HVOF sprayed NiCoCrAl coating.

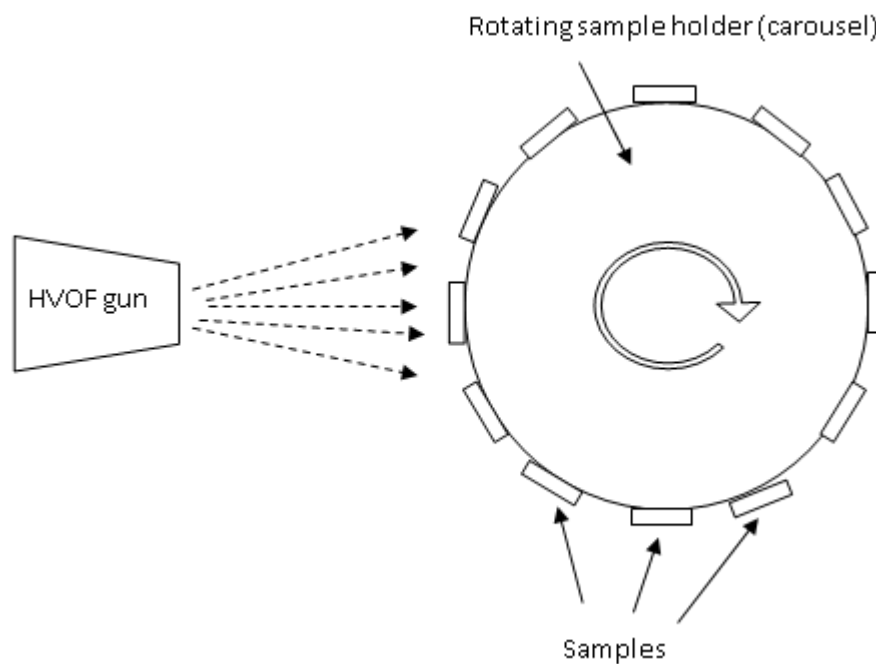


Figure 3.8 Schematic of the HVOF spray process [165]

The chemical composition of NiCoCrAlY (Ni191-4, Praxair) powder is shown in Table 3.3. The NiCoCrAlY coating was expected to have both good oxidation and corrosion resistance for industrial benchmark. The detailed HVOF spray parameters are shown in Table 3.4. The rotation speed of the carousel was set constant at 73 rpm. The substrates for NiCoCrAlY coating were M247 with 20 mm in diameter and 5 mm thickness. The surface treatment of the substrates before the HVOF

process was carried out within a Guyson Formula 1400 sandblasting cabinet using F20 brown alumina (average size 1000 μm , Guyson). The substrates were ultrasonically washed and oven dried before the spraying process. In addition, the sprayed bond coats were heat treated at 1100°C in a vacuum furnace (Elite, TVH12/75/600, section 3.6) for 2 h after the HVOF spraying.

Table 3.3 Chemical compositions of the Ni191-4 powders.

Elements (wt. %)	Co	Ni	Cr	Al	Y	other
Ni191-4	20.51	Bal.	17.80	12.60	0.58	0.13

Table 3.4 HVOF spray parameters of the Ni191-4.

Parameters	Ni191-4
Spray distance	356 mm
Carrier gas	6 l/min
Oxygen	920 l/min
Kerosene	475 ml/min

3.3 Ceramic Top Coat

A 8 wt.% Y_2O_3 -doped ZrO_2 (8YSZ, Al1075 Praxair) ceramic coating was applied as the top coat, in order to study the performance of the prepared bond coats in a TBC system after the bond coat preparation. The top coat was sprayed by the conventional air plasma spray (APS).

The APS was carried out using a TAFA SG-100 plasma torch and a 3710 plasma control unit. The same sample holder and robot arm used in the HVOF process were also used for the APS. A different powder feeder (Model 1264, Praxair) was used to avoid the powder cross contamination. The carrier gas was switched to Ar and Ar and H_2 were utilised to generate the plasma and accelerate the plasma

flame to increase the gun outlet temperature. The sample holder was operated at the same condition as in the HVOF process.

The chemical composition of Al1075 is shown in Table 3.5. Due to the shorter plasma flame length, the spray gun is much closer to the samples than in the HVOF spray gun. The detailed parameter settings are shown in Table 3.6. Due to the original setting unit of 3710 control unit is psi, so the actual flow rates of the primary gas, carrier gas and secondary gas were converted to psi unit according to industrial conversion method. The voltage and current used were maintained at around 37 V and 800 A. The rotation speed of the powder feeder (model 1264) was 6 rpm.

Table 3.5 Chemical composition of Al1075 ceramic powder.

Elements (wt. %)	Y ₂ O ₃	ZrO ₂
Al1075	7.5	Bal.

Table 3.6 APS parameters for spraying Al1075 ceramic powder.

Parameters	Al1075
Spray distance	90 mm
Carrier gas/Ar	40 psi
Primary gas/Ar	34 psi
Hydrogen/H ₂	12 psi

For 8YSZ coatings sprayed on the NiCoCrAlY bond coat, the samples were cleaned by a high pressure air gun before the APS. No further surface treatment was carried out before the process. However, due to the flat surface of Pt group coatings after aluminising, sandblasting was performed before spraying the 8YSZ top coat. F20 (Guyson) and F100 (average size 162 μm) brown alumina were used to create a rough surface for the 8YSZ coating in the Guyson Formula 1400

sandblasting cabinet. The F100 was used to create a medium rough surface to hold APS sprayed 8YSZ coating, because the F20 alumina could remove a large amount of bond coat materials (as shown in Figure 3.9). To give a brief understanding of the surface roughness created by different sized alumina, R_a values of the sandblasted surfaces were measured by a surface profile meter (Surftest SV-600) and the results are summarised in Table 3.7. Even though the F100 alumina can create the medium rough surface, some APS sprayed 8YSZ coatings may still detach from the diffused bond coats, the F20 was then chosen as the only surface treatment if this detachment occurred. The surface treatment information of bond coats is summarised in Table 3.8.

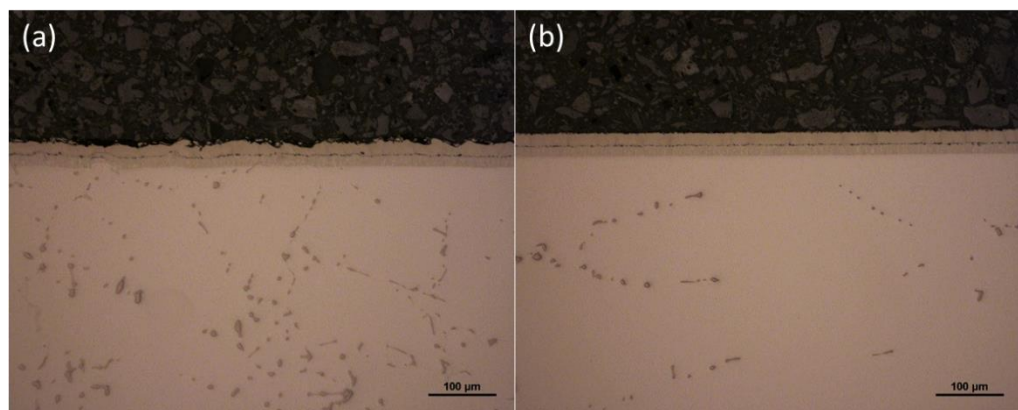


Figure 3.9 Optical images of the sandblasted PtAl coatings using (a) F20 and (b) F220 alumina.

Table 3.7 R_a value of different sized alumina blasted surfaces.

	$R_a / \mu\text{m}$
F20	6.5
F100	2.8
F220	0.5

Table 3.8 Sandblasting treatments of aluminide bond coats before APS.

Samples	Sandblasting	Samples	Sandblasting
PtAl 50 h (PA50h)	F100	PtAl 50 C (PA50C)	F100
PtAl 100 h (PA100h)	F100+F20	PtAl 100 C (PA100C)	F100+F20
PtAl 200 h (PA200h)	F100+F20	PtAl 200 C (PA200C)	F100+F20
ZrO ₂ -PtAl 50 h (PZ50h)	F100+F20	ZrO ₂ -PtAl 50 C (PZ50C)	F100
ZrO ₂ -PtAl 100 h (PZ100h)	F100	ZrO ₂ -PtAl 100 C (PZ100h)	F100+F20
ZrO ₂ -PtAl 200 h (PZ200h)	F100	ZrO ₂ -PtAl 200 C (PZ200h)	F100+F20
Pd-PtAl 50 h (PD50h)	F20	Pd-PtAl 50 C (PD50C)	F20
Pd-PtAl 100 h (PD100h)	F20	Pd-PtAl 100 C (PD100C)	F20
Pd-PtAl 200 h (PD200h)	F20	Pd-PtAl 200 C (PD200C)	F20

3.4 High Temperature Oxidation Test

The thermal cyclic oxidation test was performed in a rapid high temperature furnace (CM Inc. 1608 BL). Each thermal cycle consisted of 10 min heating up to 1100°C, 1 h dwell time at 1100°C and 20 min forced air cooling. Another 2 min were added to the dwell time to stabilise the temperature inside the furnace chamber. Coatings on Mar-M247 and Mar-M246 substrates were tested for 50, 100 and 200 cycles, and the coatings on In718 were tested for 50 and 200 cycles. Figure 3.10 shows the setup of the thermal cycling rig. Samples were placed on the sample table and lifted up to the heating chamber during the heating process. Isothermal oxidation test was carried out in a Carbolite HTF 17/5 chamber furnace. The ramping rate was 8 °C/min and the samples were cooled inside the furnace at 15 °C/min cooling rate.

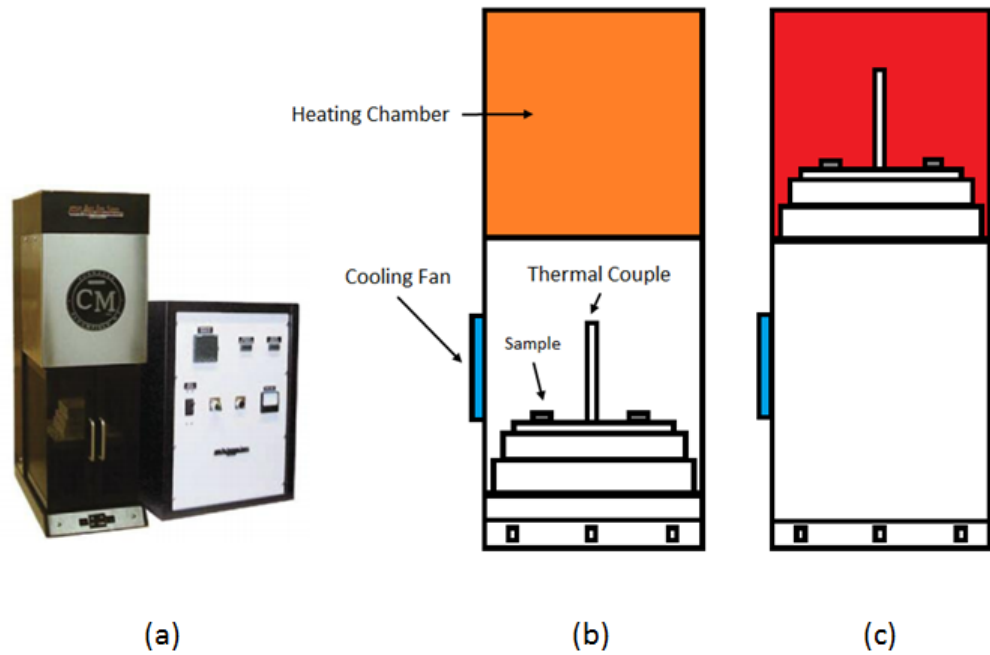


Figure 3.10 Schematic diagram of thermal cycling test rig. (a) Image of the furnace used for thermal cycling; (b) Cooling stage setup and (c) Heating stage setup.

3.5 Characterisation

3.5.1 Scanning Electron Microscopy (SEM)

Samples were sectioned for microstructure characterisation after the coating fabrication and oxidation test. An ATM Brilliant 220 cutting machine was used to cut the samples into small pieces for mounting using a BUEHLER AcuThin Abrasive Cut-off wheel. The cutting speed was set to 0.005m/s in order to keep the minimum damage to coating cross sections. Normally, the sectioned samples were mounted using conductive epoxy resin for SEM characterisation. However, for the TBC samples (samples with ceramic top coats), non-conductive resin was firstly used to hold the TBC samples before the cutting in order to protect the ceramic coatings. When the cutting was finished, the TBC samples were re-mounted using the same non-conductive resin.

All the mounted samples were ground by 240p, 400p, 800p and 1200p grit abrasive papers and polished by 6 μm and 1 μm diamond paste. Finally, for the SEM characterisation, a final polish was carried out using 0.02 μm silica. For the TBC samples, carbon coating was used to enhance the surface electrical conductivity. The microstructure characterisation was conducted on a Phillips XL30 ESEM-FEG SEM operated with 20kV voltage. The spot size of the electron beam was set to 3 in order to reduce the deadtime when performing energy dispersive X-ray analysis (EDX). Backscattered electron (BSE) mode was also used to detect the formed phases after coating fabrication and oxidation processes.

3.5.2 Energy Dispersive X-ray Analysis (EDX)

An Energy-dispersive X-ray spectroscopy (EDX, INCA, Oxford Instrument Link ISIS-3000) was used to help the elemental analysis in the coatings, combined within the Phillips XL30 ESEM-FEG SEM. X-rays emitted from different elements in the coating were examined by an EDX detector. When performing the area detection, a minimum 2 μm X 2 μm area was examined to give accurate results due to the precision of the detector. For some smaller areas in the coating, i.e. precipitates, a point scan was performed, but the influence of other elements in nearby area was also considered. In general, the EDX detector was operated at 20 kV, but for detecting ZrO_2 nanoparticles, the operating voltage was increased to 30 kV to distinguish Pt and Zr. In addition, because of the very small gap between Pt Ma line (2,050.5 KeV) and Zr La1 line (2,042.36 KeV), the Zr index was changed to $\text{K}\alpha_1$ line (15,775.1 KeV) which made it easier to detect Zr content in the coating. General errors in EDX analysis are considered in later discussion.

3.5.3 X-ray Diffraction (XRD)

The prepared coatings and powder mixtures were characterised by a Siemens D500 X-ray diffractometer to determine the formed phases. The instrument was operated at 25 mA and 40 kV using a Cu-K α source with a scanning range of 2-theta (2θ) from 10° to 90° and a scanning step of 0.02°. The XRD results were analysed using an Eva software to determine the crystalline phases.

3.5.4 Transmission Electron Microscopy (TEM)

Cross sections of the ZrO₂-PtAl electroplating layer on Mar-M-247 after oxidation were prepared for transmission electron microscopy (TEM) analysis using a focused ion beam microscope (FEI Nova Nanolab 600). Microstructure characterisation of the cross-sections and composition mapping were performed using a FEI Tecnai F20 G2 S-Twin field emission gun (FEG) TEM. The TEM was operated at 200kV and equipped with an Oxford Instruments X-Max 80 mm² TLE detector for energy dispersive X-ray (EDX) spectroscopy. Scanning TEM bright field images of the layer were also collected simultaneously with an electron probe diameter $\sim$ 1 nm convergence semi-angle 10 mrad.

3.5.5 Image Analysis

The thickness of the thermally grown oxide layer was calculated using Matlab software (R2015b) from at least 10 images evenly taken from cross-sectional SEM observation. The main theory of the Matlab calculation was to obtain the area and length of oxide layer by calculating the pixels of TGO. The average TGO thickness was determined by dividing the TGO area by the length of the TGO/substrate interface. The SEM images of oxidised samples were

first processed into a binary diagram. This process was carried out using an image tool (GIMP 2.8). The oxide layer was chosen by the Fuzzy Select Tool with the threshold set to 10. However, manual selection using the GIMP Free Select Tool was still needed to refine the oxide selection. When the oxide layer was selected, the processed image was then transferred to black and white binary image. The processed image is shown in Figure 3.11a and 3.11b. In the Matlab program, the 'bwperim' function was used to find the perimeter of an object in binary form. The processed image is shown in Figure 3.11c.

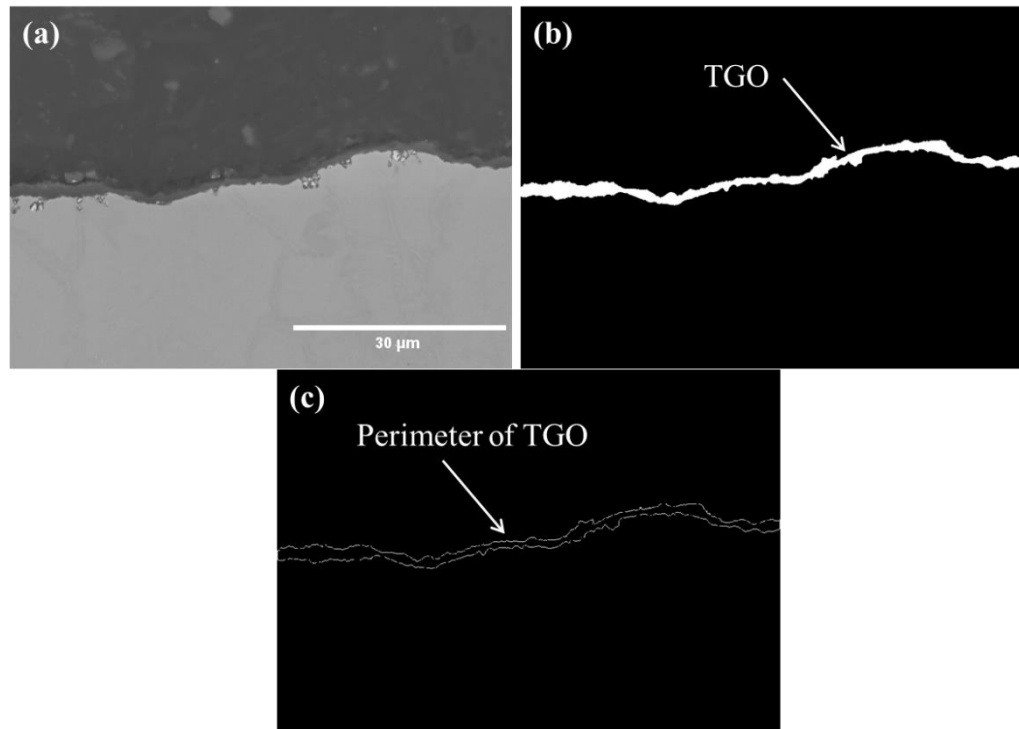


Figure 3.11 Processes of cross-sectional images using Matlab analysis. (a) Original image; (b) Processed binary image of the TGO and (c) Calculated perimeter of TGO.

In addition, the total pixel numbers of the oxide layer can be obtained from the GIMP histogram. The total pixel numbers of the oxide layer

were shown in the histogram by choosing the grey scale value of the oxide layer which was 255. The total pixel number of the cross-sectional image was also shown in the histogram which was used to calculate the area of the oxide layer. The GIMP software only gave the value of pixel numbers, so another image tool (ImageJ) was applied to calculate the actual distance by obtaining the single pixel length by determining the length of the scale bar in pixels.

Because the retrieved data from GIMP gave the total number of pixels in the perimeter, the edge pixels should be removed and the two long side pixels should be averaged to give the average number of pixels for the oxide layer length. To calculate the actual length of the oxide layer, the length between the two side connected pixels were considered to be one-pixel length and the length between two diagonally connected pixels would be considered to have $\sqrt{2}$ pixel length.

A schematic diagram shown in Figure 3.12 illustrates the principle for calculating the total oxide layer pixels. In Matlab, the program could find the pixels which were side connected. The left pixels would be considered diagonally connected and the length between each pixel was $\sqrt{2}$ pixel length. Finally, the pixel area and pixel length were converted to actual scale and the thickness could be calculated. Standard error was used to reflect the variation of calculated thicknesses. A detailed Matlab program for calculating TGO thicknesses can be found in Appendix 1.

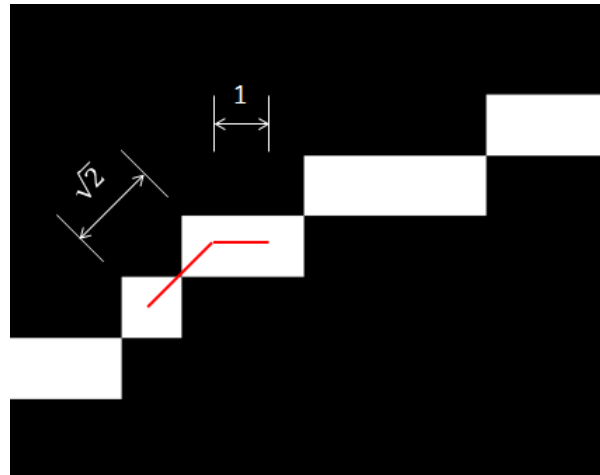


Figure 3.12 Principle of calculating oxide length based on single pixel length.

In order to investigate the rumpling level of bond coats, the TGO roughness was calculated by Matlab to indicate the rumpling behaviour of bond coats. Based on the perimeter results, as shown in Figure 3.13, the lower part of the perimeter and the edges were removed for image setup. The principle of calculating TGO roughness is shown in Figure 3.13, the upper part remained after GIMP process for roughness calculation because only the upper part roughness directly contacted with the top coat. R_p (the maximum peak difference to average height) and R_v (maximum valley difference to average height) can be obtained afterwards (Figure 3.13). The sum of R_p and R_v , R_t ($R_t = R_p + R_v$) was utilised to evaluate the rumpling resistance of the prepared coatings. The Matlab program used to calculate TGO roughness is shown in Appendix 2.

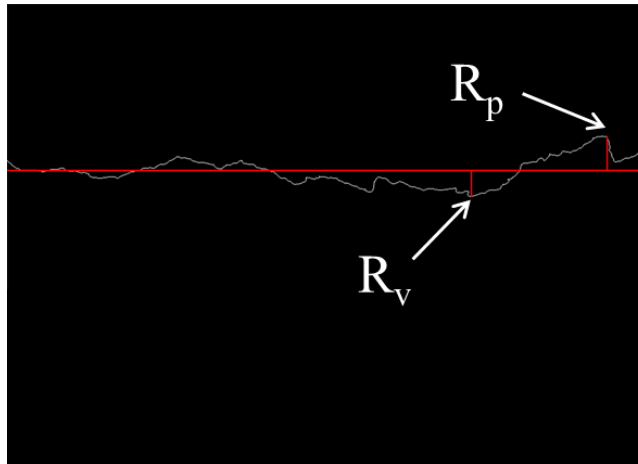


Figure 3.13 Principles of calculating TGO roughness by Matlab.

Chapter 4 Fabrication and Oxidation Behaviour of ZrO₂ Nanoparticle-modified PtAl Coating

Reactive elements have been reported to enhance the thermally grown oxide (TGO) adhesion and reduce the growth rate of TGO [12, 133-135]. According to the dynamic segregation theory, reactive elements can form oxides at the interface between the TGO and bond coat, and these oxide pegs increase the bonding strength of TGO [132]. In addition, the oxides of reactive elements can slow down the outward diffusion of Al and change the growth mechanism of TGO so that inward diffusion of oxygen becomes predominant, which can further reduce the growth rate of TGO [9, 132, 138]. As one of the reactive elements, Zr has shown great capability to improve the oxidation resistance and enhance the TGO adhesion of aluminide coating [138, 166]. Even so, the investigation of Zr is mostly limited to alloys rather than coatings [138, 167]. Only a few studies have reported the effects of Zr in Pt-modified aluminide (PtAl) coating [137] and the methods of introducing Zr are either costly or under studied [137, 168]. In theory, the oxides of reactive elements are also expected to achieve similar improvements as pure reactive elements [132]. However, related mechanisms on the effects of these oxides have not been clearly established.

In this chapter, ZrO₂ nanoparticles are incorporated into the PtAl bond coats, in an attempt to enhance their performance by exploiting the effect of reactive element oxides. Additionally, the ceramic top coat is normally made of ZrO₂. The embedded ZrO₂ particles may help to increase the mechanical strength of bond coats and also reduce the thermal mismatch. Incorporation of ZrO₂ particles in Pt (ZrO₂/Pt) coating is achieved by co-electrodeposition [157]. The ZrO₂-modified

PtAl coatings (ZrO₂-PtAl) are evaluated on different Ni superalloy substrates using thermal cyclic oxidation tests.

The evolution of ZrO₂ particles and their role in TGO growth are discussed, as well as the influences of substrate compositions on ZrO₂ nanoparticles and on the oxidation behaviours of the bond coats. Furthermore, the effects of pure Zr addition on coating oxidation behaviour are investigated by co-diffusing Zr and Al (ZrAl) into the substrate. The oxidation results of ZrAl coatings are discussed to give a deeper understanding of the behaviours of pure Zr and ZrO₂ in aluminide bond coats.

4.1 Co-electrodeposition of ZrO₂/Pt Composite Coating

4.1.1 Microstructure of ZrO₂/Pt Coating

Prior to co-electrodeposition, the as-received ZrO₂ nanoparticles are characterised as shown in Figure 4.1. The ZrO₂ nanoparticles have sizes ranging from 50 ~ 100 nm. Backscattered electron (BSE) images of cross sections of the pure Pt coating and the ZrO₂/Pt coating on M247 are shown in Figure 4.2a and 4.2b. The size of ZrO₂ nanoparticles makes it difficult to detect the small amount of ZrO₂ composition within the Pt coating. In addition, due to the very small gap between Pt Ma line (2,050.5 keV) and Zr La1 line (2,042.36 KeV), the analysis software could not easily distinguish the Zr content from the Pt matrix. By changing the Zr index to K α ₁ line (15,775.1 keV), it makes it easier for the analysis software to detect Zr content. Table 4.1 indicates a distinctly the ZrO₂ composition within the Pt matrix shown in the inset of Figure 4.2b. With the same electroplating time, the ZrO₂/Pt electroplating yields slightly thicker coating than that of

pure Pt plating, indicating that the dispersed nanoparticles may help the nucleation of Pt deposition.

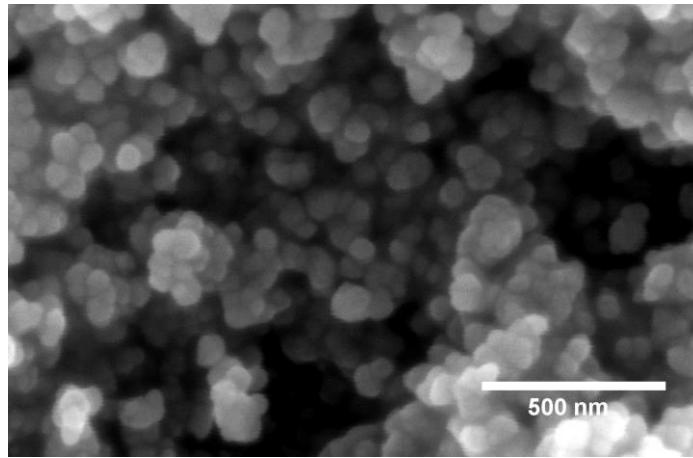


Figure 4.1 SEM image of ZrO₂ nanoparticles (coated with Pt).

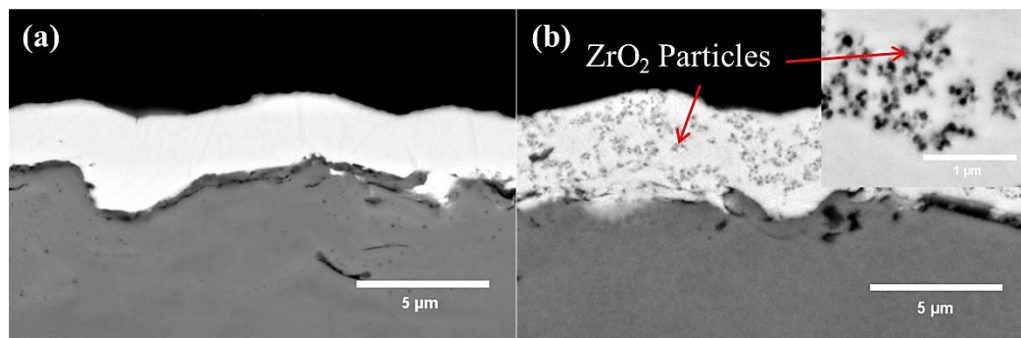


Figure 4.2 SEM and BSE images of the ZrO₂/Pt coating. (a) A cross-section of pure Pt coating on M247 and (b) A cross-section of the ZrO₂/Pt coating on Mar-M247. The inset of (b) shows the enlarged image of nano ZrO₂ particles.

Table 4.1 EDX result of the ZrO₂ particles in ZrO₂/Pt coating.

Elements / at. %	Pt	Y	Zr	O
	21.0	0.6	11.8	66.6

4.1.1.1 Effect of Particle Size

Co-electrodeposition of ZrO₂/Pt coating using ZrO₂ micro-particles is shown in Figure 4.3. Micro ZrO₂ particles yield much thicker coatings than ZrO₂ nanoparticles with the same plating time. The result of ZrO₂/Pt coating with micro-particles indicates that micro-particles are easier being co-deposited. The phenomenon may be attributed to the fact that the large particles have more surface area for the nucleation of Pt ions and then help the growth of Pt coating. However, micro-particles may cause larger internal stress than nanoparticles. In addition, it is hard to maintain a good dispersion of micro-sized particles in the electrolyte. Because the usual Pt coating thickness is 3 ~ 5 μm , nanoparticles are more desirable as they are able to produce finely distributed particles inside the Pt coating with appropriate thickness.

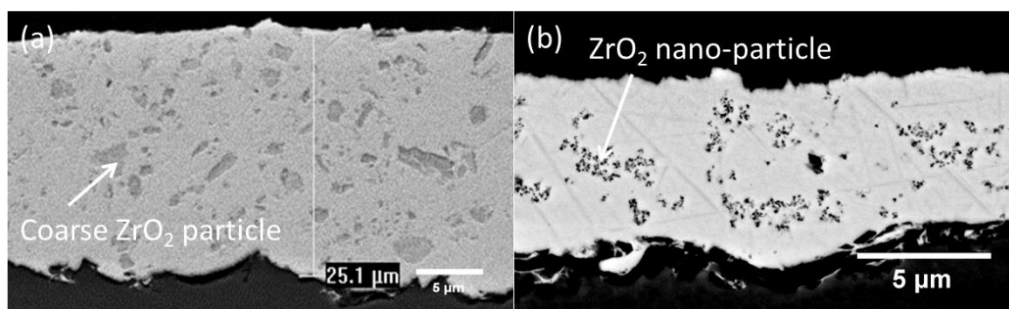


Figure 4.3 BSE images of the co-electrodeposited ZrO₂/Pt coatings with different sizes of ZrO₂ particles. (a) ZrO₂ micro-particles (1 ~ 5 μm) and (b) ZrO₂ nanoparticles (50 ~ 100 nm).

4.1.1.2 Effect of Particle Concentration in Electrolyte

Particle concentration has different effects on coating thickness with ZrO₂ micro- and nanoparticles. Low concentration (5 g/L) of ZrO₂ micro-particles can generate thicker Pt coating than high concentration (50 g/L), but the obtained thickness is still thinner than general concentration (20 g/L) deposited coating, which is shown in Figure 4.4a and 4.4b. Figure 4.4b also indicates that when the concentration is high, only fine particles in the solution can be co-deposited. However, the concentration does not have a significant effect on coating thickness with ZrO₂ nanoparticles. As shown in Figure 4.4c and d, high concentration (100 g/L) of ZrO₂ nanoparticles results in a similar microstructure to low concentration (5 g/L) deposited ZrO₂/Pt coating.

In addition, agitation is mandatory to maintain the dispersion of ZrO₂ nanoparticles and the transportation of Pt ions. It is shown in Figure 4.5 that no particles will be co-deposited without agitation. Because the particles are all settled at the bottom of the flask, the plain Pt layer is formed. When agitation is applied, the co-deposited layer can be observed in Figure 4.5.

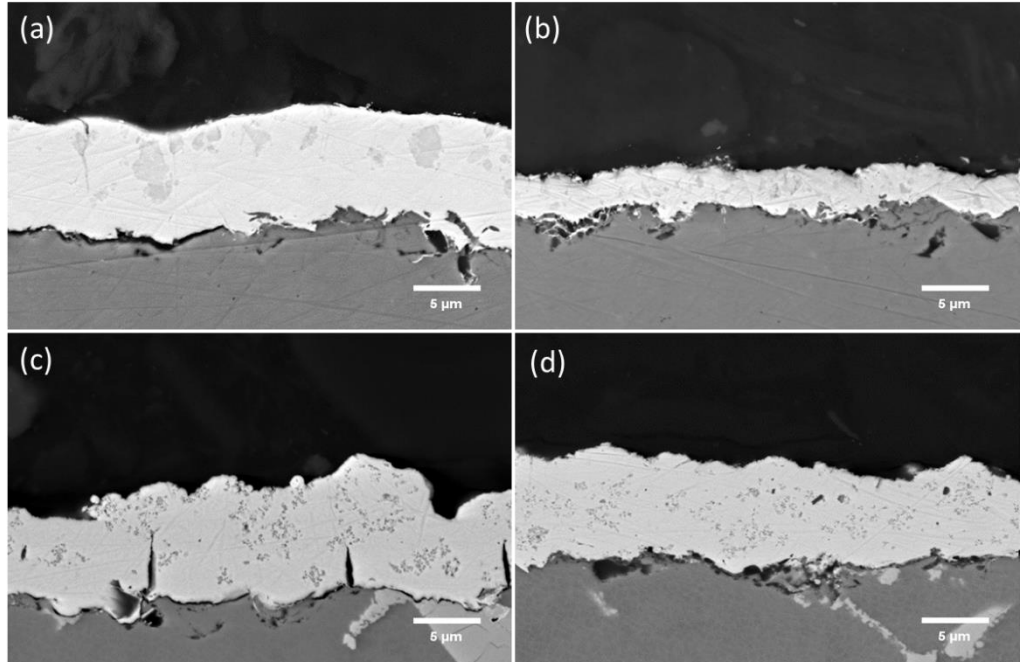


Figure 4.4 Influence of particle concentration on co-electrodeposited coating microstructures. (a) 5 g/L with coarse ZrO_2 particle; (b) 50 g/L with coarse ZrO_2 particle; (c) 5 g/L with ZrO_2 nano particle; (d) 100 g/L with ZrO_2 nano particles.

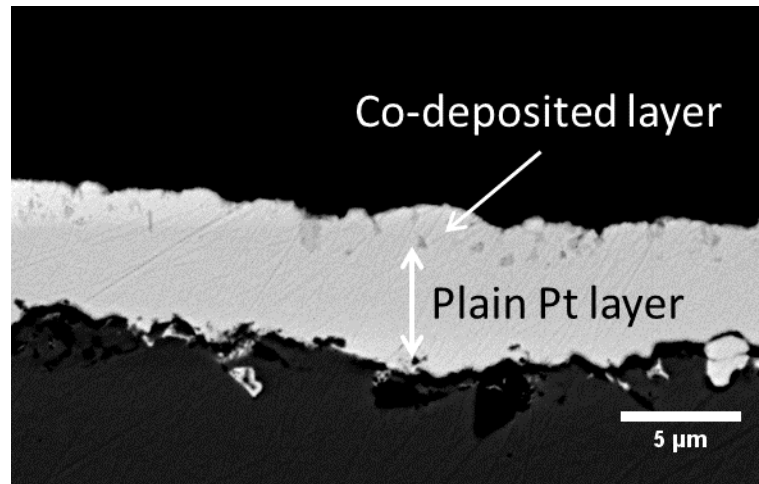


Figure 4.5 BSE image of ZrO_2/Pt coating without agitation in the first 30 min and with agitation in the next 30 min (total plating time: 1 h).

4.1.2 Discussion

During the current investigation, ZrO₂ nanoparticles have been co-electrodeposited with Pt using direct current. Even though pulse current is reported to be better than direct current to perform co-electrodeposition [146, 157, 169], direct current is still used in this study because it is easier to control compared to pulse electroplating. In addition, electroplating of Pt is well-established using direct current, i.e. the modification of parameters to carry out co-electrodeposited Pt-ZrO₂ coating is minimised.

The particle size of incorporated ZrO₂ particles has significant effect on co-deposited coating thickness. It is easier to co-deposit micro-particles than the nanoparticles because they can absorb more Pt ions to help deposition. Nevertheless, to achieve well-distributed micro-particles, the Pt coating thickness needs to be much thicker than 5 μm , however it is not economically viable.

In addition, effects of particle concentration vary with particle sizes. The co-electrodeposition of ZrO₂ micro-particles is influenced by both low and high particle concentrations. For low particle concentration, micro-particles are less co-deposited due to low particle concentration, thus fewer particles will be moved to the sample surface. For high particle concentration, more Pt ions will be absorbed by the particles, and agglomeration and precipitation may occur. This will reduce the Pt concentration in electrolyte, thereby decrease the deposition efficiency. Moreover, particles agglomerated near the sample surface may act a barrier to the particles far from the surface, i.e. block the particles to be co-deposited. In addition, the micro-particles are dispersed in the solution, and the movement of micro-particles may lead to the spallation of already co-deposited particles. Only the early

formed composite coating remains. These possible mechanisms are demonstrated in Figure 4.6.

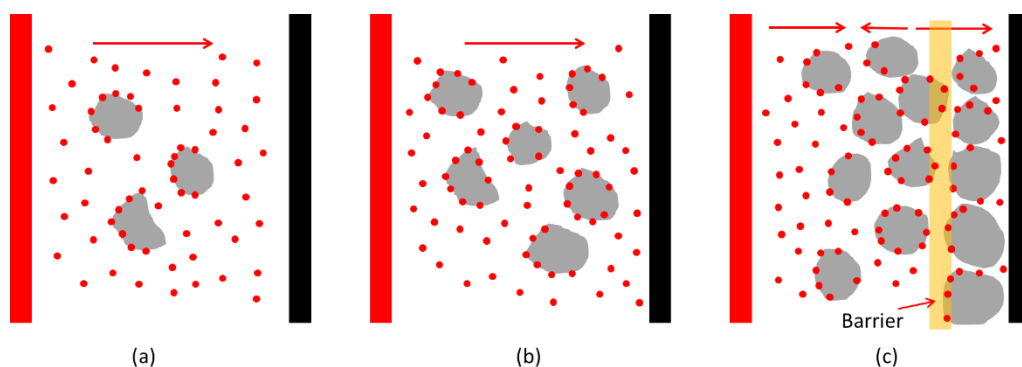


Figure 4.6 A possible mechanism of the effects of particle concentration on co-electrodeposition with ZrO₂ micro-particles. (a) low concentration (5 g/L); (b) general concentration (20 g/L); and (c) high concentration (50 g/L), barrier formed due to micro-particles agglomerated at the sample surface.

It is interesting that either using 100 g/L or 5 g/L nanoparticles, ZrO₂/Pt coating still has the similar coating thickness compared to the general concentration (20 g/L) deposited coating. Due to the size of the ZrO₂ nanoparticles, the deposition of Pt ions is not significantly affected by the ZrO₂ particles, because the Pt ions are not effectively absorbed by the nanoparticles. However, the micro-sized ZrO₂ particles could absorb more Pt ions when they have a large concentration, which will lead to the reduction of Pt deposition. In the situation of nanoparticles, the specific surface area of nanoparticles may also eliminate the effect caused by low particle concentration. Further studies need to be carried out to systemically investigate the effects of particles concentration with ZrO₂ nanoparticles.

4.2 Microstructures of ZrO₂-PtAl Coatings

4.2.1 Effects of Heat Treatments and Aluminising Process

Figure 4.7 reveals the microstructure development of pure Pt and ZrO₂/Pt coatings after vacuum heat treatment at 1100°C for 1 h. The line scan shows the inward diffusion of Pt and outward diffusion of substrate elements, such as Ni and Cr (Figure 4.8). In Figure 4.7b, the positions containing ZrO₂ particles are confirmed by EDX results (Table 4.2). Compared with the as-deposited ZrO₂/Pt coating, the volume of ZrO₂ nanoparticles is reduced after vacuum heat treatment. The alumina, which is used as the sandblasting media, remains after heat treatment as a marker to indicate the original surface.

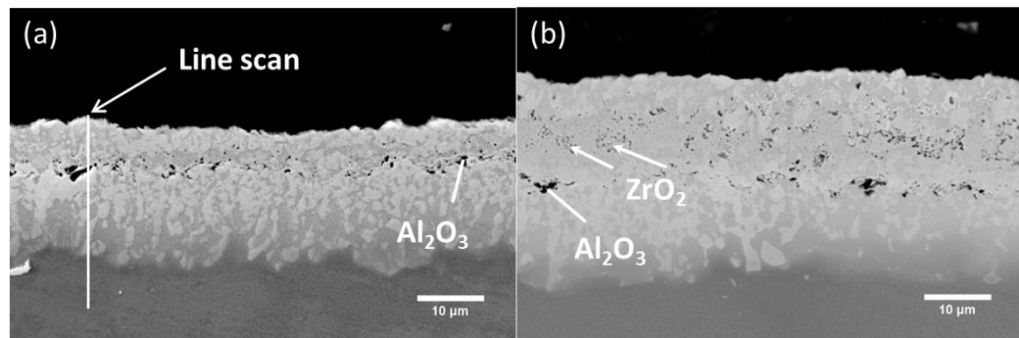


Figure 4.7 Microstructures of vacuum diffusion heat treated (a) pure Pt coating with line scanned position indicated and (b) ZrO₂/Pt coating.

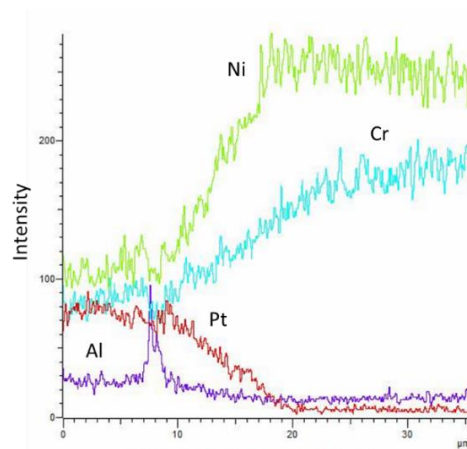


Figure 4.8 Line scan across the vacuum heat treated Pt coating.

Table 4.2 ZrO₂ composition in vacuum heat treated ZrO₂/Pt coating.

Elements	Pt	Ni	Zr	O	Al	Other
wt. %	60.9	15.9	4.4	6.0	6.0	Bal.

A step by step heating process is carried out to clarify the evaluation of ZrO₂ nanoparticles after vacuum heat treatment. Figure 4.9 demonstrates the microstructure development of ZrO₂/Pt coating in step vacuum heat treatment. ZrO₂ nanoparticles start to disappear at 1000°C. This observation confirms the disappearance of ZrO₂ nanoparticles.

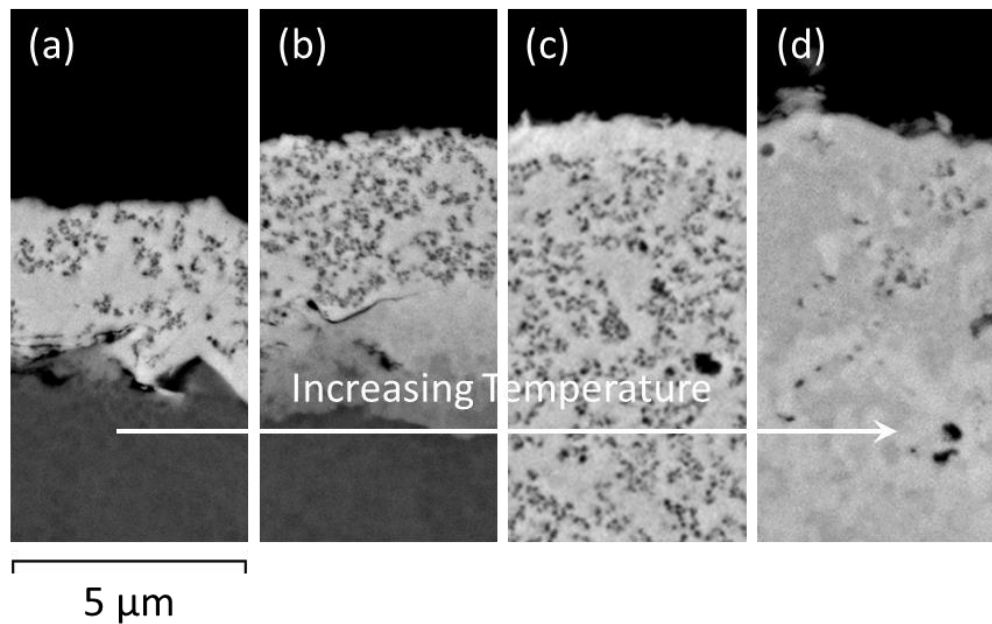


Figure 4.9 Microstructure development of step by step heat treated ZrO₂/Pt coating. (a) 700°C for 1 h, (b) 800°C for 1 h (c) 900°C for 1 h and (d) 1000°C for 1 h.

Generally, the high temperature low activity aluminising process would finalise the microstructure of the PtAl bond coat. A post vacuum heat treatment after aluminising can optimise the microstructure of aluminised coatings. Figure 4.10 shows the final microstructures of

PtAl and ZrO₂-PtAl bond coats. A sketch of the PtAl bond coat with key features is shown in Figure 4.11. An outlayer of β -(Ni, Pt)Al phase region and an inter-diffusion zone (IDZ) constitute the basic microstructure of PtAl bond coat. EDX results of the β phase region in PtAl and ZrO₂-PtAl bond coats are shown in Table 4.3, which indicate the very similar compositions of the β phase region and IDZ in both bond coats. Some ZrO₂ nanoparticles disappeared after diffusion vacuum heat treatment, but no ZrO₂ nanoparticles are detected in the co-electrodeposited layer in the final coating microstructure, indicating a kind of 'dissolution' of the particles during heat treatment stages. In the IDZ, precipitates containing refractory elements, such as W, are observed (as shown in Table 4.3).

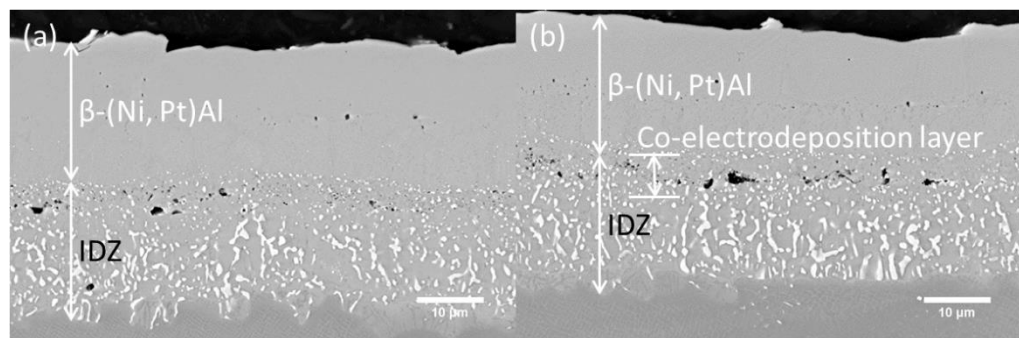


Figure 4.10 Microstructures of final (a) PtAl and (b) ZrO₂-PtAl bond coats.

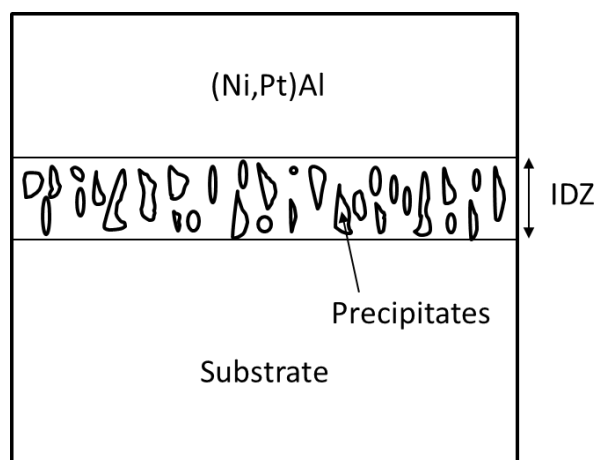


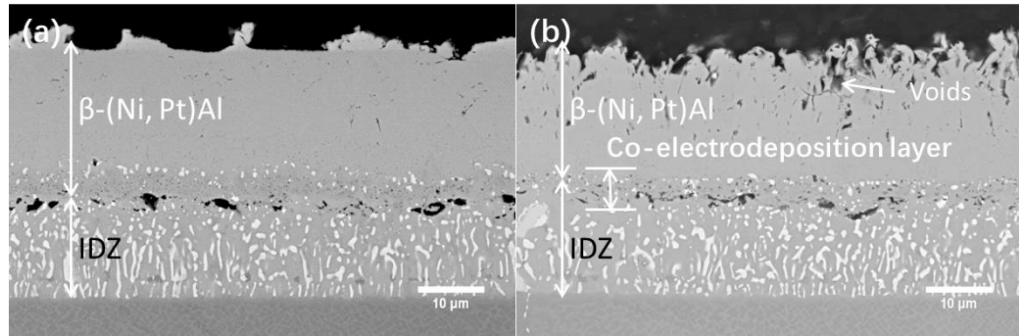
Figure 4.11 Sketch of Pt-modified aluminide bond coat.

Table 4.3 EDX results of β phase region and IDZ in PtAl and ZrO₂-PtAl bond coats.

Elements / wt. %	Pt	Ni	Al	Ti	Cr	Co	W
β region (PtAl)	34.7	40.8	14.8	0.4	3.8	5.6	/
β region (ZrO ₂ -PtAl)	31.7	42.8	15.0	0.4	4.4	5.7	/
IDZ (PtAl)	16.6	17.7	3.9	0.4	10.0	2.8	48.6
IDZ (ZrO ₂ -PtAl)	18.5	23.7	7.2	0.6	8.6	7.3	34.2

4.2.1.1 Effects of Substrate Compositions on Coating Microstructure

Because the main difference between M246 and M247 is the Hf content, similar microstructures of PtAl and ZrO₂-PtAl bond coats are expected. Figure 4.12 shows the microstructures of PtAl and ZrO₂-PtAl bond coats on M246 substrate. The PtAl coating reveals similar microstructure to the PtAl coating on M247 substrate. Some voids are found in the β phase region after the post-vacuum heat treatment in the ZrO₂-PtAl bond coat. In the co-electrodeposited layer, the ZrO₂ nanoparticles are still not detected. Table 4.4 gives the EDX results of the detected β phase region of both coatings. Similar β phase compositions are found in both coatings. The composition of the precipitates in IDZ is also shown in Table 4.4. Because of the higher content of Mo, the precipitates contain a certain amount of Mo which is not found in the coatings on M247.

Figure 4.12 Microstructures of PtAl and ZrO₂-PtAl bond coats on M246.Table 4.4 Compositions of detected β phases in PtAl and ZrO₂-PtAl bond coats on M246.

Elements / wt. %	Ni	Al	Cr	Co	Pt	Mo	W
β phase (PtAl)	41.3	14.9	3.6	4.6	35.2	-	-
β phase (ZrO ₂ -PtAl)	46.0	15.8	4.2	5.3	28.2	-	-
IDZ (PtAl)	13.3	0.6	8.8	5.8	15.5	15	39.6
IDZ (ZrO ₂ -PtAl)	13.5	0.8	8.7	5.5	18.2	14.8	35.2

Because In718 has significant differences in chemical composition compared to M247, the ZrO₂-PtAl bond coats were compared from the co-electrodeposition step with PtAl bond coats to study the development of microstructures. Figure 4.15a and 4.15b show the microstructures of as-deposited Pt and ZrO₂/Pt coatings. Both coatings have similar microstructures to those on M247 substrate. The ZrO₂ nanoparticles are incorporated in Pt coating as shown in Figure 4.13b. Some ZrO₂ nanoparticles remain after diffusion vacuum heat treatment. Table 4.5 gives the EDX composition of the ZrO₂ nanoparticles area. Because In718 contains less Al than M247, the detected Al content is dramatically lower. Other elements found in the area are Ti, Cr and Fe.

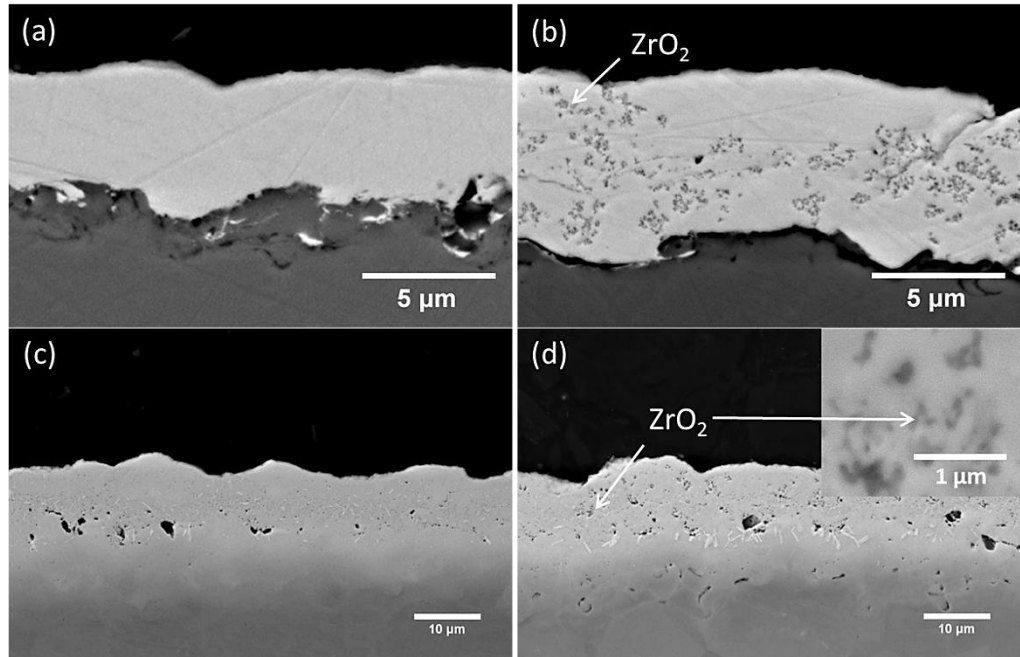


Figure 4.13 Microstructures of Pt and ZrO₂/Pt coatings on In718 substrate after electroplating and vacuum diffusion heat treatment. (a) As-coated Pt coating; (b) As-coated ZrO₂/Pt coating; (c) Diffused Pt coating and (d) Diffused ZrO₂/Pt coating. The inset of (d) shows the enlarged image of ZrO₂ nanoparticles.

Table 4.5 EDX result of the ZrO₂ nanoparticles in In718 after diffusion vacuum heat treatment.

Elements	Pt	Ni	Zr	O	Al	Other
wt. %	46.6	16.8	11.7	9.8	1.5	Bal.

Final coating microstructures of PtAl and ZrO₂-PtAl bond coats are shown in Figure 4.14. Table 4.6 gives the EDX results of identified β phase region, IDZ and dark spot precipitates in Pt and ZrO₂-PtAl coatings on In718. ZrO₂ nanoparticles disappear in the co-electrodeposited layer. EDX analysis reveals the presence of Cr precipitates in both coatings on In718, attributed to the high concentration of Cr. The reduced inter-diffusion region on this substrate may be due to the low concentration of refractory elements.

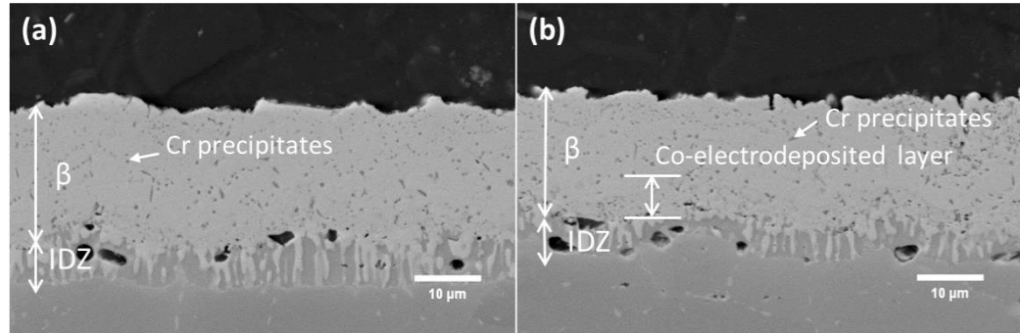


Figure 4.14 Microstructures of (a) PtAl and (b) ZrO₂-PtAl aluminide bond coats on In718 substrate after post heat treatment.

Table 4.6 EDX analysis of the β phase region, IDZ and dark spot precipitates in Pt and ZrO₂-PtAl coatings on In718.

Elements (wt. %)	Cr	Ni	Ti	Al	Pt	Fe	Mo	Nb	S
β phase (PtAl)	3.1	35.9	0.7	13.9	40.4	6.0	-	-	-
β phase (ZrO ₂ -PtAl)	3.2	39.5	0.7	14.1	35.7	6.8	-	-	-
Dark spot (PtAl)	25.0	27.6	0.4	9.2	28.6	9.3	-	-	-
Dark spot (ZrO ₂ -PtAl)	25.4	30.4	0.6	8.8	24.4	9.8	-	-	0.5
IDZ (PtAl)	13.2	29.5	0.8	11.2	31.9	8.9	3.0	1.5	-
IDZ (ZrO ₂ -PtAl)	12.4	32.4	0.7	12.0	28.4	9.2	2.8	1.7	0.4

4.3 Oxidation Behaviour of ZrO₂-PtAl Coatings

4.3.1 Microstructures of Oxidised ZrO₂-PtAl Coatings

The microstructure evolution of PtAl and ZrO₂-PtAl bond coats after cyclic thermal oxidation tests at 1100°C on M247 is shown in Figure 4.15. Growth of the TGO layer is observed in both coatings. Table 4.7 provides the EDX analysis of the TGO layer, indicating that Al₂O₃ is the main composition of the TGO layer. However, Al depletes after cyclic thermal oxidation because the γ' (Ni₃Al) phase is formed (dark area in both bond coats). The compositions of the detected γ' phases are shown in Table 4.7.

The γ' phase area increases with increasing as thermal cycles increase because more Al is consumed to form the TGO layer. Figure 4.16 demonstrates the formation mechanism of γ' phase after thermal cycling. At the early stages of oxidation, γ' phase mostly occurs at the interface of β phase region and IDZ because of the inward diffusion of Al. As the oxidation continues, γ' phase will also occur within the β phase region and top coating surface adjusting to the oxide layer due to the further outward diffusion of Al. In current investigation, no γ phase is detected in both bond coats, which is the next transformation of γ' phase when Al depletion continues [5]. Because the β phase still exists in the coating, further protection of both bond coats is expected.

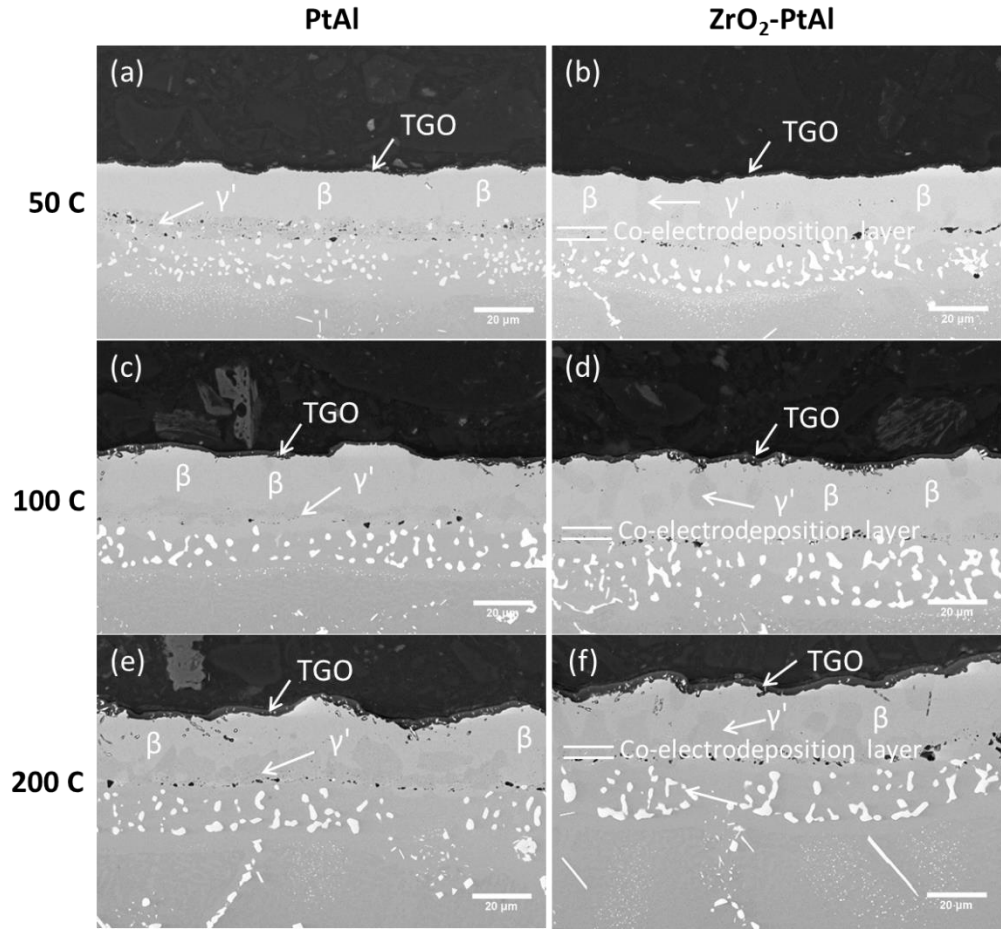


Figure 4.15 Microstructure evolution of PtAl and ZrO₂-PtAl bond coats in cyclic thermal oxidation test at 1100°C. (a) PtAl 50 cycles; (b) ZrO₂-PtAl 50 cycles; (c) PtAl 100 cycles; (d) ZrO₂-PtAl 100 cycles; (e) PtAl 200 cycles; (f) ZrO₂-PtAl 200 cycles.

Table 4.7 EDX analysis of the TGO layer and γ' phase in PtAl and ZrO₂-PtAl bond coats after cyclic oxidation test.

Elements (wt. %)	O	Ni	Ti	Al	Pt	Cr	Co
TGO (PtAl)	50.3	-	-	40.1	-	-	-
TGO (ZrO ₂ -PtAl)	52.9	-	-	42.2	-	-	-
γ' phase (PtAl)	-	48.9	1.2	8.9	30.3	4.3	6.5
γ' phase (ZrO ₂ -PtAl)	-	52.2	1.0	9.7	22.7	4.4	7.1

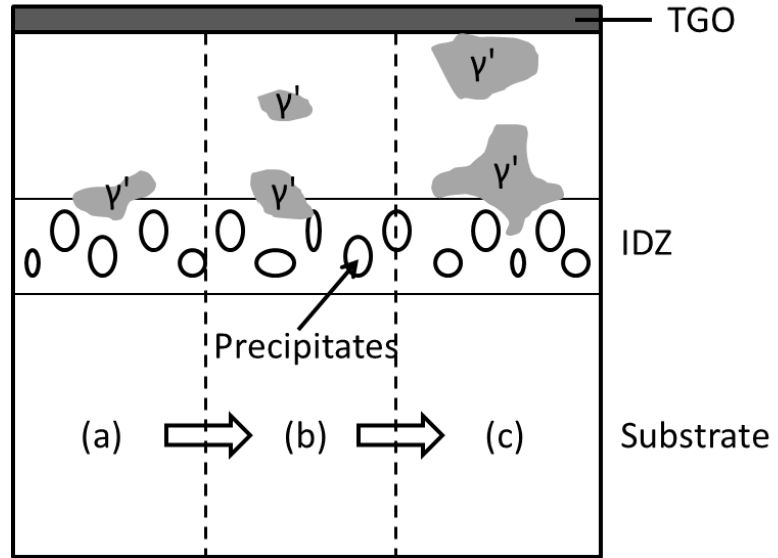


Figure 4.16 Sketch of γ' phase area develops after (a) 50 cycles, (b) 100 cycles and (c) 200 cycles.

Hafnium oxide is heavily formed within the TGO layer and near surface area in both coatings after the cyclic thermal test, especially for the longer period tested samples. Figure 4.17 shows the Hf rich oxides formed in both bond coats after 200 cycles. The EDX analysis shown in Table 4.8 indicates that Hf rich oxide in ZrO_2 -PtAl coating contains Zr, while there are only a few Hf rich oxides with Zr in the PtAl coating. In addition, the dark phase formed around the Hf rich oxide is confirmed by EDX analysis to be an aluminium rich oxide. Because ZrO_2 nanoparticles disappear in the final coating microstructure, the Zr content found in Hf-rich oxide may come from the disappeared ZrO_2 nanoparticle. However, investigations need to be carried out to verify whether Zr comes from the disappeared ZrO_2 particles or from the substrate, because M247 contains 0.05 wt. % of Zr.

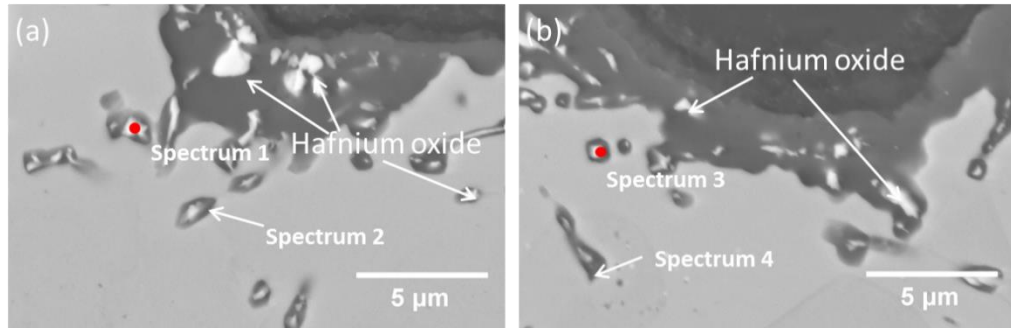


Figure 4.17 Microstructures indicate the Hafnium oxides formed in PtAl and ZrO₂-PtAl bond coats in cyclic thermal oxidation test at 1100°C. (a) Hafnium oxides in PtAl coating after 200 cycles; (d) Hafnium oxides in ZrO₂-PtAl coating after 200 cycles.

Table 4.8 EDX results of Hf oxides in PtAl and ZrO₂-PtAl coating after 200 cycles.

Elements / wt. %	Ni	Al	Hf	O	Zr	Co	Cr
Spectrum 1	4.5	4.0	73.6	17.9	-	-	-
Spectrum 2	29.4	26.5	-	27.3	-	3.0	2.7
Spectrum 3	12.6	10.0	37.2	27.4	9.7	1.5	1.6
Spectrum 4	27.4	28.9	-	29.0	-	3.2	2.9

4.3.1.1 Effects of Substrates on Microstructure Development of ZrO₂-PtAl Coatings

The microstructure evolution of PtAl and ZrO₂-PtAl bond coats on M246 substrate after cyclic thermal oxidation at 1100°C is shown in Figure 4.18. Because M246 does not contain any Hf, the Hf rich oxides have not been detected in either coating after oxidation. In addition, spinel is formed during the oxidation test. Table 4.9 provides the EDX results of detected spinel phases which are formed after 50 cycles in both bond coats. The high content of Ni supports that NiAl₂O₄ is predominant in spinel phases. In both coatings, a few Pt precipitates

are detected in the spinel phase region which is not seen in the coatings on M247 substrate. However, the formation of spinel and Pt precipitates is not usual in PtAl coatings and may be caused by the original coating surface morphology, which will be discussed later.

Similar to the PtAl coatings on M247 substrate, the β phase depletes during the cyclic oxidation test. However, the β to γ' transformation is almost completed after 200 cycles because little β phase is detected in both coatings. Table 4.9 indicates that the Al content in γ' phase is around 8 wt. %, which is close to the 5-6 wt. % in γ phase. Though γ phase has not been detected in ZrO₂-PtAl coating, a good amount of γ phase is detected in PtAl coating (shown in Table 4.9).

For the 200 cycle samples, the TGO layer in PtAl coating has already suffered from severe spallation, but the TGO layer continues to grow after 200 cycles in ZrO₂-PtAl coating. Although ZrO₂ nanoparticles still disappear from the bond coat, some particles are observed in the co-electrodeposited layer after oxidation. EDX analysis (Table 4.9) reveals that the compositions of the particles in the co-electrodeposited layer of ZrO₂-PtAl coating on M246 are Al₂O₃, which is not observed in the ZrO₂-PtAl coating on M247 or any of the PtAl coatings.

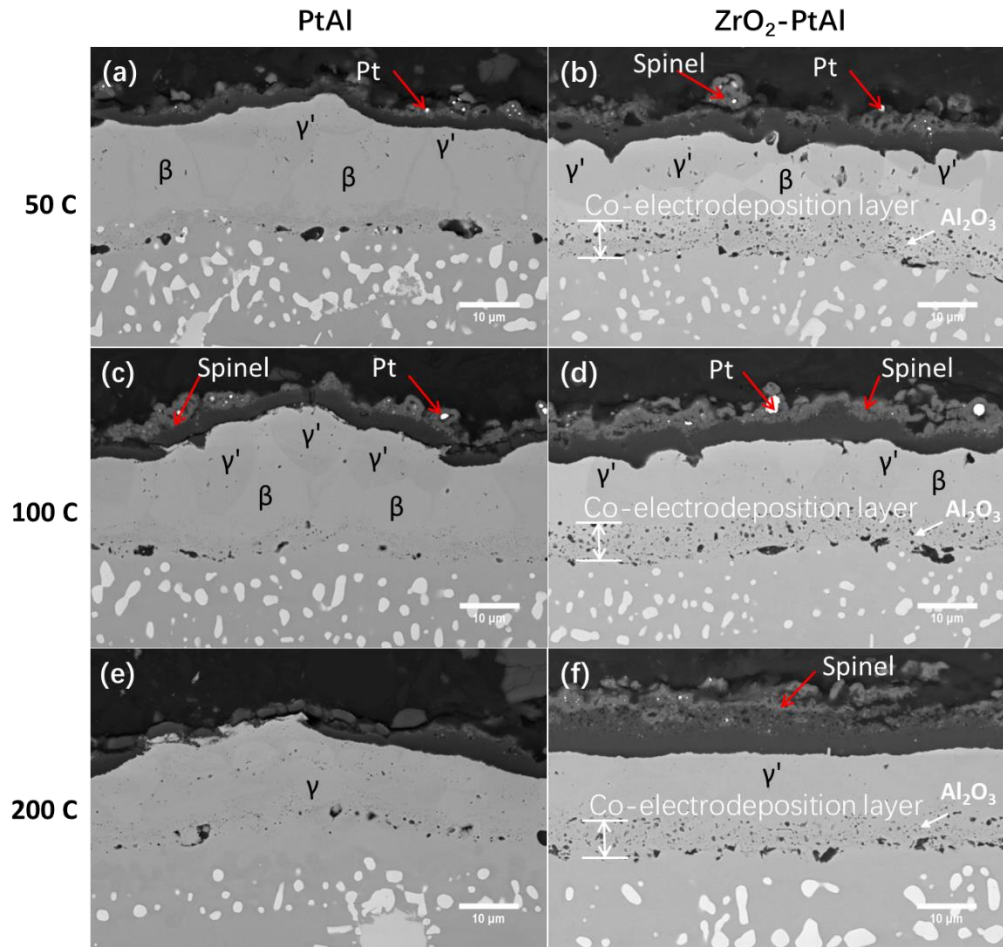


Figure 4.18 Evolution of microstructures of PtAl and ZrO₂-PtAl coatings on M246 substrate after thermal cyclic oxidation test at 1100°C. (a) PtAl 50 cycles; (b) ZrO₂-PtAl 50 cycles; (c) PtAl 100 cycles; (d) ZrO₂-PtAl 100 cycles; (e) PtAl 200 cycles and (f) ZrO₂-PtAl 200 cycles.

Table 4.9 EDX analysis of key features in PtAl and ZrO₂-PtAl bond coats on M246 after cyclic thermal oxidation test.

Elements / wt. %	Ni	Al	O	Pt	Co	Cr	W
Spinel (PtAl)	20.1	28.0	39.2	-	4.1	3.1	-
Spinel (ZrO ₂ -PtAl)	22.5	26.0	40.1	-	3.8	3.6	-
Pt precipitate (PtAl)	2.3	-	3.0	91.2	-	-	-
Pt precipitate (ZrO ₂ -PtAl)	2.4	-	3.5	89.3	-	-	-
γ' phase (PtAl)	50.2	7.8	-	27.6	5.6	3.8	2.8
γ' phase (ZrO ₂ -PtAl)	49.7	8.0	-	28.7	5.3	4.3	2.3
γ phase (PtAl)	56.4	6.6	-	14.5	7.1	6.6	6.7
Particles (co-electrodeposited layer)	34.0	22.7	25.6	9.8	3.9	2.8	-

Because In718 is used as the bench mark to investigate the behaviour of ZrO₂ nanoparticles, samples are only characterised after 50 and 200 cycles. Figure 4.19 shows the microstructures of the two bond coats after 50 and 200 cycles. The inter-diffusion zone disappears after 50 cycles because of Al depletion, which is not observed in the coatings on M247 and M246. Table 4.10 gives the EDX analysis of the bond coats after cyclic oxidation tests. The low Al content proves that β to γ transformation is already completed in both coatings. The consumption of Al is faster in In718 at 1100°C because γ'' phase is the main strengthening phase [29] rather than the γ' phase which is more stable at a higher temperature. Because of the fast consumption of Al, further oxidation resistance of the bond coats is deteriorated.

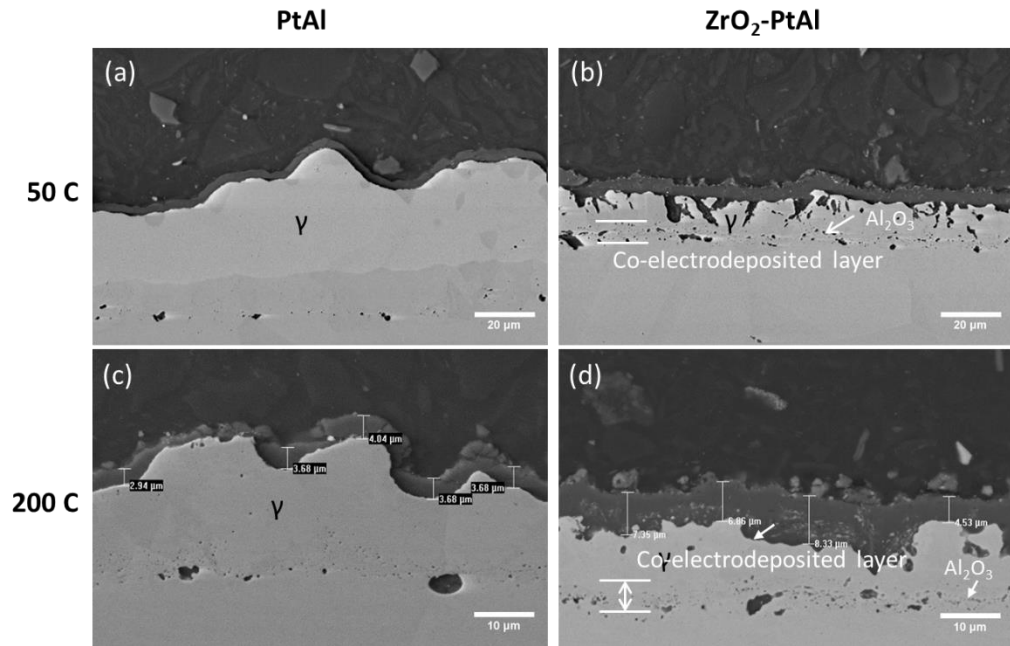


Figure 4.19 Microstructures of PtAl and PtZrO₂ aluminide bond coats on In718 substrate after thermal cyclic oxidation test at 1100°C. (a) PtAl 50 cycles; (b) ZrO₂-PtAl 50 cycles; (c) PtAl 200 cycles and (d) ZrO₂-PtAl 200 cycles.

Table 4.10 EDX analysis of the coating area of PtAl and ZrO₂-PtAl bond coats on In718 after 50 and 200 cycles.

Elements / wt. %	Ni	Al	Pt	Ti	Fe	Cr
50 cycles PtAl	47.3	2.4	19.4	1.3	14.3	15.4
50 cycles ZrO ₂ -PtAl	49.1	2.3	18.7	1.2	12.9	15.8
200 cycles PtAl	51.2	2.0	12.5	1.2	15.7	16.8
200 cycles ZrO ₂ -PtAl	53.4	1.6	9.6	1.3	16.2	17.1

Similar to the ZrO₂-PtAl coating on M246, a few Al₂O₃ particles are observed in the co-electrodeposited layer (shown in Figure 4.19b and 4.19d). Nevertheless, the volume of detected Al₂O₃ particles in the co-electrodeposited layer makes it difficult to distinguish them from sandblasting alumina. Furthermore, severe internal oxidation is found in ZrO₂-PtAl coating. Figure 4.20a shows the detailed microstructure of internal oxides. EDX analysis in Table 4.11 indicates that the main

composition of internal oxide is aluminium oxide and the bright phase in internal oxide containing certain Zr. In addition to internal oxides, Zr is also detected in the TGO layer in Figure 4.20b. However, In718 does not contain Zr so the Zr found in the TGO layer and internal oxides on In718 can be confirmed as coming from the disappeared ZrO₂ nanoparticles.

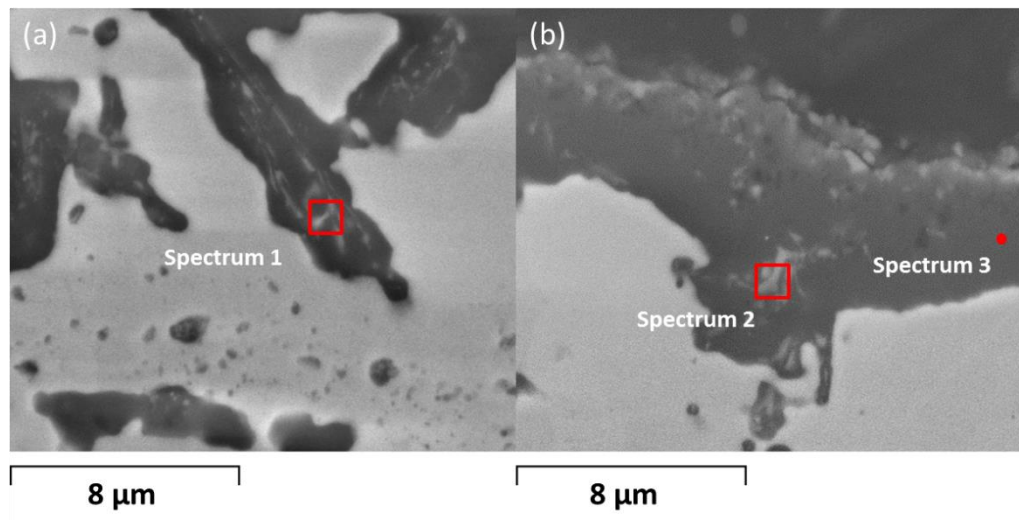


Figure 4.20 Microstructures of internal oxides and Zr oxides found in PtZrO₂ aluminide coating on In718 substrate after (a) 50 cycles and (b) 200 cycles.

Table 4.11 EDX analysis of labelled locations in Figure 4.20.

Elements (wt. %)	O	Cr	Ni	Fe	Al	Zr	Pt
Spectrum 1	43.6	1.9	4.8	1.7	34.7	11.4	1.8
Spectrum 2	37.2	2.7	8.1	2.6	31.8	12.3	5.1
Spectrum 3	50.2	0.2	0.5	0.3	48.7	-	-

Although the ZrO₂-PtAl coating has a larger TGO thickness than PtAl coating, the coating rumpling level of ZrO₂-PtAl bond coat is lower than that of the PtAl coating on In718, which is not clearly shown on other two substrates. Figure 4.21 gives the low magnification images of the both bond coats on In718 substrate after the cyclic thermal oxidation test. It suggests that the internal oxides formed due to the incorporation of ZrO₂ nanoparticles, may act as oxide pegs to increase the rumpling resistance of the ZrO₂-PtAl bond coat.

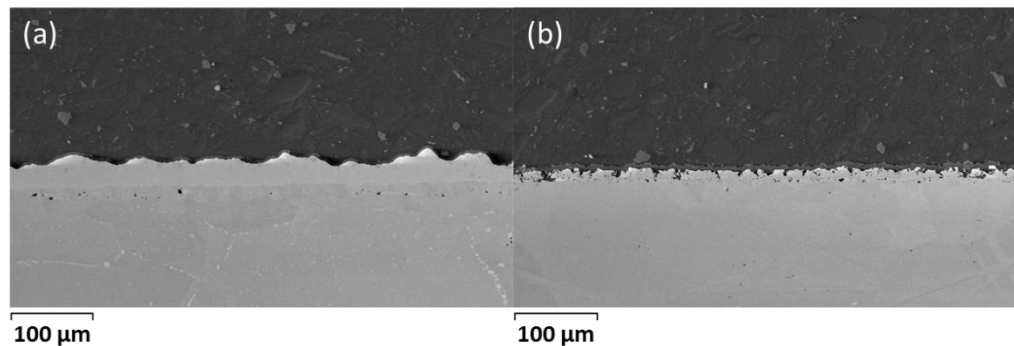


Figure 4.21 Surface roughness changes of PtAl and PtZrO₂ aluminide bond coats on In718 substrate after thermal cycling. (a) PtAl 50 cycles; (b) PtZrO₂ 50 cycles.

4.3.2 TGO Growth of ZrO₂-PtAl Coatings on Different Substrates

TGO thickness changes in PtAl and ZrO₂-PtAl coatings during cyclic thermal oxidation test are summarised in Figure 4.22. There is an indication that TGO growth in the M247 samples is slowed by the addition of ZrO₂. However increased TGO growth rates are observed in the ZrO₂-PtAl coatings on both M246 and In718. The TGO thickness decrease in the ZrO₂ modified coating on In718 is due to TGO spallation.

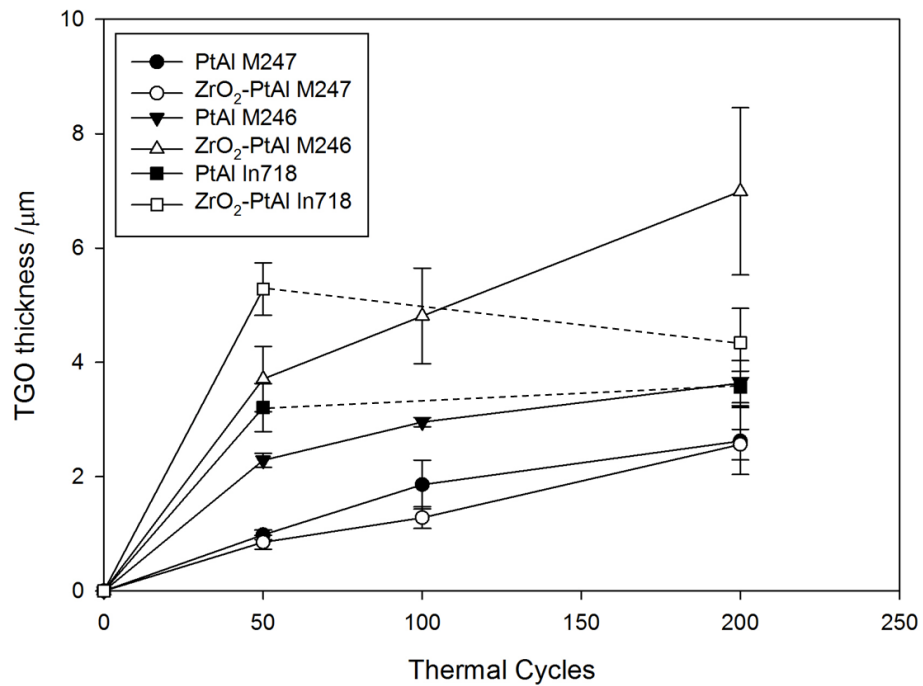


Figure 4.22 Changes of TGO thickness of PtAl and ZrO₂-PtAl coatings on different substrates versus thermal cycles (error bar: standard deviation).

The surface roughness profile of TGO in PtAl and ZrO₂-PtAl coatings before and after thermal cycling is shown in Figure 4.23. An increase of TGO roughness is found in both coatings on M247 after 200 cycles, with little difference between the two coating types. On M246 substrate, the TGO roughness increases in the PtAl coating. Nevertheless, the roughness of ZrO₂-PtAl coating remains unchanged between 50 and 200 cycles. On In718 substrate, there is no significant change in TGO roughness for either coating between 50 and 200 cycles, but a huge increase in roughness is observed as compared to the original surface. The PtAl coating has a remarkably higher TGO roughness than the ZrO₂-PtAl coating on In718.

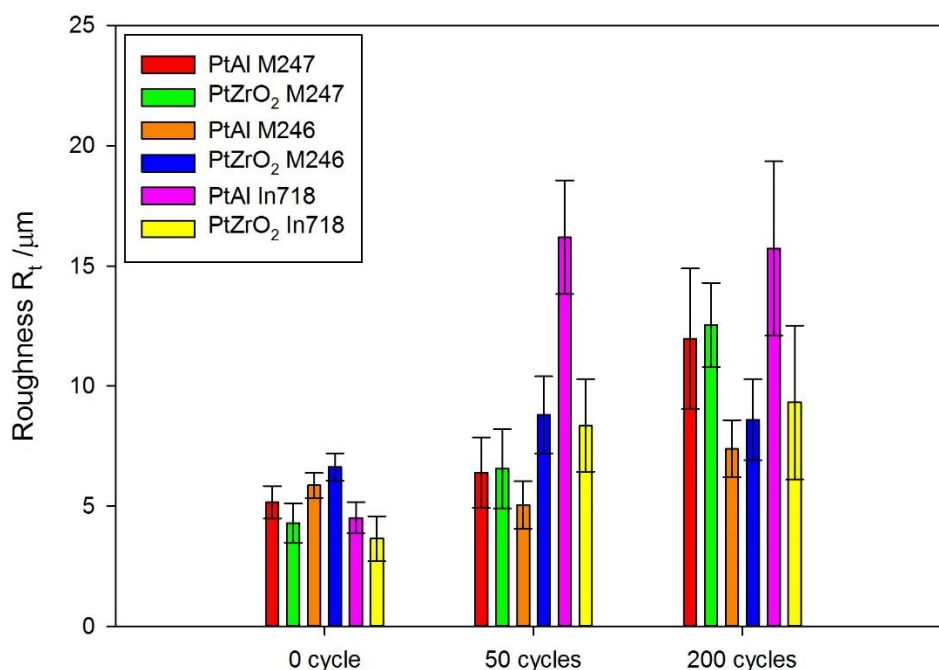


Figure 4.23 Surface roughness profile of PtAl and ZrO₂-PtAl coatings before and after thermal cycling (error bar: standard deviation).

4.4 Reaction between ZrO₂ and Al at 1100°C

The microstructure of the co-electrodeposition layer is carefully characterised to investigate the behaviour of ZrO₂ nanoparticles. Figure 4.24 and Table 4.12 provide detailed microstructures and EDX analysis of the electroplated layers on M247. Hf rich precipitates are formed in the electroplating layer on M247 and appear to be associated with Al rich regions. Moreover, in the ZrO₂-PtAl coating, Zr is detected in the Hf rich precipitates (spectrum 2). Hf-rich precipitates are also found in similar locations within the PtAl coating (Figure 4.24b), however no Zr is detected (spectra 5-7).

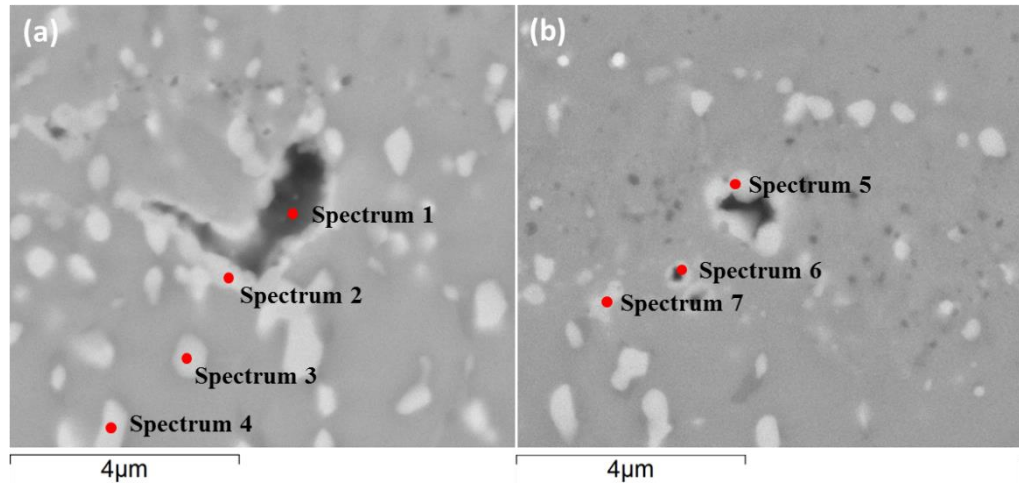


Figure 4.24 BSE images of ZrO₂-PtAl (a) and PtAl (b) bond coats after final vacuum heat treatment.

Table 4.12 EDX results of labelled spectra in Figure 4.24.

Elements (wt. %)	O	Cr	Ni	Co	W	Al	Zr	Hf	Pt
Spectrum 1	32.7	3.0	15.7	3.2	-	14.0	4.8	18.4	-
Spectrum 2	22.8	-	7.1	-	-	3	8.3	42.5	-
Spectrum 3	-	7.4	26.3	7.1	31.2	-	-	-	21.1
Spectrum 4	-	11.1	19.0	10.4	42.5	3.6	12.2	-	-
Spectrum 5	13.9	1.7	13.0	2.1	-	3.4	-	53.4	12.6
Spectrum 6	9.9	2.2	17.9	2.8	-	5.7	-	43.4	17.6
Spectrum 7	8.7	2.5	16.7	3.0	-	5.7	-	44.5	18.2

For the M246 substrate shown in Figure 4.25, no Hf precipitate is formed in the electroplating layer, which is not surprising given that there is no Hf present in M246. Nevertheless, in the labelled location shown in Figure 4.25, a small amount of Zr is detected (Table 4.13). As mentioned before, because of the presence of Zr in both M247 and M246, it is difficult to verify whether the observed Zr comes from the ZrO₂ particles or the substrate.

The ZrO₂ nanoparticles start to disappear in diffusion vacuum heat treatment and totally disappear in the final coating after post vacuum heat treatment. In addition, the Al₂O₃ found in the co-electrodeposition layer of ZrO₂-PtAl coating on M246 may suggest that Al₂O₃ could be a reaction product from the reaction of ZrO₂ nanoparticles. Therefore, the reaction between Al and ZrO₂ is considered.

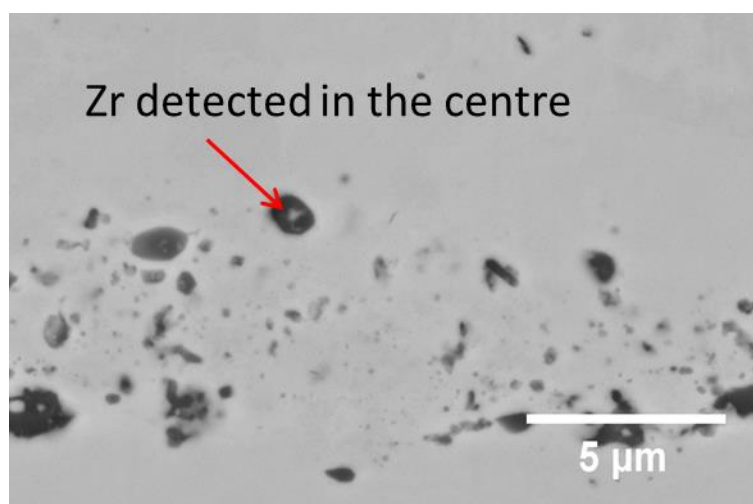


Figure 4.25 BSE image of Zr contained Al₂O₃ found in ZrO₂ modified PtAl coating on M246 substrate after 200 cycles oxidation at 1100°C.

Table 4.13 EDX analysis of the Al₂O₃ particle contains central bright phase in Figure 4.25.

Elements	O	Cr	Ni	Co	Al	Zr	Pt
wt. %	24.6	2.8	34.0	3.9	22.2	1.5	9.8

Figure 4.26 shows a bright field scanning TEM image of a typical position in the ZrO₂-PtAl electroplating layer on Mar-M-247 after 200 thermal cycles, Fig. 8b-8e are the corresponding maps of Al, O, Hf and Zr. Figure 4.26b and 8c confirm that the detected Al₂O₃ particle size is less than 200 nm, similar to the original size of the incorporated ZrO₂ particles. Fig. 8c indicates a less oxygen concentrated area as labelled. However, Fig. 8d reveals that Hf is slightly concentrated in the same location of less oxygen concentrated area and surrounding the formed Al₂O₃. In addition, Al content is also relatively high in the Hf concentrated area. Because the indicated area is concentrated with Al and Hf, it suggests a formation of HfAl solid solution around the Al₂O₃. Due to the original Zr content in Mar-M-247, zirconium map in Figure 4.26e could not confirm the source of zirconium.

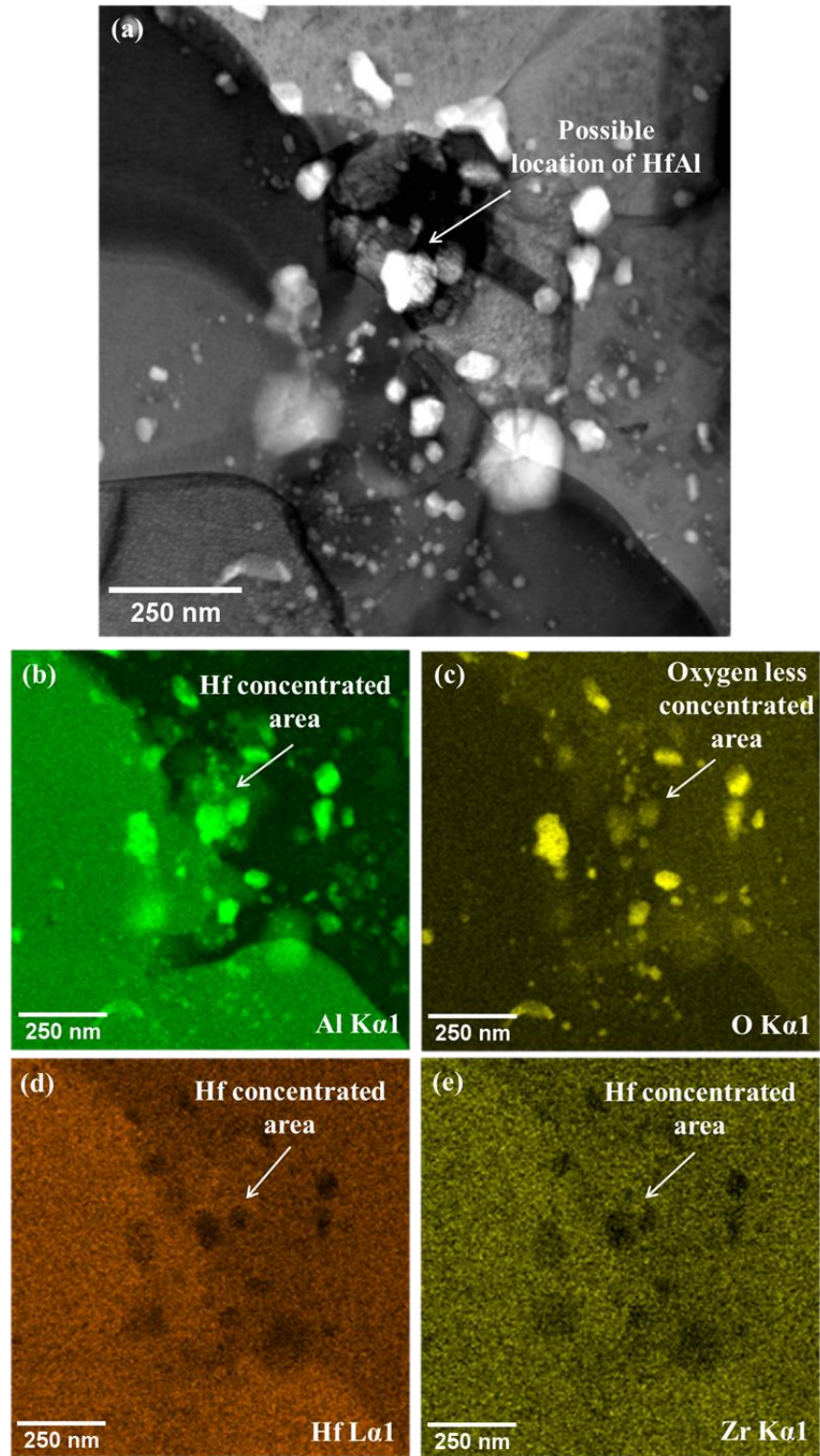


Figure 4.26 STEM/EDX analysis of ZrO₂-PtAl layer: (a) Bright field image of particles formed in the electroplating layer (b) aluminium distribution, (c) oxygen distribution, (d) hafnium distribution and (e) zirconium distribution in this area.

Mixtures of Al and ZrO₂ particles were characterised by XRD after vacuum heat treatment at 1100°C as shown in Figure 4.27. Al₃Zr phase is clearly identified, while Al₂O₃ is also detected with significantly lower peaks. These XRD results confirm that Al and ZrO₂ react during vacuum heat treatment to form Al₃Zr. The XRD results of the heat treatment in the controlled environment (5%H₂/95%Ar) with a higher Al/ZrO₂ ratio again confirms the formation of Al₂O₃ and Al₃Zr (Figure 4.28).

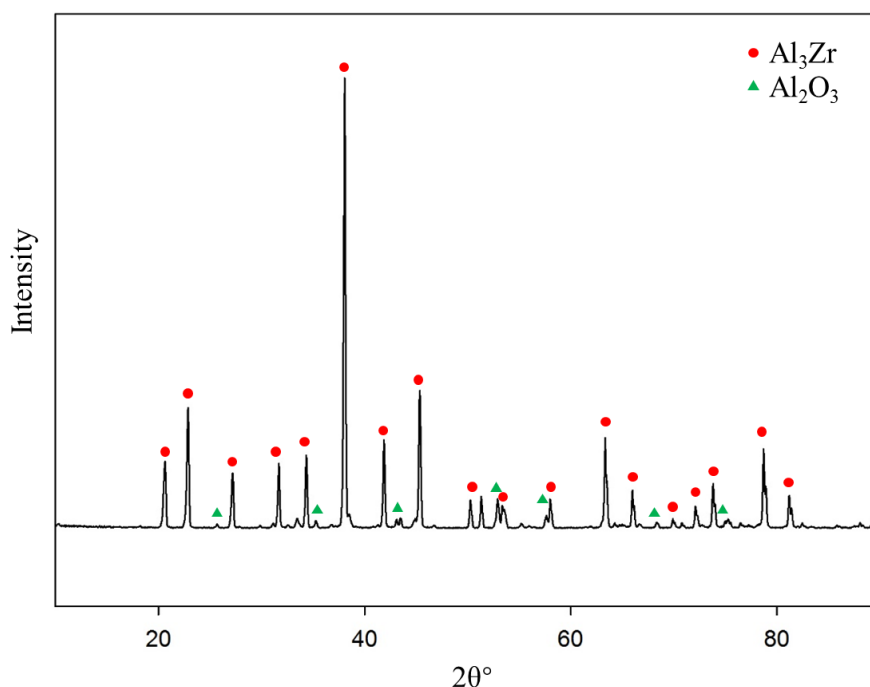


Figure 4.27 XRD result of Al and ZrO₂ powder mixture (1.5 g Al + 1.5 g ZrO₂) heat treated under vacuum.

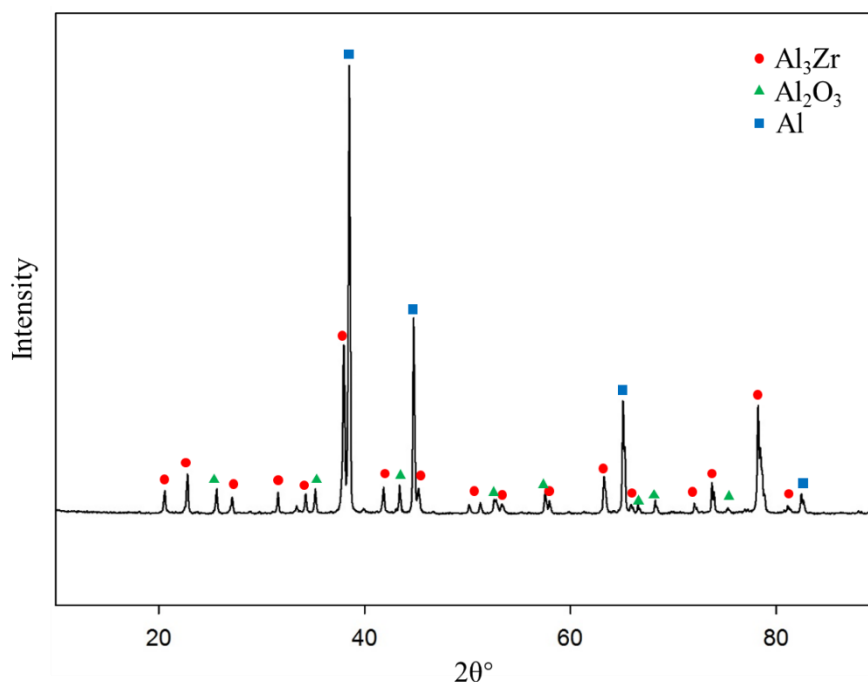


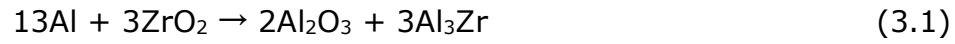
Figure 4.28 XRD result of Al and ZrO₂ powder mixture (1.5 g Al + 0.5 g ZrO₂) heat treated under controlled environment (5%H₂/95%Ar).

4.5 Discussion

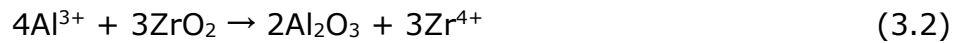
4.5.1 Reaction Mechanism of ZrO₂ Nanoparticles

An interesting phenomenon from the above investigation is the disappearance of the ZrO₂ particles after heat treatment. Therefore, possible reaction mechanisms of ZrO₂ particles are discussed to clarify the behaviour of ZrO₂ in aluminide coatings. The importance of Al has been highlighted in Section 4.4 which confirms that Al and ZrO₂ can react during the heat treatment. Nevertheless, the reaction between Al and ZrO₂ mainly depends on the environment, such as very low oxygen pressure or vacuum [170]. In general atmosphere, Al has great driving force to form Al₂O₃ with oxygen rather than react with ZrO₂ to form Al₂O₃. When in a vacuum or low oxygen pressure environment, the reaction between Al and ZrO₂ becomes thermal

dynamically available [170]. The reaction between Al and ZrO₂ was reported as below [170]:



The reaction has been confirmed by the XRD results. In this situation, Al can be provided either by the substrate or aluminising process, and higher Al content is desired for the reaction. However, the Al₂O₃ phase peaks are weak in the XRD result after vacuum heat treatment. The formed Al₂O₃ may lose oxygen because of the very high vacuum level (10⁻⁶ mbar) [171]. Though Al₃Zr is identified in XRD the result, it is not detected in the electroplating layer of ZrO₂-PtAl coating. In this case, Zr⁴⁺ is proposed as the reaction product rather than Al₃Zr [26]. In Tremouilles's work, only Al₂O₃ was observed at the interface between Al and ZrO₂ [26]. Reaction (1) then can be written as follows [26]:

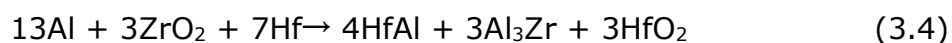


The formed Zr⁴⁺ may be free to diffuse into the substrate and ready for diffusion in the subsequent oxidation period.

Hf rich precipitate formed at the interface between the bond coat and inter-diffusion zone on M247 is not commonly reported [172]. It has a different formation mechanism from the hafnium oxides formed inside the TGO layer [133], in which Hf is considered to react due to high oxygen reactivity. Hf is reported to react with Al₂O₃ [173]. The reaction is shown below:



HfO₂ is a confirmed product in the current experimental results on M247, but HfAl phase could not be detected by EDX analysis. Furthermore, Al₂O₃ source can be provided by embedded sandblasting alumina. It means that the Hf-rich precipitate formed in PtAl coating may be a result of the interaction of Hf with the sandblasting media. However, the reaction between Al and ZrO₂ can also provide Al₂O₃ for the reaction. When reactions 3.2 and 3.3 are combined, i.e. Al₂O₃ formed in reaction 3.2 can participate in reaction 3.3, reaction 3.4 can be written as:



From reaction 3.3, it is suggested that the combination of reactions between Hf, Al and ZrO₂ can form hafnium oxide and solid solutions of HfAl and Al₃Zr. This matches with the identified Zr in Hf rich precipitates found in ZrO₂-PtAl coating (Figure 4.20, spectrum 2). Because of the direct reaction between Al₂O₃ and Hf, it can also form Hf rich precipitates without Zr. In spectrum 2, the Al content is much lower than expected. Decomposition of Al₃Zr and HfAl may occur after reaction 3.3. Al can easily dissolve in the substrate to form a solid solution with Ni because Hf forms a more stable oxide. Meanwhile, Zr may partially dissolve in the coating substrate and also form oxides together with Hf [138]. Even though the original Zr content in M247 can affect the reactions of ZrO₂ particles, the results on In718 confirm the reaction between Al and ZrO₂ particles and further diffusion of Zr in cyclic oxidation.

For the coatings on the M246 substrate, no hafnium rich oxide or precipitate is formed, but Figure 4.25 reveals a Zr containing phase in the centre of the aluminium phase. In addition, some Al₂O₃ particles

are found in the particle regions on M246 and In718, which indicates Hf can consume Al₂O₃ particles from the reaction between Al and ZrO₂. Furthermore, hafnium-rich precipitates are commonly formed at the edges of Al₂O₃ particles.

Based on the above results, Figure 4.29 illustrates the possible mechanism of the reaction. The ZrO₂ particles are first attacked by Al to form an outer ring of Al₂O₃. The Al₂O₃ can act as a diffusion barrier to Al, which can slow down the reaction between Al and ZrO₂, this may leave a central un-reacted ZrO₂ particle. Meanwhile, the formed Al₃Zr phase decomposes to Al and Zr, both of which can dissolve into the coating substrate. When Hf is present, it can react with the outer Al₂O₃ to form hafnium oxide and HfAl. Once the Al₂O₃ is consumed, the residual ZrO₂ can continue to react with Al. Because of the congener effect, the released Zr from ZrO₂ particles can form oxides and precipitates together with hafnium. In addition, some Hf and Al from HfAl may have the chance to dissolve into coating substrate. Al can initiate the reaction with ZrO₂ and release Zr by forming Al₃Zr.

The effects of Hf are mainly to react with Al₂O₃ to release Zr from ZrO₂ particles and form oxides or precipitates with Zr simultaneously. Hf is further expected to be useful if the incorporated ZrO₂ has a larger particle size. When the particle size is small (such as nanoparticles), Al can complete the reaction with ZrO₂ as it was seen in Figure 4.25. When the particle is large enough (such as micro-particles), the unreacted ZrO₂ core is expected. In this situation, Hf can react with the Al₂O₃ shell formed and release Zr from ZrO₂. However, the dispersion of large particles in the electrolyte is not desirable for co-electrodeposition. In current investigation, M247 has 1.5 wt. % Hf which is thought to be enough to react with Al₂O₃. However,

incomplete reaction with Al₂O₃ can be foreseen if there was not enough Hf in the substrate, resulting in unreacted ZrO₂ particles. The sandblasting alumina is then considered as harmful to oxidation resistance because it can consume Hf through the reaction between Hf and Al₂O₃.

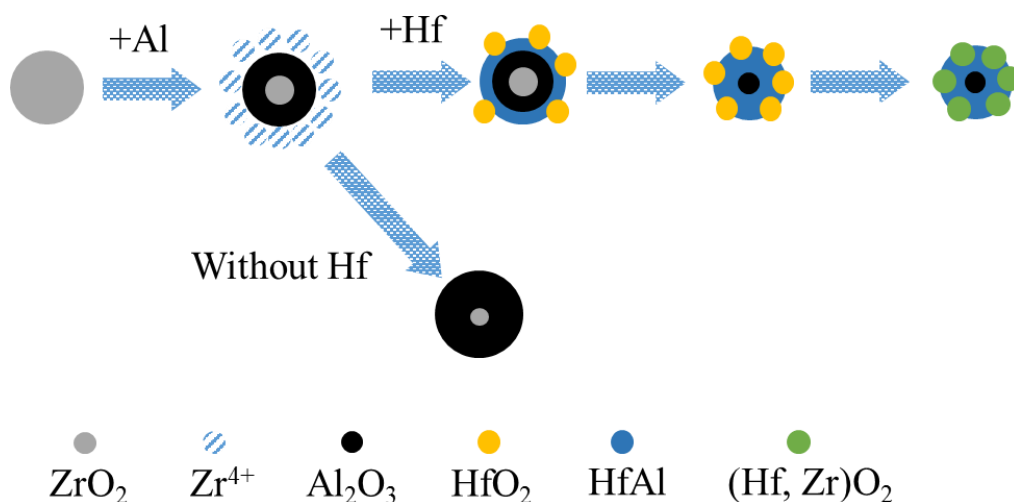


Figure 4.29 Reaction mechanism of nano ZrO₂ particles.

The reaction mechanism of ZrO₂ particles can be used to further explain the dynamic segregation theory in the case of ZrO₂. In theory, the reactive elements can improve the oxidation resistance even in their oxide form [132]. In current study of ZrO₂, Zr is finally released from ZrO₂ particles and participates in oxidation because of the reactions with Al and Hf. However, in another report, the ZrO₂ particles were segregated at grain boundaries in a powder metallurgy fabricated ZrO₂ strengthened NiAl/Cr(Mo, Hf) (33Ni-33Al-31Cr-2.8Mo-0.2Hf at.%) composite alloy instead of reacting with Al [174]. Considering the processing environment of powder metallurgy, the ZrO₂ particles have the potential to react with Al. Because the reported alloy powder had a size ranging from 10 μm to 20 μm and

the size of the ZrO₂ particle is around 1 μm , the ZrO₂ particles may stay in the interspaces between the large alloy powders. In addition, even though the heat treatment temperature was 1250°C, the alloy powder will not melt, maintaining the minimal contact between ZrO₂ and alloy particles, which may inhibit the reaction between ZrO₂ and Al. In the case of Al-ZrO₂ powder mixture, Al will melt at around 650°C, which ensures good contact with ZrO₂ particles. Another reason may be that the ZrO₂ particle with a smaller size in the current study ($\leq 200\text{ nm}$), possess higher specific surface area and activity. Since the ZrO₂ particles already segregate at grain boundaries, further heat treatment can be carried out on the composite alloy to see whether the ZrO₂ particle disappears.

The current investigation can explain the behaviour of ZrO₂ but not the HfO₂, because the hafnium oxide still exists in the particle region after oxidation. More investigation should also be carried out to study the decomposition of transition phases, such as Al₃Zr and HfAl in the coating, in order to determine the diffusion mechanisms of Zr and Hf.

4.5.2 Effects of ZrO₂ Nanoparticles on Oxidation Resistance

Once the oxidation starts, Zr will diffuse to the surface to form oxides together with Hf. Like other oxygen reactive elements, Zr is reported to have a similar effect to Hf [137, 175, 176]. The result of ZrO₂ modified PtAl coating shows that the Zr did not reduce the growth rate of TGO, but it can significantly improve the rumpling resistance because the roughness of TGO in ZrO₂-PtAl coating after thermal cycling remains stable from 50 cycles to 200 cycles on M246 and In718. On the other hand, the ZrO₂-PtAl coating on M247 demonstrates reduced growth rate of TGO compared to the result using M246 substrate, which could be the influence of Hf. Even though

the Hf content in M247 is much higher than the optimized value (500 ppm) [177, 178], the growth of the TGO layer in both coatings is still retarded on M247. It is reported that Hf would improve the spallation resistance by forming oxide pegs at the interface between the TGO and bond coat [179]. Nevertheless, the rumpling resistance is decreased by Hf as the roughness of PtAl coating on M247 is much higher than that on M246 substrate. Because the Hf content in M247 is much higher than that in general single crystal Ni superalloys, massive internal oxides are formed, and this may be the reason for the roughness of the TGO increasing.

It is also of interest to discuss the combined effects of Hf and Zr. Because Zr is detected in hafnium precipitates and the different features of ZrO₂-PtAl coating are found on different substrates, the Hf-rich precipitates may act as Zr reservoirs and slowly release Zr to the surface to help improve oxidation resistance. Once the interfacial oxide pegs are formed, the effect of Hf or Zr will be optimised by forming joint oxides to further retard the outward diffusion of Al and reduce the growth rate of TGO [13]. However, because Zr from the added ZrO₂ particles is released by the reaction between Al and ZrO₂, the effects of Zr from pure Zr addition and ZrO₂ particles may be different. When pure Zr is incorporated by EB-PVD (electron beam physical vapour deposition) on the coating surface, the Zr-rich phase is formed after heat treatment and helps reduce the growth rate of TGO at early stages of oxidation [16]. However, Zr which comes from ZrO₂ particles, needs to first diffuse to the coating surface because ZrO₂ particles are present inside the bond coat. A longer vacuum heat treatment on ZrO₂ containing coating may achieve similar effects to pure Zr. Nevertheless, the incorporation of ZrO₂ nanoparticles provides an alternative possible cost effective method to achieve the

advantages of Zr addition than directly introduce pure Zr into the PtAl coating.

4.5.3 Influence of Substrate Compositions

In current study, substrates have played an important role in the reaction of ZrO₂ nanoparticles. Al content is a key factor in substrate composition. The reaction between ZrO₂ nanoparticles and Al can be completed during diffusion vacuum heat treatment when the substrate has high Al concentration. This may be useful when there is no further aluminising process after vacuum heat treatment, such as the Pt-modified $\gamma+\gamma'$ coating. Though Al can be provided by the aluminising process, Hf is coming from the substrate, which is desirable to promote the effects of ZrO₂ particles. Because some Hf reacts with Al₂O₃ to form HfO₂, the optimised content of Hf in the substrate is expected to be higher than the reported 500 ppm [177] to maintain the benefits of Hf. For ZrO₂ modified PtAl coating, a substrate with a high Al content and certain amount of Hf (larger than 500 ppm) is desired.

4.5.4 Influence of As-prepared Coating Surface Roughness

M246 has a similar composition as M247, but without Hf content. However, only the coatings on M246 forms spinel during cyclic thermal oxidation test. This is considered to be the influence of the as-prepared coating microstructure before the oxidation test. In Figure 4.12, both coating surfaces show micro-roughness after post heat treatment. When compared with the oxidised microstructures, the formed spinel phase also shows micro-roughness. The small convex area on the coating surface may be the reason for the formation of spinels.

Figure 4.30 demonstrates the formation mechanism of spinels on M246. Figure 4.30a indicates a convex area in the as-prepared bond coat. When the oxidation starts, the convex area will be oxidised to form Al₂O₃ (Figure 4.30b). However, Al in the convex area will be consumed in the early stages of oxidation because the Al content in the convex area is not enough (Figure 4.30b) and the diffusion of Al from the bond coat cannot provide enough Al to protect the surface. The NiO can be formed when Al concentration in the convex area reduces to a certain level (Figure 4.30c). Figure 4.30d shows the final stage of the transformation from Al₂O₃ to spinel (NiAl₂O₄). The interaction between Al₂O₃ and NiO will finally form the spinel phase. The actual size of the convex area is in the range of several square microns so that Pt will precipitate out from the spinel matrix (Figure 4.30d) because it is noble at 1100°C.

For the coatings on M247 and In718, the coating surface is relatively smoother than the coatings on M246. Therefore, the formation of spinel is not detected. However, the convex area and the ratio of convex height to width could be the important factors to affect whether spinel can be formed. For example, Al₂O₃ can be formed in that area, but there is not enough Al to provide further protection, then NiO (other spinel formation oxide) can form and combine with Al₂O₃ to generate spinel.

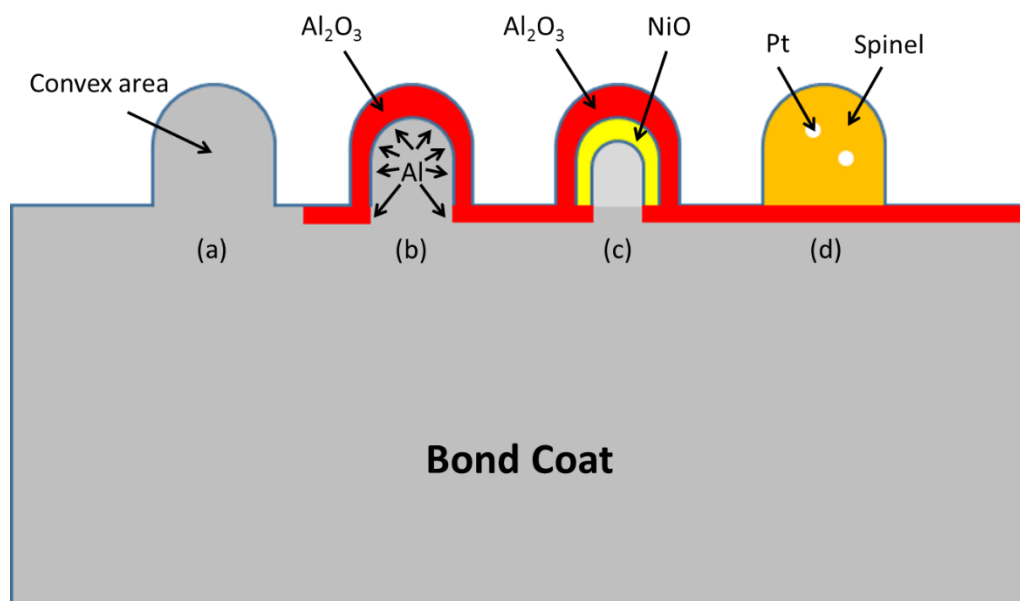


Figure 4.30 Mechanism of the spinel formation on M246. (a) Convex area in as-prepared bond coat, (b) formation of outer Al_2O_3 at early stages of oxidation, (c) formation of NiO when Al is depleted and (d) formation of spinel (NiAl_2O_4) and Pt precipitates out from the coating.

4.6 Effects of Pure Zr on Oxidation Behaviour

It has been mentioned in section 4.5.2 that the incorporation of ZrO_2 nanoparticles provides an alternative method to introduce Zr into aluminide coatings. A ZrAl coating is designed based on the reaction between Al and ZrO_2 . Al_3Zr which comes from the reaction, can be used as the resource of both Al and Zr to co-diffuse these two elements into substrates. Therefore, a pack aluminising method is applied to give better contact between samples and the Al_3Zr compound.

When preparing the packing powders, Al powder and ZrO_2 nanoparticles are the main components in the mixture. Al_2O_3 which also comes from the reaction, can act as the stabiliser similar to that in the general aluminising process. NH_4Cl is utilised as the activator

in the packing powders to guarantee that the aluminising process can proceed. In addition, ZrCl₄ is used as another source of Zr to diffuse Zr into the substrate. Furthermore, a Pt coating is electroplated prior to pack aluminising to prepare Zr-modified PtAl (Zr-PtAl) coating. A cyclic thermal oxidation test is carried out on the ZrAl and Pt-ZrAl coatings to give better understanding of the different effects of pure Zr and ZrO₂ nanoparticles on oxidation behaviour.

4.6.1 Microstructures of ZrAl coatings

In total, five powder mixtures were used for preparing ZrAl coatings. The compositions of prepared powder mixtures were summarised in Table 3.2. ZA1 coating is treated as the bench mark for ZrAl coatings. Figure 4.31a shows the microstructure of ZA1 coating after vacuum heat treatment. Table 4.14 gives the EDX analysis of the different regions in ZA1 coating, indicating five regions in the coating. Figure 4.32 illuminates the possible microstructures of ZA1 coating. The top layer is made of Al-Zr-Ni which is rich in Al. The second layer could be a transition layer of Al-Zr-Ni. The third layer consists of mainly Al-Zr-Ni but rich in Ni. There are also a little β -NiAl formed in this layer. The next layer is made of β -NiAl but with some Ni-Zr precipitates. The final layer of the coating contains mainly Ni-Zr which has high content of Ni.

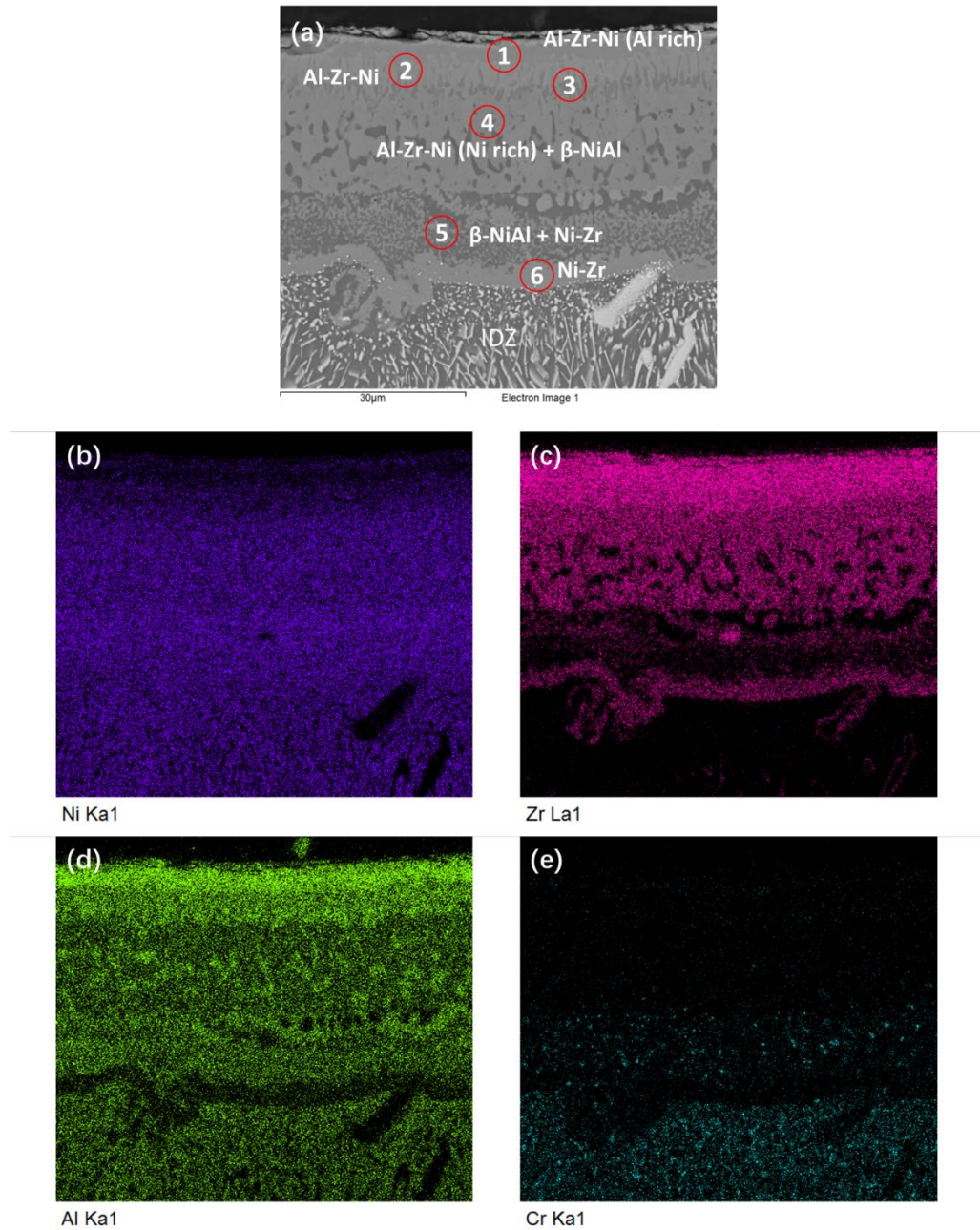


Figure 4.31 Microstructure of ZA1 coating (a) after vacuum heat treatment, and the elements mapping of (b) Ni, (c) Zr (d) Al and (e) Cr.

The microstructure of ZA1 coating indicates an outward diffusion of Ni because the concentration of Ni increases inward. Both Al and Zr show inward diffusion due to reduced concentration of both elements. Based on the detected Zr content, the fabricated ZA1 coating is

considered as an aluminide coating with high Zr addition (≥ 20 wt. %) in current investigation.

Table 4.14 EDX analysis of the different regions in ZA1 coating after vacuum heat treatment.

Elements / wt. %	Ni	Al	Cr	Zr	Co	W
1	14.3	24.0	-	60.8	1.0	-
2	27.3	16.0	0.4	53.3	3.1	-
3	33.4	18.8	1.2	42.8	3.8	-
4	27.9	17.8	1.3	50.1	2.9	-
5	59.3	22.5	5.1	3.2	8.7	-
6	47.3	7.7	2.3	34.7	8.1	-
Precipitates in IDZ	20.3	8.8	9.1	8.6	9.5	42.8

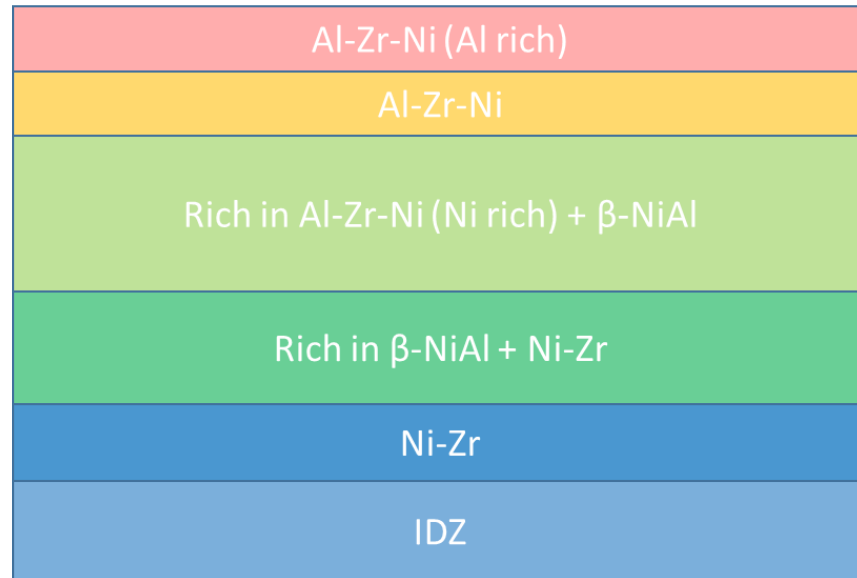


Figure 4.32 Schematic of the microstructures of ZA1 coating.

4.6.1.1 Effects of Packing Mixture Compositions on Coating Microstructure

Figure 4.33 gives the XRD results of ZrAl coatings fabricated by different packing powder mixtures. Al_{1.7}Ni_{0.3}Zr phase is mainly

detected in ZA1 coating, which is consistent with the EDX result in Table 4.14. Though ZrCl₄ has been added into Mixture2 to provide an extra Zr source, the microstructure of ZA2 coating (shown in Figure 4.34) indicates a similar microstructure to ZA1 coating. The XRD result of ZA2 coating reveals that there are some other phases in the coating but with weak peaks, such as Al₂Zr and Ni₇Zr₂. This result may suggest that the top surface of ZA2 coating is made of Al₂Zr and the NiZr region mainly consists of the Ni₇Zr₂ phase. However, the β -NiAl phase could not be confirmed by the XRD results. Because ZA1 and ZA2 coatings have similar microstructures and phases, ZrCl₄ is considered as unnecessary to provide an extra Zr source.

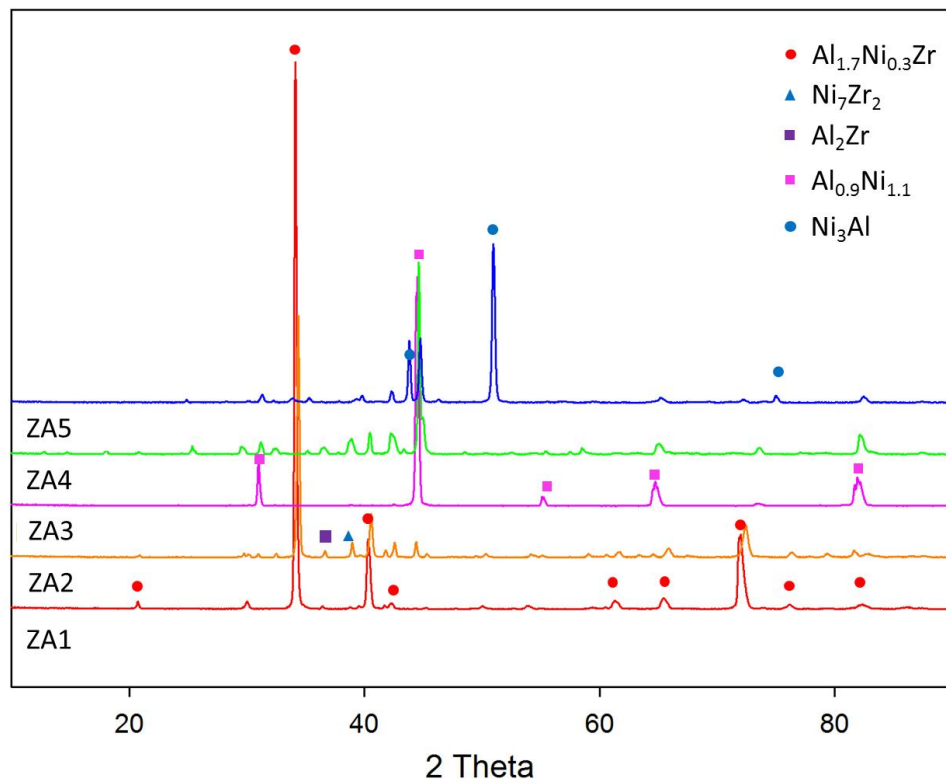


Figure 4.33 XRD results of aluminide coatings by different packing powder mixtures.

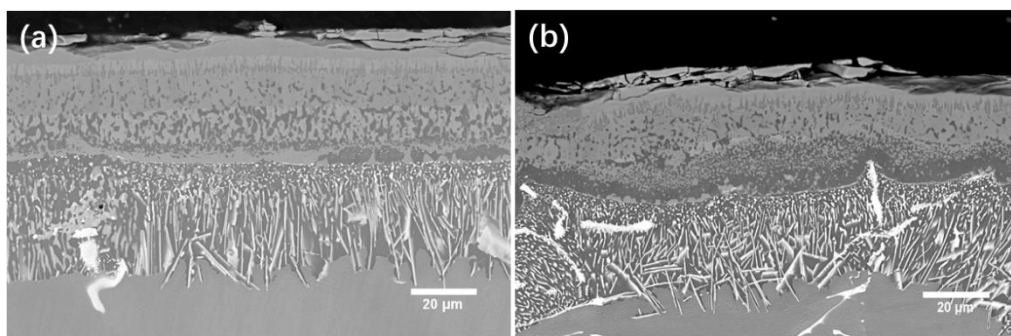


Figure 4.34 Microstructures of (a) ZA1 and (b) ZA2 coatings after vacuum heat treatment.

Both Mixture1 and Mixture2 yield good Zr-doped aluminide coating due to the formation of the Al_{1.7}Ni_{0.3}Zr phase. However, it has not been detected in samples fabricated from the other three mixtures. The XRD result of ZA3 coating only shows the peaks of the β -NiAl phase. There is no any Zr-rich phase detected in ZA3 coating, but a small amount of Zr-rich precipitates is formed in the coating from the EDX analysis shown in Table 4.15, which is arrowed in Figure 4.35a. Figure 4.35b shows the microstructure of ZA4 coating, indicating a typical microstructure of aluminide coating. The EDX analysis could support any Zr compositions in ZA4 coating. Because the XRD result of ZA5 coating only indicates the Ni₃Al phase in the coating, thus the Mixture5 (ZrO₂ + NH₄Cl) cannot yield a Zr doped aluminide coating.

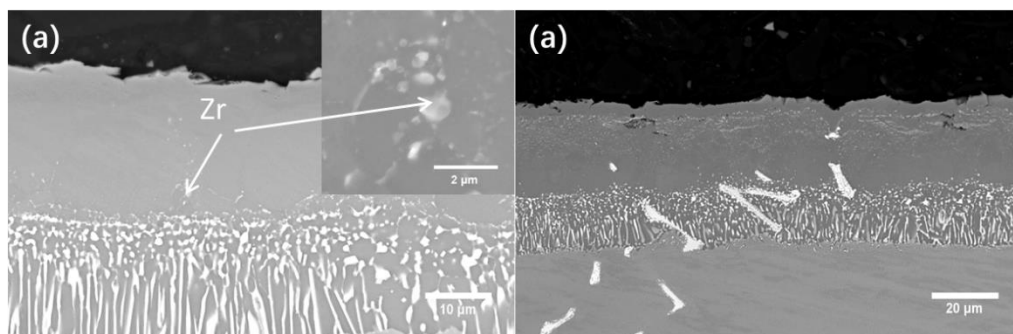


Figure 4.35 Microstructures of (a) ZA3 coating with enlarged insert of Zr containing area and (b) ZA4 coatings after vacuum heat treatment. The inset of (a) reveals the enlarged image of Zr containing precipitate.

Table 4.15 Detected Zr composition in ZA3 coating.

Elements	Ni	Al	Zr	Hf	O	Cr	Co
wt. %	54.2	15.8	9.0	3.1	4.0	5.3	7.8

4.6.2 Microstructure of Zr-modified PtAl Coatings

Figure 4.36 reveals the microstructure of Zr-modified PtAl (Zr-PtAl) coating on M247 after vacuum heat treatment. A similar microstructure to ZA1 coating is achieved in Zr-PtAl coating. An EDX analysis of the different regions is shown in Table 4.16. Pt is absent in the top surface of the Zr-PtAl coating. Because the main effect expected from Pt is to stabilise the aluminide phases and improve the adhesion of formed TGO during oxidation [180], the top surface of the Zr-PtAl will be oxidised without the addition of platinum.

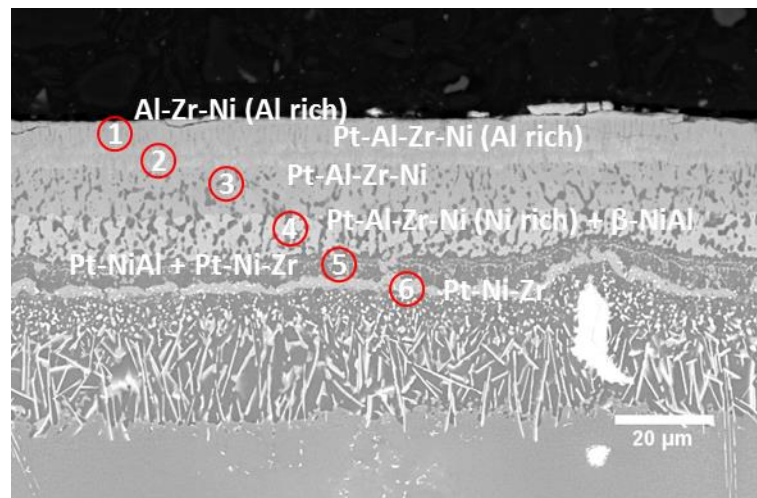


Figure 4.36 Microstructures of Pt-modified ZrAl coating after vacuum heat treatment.

Table 4.16 EDX analysis of the different regions in Zr-PtAl coating after vacuum heat treatment.

Elements / wt. %	Ni	Al	Cr	Zr	Co	Pt	W	Hf
1	27.8	14.4	-	53.8	2.1	1.9	-	-
2	29.3	16.7	0.8	40.3	2.4	10.5	-	-
3	37.4	9.9	0.6	37.5	4.7	10.0	-	-
4	41.9	5.5	2.0	28.7	6.6	15.3	-	-
5	58.0	20.4	5.4	1.8	7.9	5.0	-	-
6	38.1	5.9	2.8	29.8	5.9	10.3	4.7	2.5

4.6.3 Oxidation Results of ZrAl and Zr-PtAl Coatings

A cyclic thermal oxidation test is carried on the ZA1 and Zr-PtAl coatings. The result of thermal cyclic oxidation on Zr doped aluminide coating is shown in Figure 4.37. There is no any protective oxide layer formed in ZA1 coating after 50 cycles. The oxidised region has exceeded the original coating thickness and reaches about 200 μm after 50 cycles. Spinel is formed on the surface rather than a protective Al₂O₃ scale. On the other hand, Al₂O₃ is formed at the interface between spinel and substrate. Because zirconium oxide is not clearly detected in the oxide layer, it is considered that the original formed oxide layer has spalled off at the early stage of thermal cycling.

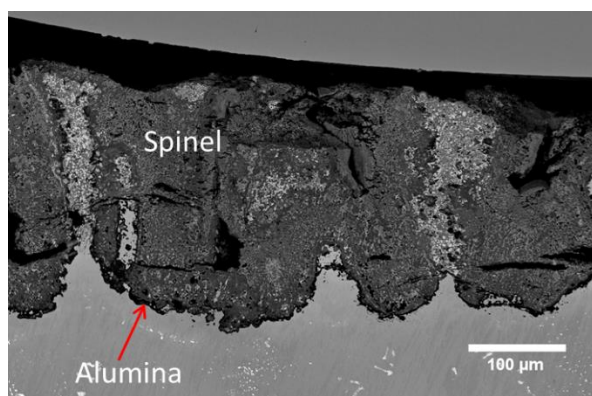


Figure 4.37 Microstructure of ZA1 coating after 50 cycles at 1100°C.

The microstructure of Zr-PtAl coating after 50 cycles is shown in Figure 4.38. It is clear that the early formed oxide layer spalled off during thermal cycling because the fracture interface can be observed at the top surface of the residual oxide layer. Hafnium oxide is formed at the oxide interface from EDX analysis, which is expected on the M247 substrate due to the high oxygen reactivity of Hf. Some concentrated Pt precipitates are detected in the spinel phase. Because Pt is noble at high temperatures, the formation of concentrated Pt may indicate massive and rapid oxidation of the coating. The possible mechanism has been discussed in Section 4.5.4.

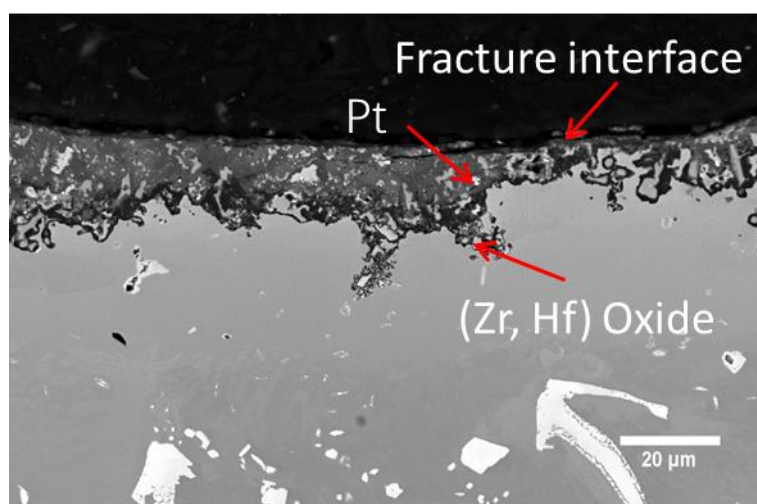


Figure 4.38 Microstructure of Zr-PtAl coating on M247 substrates after 50 cycles at 1100°C.

Because the oxide layer in Zr-PtAl coating has spalled off after 50 cycles, the early stage of cyclic thermal oxidation is investigated through short-time annealing (10 min heating up to 1100°C, holding for 30 min at 1100°C and cooling down by forced air). Figure 4.39a shows the microstructure of Zr-PtAl coating after short time annealing, indicating a severe internal oxidation. Table 4.17 provides the EDX analysis of different regions in Zr-PtAl coating after short time

annealing on M247. Only the β phase region remained but still suffered from internal oxidation as shown in Figure 4.39b. Zirconium oxides are detected throughout the Zr-PtAl coating as indicated in Table 4.17, which is consistent with the zirconium oxide formed at the early stage of oxidation and spalled off during thermal cycling. Because the annealing is only carried out for 30 min, the depth of formed zirconium oxides indicates that oxygen has a fast diffusion rate in Zr-PtAl coating. Table 4.17 also shows a high Pt concentration in β phase region. This may suggest an inward diffusion of Pt and Pt could not slow down the oxidation rate.

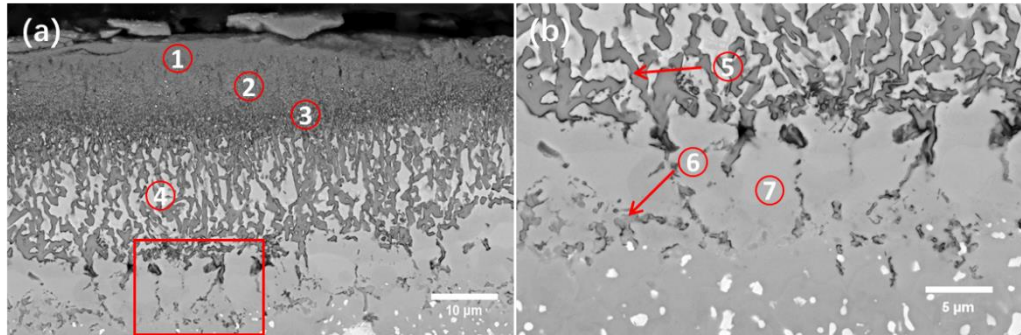


Figure 4.39 Microstructure of (a) Zr-PtAl coating after short time annealing (30 min at 1100°C) on M247 substrate. (b) shows the enlarged β phase region.

Table 4.17 EDX analysis of the different regions in Zr-PtAl coating after short time annealing (30 min at 1100°C) on M247.

Elements / wt. %	Ni	Al	Cr	Zr	Co	Pt	Hf	O	W
1	6.2	12.6	-	42.3	-	-	-	36.4	1.7
2	6.3	14.7	-	38.9	-	-	-	38.0	1.3
3	9.7	17.9	1.3	34.9	1.5	1.7	-	33.0	-
4	25.6	9.8	1.6	26.9	3.1	12.1	-	20.9	-
5	4.4	2.4	-	61.4	-	-	3.4	27.5	-
6	19.6	6.2	3.3	33.1	3.1	6.9	9.2	18.7	-
7	43.2	13.4	4.8	-	5.4	30.7	-	-	2.0

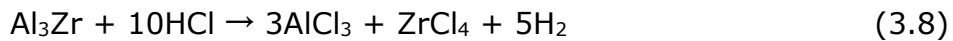
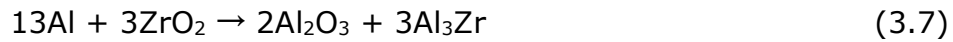
4.6.4 Discussion

4.6.4.1 Mechanism of Zr doped Aluminising

In the current investigation, Zr-modified aluminide coatings are fabricated by a pack aluminising method via the reaction between Al and ZrO₂, which is different to the reported CVD method via ZrOCl₂ [168]. The reactions in CVD process are given below [181]:



Where ZrCl₄ comes from the decomposition of ZrOCl₂. In the current study, the possible reactions in the pack aluminising process can be proposed as follows:



In addition, Reactions 3.5 and 3.6 both happen in the pack aluminising process as the final diffusion processes of Al and Zr. NH₄Cl is a necessary activator in the powder mixture to provide HCl for generating AlCl₃ and ZrCl₄, but it cannot directly react with ZrO₂ particles because ZA5 coating could not yield a Zr doped aluminide coating. Al can react with ZrO₂ to provide Al₃Zr for further reaction, it

can also directly react with HCl. When Al is consumed by the reaction with HCl, there may be not enough Al to react with ZrO₂. This could explain why the ZA4 coating does not contain Zr composition in the coating with 15 wt. % Al in powder mixture (25 wt. % Al in Mixture1 and Mixture2). Because Al₂O₃ can be produced in Reaction 3.6, the Al₂O₃ content in the powder mixture may inhibit or slow down the Reaction 3.6 as a barrier between Al and ZrO₂ particles, which could be another reason for the result of ZA4 coating. The result of ZA3 coating indicates that the Zr cannot diffuse into Ni superalloy substrate. It is surprising that there is a small amount of Zr detected inside the ZA3 coating. This could be the ZrO₂ nanoparticles embedded in the coating when the aluminising process begins.

The microstructure of ZrAl coating is formed due to the outward diffusion of Ni and inward diffusion of Al and Zr. The Ni-Zr region has drawn attention because it may suggest that Zr diffuses faster than Al because the Ni-Zr region forms just above the IDZ. However, the microstructure is characterised after vacuum heat treatment. The inward diffusion of Al may leave concentrated Zr to form solid solution with Ni.

4.6.4.2 Effects of High Content of Zr on Oxidation Behaviour

The high content of Zr in aluminide coatings is harmful to coating oxidation resistance. The oxidation result of short time annealing has indicated that the oxygen inward diffusion predominates in Zr-PtAl coating during the oxidation test. In addition, Zr is more reactive to oxygen so a large amount of zirconium oxides are formed inside the coating after short time annealing. However, high Zr concentration has caused severe internal oxidation by forming zirconium oxide. This

may indicate that a high content of Zr can create oxygen diffusion paths by forming zirconium oxide inside the coating.

4.7 Summary

ZrO₂ nanoparticles were successfully incorporated into electrodeposited PtAl coatings by co-electrodeposition. Performance of the ZrO₂-PtAl coatings was investigated through thermal cyclic oxidation on different substrates. The results can be summarised as: (i) The addition of the ZrO₂ nanoparticles produces a minor improvement in TGO growth on M247. It also improves TGO rumpling resistance of the PtAl coating on In718; (ii) ZrO₂ particles disappeared during both vacuum (10^{-6} mbar) and controlled environment (5%H₂/95%Ar) heat treatment. The disappearance of the particles is because of the reaction with Al, proved with TEM characterisation. The reactions of the ZrO₂ particles are observed to vary with substrate composition, and the presence of Hf plays an important role in the reaction; (iii) When Al is present without Hf, ZrO₂ particles disappear through the reaction between Al, which may leave un-reacted ZrO₂ in the coating. In the presence of Hf, the reaction can further release Zr and form a Zr reservoir to help improve oxidation resistance. Synergistic actions of Zr and Hf are found to be better on improving the oxidation resistance; (iv) Because of the reactions with Al and Hf, Zr is finally released from ZrO₂ particles and helps improve the rumpling resistance of PtAl bond coat during thermal cyclic oxidation. The reaction mechanism of ZrO₂ nanoparticles gives a deeper understanding of the reactions of ZrO₂ and the influence of substrate on bond coat compositions.

Zr-modified aluminide coatings were developed based on the reaction between Al and ZrO₂ using the pack aluminising method. High Zr content aluminide coatings were successfully fabricated using Al (25 wt.%), ZrO₂ (74.8 wt.%) and NH₄Cl (0.2 wt.%) powder mixture. Al and ZrO₂ particles are the two main compositions in the powder mixture. NH₄Cl acts as an activator which is necessary to generate AlCl₃ and ZrCl₄ as the sources of Al and Zr for diffusion. Because Al can also directly react with HCl released from NH₄Cl, enough Al content is desired to co-diffuse Zr into the substrate. Al₂O₃ may be harmful to the process because it can act as a barrier to the reaction between Al and Zr. In addition, ZrCl₄ is unnecessary to provide an extra Zr source.

The performances of fabricated ZrAl and Zr-PtAl coatings were investigated by cyclic thermal oxidation tests and a short time annealing compared with ZrO₂-PtAl coating. However, severe oxidation and spallation of the TGO layer occurred after oxidation tests. A high content of Zr in aluminide coatings is harmful to coating oxidation resistance because it leads to fast inward diffusion of oxygen and formation of internal zirconium oxides. The oxidation results of Zr-modified aluminide provide an understanding of the influence of pure Zr in aluminide coating.

Chapter 5 Influences of Ir and Pd Additions on Oxidation Behaviour of PtAl Coatings

Platinum group metals (PGMs) exhibit high potentials for improving the oxidation resistance of NiAl coating. General Pt-modified aluminide coating has been used as the bond coat for many years in aircraft engines [5]. Efforts have been made to reduce or eliminate the high cost of Pt via replacement with lower-cost elements [182]. Pd has been reported to be a good alternative for Pt due to their similar chemical properties. However, the effects of Pd are still being argued because both improvement and setback have been reported [100, 183]. This causes confusion when investigating the influence of Pd on PtAl coating with multiple aspects.

In PGMs, Ir has received more attention due to its high melting point (2716 K), excellent corrosion resistance and higher mechanical strength than Pt [140, 184]. In addition, Ir also has excellent oxidation resistance and low oxygen permeability, which makes it possible to act as an oxygen diffusion barrier (ODB) [185]. Even though Ir has a great potential to replace Pt to further improve the oxidation resistance of bond coats, the problem remains on how to deposit thick Ir coating as thin Ir coating could not effect an improvement on PtAl coating [143]. A sputtering method is usually used to prepare the Ir layer for Pt-Ir coating applications [158-160], the high cost and low thickness are not satisfactory. Only a few reports are available on the electrodeposition of Ir, and the Ir halogens can be used as starting materials [161, 162]. Among them, Ir bromide was reported to have the potential to prepare thick Ir coatings [162, 163].

The overarching goal of this chapter is to investigate the effects of Ir and Pd additions on the oxidation behaviour of PtAl coating. In this work, Ir coating is electroplated by IrBr_3 aqueous solution. The electroplating parameters are optimised to produce thick Ir coating for Ir-modified PtAl (Ir-PtAl) coating. Electroless deposition of Pd is used to prepared Pd-modified PtAl (Pd-PtAl) coating as a different approach to investigate the Pd-PtAl coating with different fabrication methods. A cyclic thermal oxidation test is carried out on both aluminide coatings. General PtAl coating is used as the bench mark for comparison.

5.1 Preparation of Pd-Pt and Ir-Pt Coatings

5.1.1 Microstructure of Pd-Pt Coating

Figure 5.1 shows the microstructures of electroless deposited Pd coatings with different deposition times on M246. Around 3 μm thick Pd coating can be produced after 60 min deposition, but the coating thickness decreased dramatically with reduced deposition time. The thickness of deposited Pd coating is 1 μm after 30 min, but 2.5 μm and 3 μm after 45 min and 60 min, respectively. In Figure 5.1a and 5.1b, the labelled locations indicate the possible nucleated Pd clusters at the early stage of the reaction, but no obvious clusters are found in the cross section of Pd coating after 60 min. In addition, cracks are found in the 60 min deposited Pd coating as revealed in Figure 5.1c.

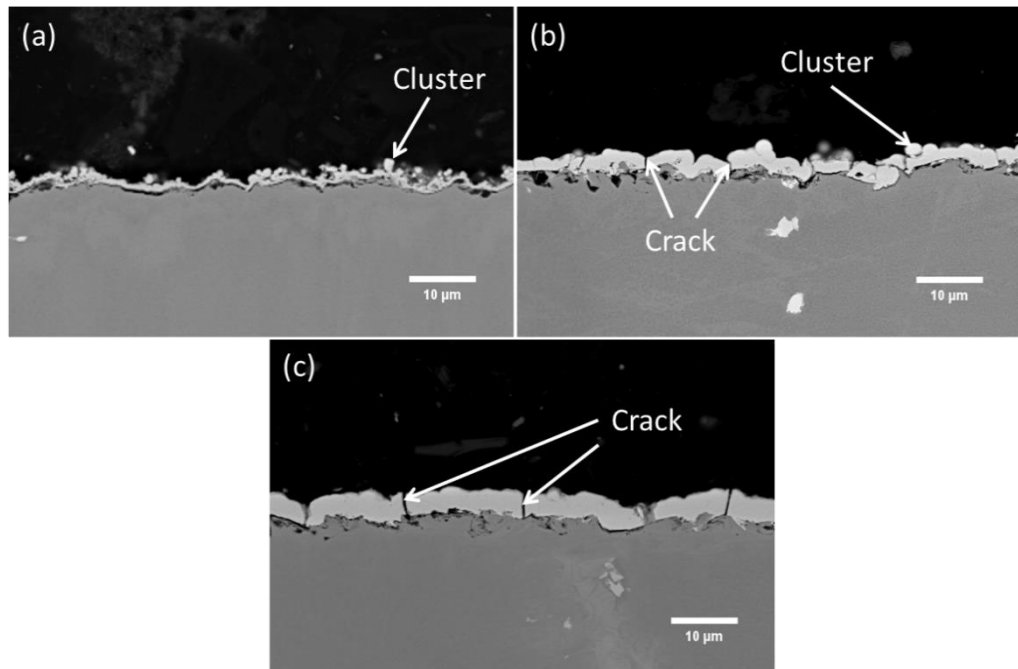


Figure 5.1 BSE images of the cross-sections of the Pd coatings on M246 with different deposition times, (a) 30 min, (b) 45 min and (c) 60 min.

The surface morphologies of as-deposited Pd coatings after 45 min and 60 min are shown in Figure 5.2. In both coatings, the Pd deposit clusters are observed on the surface and large clusters are found in the 60 min coating. Cracks are found in the coating after 60 min, but only a few cracks are observed in the coating after 45 min. The EDX result of deposited Pd coating shown in Table 5.1, reveals that the Pd coating contains certain amount of P, which is reported as a side effect of applied electroless method [186]. For Pd-Pt coating after 20 min electroplating of Pt, the microstructure is shown in Figure 5.3. The cracks are fully filled with Pt during the Pt electrodeposition.

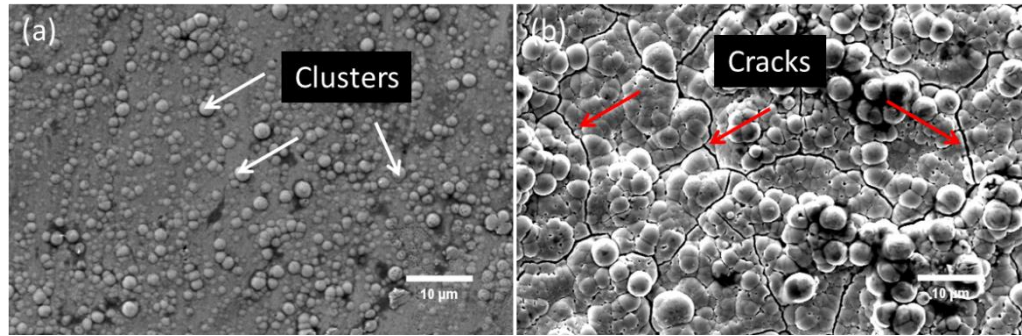


Figure 5.2 Surface morphologies of as-deposited Pd coatings after (a) 45 min and (b) 60 min. The labelled locations from top view indicate the clusters and cracks after deposition.

Table 5.1 EDX result of as-deposited Pd coating.

Element	Weight %
Pd	96
P	4

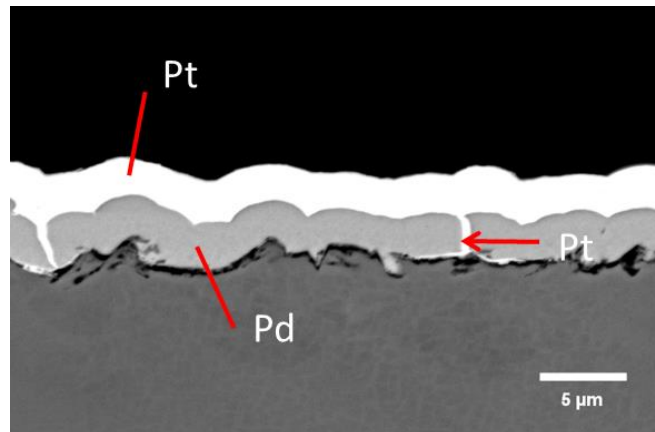


Figure 5.3 BSE image of the microstructure of layered Pd and Pt coatings. The Pt pegs can be found in the cracks from electroless deposition of Pd.

It can be seen from Figure 5.1 that the thickness of electroless deposited Pd coating mainly depends on the deposition time. Because of the spontaneous reduction reaction, the deposition can only generate a very thin layer of Pd clusters at the early stage. When the thin cluster layer is formed, it can act as the seed layer for the growing Pd layer, which is presented in Figure 5.1b, showing that the Pd

coating after 45 min has a dramatic increase in thickness. The small difference in thickness between the Pd coatings after 45 min and 60 min indicates a relatively steady growth of the Pd layer, but the depositing rate of Pd is reduced because the Pd source is consumed during the deposition. Though the electroless deposited Pd coating shows a dense coating microstructure that can be used for Pd-Pt double layer coating as a base layer for Pt, cracks are also observed after 60 min. In general, cracks can influence the mechanical properties of deposited coatings and may cause spallation. However, as a base layer, the cracks could help to form strong bonded Pd-Pt double layer coating because the electroplated Pt can penetrate through the cracks and improve the adhesion between Pt and Pd coatings.

5.1.2 Microstructure of Ir-Pt Coating

Figure 5.4 shows the results of electroplated Ir coatings on M246 using early reported parameters [162]. The coating thickness is less than 1 μm even after 2 h electrodeposition, as shown in Figure 5.4a and 5.4b. During the deposition process, black deposits were formed not only around the two electrodes but also within the solution. The black deposits were then detected by EDX and the result is shown in Table 5.2. The oxygen content confirms the presence of oxides, but the black deposits can be the complex of Ir, Br and O rather than single Ir or Br oxide. In addition, Iron was also detected within the coating because the steel electrode slightly dissolved due to the low pH value.

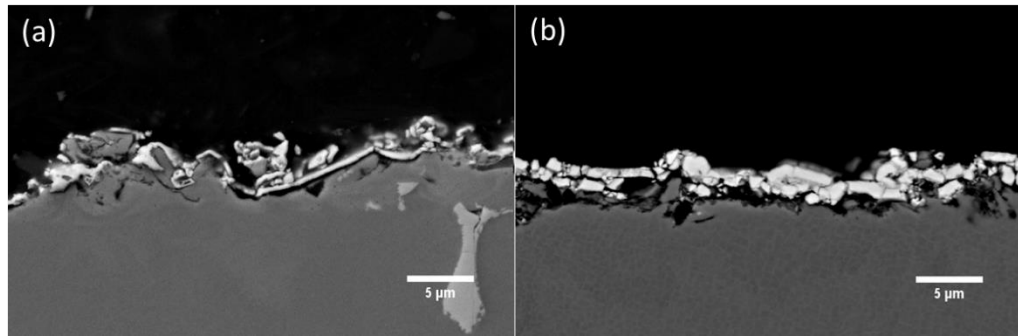


Figure 5.4 BSE images of the microstructures of electroplated Ir coatings on M246. The electroplating time are (a) 1 h and (b) 2 h.

Table 5.2 EDX results of as-received IrBr_3 particle and the black deposits formed during electroplating.

Elements /wt. %	Ir	Br	O	Fe	Other
IrBr_3 Particle	28	70	-	-	2
Black Deposits	44	23	20	9	4

5.1.2.1 Effects of Ir Electroplating Parameters

In order to achieve thick enough Ir coating ($\geq 2 \mu\text{m}$), the electroplating parameters were optimised to improve the deposition efficiency. Totally, the current density and Ir concentration were modified individually to find out the best setting for Ir electroplating. When the current density or the Ir concentration were doubled, the black deposits formed much quicker than normal process and the sample surface was covered by black deposits. The black deposits can be easily removed by ultrasonic bath, but no visible metallic coating was observed by visual examination. In addition, bubbles were also formed when the current density was doubled. Though the high bath operating temperature can increase the deposition efficiency, the increase in temperature was limited. The pH value remained unchanged because the lower pH value accelerated the corrosion of steel electrode and cause contaminations.

The problem came from the formation of possible complex oxides because the Ir ions in the electrolyte were consumed by forming oxides rather than deposited as a metallic layer. Although low pH value means low concentration of hydroxide ions, the dissolved oxygen in the electroplating solution can still oxidise the Ir ions and form complex oxides. A 5% H_2 /95%Ar gas was then used to remove the dissolved oxygen by bubbling the gas through the solution. The de-oxygen process was carried out for 2 h before electroplating. The final parameter settings are summarised in Table 5.3. The current density increased from 0.2 A/dm² to 0.3 A/dm² to reduce the side reaction at cathode and the Ir concentration was doubled to maintain the concentration of Ir ions. The operating temperature remained unchanged to protect the steel electrode from fast high temperature corrosion. Finally, a de-oxygen process was carried out before the electrodeposition.

Table 5.3 Deposition parameters of Ir electroplating.

Parameters	Setting
De-oxygen	2 h
Current Density	3 mA/dm ²
Temperature	75 °C
Ir Concentration	4 g/L

The as-deposited single Ir and Ir-Pt coatings on M246 by optimised parameters are shown in Figure 5.5a and b. With these electroplating parameters, the thickness of Ir coating has reached 2 μm . In addition, the Pt coating can also be successfully electrodeposited on the Ir coating. Surface morphologies of the Ir coatings prepared by reported and optimised parameters are shown in Figure 5.5 (c) and (d), respectively. The nucleated clusters of Ir and the original substrate features still can be seen from Figure 5.5 (c), but the surface is fully covered by the grown Ir grains which form the Ir coating in Figure 5.5

(d). Similar to the electroless plated Pd coating, cracks are found in the Ir coating deposited by optimised parameters.

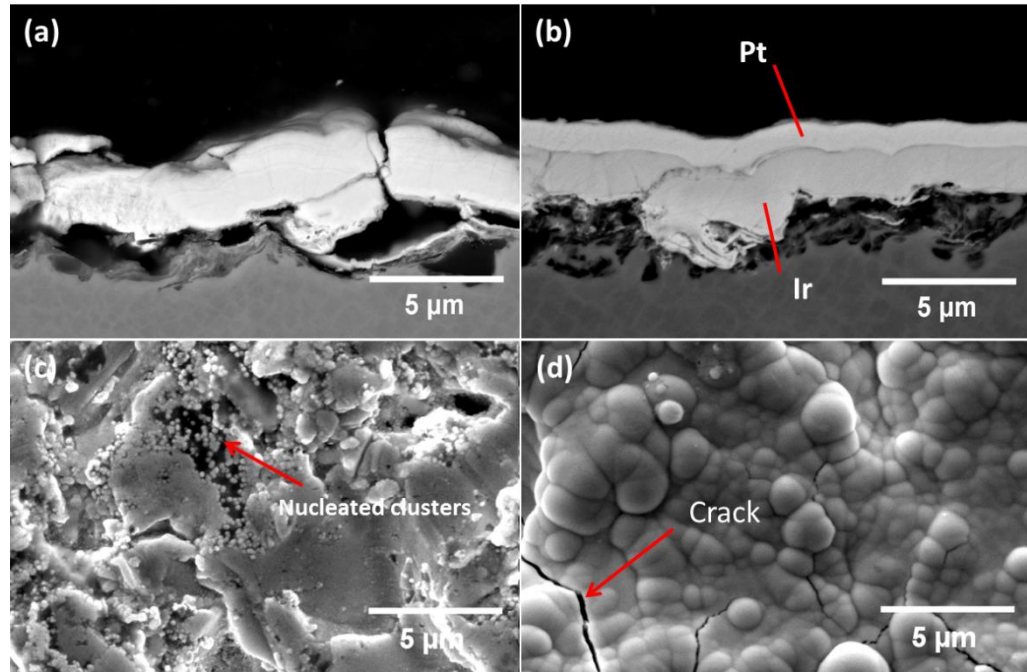


Figure 5.5 Microstructures of (a) as-deposited Ir coating by modified parameters and (b) Ir-Pt double layer. (c) Surface morphology of Ir coating deposited by reported parameters and (d) surface morphology of Ir coating deposited by optimised parameters.

Because Ir has many oxidation states, it makes it difficult to be oxidised to metal during the electroplating [187]. Both the disproportionation and comproportionation reactions can occur during the process, thus enough current density should be applied to reduce Ir^{3+} ions to Ir. Meanwhile, the current density also needs to be controlled because of high concentration of H^+ ions. When the current density is high enough, the H^+ ions can also be reduced and generate hydrogen gas which can prevent the nucleation of Ir atoms. In this investigation, current density was set to 0.3 mA/cm^2 to increase the

deposition of Ir and avoid the formation of H_2 . In addition, Ir^{3+} ions can easily form oxides with OH^- ions and the dissolved oxygen. Once the oxides are formed, they may cover the sample surface and prevent the deposition on the original sample surface, indicating no effective coating can be produced. The de-oxygen process was performed to ensure the deposition of Ir to avoid the formation of Ir oxide, via the removal of the dissolved oxygen. Furthermore, high concentration Ir ions can increase the deposition rate and also ensure a thick Ir coating can be produced.

The Ir-Pt coating can also be prepared by co-electrodeposition, but the thickness of the Ir-Pt coating is very limited (around $2\text{ }\mu\text{m}$) [142]. It has been reported that insufficient Ir content could not act as an oxygen diffusion barrier [140], thus a thick Ir coating is required for investigating the behaviour of Ir in bond coats. In this study, the prepared thick Ir coating may have the potential to provide an oxygen diffusion barrier and improve the oxidation resistance of bond coats with further applied Pt coating and the aluminising process.

As a summary, Pd coating was successfully deposited by electro-chemical method. The coating thickness of the Pd layer was around $3\text{ }\mu\text{m}$ after 60 min deposition. P is detected within the Pd coating as a side effect of the utilised electrolyte solution. The deposition of Ir coating using reported parameters resulted in a very limited coating thickness. However, with increased current density and Ir concentration, the deposited Ir coating thickness can reach more than $2\text{ }\mu\text{m}$. Furthermore, a de-oxygen process needs to be carried out to reduce the formation of black deposits and maintain Ir concentration during the electrodeposition.

5.2 Microstructure Evolution of Ir and Pd-modified PtAl Coatings

Figure 5.6 gives the microstructures of Ir-Pt and Pd-Pt coatings on M246 after vacuum diffusion heat treatment at 1100°C. The difference between the Ir-Pt coatings after 1 h and 4 h (Figure 5.6a) vacuum heat treatments is that the diffusion distance is around 20 μm after 4 h and only 10 μm after 1 h. The diffusion distance in Ir-Pt coating is relatively shorter than that in Pd-Pt coating. The inter-diffusion between Ir-Pt coating and Ni substrate is retarded, which may be due to the existence of Ir because the Pd-Pt coating has a similar diffusion distance as pure Pt coating. EDX results shown in Table 5.4 indicate that the inward diffusion of Ir is slower than Pt. On the other hand, Pd has diffused from the deposition layer to the substrate but is concentrated underneath the deposition layer with Pt. Because Al content in this concentrated layer is slightly higher than that in the substrate, Pd may form a solid solution with Al, similar to Pt [5].

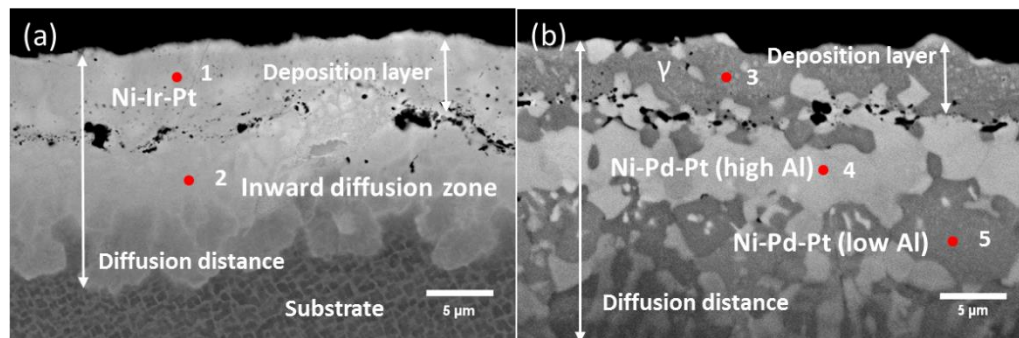


Figure 5.6 Microstructures of Ir-Pt and Pd-Pt coatings on M246 after vacuum diffusion heat treatment at 1100°C. (a) Ir-Pt coating after 4 h and (b) Pd-Pt coating after 1 h.

Table 5.4 EDX results of marked area in Figure 5.6.

Elements/wt. %	Ni	Al	Ir	Pt	Pd	Cr	Co	W
Spectrum 1	32.3	2.1	31.0	10.7	-	11.5	7.1	3.8
Spectrum 2	45.4	4.7	13.6	15.8	-	4.0	5.5	9.3
Spectrum 3	43.2	2.4	-	18.8	4.0	11.1	10.8	9.4
Spectrum 4	42.7	6.6	-	25.2	14.4	2.2	3.9	3.7
Spectrum 5	48.5	2.5	-	11.1	3.7	10.0	11.2	13.0

Microstructures of Ir (Ir-PtAl) and Pd (Pd-PtAl) modified PtAl coatings are shown in Figure 5.7. The β phase region in Ir-PtAl coating varies with different diffusion heat treatment durations. Less than 15 μm of aluminide layer is achieved in Ir-PtAl-1h coating, but around 30 μm of aluminide layer is formed in Ir-PtAl-4h coating. On the other hand, Pd-PtAl coating (Figure 5.7c) has similar microstructures to the conventional PtAl coating. The compositions of detected bond coat regions are shown in Table 5.5. γ' phase is only detected in the bond coat region of Ir-PtAl-1h coating. For both Ir-PtAl coatings, a high content of Ir is detected in the β phase. However, Ir-PtAl-4h coating shows a different coating structure which has separated aluminide layers with enriched Pt and Ir, respectively. The Ir-PtAl-4h coating has an upper Pt-enriched β phase region and lower Ir enriched phases. In Pd-PtAl coating, P is found enriched at the interface between the β phase region and inter-diffusion zone after post heat treatment as a result of the side reaction of electroless deposition. The EDX result of P precipitate is also given in Table 5.5.

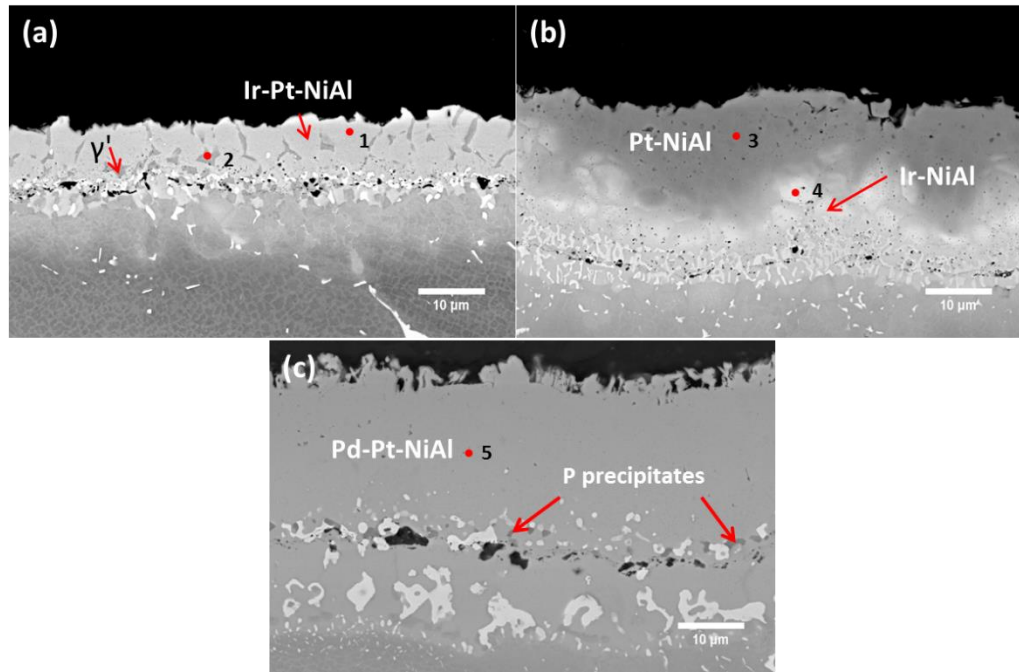


Figure 5.7 Microstructures of (a) Ir-PtAl-1h coating, (b) Ir-PtAl-4h coating and (c) Pd-PtAl coating.

Table 5.5 EDX results of marked areas shown in Figure 5.7.

Elements/wt. %	Ni	Al	Ir	Pt	Pd	Cr	Co	W	P
1	38.0	13.5	22.5	16.1	-	4.5	3.8	-	-
2	50.1	8.7	12.6	13.5	-	3.9	5.4	3.4	-
3	51.0	24.5	-	16.5	-	2.6	4.6	-	-
4	32.8	18.2	39.6	-	-	2.4	5.3	-	-
5	45.8	17.6	-	14.5	13.2	3.4	5.0	-	-
P precipitate	18.2	2.1	-	-	2.0	14.5	12.8	13.6	16.2

The microstructure of Ir-PtAl coatings also indicates that the inward diffusion of Al is retarded because the length of the inter-diffusion zone is shorter than that of a common inter-diffusion zone. In general, the inward diffusion of Al leads to the formation of an inter-diffusion zone with precipitates of refractory elements [9]. The thickness of the Ir-modified PtAl coating has a 10 μm thick inter-diffusion layer, but the thickness of inter-diffusion in conventional Pt-modified aluminide coating is 20 μm . The difference in thicknesses is important in showing the different behaviour of Ir-modified PtAl coating. The Al

mapping of Ir-PtAl coatings shown in Figure 5.8 reveals that the inward diffusion of Al is retarded, but the Ir-PtAl-4h coating shows a thicker inter-diffusion zone than the Ir-PtAl-1h with increased vacuum diffusion heat treatment time.

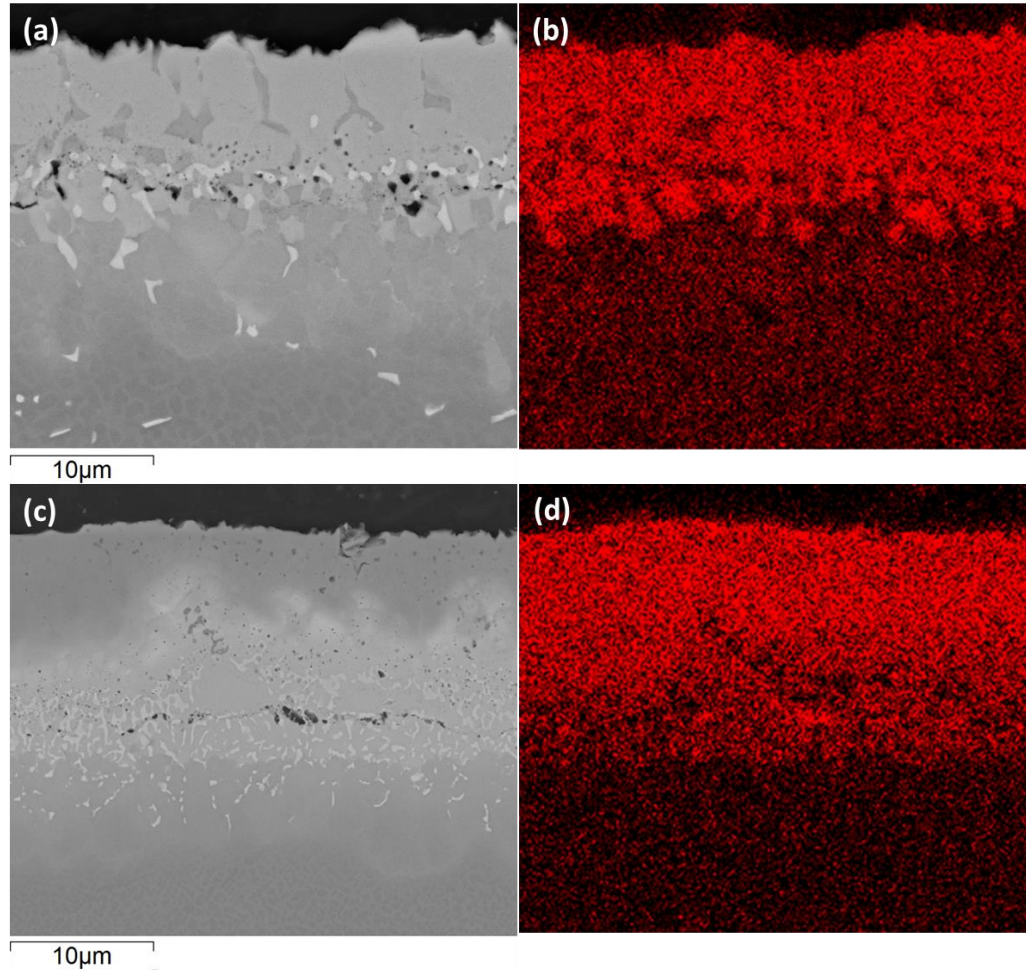


Figure 5.8 Al mapping of prepared Ir-PtAl coatings (a) BSE image of Ir-PtAl-1h coating, (b) Al mapping of Ir-PtAl-1h coating, (c) BSE image of Ir-PtAl-4h coating and (d) Al mapping of Ir-PtAl-4h coating.

5.3 Cyclic Thermal Oxidation on Ir and Pd-modified PtAl Coatings

5.3.1 Growth Behaviour of TGO

TGO thickness changes of Ir-PtAl-4h, Pd-PtAl and general PtAl coatings on M246 substrate after thermal cyclic oxidation are shown in Figure 5.9. All the three coatings show fast TGO growth in the first 50 cycles and a slowed growth rate from 50 cycles to 200 cycles. The Ir-PtAl-4h coating has the slowest growth in TGO thickness during 200 cycles among the three coatings, which indicates superior oxidation resistance than the other two coatings. Both Pd-PtAl and general PtAl coatings have similar TGO growth behaviour, but the Pd-PtAl coating shows the trend of TGO flat growth in further oxidation cycles. On the other hand, the thickness of Ir-PtAl-1h coating reached around 3 μm only after 50 cycles. The further thickness was not measured due to the massive formation of spinel after 100 cycles.

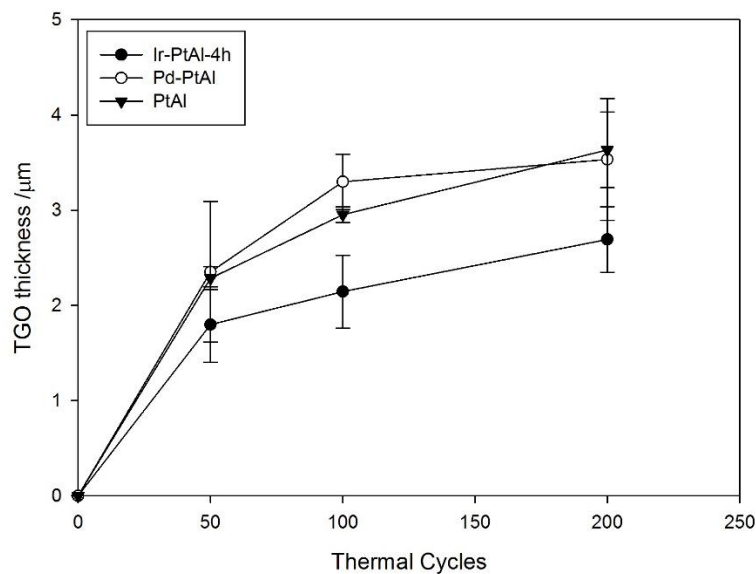


Figure 5.9 TGO thickness changes of Ir-PtAl-4h, Pd-PtAl and general PtAl coatings on M246 substrate after thermal cyclic oxidation (error bar: standard deviation).

Figure 5.10 reveals the changes of surface roughness of Ir-PtAl-4h, Pd-PtAl and PtAl coatings before and after thermal cycling. Minimum increase in surface roughness is found in the Ir-PtAl-4h coating from 0 cycle to 200 cycles. Both Pd-PtAl and PtAl coatings show larger increase in roughness than Ir-PtAl-4h coating after cyclic thermal oxidation. Significant roughness increase after 50 cycles is observed in Pd-PtAl coating, but a small difference is found between the results of 50 cycles and 200 cycles.

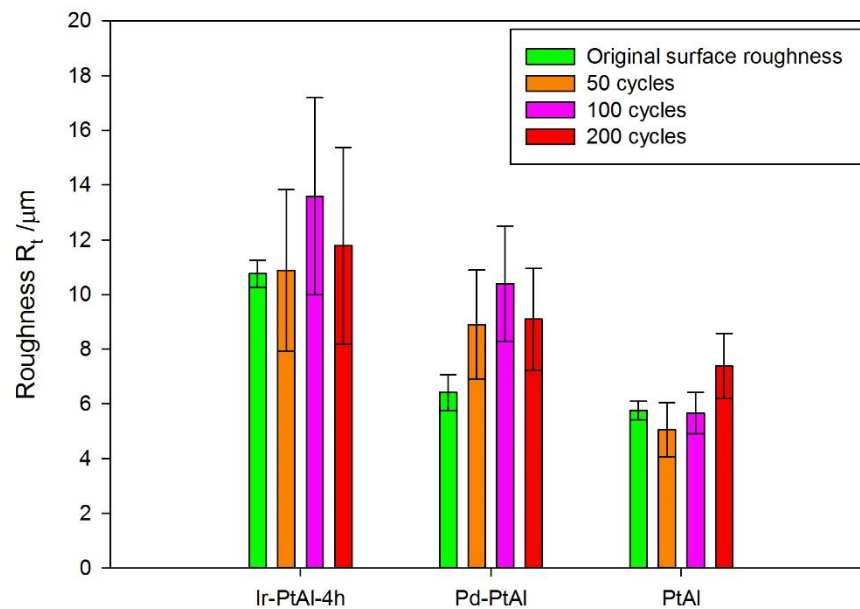


Figure 5.10 Surface roughness of Ir-PtAl-4h, Pd-PtAl and PtAl coating on M246 substrate before and after cyclic thermal oxidation (error bar: standard deviation).

5.3.2 Microstructure Evolution of Ir- and Pd-PtAl Coatings

Massive growth of spinel phase was observed in the Ir-PtAl-1h coating, suggesting rapid depletion of Al and poor oxidation resistance. The TGO thickness of the Ir-PtAl-1h coating could not be used to evaluate the performance of a typical Ir-PtAl coating. The microstructure of oxidised Ir-PtAl-1h coating after 50 and 100 cycles at 1100°C is shown in Figure 5.11. Massive formation of spinel can be seen in Figure 5.11b. EDX results of the labelled area shown in Table 5.6 indicate that the β phase is consumed and almost all the bond coat region has changed to γ phase. In addition, the reduced Ir content in a similar area reveals the inward diffusion of Ir. Fast consumption of Al and small coating thickness may result in the disappearance of the inter-diffusion zone after 50 cycles.

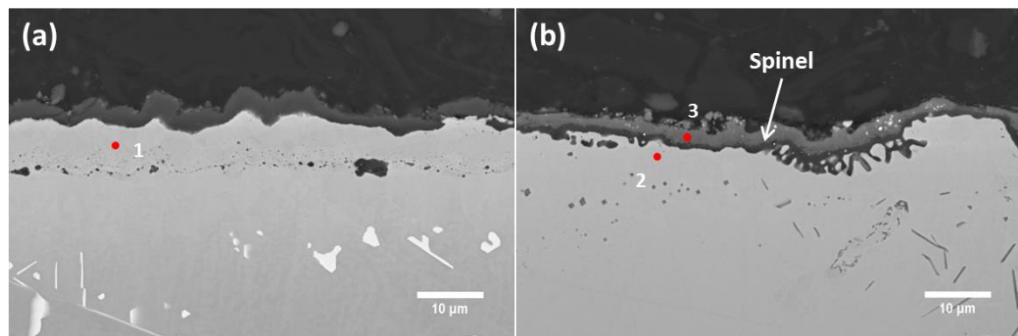


Figure 5.11 Microstructures of Ir-modified PtAl coating on M247 substrate after (a) 50 cycles and (b) 100 cycles oxidation at 1100°C. The arrowed grey layer in the formed TGO layer is the spinel phase.

Table 5.6 EDX results of labelled areas in Figure 5.11.

Elements/at. %	Ni	Al	Ir	Pt	Cr	Co	Ti	W	Mo	O
1	57.2	12.6	3.7	2.0	8.5	7.8	2	3.0	1.5	-
2	61.3	8.0	2.3	2.2	9.8	9.2	1.2	3.8	-	-
3	21.5	19.8	-	-	3.3	1.9	0.2	-	-	65.1

Figure 5.12 reveals the microstructure evolution of Ir-PtAl-4h and Pd-PtAl coatings on M246 substrate after a thermal cyclic oxidation test. The Ir-PtAl-4h coating presents much better oxidation resistance than Pd-PtAl and PtAl coatings, which exhibits a retarded transition from β to γ' . The transition of β to γ' is effectively retarded in Ir-PtAl-4h coating, indicating few formations of γ' phase after 50 cycles, but slightly increased transformation of γ' is observed after 200 cycles. The Pd-PtAl coating shows similar microstructure evolution as general PtAl coating on M246 with an increased γ' phase region during thermal cycles, but the formed γ' phase in Pd-PtAl coating has a larger area than that in Ir-PtAl-4h coating. In addition, the phosphorus precipitates are not found in Pd-PtAl coating after the cyclic thermal oxidation test.

EDX results of detected β and γ' phases in Ir-PtAl-4h and Pd-PtAl coatings are shown in Table 5.7. Compared to the Pd-PtAl coating, Ir content in β phase decreases with the increasing thermal cycles, but the concentration of Pd in β phase is not changed. The reduced Ir concentration of Ir may indicate an inward diffusion of Ir. In addition, Pt content in both coatings remains stable with different thermal cycles. With respect to the formed γ' phases, the composition of detected γ' phase after 100 cycles shows a big difference from the one detected after 200 cycles in Ir-PtAl-4h coating, because there is no Ir content found in the γ' phase after 100 cycles. The dissimilar γ' compositions may be caused by the original coating microstructure shown in Figure 5.7b. So, the formed γ' phase after 100 cycles may be a result of the degradation of general β -NiAl phase rather than the Ir-enriched β phase.

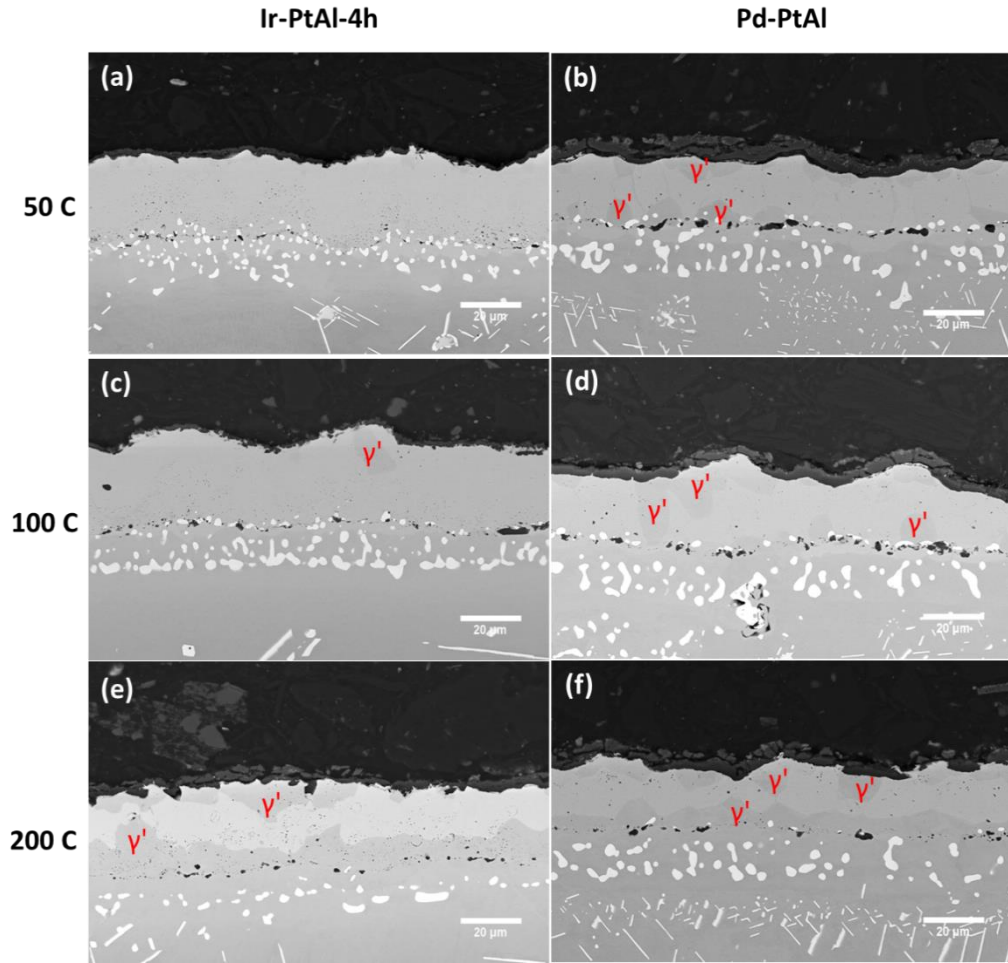


Figure 5.12 Microstructure evolution of Ir-PtAl-4h and Pd-PtAl coatings during cyclic thermal oxidation test at 1100°C. (a) Ir-PtAl-4h coating, 50 cycles; (b) Pd-PtAl coating, 50 cycles; (c) Ir-PtAl-4h coating, 100 cycles; (d) Pd-PtAl coating, 100 cycles; (e) Ir-PtAl-4h coating, 200 cycles and (f) Pd-PtAl coating, 200 cycles.

Table 5.7 EDX results of detected β and γ' phases in Ir-PtAl-4h and Pd-PtAl coatings after thermal cyclic oxidation test.

Elements/wt. %	Ni	Al	Ir	Pt	Pd	Cr	Co	W
β 50 cycles (Ir-PtAl-4h)	40.6	12.5	21.5	15.4	-	4.2	4.1	-
β 100 cycles (Ir-PtAl-4h)	44.5	13.8	16.4	15.1	-	4.4	4.4	-
β 200 cycles (Ir-PtAl-4h)	41.0	13.8	14.5	14.9	-	4.4	3.7	-
β 50 cycles (Pd-PtAl)	48.7	15.0	-	13.0	14.0	4.0	4.6	-
β 100 cycles (Pd-PtAl)	47.4	14.8	-	14.2	14.4	3.8	4.7	-
β 200 cycles (Pd-PtAl)	47.0	14.7	-	13.5	16.3	3.8	4.0	-
γ' 50 cycles (Pd-PtAl)	59.2	9.7		9.2	5.3	3.8	6.9	4.2
γ' 100 cycles (Pd-PtAl)	59.9	8.9	-	9.9	4.1	4.0	6.7	4.5
γ' 200 cycles (Pd-PtAl)	61.1	8.9	-	8.7	4.8	4.0	6.5	4.4
γ' 100 cycles (Ir-PtAl-4h)	59.3	8.8	-	2.7		4.4	6.8	5.9
γ' 200 cycles (Ir-PtAl-4h)	51.2	7.2	11.9	13.5		6.6	6.5	-

Since the depletion of Al in Ir-PtAl-4h coating starts to increase during 100 cycles to 200 cycles, the relationship between Ir concentration and Al depletion is considered. Figure 5.13 shows the Al mapping of Ir-PtAl-4h coating after different thermal cycles, indicating that the consumption of Al due to inward diffusion of Al occurs during the 100 cycles to 200 cycles when the concentration of Ir reduces below around 15 wt.%. This may suggest that the inward diffusion of Al is retarded when there is a high concentration of Ir in the coating. The inward diffusion of Al may occur if the concentration level of Ir is reduced below 15 wt.%.

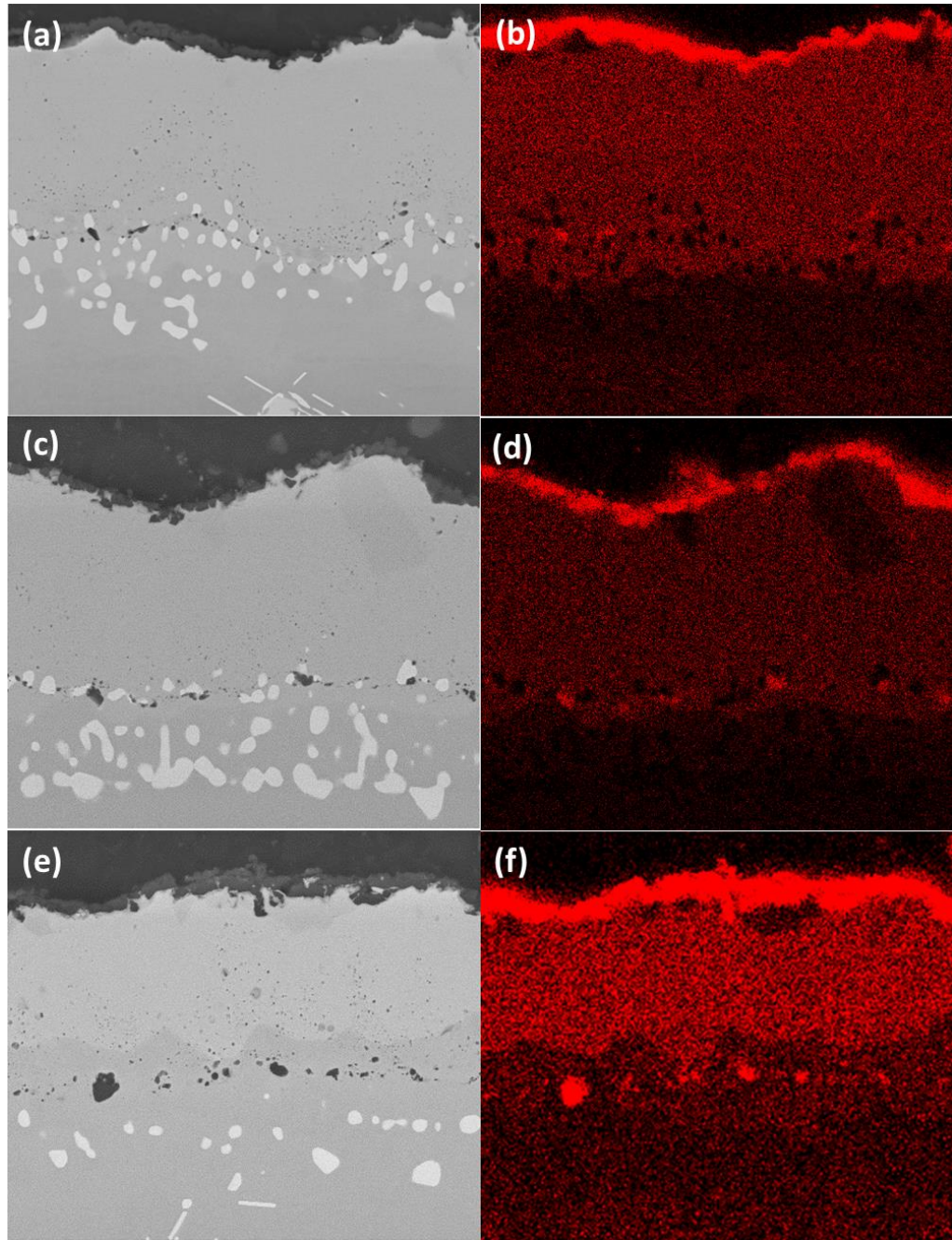


Figure 5.13 Al mapping of Ir-PtAl4h coating after thermal cyclic oxidation. (a) BSE image after 50 cycles at 1100°C; (b) Al mapping after 50 cycles; (c) BSE image after 100 cycles; (d) Al mapping after 100 cycles; (e) BSE image after 200 cycles and (f) Al mapping after 200 cycles.

5.4 Discussion

5.4.1 Influences of Ir on Oxidation Resistance

In this investigation, the Ir-PtAl-4h coating shows superior oxidation resistance compared with Pd-PtAl and PtAl coatings. The microstructure of Ir-PtAl coatings varies with different vacuum diffusion heat treatments. In general, the growth of β -NiAl phase is performed by the reaction between AlCl and Ni at high temperature [9]. However, this reaction may be retarded in Ir-PtAl-1h coating because a very limited β phase region is formed. Basically, the longer heat treatment can distribute the Ir more evenly. The results of Ir-PtAl-1h coating may indicate that the high concentration of Ir can prohibit the formation of the β phase during the aluminising process. On the other hand, the results of Ir-PtAl-4h coating shows that the aluminising process can be successfully performed after 4 h vacuum heat treatment. Because the formation of β can be a chemical attack of AlCl, the high corrosion resistance of Ir may prevent the reaction. In addition, as shown in Figure 5.7, the longer vacuum diffusion heat treatment may also lead to more outward diffusion of Ni, which could ensure the formation of β phase during the aluminising process.

The most frequently reported effect of Ir is the low oxygen permeability which makes Ir a potential oxygen diffusion barrier (ODB), but the TGO growth behaviour of Ir-PtAl-4h coating could not clarify the ODB effect. Instead, Ir is found to act as a diffusion barrier to Al because the inward diffusion of Al in Ir-PtAl-4h coating after aluminising is prevented after 1 h post vacuum heat treatment. This makes the coating have enough Al reservoir to form protective Al_2O_3 layer during oxidation. It is suggested that the possible strong bonding effect between Ir and Al may prevent the diffusion of Al even

though there is a significant concentration gradient of Al between the coating and substrate. Further investigations can be carried out to investigate the microstructure of the interface between the bond coat and substrate by TEM.

A phase diagram of Ir-Al is shown in Figure 5.14. The IrAl phase has the highest melting point among the Ir-Al phase, which is over 2000°C compared to the 1638°C of NiAl [41, 188]. This makes the IrAl phase more stable at higher temperatures than NiAl. The more stable the IrAl phase is, the slower that Al can diffuse from the IrAl phase at high temperature. However, the formation of the IrAl phase cannot be confirmed in this investigation according to EDX analysis.

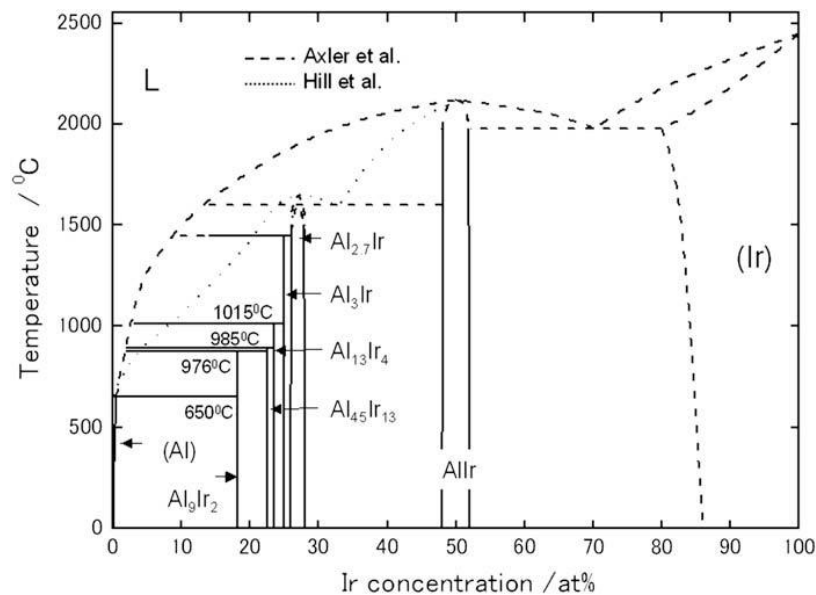


Figure 5.14 Phase diagram of Ir-Al [188].

Despite the inward diffusion of Al is prevented at the early stages of oxidation, EDX analysis shows that the inward diffusion of Ir never stops in Ir-PtAl-4h coating during oxidation test. It will be easier for Al to diffuse when the Ir concentration is reduced. It can be seen from Figure 5.14 that the melting point of the Ir-Al phases decreases with

lower Ir contents. As a result, the Ir-PtAl-4h coating will suffer from the transformation from β to γ' in long term oxidation due to decreasing Ir concentration. Therefore, the concentration and diffusion of Ir should be carefully monitored to optimise the advantages of Ir. Further investigations can be focused on reducing the inward diffusion of Ir by diffusing an initial Ir layer before fabricating the Ir-modified PtAl coating. The initial diffused Ir layer may narrow the concentration gradient between the bond coat and substrate, thus reducing the inward diffusion of Ir.

5.4.2 Effects of Pd on Oxidation Resistance

Pd-PtAl coating shows similar microstructure and oxidation behaviour to PtAl coating because as a PGM, Pd may have the same ability to stabilise the β phase [183]. Even though the Pd-PtAl coating shows a slightly higher rumpling rate of the TGO layer than the PtAl coating after thermal cyclic oxidation, steady growth in the rumpling level is observed after 200 cycles. Because of the significant increase in surface roughness, damage of the Pd-PtAl may occur at early stages of cyclic thermal oxidation.

Pd may form solid solution with Al because Al is concentrated in Pd and Pt solid solutions. This could be used to form an Al reservoir at high temperature. However, the Al concentrated Pd solid solution disappears in further heat treatments, which leaves Pd in the β phase, similar to Pt. In addition, because of the side reaction of electroless deposition, the residual P precipitates are detected after post heat treatment. It may help to grow an oxide layer but either acceleration or retardation on TGO growth could occur, which may depend on the volume of P. Further investigations should be carried out to investigate the effects of P on the growth rate of TGO. In current

investigation, the electroless deposited Pd-modified PtAl coating has similar oxidation behaviour as general PtAl coating. There is no any improvement of Pd addition in cyclic thermal oxidation. However, it is still considered that due to economic reasons, Pd can be a good candidate to reduce the use of Pt in bond coat preparation.

5.5 Summary

In this chapter, Ir and Pd coatings were prepared by electroplating and electroless deposition methods respectively to investigate the influences of Pd and Ir additions on oxidation resistance of PtAl coating. Parameters of electrodepositing Ir coating were optimised by increasing the current density and Ir concentration. More importantly, the de-oxygen process is necessary to avoid the oxidation of Ir ions and ensures thick Ir coating deposition.

The results of cyclic thermal oxidation showed that Ir-PtAl-4h coating has better oxidation resistance than Pd-PtAl and PtAl coatings. Both Pd-PtAl and PtAl coatings had similar oxidation behaviour. The Ir-PtAl-4h coating also exhibited a lower rumpling level but the Pd-PtAl coating showed a significant increase in rumpling level after 50 cycles than the other two coatings. In addition, general PtAl coating showed steady growth in surface roughness.

The ODB of Ir was not observed in this work. However, Ir had been found to retard the inward diffusion of Al. This might be caused by the formation of high temperature stable solid solution between Al and Ir. Since the inward diffusion of Al is retarded, there is more Al reserved for oxidation resistance and the growth rate of TGO might also be reduced due to the stable solid solution. It was also suggested that the inward diffusion of Al started when the Ir concentration was

below 15 wt.% in the coating. On the other hand, Pd did not lead to any improvement on PtAl coating. The reason might be that Pd has very similar chemical properties as Pt. Therefore, the addition of Pd might not have a great influence on the oxidation behaviour of Pd-PtAl coating.

Chapter 6 Oxidation Behaviour of Prepared Bond Coats with Ceramic Top Coat

In a thermal barrier coating (TBC) system, the bond coat is applied underneath the ceramic top coat. Since the TGO growth behaviour is determinant to the TBC lifetime, it is worth to investigate the capability of prepared bond coats with integrated ceramic top coat. The ZrO_2 -PtAl coating has shown great potential for anti-oxidation and rumpling resistance, and it is expected to exhibit good compatibility with the ceramic top coat. The Pd-PtAl coating did not lead to any improvement on oxidation resistance of the bond coat, but the integrated ceramic top coat may truly reveal the oxidation behaviour of Pd-PtAl.

In this chapter, oxidation behaviour of the ZrO_2 -PtAl and Pd-PtAl bond coats were investigated with air plasma sprayed ceramic top coat to determine the performance of the bond coats in thermal barrier coating systems. Conventional high velocity oxygen fuel (HVOF) sprayed NiCoCrAlY and Pt-modified aluminide bond coat were used as benchmarks. In addition, isothermal oxidation was also carried out to test the bond coats at constant high temperature for long duration compared with the short-term cycles of the cyclic thermal test. The growth rate and rumpling level of TGO were used to evaluate the performance of bond coats and lifetime of coating systems. The difference between the bond coats with and without ceramic top coats was discussed, as well as the influence of different oxidation conditions.

6.1 Isothermal Oxidation Behaviour of ZrO₂-PtAl and Pd-PtAl Bond Coats

Isothermal oxidation behaviour of ZrO₂-PtAl and Pd-PtAl coatings were investigated prior to the study of bond coats with ceramic top coat, because only the cyclic thermal oxidation behaviour was discussed in the previous chapters. General PtAl coating was treated as the bench mark.

Figure 6.1 and Figure 6.2 give the microstructure evolution of PtAl, ZrO₂-PtAl and Pd-PtAl coatings on M247 substrate during isothermal oxidation. γ' phase and hafnium oxide are formed in all the three coatings during the oxidation similar to their results in the cyclic thermal oxidation test. Table 6.1 shows the EDX results of β and γ' phases, and the hafnium oxide region in the three coatings. It is surprising that a new solid solution may be found in Figure 6.2i as labelled. The composition of the new solid solution in Table 6.1 indicates that the solid solution contains a relative high content of Al, Pt and Pd. Because the β to γ' transformation is nearly completed after 200 h in Pd-PtAl, so this formed new solid solution indicates better high temperature stability than the β phase. In addition, the Al content is similar to that in the β phase, but with lower Ni concentration and higher Pd and Pt concentrations. This may suggest that the combined effects of Pd and Pt could form a stable aluminide phase at high temperature. However, it remains unknown why this high temperature solid solution only occurs after 200 h isothermal oxidation in Pd-PtAl coating.

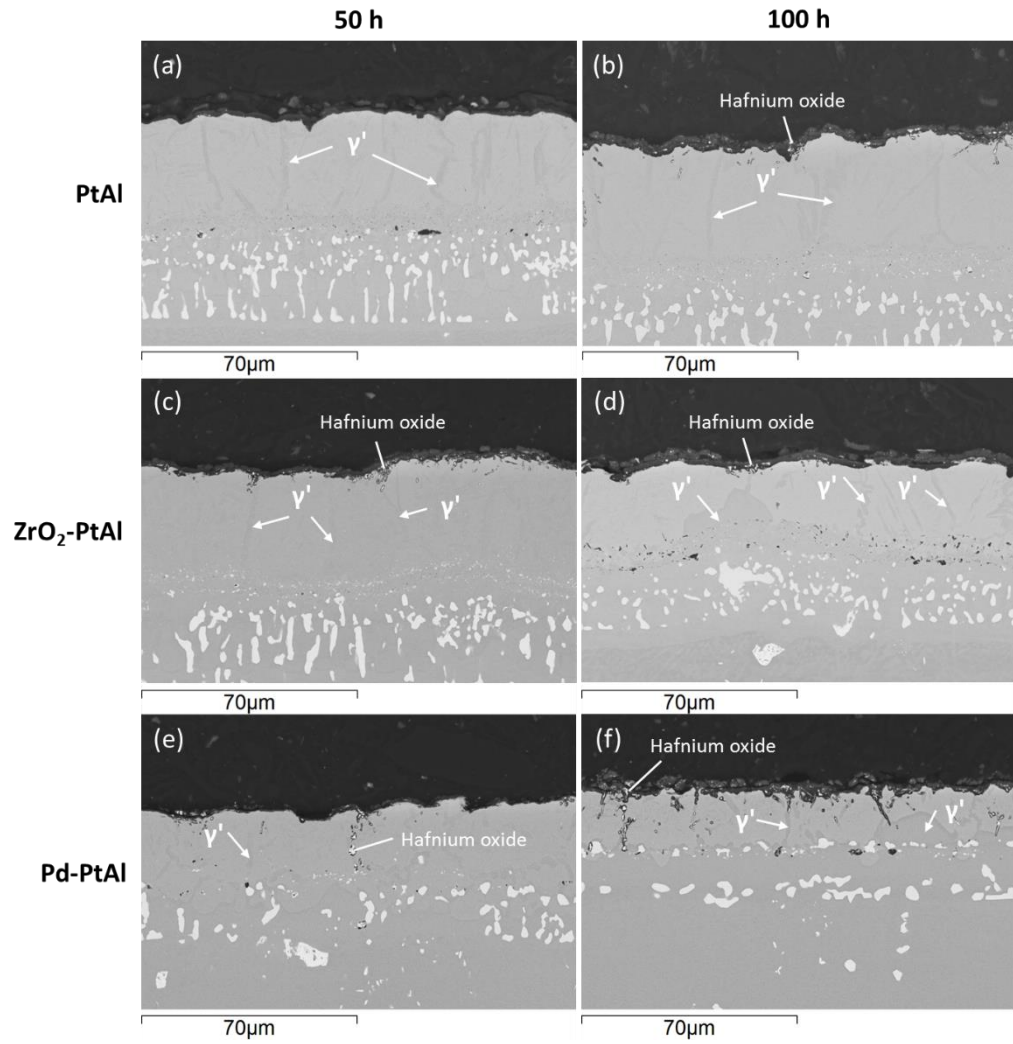


Figure 6.1 Microstructure evolution of PtAl, ZrO₂-PtAl and Pd-PtAl bond coats in isothermal oxidation test at 1100°C. (a) PtAl 50 h; (b) PtAl 100 h; (c) ZrO₂-PtAl 50 h; (d) ZrO₂-PtAl 100 h; (e) Pd-PtAl 50 h; (f) Pd-PtAl 100 h.

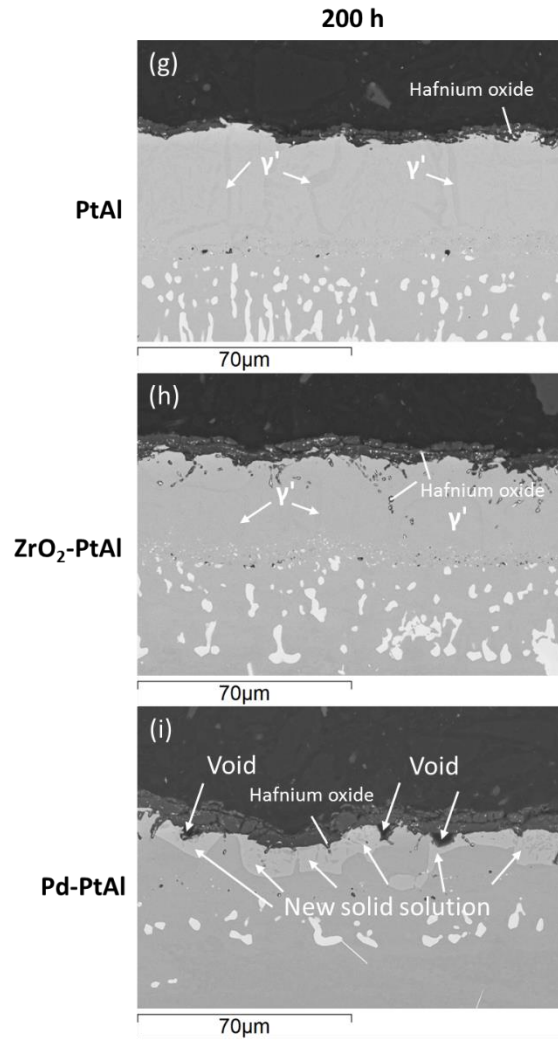


Figure 6.2 (continued) Microstructure evolution of PtAl, ZrO₂-PtAl and Pd-PtAl bond coats in isothermal oxidation test at 1100°C. (g) PtAl 200 h; (h) ZrO₂-PtAl 200 h and (i) Pd-PtAl 200 h.

Table 6.1 EDX results of β and γ' phase, hafnium oxide region in PtAl, ZrO₂-PtAl and Pd-PtAl coatings on M247 during isothermal oxidation test. The composition of the new solid solution formed after 200 h in Pd-PtAl coating is also revealed.

Elements/ wt. %	Al	Ni	Pd	Pt	Hf	Cr	Co	Zr	O
β PtAl	15.2	40.4	-	32.7	-	4.8	6.6	-	-
β ZrO ₂ -PtAl	14.9	42.5	-	32.0	-	4.1	5.7	-	-
β Pd-PtAl	16.3	48.9	11.5	13.0	-	4.5	5.6	-	-
γ' PtAl	9.5	48.3	-	31.5	-	4.3	5.3	-	-
γ' ZrO ₂ -PtAl	9.8	51.2	-	22.7	-	4.4	6.2	-	-
γ' Pd-PtAl	10.2	59.2	7.3	8.6	-	5.1	7.3	-	-
Hafnium oxide PtAl	4.5	4.1	-	--	70.2	-	-	-	23.4
Hafnium oxide ZrO ₂ -PtAl	1.6	3.0	-	-	69.2	-	-	6.9	19.8
Hafnium oxide Pd-PtAl	1.6	3.3	-	-	76.1	-	-	-	19.0
New solid solution Pd-PtAl	15.7	31.8	29.3	18.3	-	2.4	2.5	-	-

The result of microstructure evolution also indicates that the formed γ' phase in isothermal oxidation has a different feature from that generated in cyclic thermal oxidation. The formed γ' phase during cyclic thermal oxidation has an island shape but a lath shape is indicated during the isothermal oxidation. A sketch of the shape difference of γ' phase is shown in Figure 6.3. This phenomenon is considered to be a result of different oxidation conditions and will be discussed in section 6.4.2.

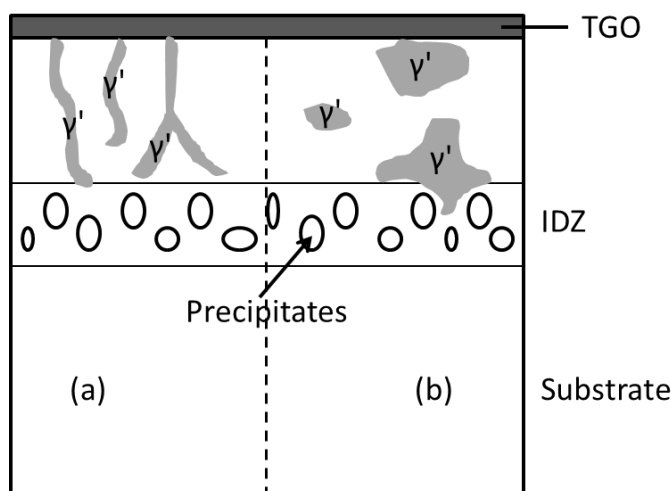


Figure 6.3 Schematic of the difference between formed γ' phases during (a) isothermal and (b) cyclic thermal oxidation.

6.1.1 TGO and Roughness Evolution

Figure 6.4 gives the TGO changes of PtAl, ZrO_2 -PtAl and Pd-PtAl coatings during isothermal oxidation. The general PtAl coating shows slower growth rate of TGO than the other two coatings. Even though the growth of TGO in both ZrO_2 -PtAl and Pd-PtAl coatings is slower than that of PtAl coating, the growth rate of TGO in ZrO_2 -PtAl and Pd-PtAl coatings increases during 50 h to 200 h. The trend of TGO thickness changes in PtAl coating, indicating a further flat increment of TGO, but the TGO thickness in both ZrO_2 -PtAl and Pd-PtAl coatings may continue to grow.

The surface roughness profile after isothermal oxidation is shown in Figure 6.5. The ZrO_2 -PtAl coating has lower surface roughness than general PtAl coating, indicating the best rumpling resistance among the three coatings. However, the surface roughness of Pd-PtAl coating increases significantly after isothermal oxidation. Thus a poor rumpling resistance is revealed.

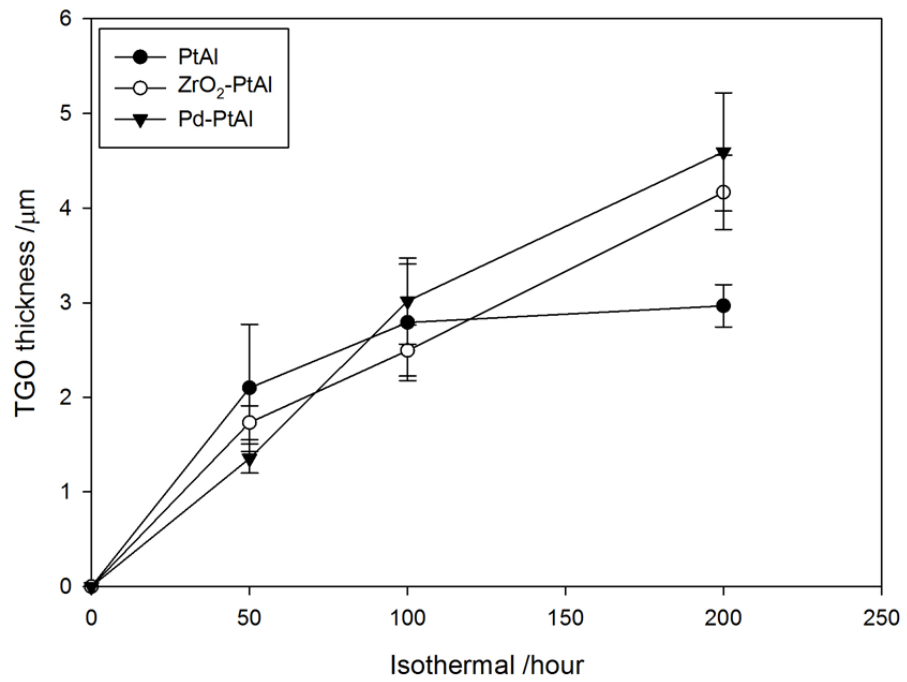


Figure 6.4 TGO thickness changes of PtAl, ZrO₂-PtAl and Pd-PtAl coating in isothermal oxidation test (error bar: standard deviation).

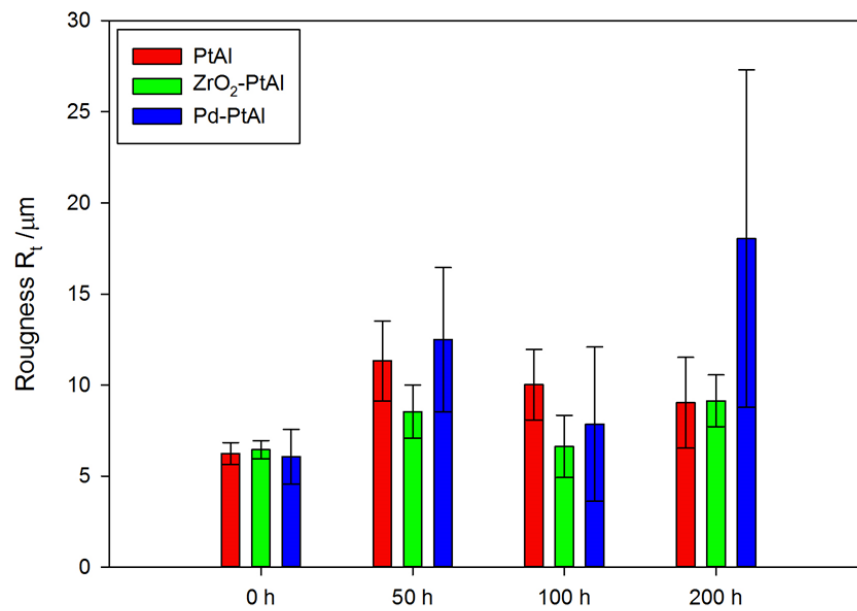


Figure 6.5 Surface roughness changes of PtAl, ZrO₂-PtAl and Pd-PtAl coatings in isothermal oxidation (error bar: standard deviation).

6.2 Microstructures of As-prepared Ceramic Coating Systems

Figure 6.6 gives the microstructures of as-sprayed coating systems, which shows the general microstructure of APS sprayed 8YSZ coating. However, surface removal of the aluminide bond coats can be observed at the interface. This is attributed to the coarse sandblasting alumina labelled in Figure 6.6a and 6.6b. For the PtAl, ZrO₂-PtAl and Pd-PtAl bond coats, the β phase regions slightly decreased in size due to the loss of bond coat material caused by sandblasting. This is expected because sandblasting will remove certain amount of the bond coat material and coarse alumina particles will remove more material than fine alumina. Some embedded coarse alumina particles can still be observed after sandblasting (Figure 6.6a and 6.6b). Only the NiCoCrAlY bond coat has kept the original coating microstructure because sandblasting is not carried out on the NiCoCrAlY bond coat. The surface roughness of as-sprayed NiCoCrAlY coating can directly hold an APS sprayed ceramic top coat. Different from the single β phase in aluminide bond coats, β and γ double phases are formed in NiCoCrAlY coating after vacuum heat treatment (as indicated in the inset of Figure 6.6d and Table 6.2). Figure 6.6c also indicates that the ceramic coating can be slightly damaged at the edges of prepared samples, in the example of the Pd-PtAl coating system.

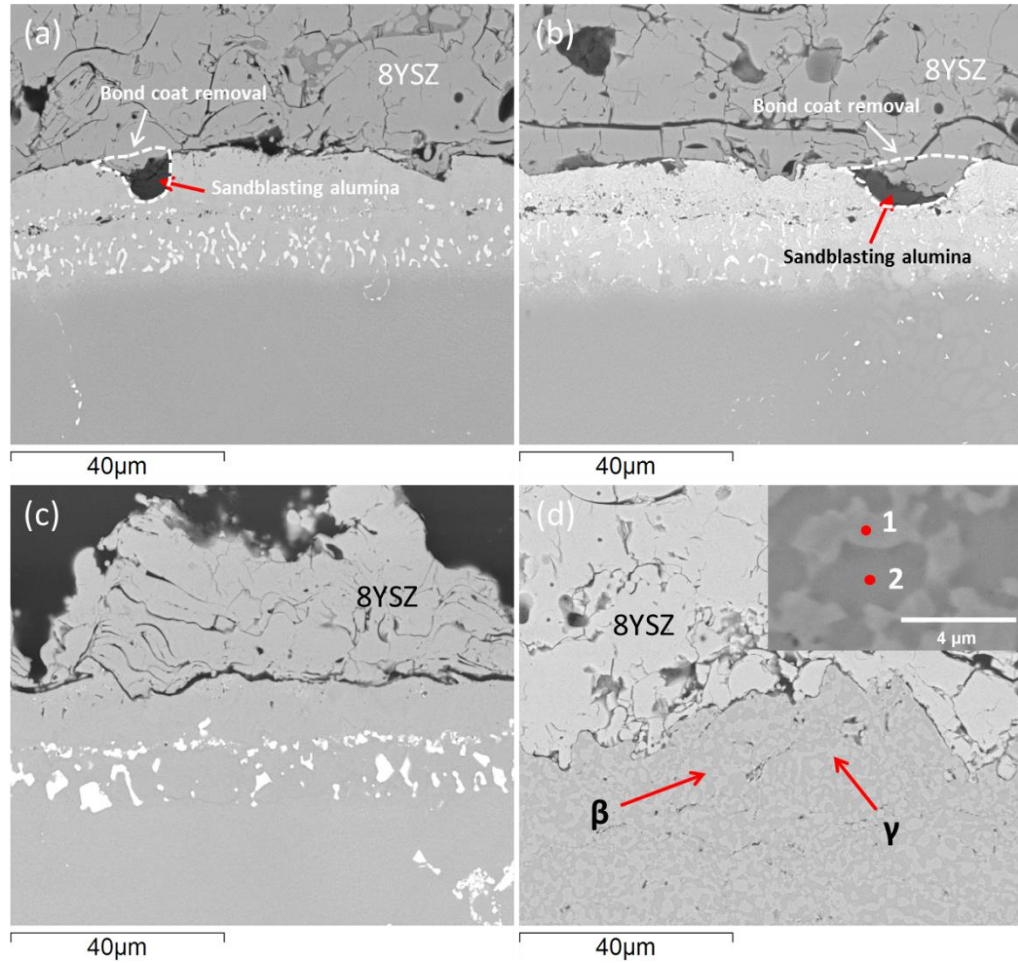


Figure 6.6 Microstructures of APS sprayed coating systems with different bond coats (a) PtAl; (b) $\text{ZrO}_2\text{-PtAl}$; (c) Pd-PtAl and (d) NiCoCrAlY after vacuum heat treatment at 1100°C for 2 h. The removal of the bond coat is illuminated in (a) and (b) by dot line. The arrows in (a) and (b) indicate the embedded sandblasting alumina. Image (c) is taken at the near edge of the Pd-PtAl coating system and the inset in (d) shows the enlarged image of detailed microstructure of NiCoCrAlY bond coat.

Table 6.2 EDX result of β and γ phases in NiCoCrAlY bond coat in Figure 6.6d.

Elements/ wt.%	Ni	Al	Cr	Co
Spectrum 1 (γ)	52.9	4.5	20.8	22.0
Spectrum 2 (β)	57.4	19.0	8.9	14.5

6.3 Results of Oxidation Tests on TBC Systems

In the current investigation, the oxidation durations in the isothermal test were set as 50 h, 100 h and 200 h at 1100°C, but they were 51 h 40 min, 103 h 20 min and 206 h 40 min respectively at 1100°C in the cyclic thermal test due to the additional 2 min in each cycle. For each isothermal test, the heating duration was constantly 137 min 30 sec and the cooling duration was usually over 12 h in the furnace. On the other hand, the totally heating and cooling duration was 25 h, 50 h and 100 h for 50 cycles, 100 cycles and 200 cycles respectively. However, samples were kept at temperatures between 300°C and 800°C for a longer time during the heating and cooling in isothermal oxidation than those in cyclic thermal oxidation due to the rapid heating and cooling rates.

6.3.1 Evolution of Microstructures during Oxidation

The microstructures of the TBC systems on the M247 substrate with different bond coats after isothermal oxidation at 1100°C are shown in Figure 6.7 and Figure 6.8. Internal cracks are formed at the ceramic/bond coat and bond coat/alloy interfaces after oxidation, which are labelled in Figure 6.7 and Figure 6.8. After 200 h oxidation, large cracks are also observed near the interface in the ceramic coating region. However, the cracks in the ceramic coating side are influenced by the initial cracks in the as-sprayed ceramic coating, which makes it difficult to identify the cracks that were caused by the isothermal oxidation test.

In all coating systems, ceramic top coats remain attached to the bond coats except that partial detachment of the ceramic top coat occurs in the $\text{ZrO}_2\text{-PtAl}$ coating system after 200 h. The $\text{ZrO}_2\text{-PtAl}$ coating

system suffers from severe internal cracks because of the preliminary detached ceramic coating as seen in Figure 6.7f, but no spallation of the ceramic top coat occurs. Figure 6.7f reveals a typical microstructure caused by incomplete aluminising as compared with the other PtAl and ZrO₂-PtAl coating in Figure 6.7 (indicated in Figure 6.7f). When the aluminising process is incomplete, the inter-diffusion zone will disappear due to low Al content and leaves the microstructure without sufficient β phase for long term oxidation resistance. In the NiCoCrAlY coating system, cracks propagate along the TGO/bond coat interface and result in some detachment of the TGO layer from the NiCoCrAlY bond coat after 200 h (Figure 6.8f), this is not observed in the other three coating systems.

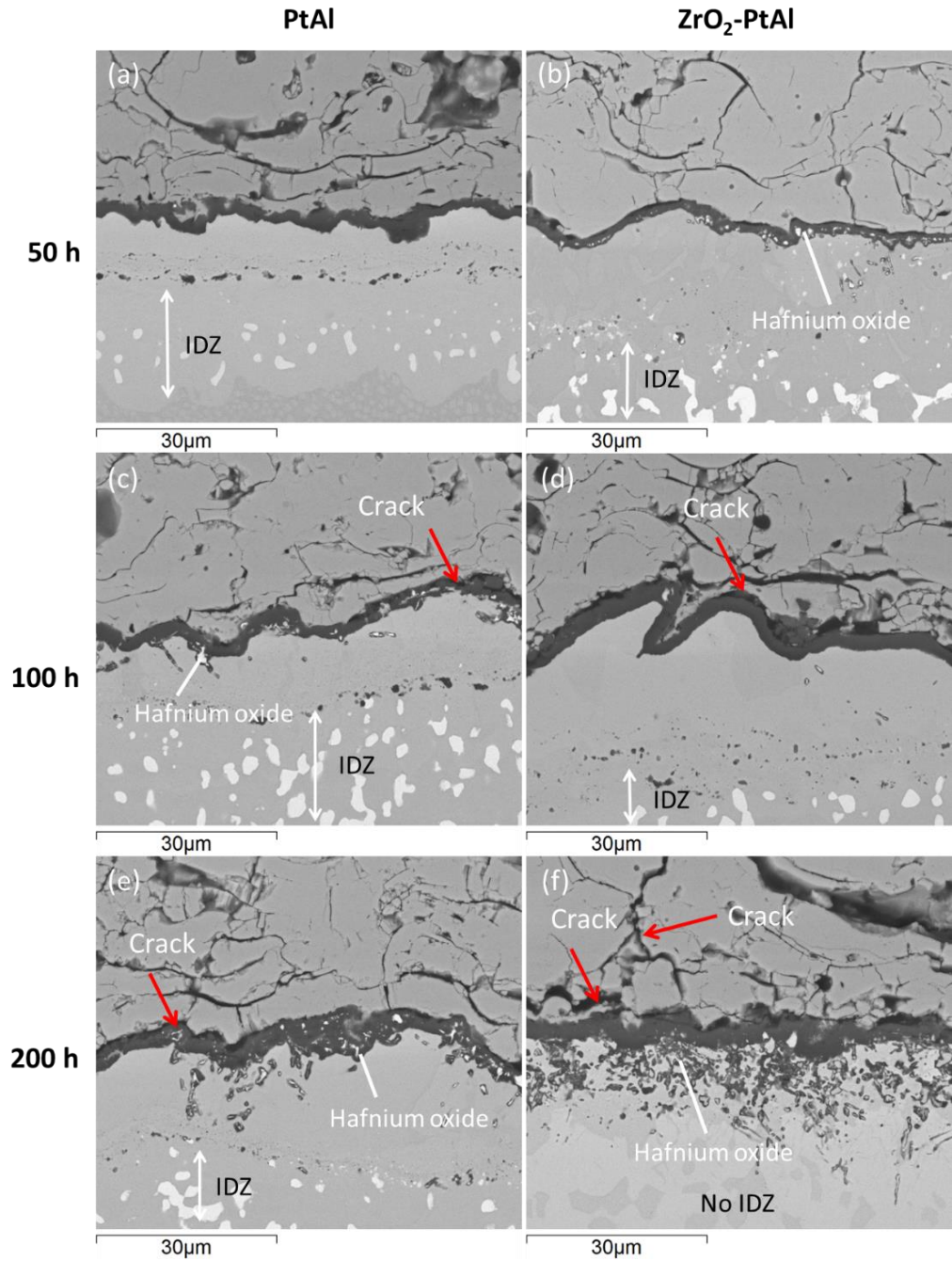


Figure 6.7 Microstructures of PtAl and ZrO₂-PtAl bond coats with 8YSZ top coat after isothermal oxidation at 1100°C. (a) PtAl 50 h; (b) ZrO₂-PtAl 50 h; (c) PtAl 100 h; (d) ZrO₂-PtAl 100 h; (e) PtAl 200 h and (f) ZrO₂-PtAl 200 h.

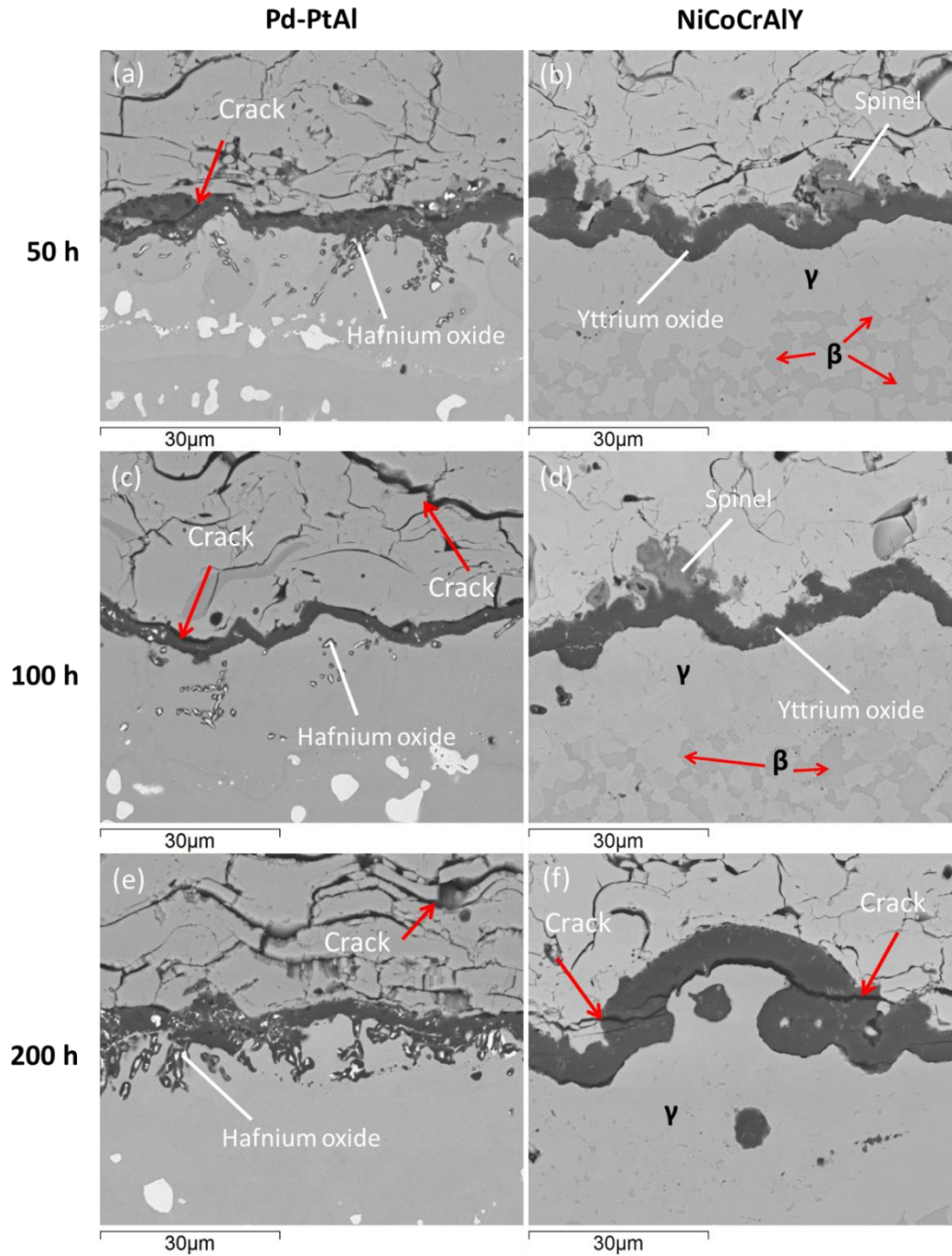


Figure 6.8 Microstructures of Pd-PtAl and NiCoCrAlY bond coats with 8YSZ top coat after isothermal oxidation at 1100°C. (a) Pd-PtAl 50 h; (b) NiCoCrAlY 50 h; (c) Pd-PtAl 100 h; (d) NiCoCrAlY 100 h; (e) Pd-PtAl 200 h and (f) NiCoCrAlY 200 h.

In aluminide coating systems, hafnium oxides are formed within the TGO layer and bond coat matrix, which is confirmed by EDX analysis. Because of the incorporated ZrO_2 nano particles, Zr contained hafnium oxides are also detected in Pt- ZrO_2 aluminide coating, which is similar to the results in Chapter 4. As another oxygen reactive element, Y forms oxide in the NiCoCrAlY coating after oxidation. The hafnium and yttrium oxides are labelled in Figure 6.7 and Figure 6.8. Degradation of aluminide bond coats in TBC systems still obeys the $\beta \rightarrow \gamma' \rightarrow \gamma$ transformation, which was discussed in Chapter 4 and Chapter 5.

However, only the $\beta \rightarrow \gamma$ transformation is detected in NiCoCrAlY coating, resulting in depletion of the β phase near bond coat surface (Figure 6.8b, d and f). Diffusion of Al from the β phase to the coating surface leads to an expanded β phase depletion zone with increased oxidation time. Furthermore, spinel phases are detected in some locations between the TGO and ceramic layer, which are labelled in Figure 6.8b and d. The EDX results of the spinel phase in Figure 6.8d is shown in Table 6.3. The spinel phase is enriched with Cr rather than Ni. The spinel phases are not found in the other three bond coats, but only in the NiCoCrAlY bond coat.

Table 6.3 EDX result of the spinel phase in isothermal oxidised NiCoCrAlY coating shown in Figure 6.8d.

Spinels	Ni	Al	Co	Cr	O
at.%	6.5	13.3	4.6	14.3	61.0

The evolution of coating microstructures in the cyclic thermal oxidation test is shown in Figure 6.9 and Figure 6.10. The microstructures of coating systems are similar to those in the isothermal oxidation test. Nevertheless, the incomplete aluminised microstructure is not observed in ZrO_2 -PtAl bond coat (Figure 6.9f), indicating a similar microstructure as the ZrO_2 -PtAl coating in Chapter 4. Unlike the isothermal test, the thermal cyclic oxidation test is more aggressive as rapid heating and cooling are applied in each cycle, also with increased holding duration at 1100°C . Delamination of the TGO layer is detected in the NiCoCrAlY coating only after 100 cycles. The Pd-PtAl coating system shows partial detachment of the ceramic top coat after 200 cycles, but no spallation occurs. Fast propagation of initial coating defects, such as damaged coating edges, under cyclic thermal oxidation can be the reason for large area detachment. Hafnium and yttrium oxides are confirmed by EDX analysis in the coating systems after thermal cyclic oxidation similar to those in isothermal tested samples. However, the spinel phase in NiCoCrAlY coating is not as obvious as observed in isothermal tested coating systems.

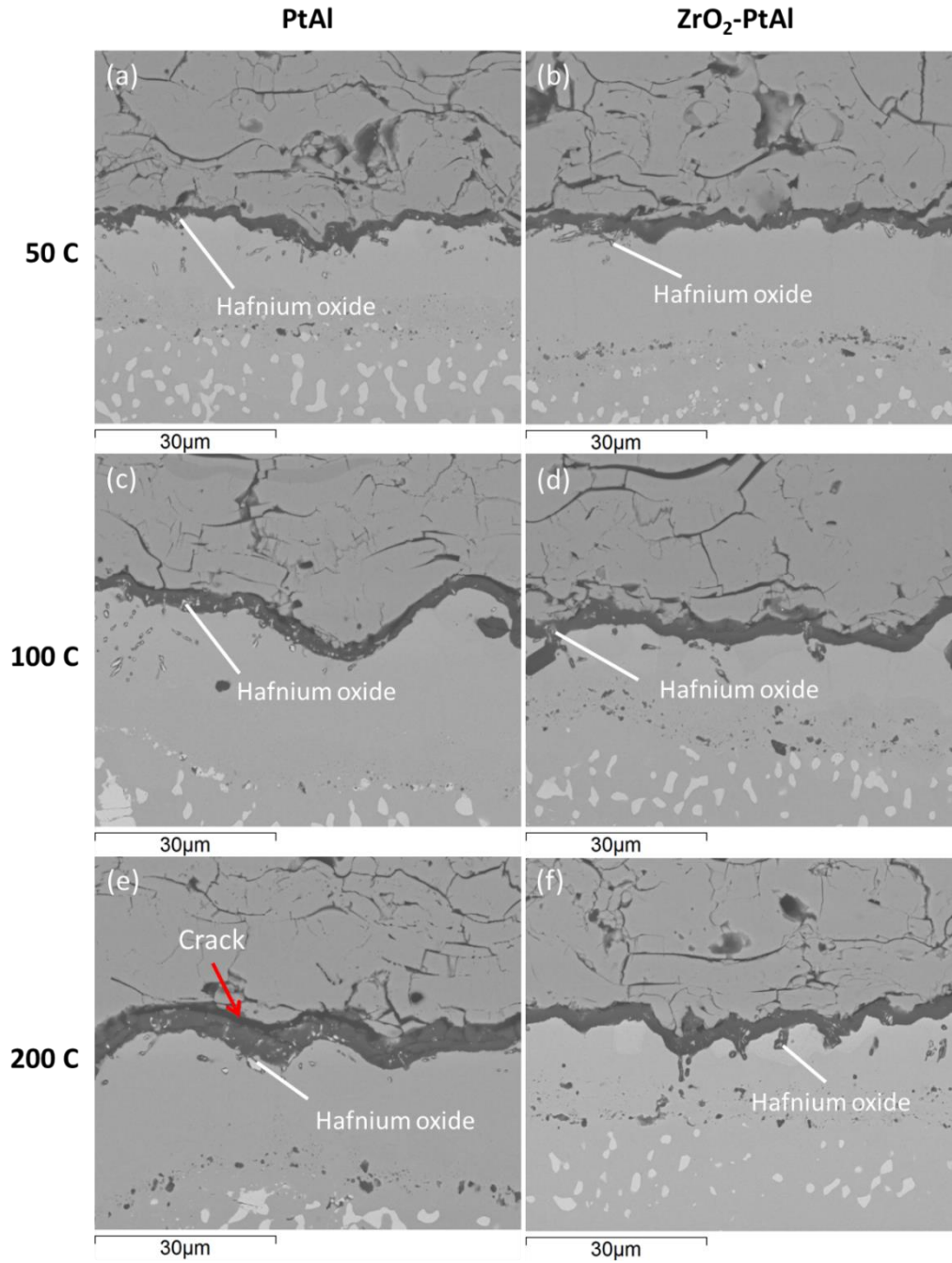


Figure 6.9 Microstructures of PtAl and ZrO₂-PtAl bond coats with 8YSZ top coat after thermal cyclic oxidation at 1100°C. (a) PtAl 50 cycles; (b) ZrO₂-PtAl 50 cycles; (c) PtAl 100 cycles; (d) ZrO₂-PtAl 100 cycles; (e) PtAl 200 cycles and (f) ZrO₂-PtAl 200 cycles.

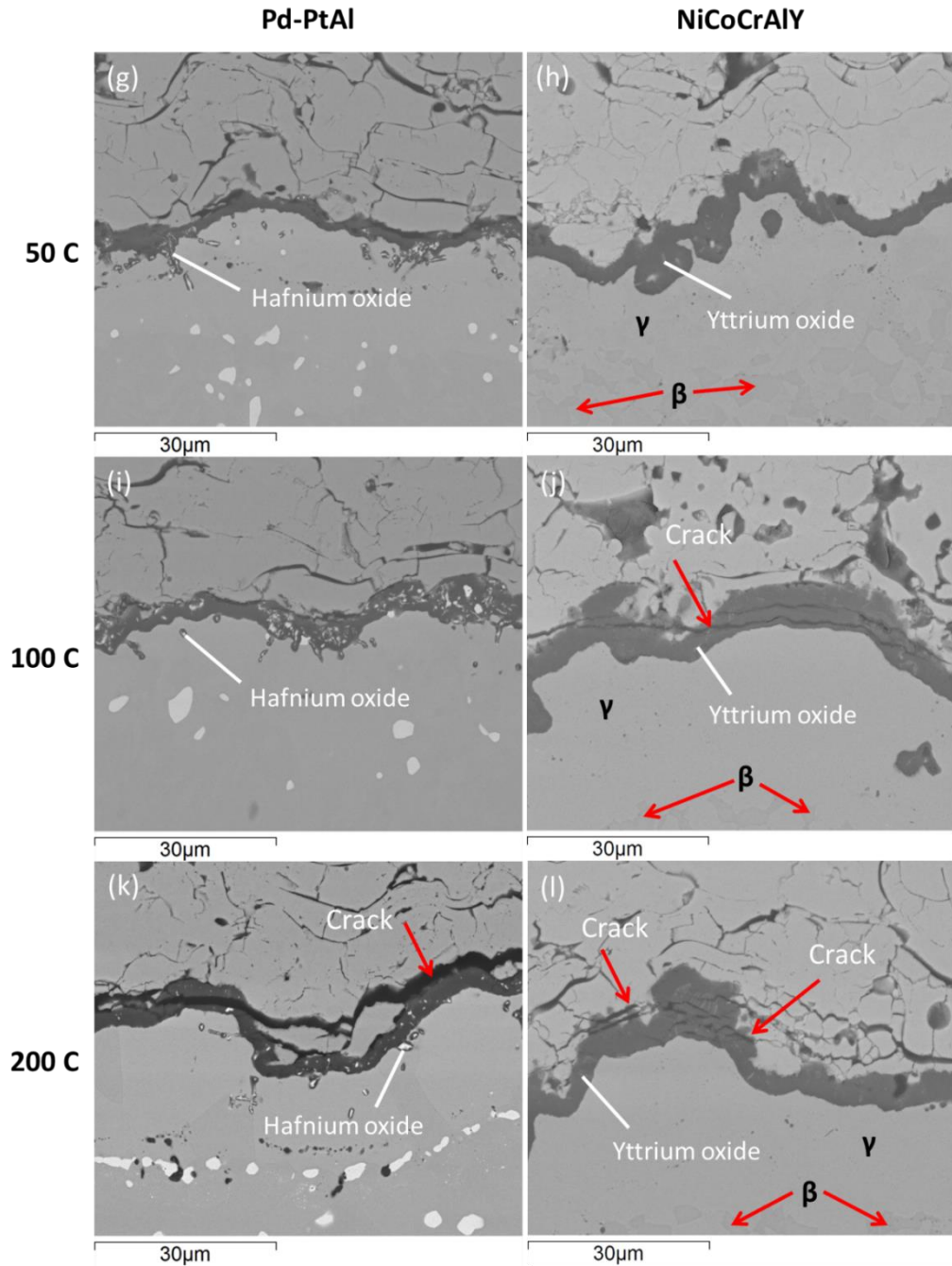


Figure 6.10 Microstructures of Pd-PtAl and NiCoCrAlY bond coats with 8YSZ top coat after thermal cyclic oxidation at 1100°C. (a) Pd-PtAl 50 cycles; (b) NiCoCrAlY 50 cycles; (c) Pd-PtAl 100 cycles; (d) NiCoCrAlY 100 cycles; (e) Pd-PtAl 200 cycles and (f) NiCoCrAlY 200 cycles.

6.3.2 Growth of TGO with Ceramic Top Coat

Figure 6.11 summarises the results of TGO thickness after isothermal and cyclic oxidation tests. In isothermal oxidation (Figure 6.11a), ZrO_2 -PtAl and Pd-PtAl coating systems have a faster TGO growth rate than the PtAl coating after 200 h. The ZrO_2 -PtAl coating system exhibits reduced TGO growth rate, indicating some improvement compared to the PtAl coating system in cyclic thermal oxidation after 200 cycles (Figure 6.11b). In both oxidation tests, the NiCoCrAlY coating system has the highest TGO thickness.

As mentioned in Figure 6.6f, severe internal cracks were observed in the ZrO_2 -PtAl coating system in the isothermal oxidation test, which may result in fast growth of TGO after 200 h. Even though the Pd-PtAl coating system also has a delaminated top coat after cyclic thermal oxidation (Figure 6.10k), the growth rate of TGO is faster in isothermal oxidation than that in the cyclic thermal oxidation. Furthermore, the Pd-PtAl coating system shows fast growth of TGO during 0-50 cycles and 100-200 cycles but slowed growth of TGO during 50 ~ 100 cycles in cyclic thermal oxidation. The overall shape of the TGO thickness changes of the Pd-PtAl coating system indicates a breakaway oxidation behaviour in cyclic thermal oxidation [9]. However, the top coat of the Pd-PtAl coating system is unbroken after 200 h, which may be caused by the Pd addition.

Figure 6.12 gives the results of TGO thickness against the square root of time/cycle numbers to help investigate the parabolic oxidation behaviour [9]. All the coating systems show parabolic oxidation behaviour before 100 h and 100 cycles (103 h 20 min) at 1100°C, except the Pd-PtAl coating system in the isothermal oxidation test. The growth rates of TGO in all coating systems are dramatically

reduced after 200 cycles (206 h 40 min) at 1100°C in cyclic thermal oxidation. In isothermal oxidation, the growth rates of TGO are slightly reduced after 200 h at 1100°C.

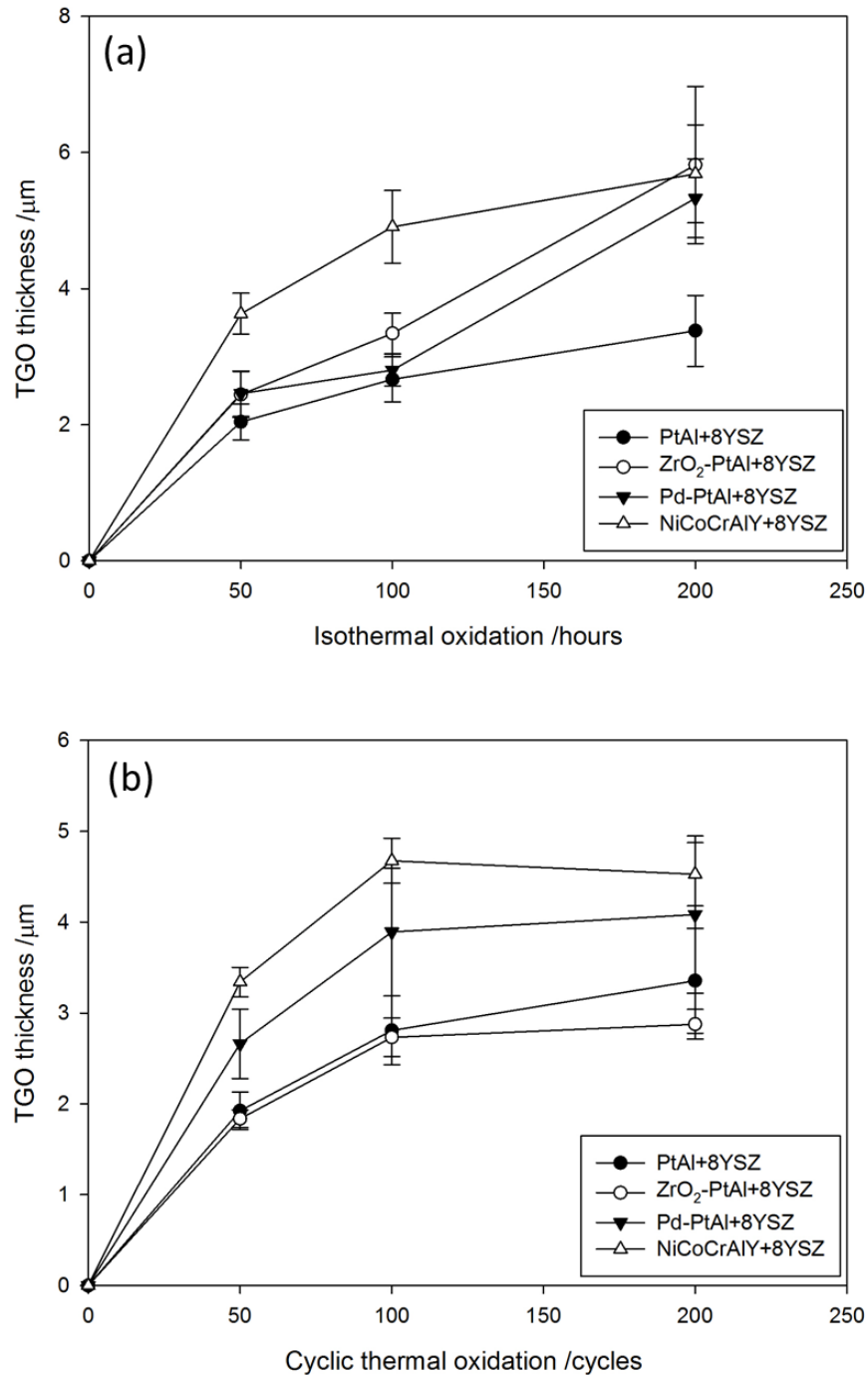


Figure 6.11 TGO growth of (a) isothermal and (b) thermal cyclic oxidation tested coating systems (error bar: standard deviation).

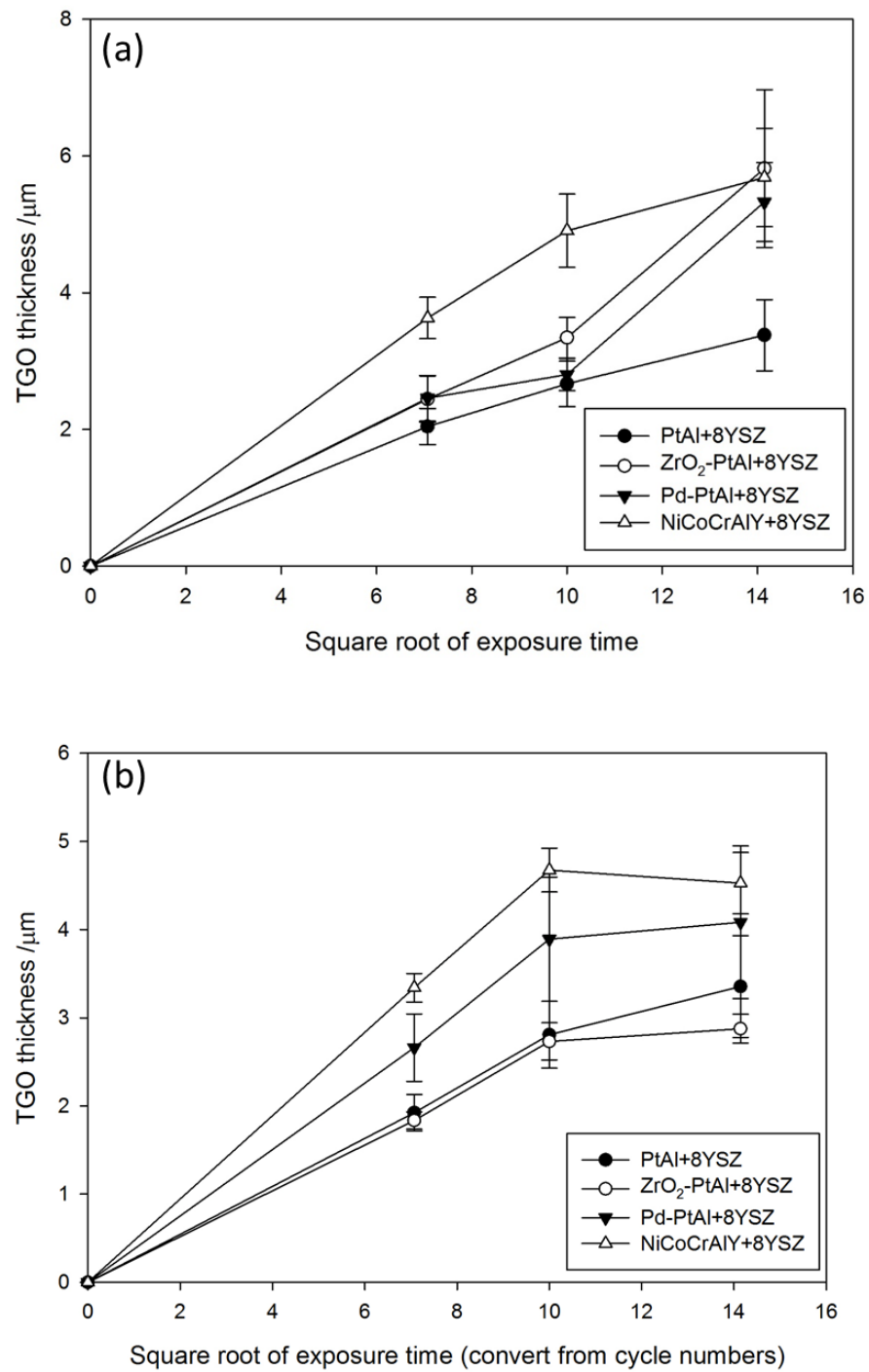


Figure 6.12 TGO growth against square root of time/cycle numbers in (a) isothermal and (b) thermal cyclic oxidation tested coating systems (error bar: standard deviation).

The influence of ceramic top coat on TGO growth in PtAl, ZrO₂-PtAl and Pd-PtAl coatings with different oxidation conditions is indicated in Figure 6.13. Overall, TGO thickness is higher in the TBC system than that in the bond coats without ceramic top coat. This is observed in cyclic thermal oxidation as well as the isothermal oxidation. It is expected that the use of ceramic top coat can help to test the actual oxidation behaviour of the bond coats, as formed TGO layer will be covered by the top coat. Thus, the disadvantage of TGO spallation during the cooling stage can be eliminated when the ceramic top coat is applied. In addition, the TGO growth behaviour in both isothermal and cyclic thermal oxidation tests is not significantly influenced by the applied ceramic top coat, except in the Pd-PtAl coating under isothermal oxidation. The growth trend of TGO indicates a slowed growth rate after 200 h without ceramic top coat, but an increasing growth rate may be suggested by the result of Pd-PtAl coating with the ceramic top coat. The testing error may be responsible for this phenomenon.

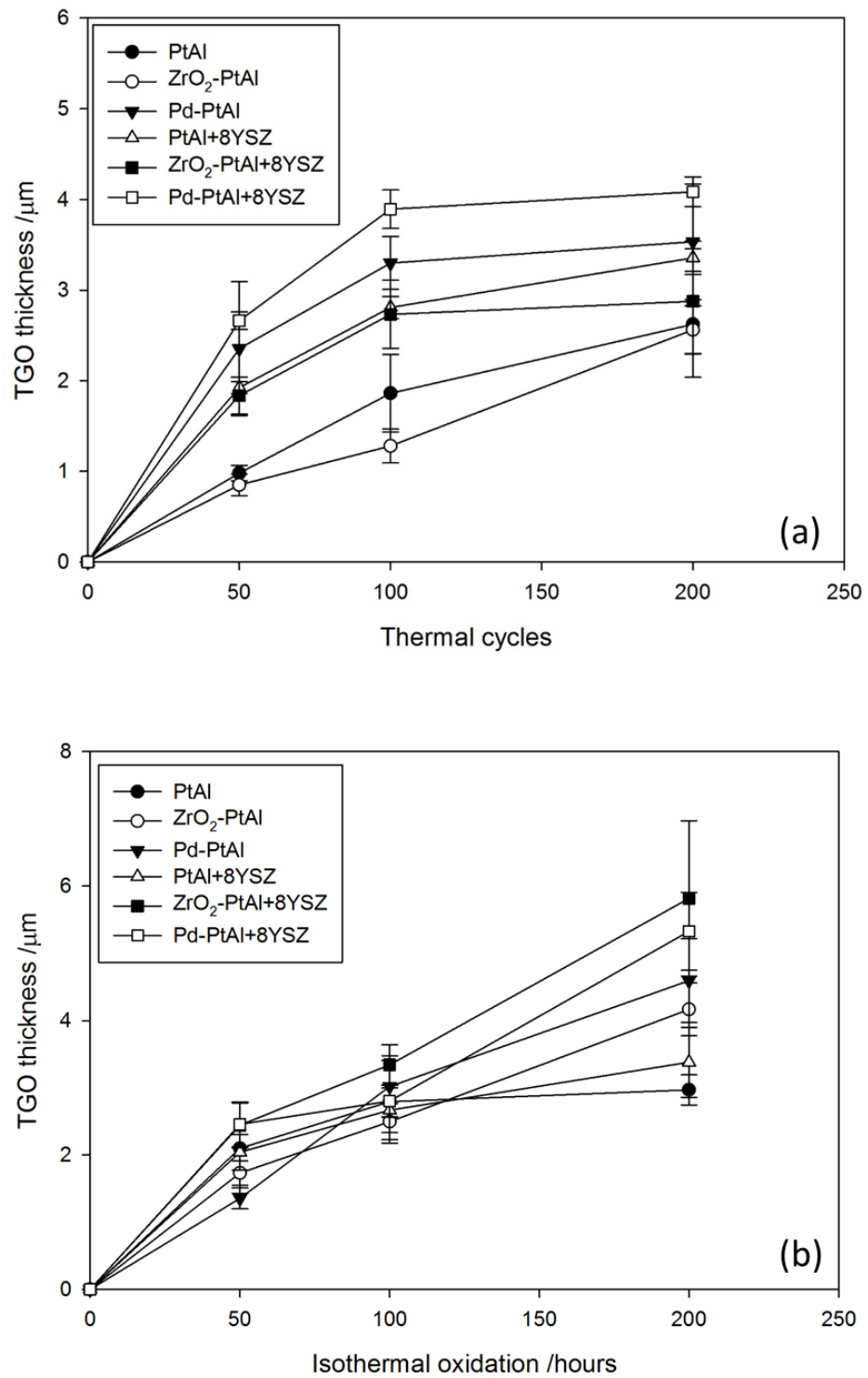


Figure 6.13 TGO thickness changes of bond coats with and without ceramic top coat in (a) cyclic thermal and (b) isothermal oxidation tests (error bar: standard deviation).

6.3.3 Rumpling of TGO

The rumpling of the TGO/ceramic interface by measuring the interface roughness profile is summarised in Figure 6.14. Because the PtAl, ZrO₂-PtAl and Pd-PtAl coatings were all sandblasted before the deposition of the ceramic top coat, so the original surface roughness of these coatings are represented by the roughness measured after the sandblasting with different sandblasting media (shown as the dot lines in Figure 6.14). In addition, the original surface roughness of HVOF sprayed NiCoCrAlY coating is also indicated as a dot line in Figure 6.14.

As the tested samples were treated by different sandblasting media, any comparison needs to consider the different original surface roughness for each sample. In isothermal oxidation (Figure 6.14a), increase in the rumpling level is observed in PtAl, ZrO₂-PtAl and Pd-PtAl coating systems, which may be due to the long term annealing and slow cooling rate. The PtAl coating system has the lowest rumpling level at 50 h, which may be caused by initial surface roughness generated by sandblasting using F100 alumina (average size 162 μm). However, different initial surface roughness may affect the roughness change in isothermal oxidation. The ZrO₂-PtAl coating system, which is sandblasted by F100 alumina, shows a significant increase in roughness after 50 h; fewer changes in roughness are found after 100 h and 200 h, which are prepared by F20 alumina (average size 1 mm). Though the NiCoCrAlY coating system has the largest rumpling level in the isothermal oxidation test, which may be caused by the original surface roughness, the roughness profile indicates lower interface roughness after 50 h and 200 h than the initial surface roughness of the NiCoCrAlY coating. On the other hand,

the interface roughness of the NiCoCrAlY coating after 100 h isothermal oxidation is similar to its original surface roughness.

Figure 6.14 (b) shows the results of rumpling in the cyclic thermal oxidation test. The rapid heating and cooling rates in cyclic thermal oxidation may lead to the formation of large internal stress, which could promote the rumpling of TGO. However, the roughness changes of each coating system are not aggressive in cyclic thermal oxidation. When considering the original surface, both PtAl and NiCoCrAlY coating systems have less increase in interface roughness. In addition, the ZrO₂-PtAl coating system has the smallest rumpling level at 200 cycles even with high initial interface roughness. Relatively large changes in interface roughness are found in the Pd-PtAl coating system after cyclic thermal oxidation. It has the highest level of rumpling among Pt-based coating systems. No improvement of rumpling resistance is found in the Pd-PtAl coating system as compared to the PtAl coating system.

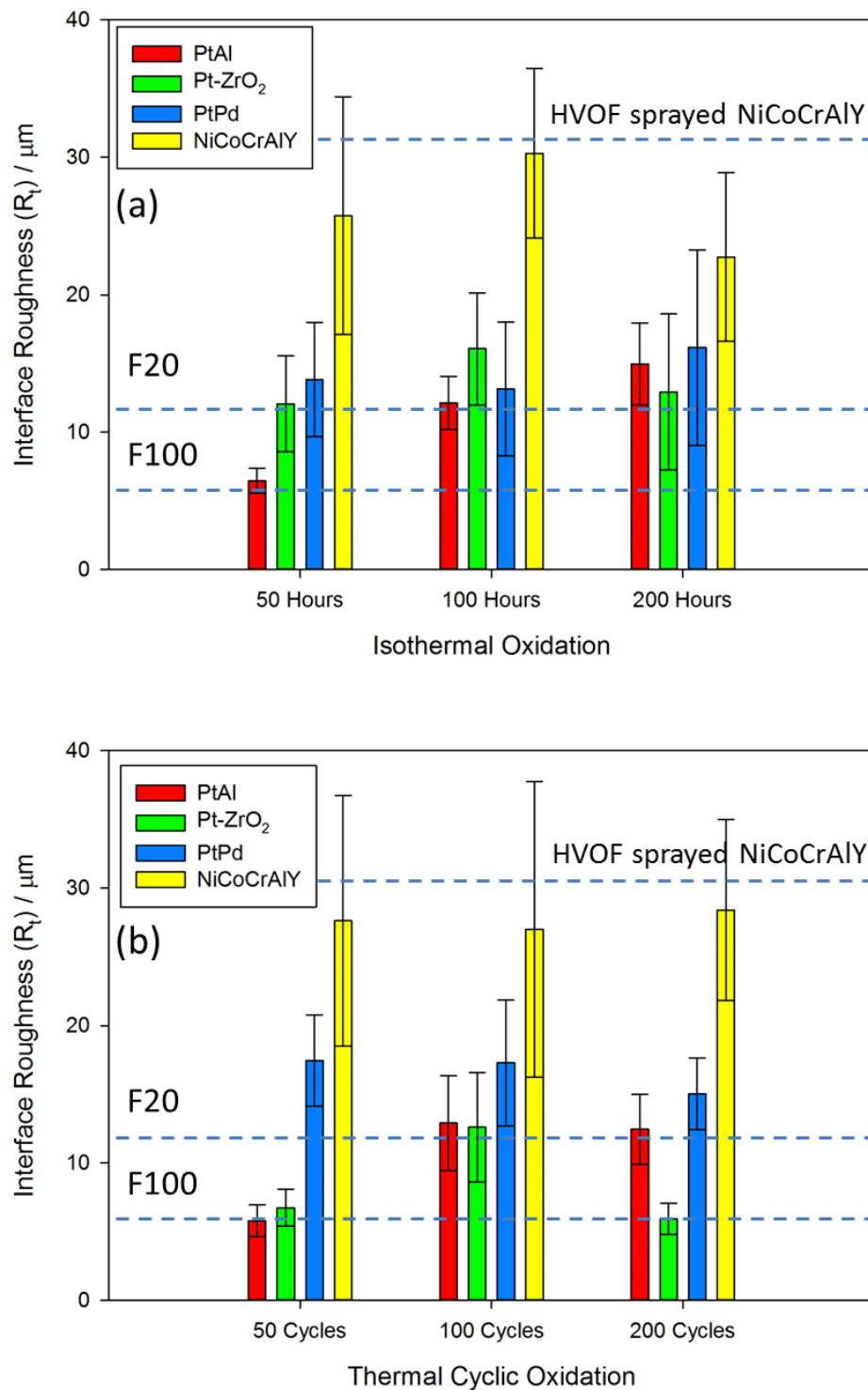


Figure 6.14 Calculated R_t values of TGO/top coat interface roughness after (a) isothermal oxidation and (b) thermal cyclic oxidation tests with dot line indicating the initial surface roughness prepared by F100 (average size 162 μm) and F20 alumina (average size 1 mm) and also the original surface roughness of HVOF sprayed NiCoCrAl coating (error bar: standard deviation).

6.4 Discussion

6.4.1 Effects of Coating Compositions

In the current investigation, ZrO_2 and Pd are found to have different effects on the PtAl bond coat. The Zr, which comes from the reaction between Al and ZrO_2 , can not only improve the oxidation resistance of the bond coat but also reduce the rumpling level of the TGO layer, which may be a result of zirconium oxide pegs (Figure 6.9f, Zr containing hafnium oxide) formed at the TGO/bond coat interface in thermal cyclic oxidation [137]. As reported, zirconium oxide can act as an ionic cluster to slow down the diffusion of Al [132, 137, 175, 176]. The effect of this ionic cluster is that Al_2O_3 scale is found to locate around the hafnium and zirconium oxides (Section 4.4). When the diffusion of Al is retarded, the growth of TGO will be dominated by the inward diffusion of oxygen [132]. Therefore the growth rate of TGO is decreased as the thickness of TGO increases [132].

In addition, 1.5 wt. % of Hf in the substrate also affects the oxidation behaviour. The study of Hf and Zr co-doped NiAl alloy indicates that the oxides of Hf and Zr are usually incorporated into one phase because they are congeners which could explain why the Zr composition is detected in hafnium oxides [138]. Moreover, the Hf and Zr can improve the oxidation resistance further rather than the effect of a single element because the ionic cluster of hafnium and zirconium oxides can operate more effectively than a single oxide. The schematic diagram of the co-effect of Hf and Zr is shown in Figure 6.15. The result of PtAl coating can then be explained by the single effect of Hf because there is less Zr in the coating to help improve the oxidation resistance.

However, drawbacks can occur due to high Hf content. The higher Hf content could accelerate the oxide growth by creating more oxygen diffusion paths which can cause severe internal oxidation and fast TGO growth. In this investigation, internal oxidation is found regularly in both the PtAl coating and also the ZrO_2 -PtAl coating, but the oxidation resistance of PtAl coating in this investigation is not obviously degraded by an initial Hf content of 1.5 wt.%, indicating that this level of Hf is low enough to be beneficial to the oxidation resistance.

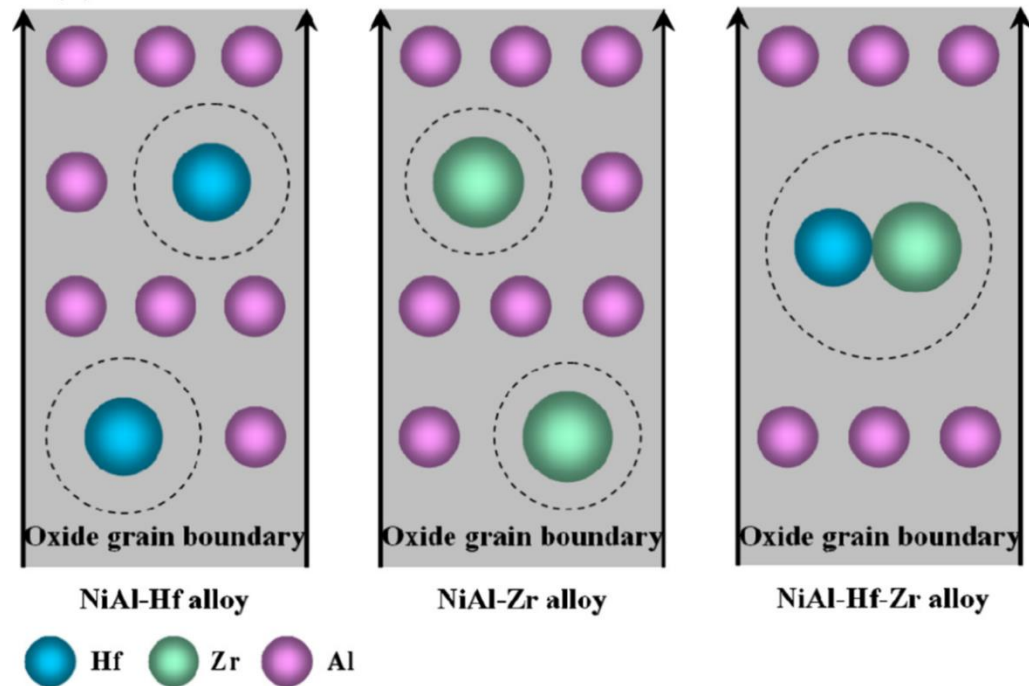


Figure 6.15 Schematic of the co-doping effects of Hf and Zr on oxide scale growth rates of NiAl-0.05 at. % Hf-0.05 at. % Zr during high-temperature oxidation [189].

Though the effects of Pd addition on aluminide coating vary in different reports [100, 182, 190-194], the enhancement of oxidation resistance due to Pd addition is not demonstrated in this study. The

Pd-PtAl coating system exhibits more rapid oxidation and a larger rumpling level than the other two Pt-based coating systems. Rather than improving the oxidation resistance, the addition of Pd may accelerate the outward diffusion of Al to grow thicker TGO than a general PtAl coating [194]. Nevertheless, it is also reported that Pd can act as a diffusion barrier to slow down the growth rate of TGO [192]. More investigations need to be carried out to identify the effects of Pd additions based on the Pd content in the bond coat. A thicker Pd layer may be desired for improving oxidation resistance.

In NiCoCrAlY coating, the formation of spinel makes it unsuitable for severe operational environments because the spinel can initiate cracks. In addition, Cr plays an important role in the formation of the spinel phase. Due to the high content of Cr, Cr_2O_3 oxides can be easily formed at lower temperatures, which could transfer into spinel with NiO and Al_2O_3 . Y_2O_3 is also considered to slow down the outward diffusion of Al and improve the oxidation resistance of the bond coat, as other reactive elements.

6.4.2 Influences of Oxidation Conditions

Despite that the isothermal oxidation behaviour of the ZrO_2 -PtAl coating system indicating reduced oxidation resistance compared to the general PtAl coating system, the ZrO_2 -PtAl coating system shows superior cyclic oxidation resistance than the other coating systems. The Pd-PtAl coating system also has different oxidation behaviours in isothermal and cyclic oxidation tests. Because both the PtAl and NiCoCrAlY coating system show expected oxidation behaviour, the reason for different oxidation behaviours in ZrO -PtAl and Pd-PtAl coating systems could be varying different effectiveness and roles of Zr and Pd in different oxidation conditions. In isothermal oxidation,

the effect of Zr may accelerate the growth rate of TGO rather than improve the oxidation resistance because of the long time ageing. The possible acceleration effect of Zr was also confirmed in Chapter 4. However, in cyclic oxidation, the Al diffusion in each cycle needs to overcome the ionic cluster to form Al_2O_3 with O, which may hold back the growth of TGO. However, further studies need to be carried out to investigate the possible acceleration mechanism and effect of Pd on TGO growth.

The diffusion mechanism of Al may be different in isothermal and cyclic thermal oxidation. As shown in Figure 6.3a, the formation of γ' phase in isothermal oxidation indicates a grain boundary diffusion of Al due to the formation of lath γ' phase. On the other hand, the island γ' phase formed during cyclic thermal oxidation may suggest a bulk diffusion of Al. The diffusion mechanism of Al can directly affect the growth of TGO. In isothermal oxidation, the long term annealing drives Al to diffuse through grain boundaries at which have higher energy. However, the annealing duration was only 1 h in each cycle and the rapid heating and cooling rates made the diffusion of Al difficult to be carried out at grain boundaries. Then the diffusion of Al may be achieved by diffusing through bulk grains to find the shortest diffusion path, and also may be driven by the Al concentration gradient in the bulk grain. An island γ' region may indicate the shape of one single β phase grain. It is then reasonable that the TGO grows faster in isothermal oxidation because the diffusion through grain boundaries is faster than that in bulk grains.

In addition to the continuous cyclic aging, the heating and cooling rates could be another reason for different oxidation behaviours between cyclic and isothermal oxidation. The slow heating up and

cooling in isothermal oxidation may result in the formation of low temperature oxides, such as NiO and Cr₂O₃, but in the cyclic oxidation, the heating up and cooling rate is more than 10 times faster, which could avoid the formation of low temperature oxides and directly build up a protective Al₂O₃ layer. This factor can be proven by carrying out two oxidation tests with the same aging time but different heat up and cooling rates. In the NiCoCrAlY coating system, the isothermal oxidation caused more spinel formation than cyclic oxidation, which could be the result of different heating up and cooling rates.

Another effect of oxidation conditions is the crack initiation and propagation promoted in cyclic oxidation. The fast heating up and cooling rates can introduce more stresses and strains within TGO, which could lead to crack initiation and bucking of TGO. The thermal mismatch between the TGO and bond coat also accelerates the bucking and leads to final rumpling failure of the coating system. However, big differences are not found between the results of rumpling levels in the two types of oxidation tests. This may also be affected by the initial interface roughness, but further investigation is needed to clarify the effects of initial interface roughness.

6.4.3 Effects of Ceramic Top Coat

In the current investigation, the use of ceramic top coat can reflect the TGO growth more relevant to the actual operation condition because TGO is formed at the interface between the top coat and bond coat. The growth of TGO with ceramic top coat could correctly indicate the oxidation and rumpling resistance of the bond coat. However, for diffusion bond coats, the pre-surface treatment before APS may be harmful to the performance of diffusion bond coats due to the removal of coating materials.

6.4.4 Life Expectancy of Tested Coating Systems

In real applications, the operating environment is closer to the cyclic oxidation which means the results of cyclic oxidation may be more relevant. In ceramic coating systems, the TGO growth rate, rumpling level and crack propagation can be the main factors to affect the life expectancy of the coating system. Based on the results of cyclic oxidation, PtAl and ZrO₂-PtAl coating are defined as good oxidation resistant coatings because of their low growth rate of TGO and rumpling level. In particular, the ZrO₂-PtAl coating system may be considered as a potential superior bond coat in long-term service because of the lower rumpling level. On the other hand, it seems that the NiCoCrAlY and PtPd aluminide coating cannot remain protective in longer oxidation tests and may be restricted to lower temperature applications.

6.5 Summary

In this chapter, the high temperature stabilities of fabricated bond coats were investigated with APS sprayed ceramic top coat. The use of top coat can correctly indicate the growth behaviour of TGO in the bond coat as the TGO is formed at the interface between the top coat and bond coat. Spallation of TGO during cooling in oxidation tests can be eliminated. The ZrO₂-PtAl coating shows better oxidation resistance than PtAl coating in cyclic thermal oxidation. However, Pd-PtAl coating cannot improve the oxidation resistance of PtAl coating. The Pd-PtAl coating only shows slightly better oxidation resistance than general NiCoCrAl coating. The effect of Pd addition is found to accelerate the TGO growth and rumpling, but more research needs to be carried out to identify the mechanism of acceleration in TGO growth.

The reason for the superior oxidation behaviour of ZrO_2 -PtAl coating is found to be the combined effects of both Hf and Zr. In the presence of both Hf and Zr, the oxidation resistance of the coating can be promoted by forming ion clusters to retard outward diffusion of Al. However, the improvement of Zr is not confirmed in the isothermal oxidation test.

The different heating and cooling rates, and the diffusion mechanism of Al could be the main reasons for different effectiveness and roles of ZrO_2 -PtAl and Pd-PtAl coatings in isothermal and cyclic thermal oxidation tests. The different heating and cooling rates may lead to the formation of unstable oxides at lower temperatures in isothermal oxidation. Faster diffusion of Al at grain boundaries in isothermal oxidation may cause faster growth of TGO than that in cyclic thermal oxidation, because Al diffuses through bulk grains in cyclic oxidation.

The NiCoCrAlY coating shows less oxidation resistance than the others at 1100°C because of the formation of spinel. The low content of Al and high content of Cr lead to the formation of low temperature oxides rather than Al_2O_3 at low temperatures, which could lead to crack initiation during oxidation. The conventional PtAl coating shows expected oxidation resistance in both isothermal and thermal cyclic oxidation tests, which means the effects of Pt may not be influenced by the different oxidation conditions.

Chapter 7 Conclusions and Future Work

7.1 Conclusions

This project aims to develop Pt-based bond coats with improved oxidation and rumpling resistance. ZrO₂ nanoparticles and platinum group metals modified PtAl bond coats were investigated. In order to improve the oxidation and rumpling resistance, the incorporation of ZrO₂ nanoparticles in PtAl coating has been presented through the co-electrodeposition method. A combination of characterisation methods and studies using different coating substrates led to a detailed description of the reaction mechanism of ZrO₂ nanoparticles in PtAl coating. In addition, an Ir layer was electroplated to improve the oxidation resistance of PtAl coating as a diffusion barrier. The improvement of Ir as a diffusion barrier candidate mainly depended on the thickness of deposited Ir layer, providing a feasible application of Ir in PtAl bond coats. Moreover, electroless deposited Pd modified PtAl coating was expected to slow down the growth rate of TGO, but no improvement from the Pd addition was observed in this study. Finally, the capability and adaptability of prepared bond coats were further investigated with 8YSZ top coat.

The effects of ZrO₂ nanoparticles in PtAl coating were investigated on Mar-M-247, Mar-M246 and Inconel 718 substrates. The co-electrodeposition of ZrO₂ nanoparticles with Pt was successful based on the general Pt electroplating. The incorporated ZrO₂ nanoparticles disappeared during both vacuum (10^{-6} mbar) and controlled environment (5% H₂/95% Ar) heat treatment on the three substrates. In cyclic thermal oxidation, ZrO₂ modified PtAl coating showed a minor improvement on the oxidation resistance of general PtAl

coating on Mar-M-247 but greater improvement of rumpling resistance on Inconel 718. However, there was no benefit in the TGO growth of ZrO₂ modified PtAl coating on Mar-M-246. The complementary combination of SEM, EDX and XRD characterisation methods indicated the interactions among Al, Hf and ZrO₂.

The reaction between Al and ZrO₂ led to the disappearance of ZrO₂ nanoparticles, which is also affected by the Hf content in substrates. When Hf existed, the reaction between Al and ZrO₂ was completed due to the reaction between Hf and Al₂O₃. Un-reacted ZrO₂ might be left in the coating in the absence of Hf. The reaction of ZrO₂ particles can be presented as: $13\text{Al} + 3\text{ZrO}_2 + 7\text{Hf} \rightarrow 4\text{HfAl} + 3\text{Al}_3\text{Zr} + 3\text{HfO}_2$. Zr was released from the reaction of ZrO₂ nanoparticles and improved the oxidation and rumpling resistance during thermal cycling. It was also found that the synergistic actions of Zr and Hf can be an advantage in increasing oxidation resistance than the single effect of Zr. In addition, a pack diffusion method was developed to co-diffuse Zr and Al according to the reaction between Al and ZrO₂ to investigate the effects of pure Zr addition. Cyclic thermal oxidation results of ZrAl coatings showed that a high content of Zr in the coating led to fast inward diffusion of oxygen and massive formation of internal oxides, which is harmful to coating oxidation resistance.

The influences of Ir and Pd on PtAl coating were investigated in order to reduce the growth rate of TGO and the cost of Pt. Ir coating was deposited by using electroplating and using IrBr₃ solution. De-oxygen process was carried out to ensure a good deposition rate of Ir. During cyclic thermal oxidation, compared with general PtAl coating, Ir-PtAl coating revealed a much slower growth rate of TGO. In addition, Ir-PtAl coating showed excellent resistance to γ' transformation. The

oxygen diffusion barrier of Ir was not verified in this study, but Ir was found as a diffusion barrier to Al, which may be due to the formation of a high temperature solid solution with Al. Owing to the high melting point of Ir-Al solid solution, the inward diffusion of Al was significantly decreased. Since the inward diffusion of Al was inhibited, more Al would remain in the coating for further oxidation. Ir concentration can also affect the strength of the diffusion barrier. When Ir concentration was reduced to less than 15 wt.%, the strength of the diffusion barrier began to degenerate.

Pd coating was successfully prepared by electroless deposition to investigate the Pd effect on PtAl coating. Improvement in oxidation resistance of Pd-PtAl coating was not observed in this study. TGO grew faster in Pd-PtAl coating than in general PtAl coating. Phosphorus precipitates were detected in the Pd-PtAl coating, which may be the reason for the fast growth of TGO, that is, phosphorus can promote the oxidation rate. It was indicated that Hf was likely to be harmful to Pd-PtAl coating because of different oxidation behaviours of Pd-modified PtAl coating on Mar-M-247 and Mar-M-246.

Selected ZrO_2 -PtAl and Pd-PtAl coatings were further studied with APS prepared 8YSZ top coat. In addition, the general PtAl and HVOF sprayed NiCoCrAlY bond coats were also prepared for comparison. ZrO_2 -PtAl bond coat showed the best oxidation and rumpling resistance with YSZ top coat. Pd-PtAl bond coats exhibited similar oxidation behaviour to the Pd-PtAl coating without ceramic top coat, which indicates rapid growth of TGO and a high rumpling level. Furthermore, the worst oxidation resistance was observed in the NiCoCrAlY bond coat due to the formation of the spinel phase. General

PtAl bond coat indicated similar oxidation resistance of ZrO_2 -PtAl coating, but a higher rumpling level with top coat.

Isothermal and cyclic thermal oxidation tests had different effects on ZrO_2 -PtAl and Pd-PtAl coatings, but the responses of PtAl and NiCoCrAlY bond coats were not sensitive to different oxidation test conditions. Influenced by the long-term annealing in isothermal oxidation, both ZrO_2 -PtAl and Pd-PtAl coatings exhibited fast growth of TGO in isothermal oxidation and a lower growth rate of TGO in cyclic thermal oxidation, thus affecting the diffusion behaviour of Al.

7.2 Future Work

In order to further investigate the influences of RE oxides and PGMs on PtAl coatings, some suggestions are put forward based on the results obtained:

- Systematic investigation on the co-electrodeposition parameters of ZrO_2/Pt coating aims to optimise the distribution and volume fraction of incorporated particles in Pt coating. Pulse co-electrodeposition is also developed to prepare ZrO_2/Pt coatings with more controllable parameters.
- Comparison between Electroplated Pd coating and electroless deposited Pd coating is necessary in order to investigate the effects of Pd addition on PtAl coating and the influence of phosphorus on coating oxidation behaviour.
- Since EB-PVD deposited 8YSZ ceramic top coat does not require a rough surface to hold the ceramic top coat, it is more appropriate to investigate the prepared Pt-based bond coats. Long term thermal cycling (≥ 500 cycles) is expected to evaluate the TGO growth behaviour of prepared bond coats. More tests are preferred to investigate the effects of isothermal and cyclic thermal oxidation on the behaviour of $\text{ZrO}_2\text{-PtAl}$ bond coat.
- TEM characterisation is proposed to verify the solid solution of Ir-Al to support the diffusion barrier activity from the involvement of Ir.

- Detailed study on specific top coat and substrates is proposed to investigate the high temperature performance of ZrO_2 -PtAl and Ir-PtAl coatings. Single crystal Ni superalloy substrates which are used in practical applications, are preferred when investigating the actual influence of substrate on diffusion bond coats.

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Appendix 1 Matlab TGO Thickness Calculation

```

function Oxide_thickness_X(filename,index)

str=(filename);
[~,name,~] = fileparts(filename);

for i=1:10
    right=size(imread([str,num2str(i),'.tif']),2);
    left=1;
    bottom=size(imread([str,num2str(i),'.tif']),1);
    top=1;
    RGB=imread([str,num2str(i),'.tif']);
    data=rgb2gray(RGB);

    %    data = imread([str,num2str(i),'.tif']);
    data = cast(data,'int16');
    uint16 oxide_top;
    uint16 oxide_bottom;
    oxide_index = index;

    %%%%%%%%% calculate oxide area %%%%%%%%%

    count_area=sum(data==index);
    oxide_area(i)=sum(count_area);

    b=oxide_area';

    %%%%%%%%% calculate oxide edges %%%%%%%%%

    column_front(:,1)=data(:,1);
    col_front=column_front(:,1);
    column_end(:,right)=data(:,right);
    col_end=column_end(:,right);
    edge_front=sum(col_front==index);
    edge_end=sum(col_end==index);
    edge_thickness=edge_front+edge_end-4;

    %%%%%%%%% calculate oxide length %%%%%%%%%

    zhou_chang = bwperim(data);
    %    figure(i);
    %    imshow(zhou_chang);

    imwrite(zhou_chang,[filename,'Rumpling',num2str(i),'.tif']);
    Count_pixel = sum(zhou_chang);
    Total_pixel = sum(Count_pixel);

    % find connected pixel in columns %

    for m=left:right
        column(:,m)=zhou_chang(:,m);
        col=column(:,m);
        column_connected_pixel=0;
        for n=top+1:bottom
            if col(n)==col(n-1) && col(n)==1

```

```

column_connected_pixel=column_connected_pixel+1;
    end
    connected_pixel_column(m)=column_connected_pixel;
end
end

total_column_connected_pixel=sum(connected_pixel_column);
P1=total_column_connected_pixel;

% find connected pixel in rows %

for m=top:bottom
    row(m,:)=zhou_chang(m,:);
    ro=row(m,:);
    row_connected_pixel=0;
    for n=left+1:right
        if ro(n)==ro(n-1) && ro(n)==1
            row_connected_pixel=row_connected_pixel+1;
        end
        connected_pixel_row(m)=row_connected_pixel;
    end
end

total_row_connected_pixel=sum(connected_pixel_row);
P2=total_row_connected_pixel;

% calculate oxide mean length %

L=((Total_pixel-P1-P2)*sqrt(2)+P1+P2-edge_thickness)/2;

mean_length(i)=L;
a=mean_length';
end

```

Appendix 2 Matlab Roughness Calculation

```

function Roughness_X(filename,index)

str=(filename);
[~,name,~] = fileparts(filename);

for i=1:10
    right=size(imread([str,num2str(i),'.tif']),2);
    left=1;
    bottom=size(imread([str,num2str(i),'.tif']),1);
    top=1;
    RGB=imread([str,num2str(i),'.tif']);
    % data=rgb2gray(RGB);

    data = imread([str,num2str(i),'.tif']);
    data = cast(data,'int16');
    uint16 oxide_top;
    uint16 oxide_bottom;
    oxide_index = index;
    height_parameter=0;
    total_height_parameter=0;
    height=0;

    for m=left:right
        column(:,m)=data(:,m);
        col=column(:,m);
        for n=top+1:bottom
            if col(n)==1
                height_parameter=n;
            end
        end

        total_height_parameter=total_height_parameter+height_parameter;
    end

    mean_height=total_height_parameter/right;

    for m=left:right
        column(:,m)=data(:,m);
        col=column(:,m);
        for n=top+1:bottom
            if col(n)==1
                height_parameter=n;
            end
        end

        height(m)=height_parameter-mean_height;
    end

    Rp(i)=max(height);
    Rv(i)=abs(min(height));
    Rt(i)=Rp(i)+Rv(i);

```

```
a=Rp';  
b=Rv';  
c=Rt';  
  
end
```