STUDY OF BOND COATS FOR THERMAL BARRIER COATING APPLICATIONS

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# NOMENCLATURE

## Nomenclature

### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>APS</td>
<td>air plasma spraying</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>DFT</td>
<td>density-functional theory</td>
</tr>
<tr>
<td>EBSD</td>
<td>electron backscatter diffraction</td>
</tr>
<tr>
<td>EBPVD</td>
<td>electron-beam physical vapour deposition</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>HVOF</td>
<td>high velocity oxygen fuel</td>
</tr>
<tr>
<td>IDZ</td>
<td>interdiffusion zone</td>
</tr>
<tr>
<td>PLPS</td>
<td>photoluminescence piezospectroscopy</td>
</tr>
<tr>
<td>RE</td>
<td>reactive element</td>
</tr>
<tr>
<td>SPS</td>
<td>spark plasma sintering</td>
</tr>
<tr>
<td>TBC</td>
<td>thermal barrier coating</td>
</tr>
<tr>
<td>TGO</td>
<td>thermally grown oxide</td>
</tr>
<tr>
<td>YAG</td>
<td>yttrium aluminium garnet</td>
</tr>
<tr>
<td>YSZ</td>
<td>yttria-stabilised zirconia</td>
</tr>
<tr>
<td>CMAS</td>
<td>calcium-magnesium-alumino-silicate</td>
</tr>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FOD</td>
<td>foreign object damage</td>
</tr>
<tr>
<td>HT-XRD</td>
<td>high temperature X-ray diffraction</td>
</tr>
<tr>
<td>LPPS</td>
<td>low-pressure plasma spraying</td>
</tr>
<tr>
<td>PSD</td>
<td>position sensitive detector</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscope</td>
</tr>
<tr>
<td>TG</td>
<td>thermogravimetry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
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</table>

### Symbols

- $\alpha_{\beta}$: lattice parameter of the $\beta$-phase
- $\alpha_{\gamma}$: lattice parameter of the $\gamma$-phase
- $\alpha_{\gamma'}$: lattice parameters of the $\gamma'$-phase
- $c_i$: atomic percentage of the element $i$
- $C_{Pt}$: platinum content
- $d_n$: $d$-spacing along the surface normal
- $d_{n}(T)$: $d$-spacing along the surface normal at high temperature
- $d_{\Psi}(T)$: $d$-spacing in a direction at an angle $\Psi$ to the surface normal at high temperature
- $e^{-2M}$: temperature factor
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>elastic modulus</td>
</tr>
<tr>
<td>$E_{hkl}$</td>
<td>elastic modulus of a ((hkl)) family</td>
</tr>
<tr>
<td>$E_{ox}$</td>
<td>elastic modulus of the oxide</td>
</tr>
<tr>
<td>$E_S$</td>
<td>elastic modulus of the substrate</td>
</tr>
<tr>
<td>$f$</td>
<td>degree of freedom</td>
</tr>
<tr>
<td>$F_{hkl}$</td>
<td>structure factor of a ({hkl}) family</td>
</tr>
<tr>
<td>$F_{hkl}^\gamma$</td>
<td>structure factor of a ({hkl}) family in the (\gamma)-phase unit cell</td>
</tr>
<tr>
<td>$G_x$</td>
<td>the fraction of the total diffracted intensity of a certain reflection from a surface layer of depth $x$</td>
</tr>
<tr>
<td>$h$</td>
<td>film thickness</td>
</tr>
<tr>
<td>$h_m$</td>
<td>metal thickness</td>
</tr>
<tr>
<td>$h_S$</td>
<td>substrate thickness</td>
</tr>
<tr>
<td>$H_\Psi$</td>
<td>full width at half maximum intensity in a direction at an angle $\Psi$ to the surface normal</td>
</tr>
<tr>
<td>$I_{i,\text{exp}}$</td>
<td>measured intensity at the frequency $i$</td>
</tr>
<tr>
<td>$I_{\text{max},\Psi}$</td>
<td>maximum peak intensity in a direction at an angle $\Psi$ to the surface normal</td>
</tr>
<tr>
<td>$L_b$</td>
<td>size of the smallest interface separation to initiate buckling</td>
</tr>
<tr>
<td>$M$</td>
<td>relative proportion of the Lorentzian component</td>
</tr>
<tr>
<td>$P_{hkl}$</td>
<td>multiplicity of a ({hkl}) family</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$V_1$</td>
<td>volume fraction of phase 1</td>
</tr>
<tr>
<td>$w$</td>
<td>full width at half maximum intensity</td>
</tr>
<tr>
<td>$x$</td>
<td>penetration depth of X-rays</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>height of point $i$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{BC}$</td>
<td>elastic modulus of the bond coat</td>
</tr>
<tr>
<td>$E_m$</td>
<td>elastic modulus of the metal</td>
</tr>
<tr>
<td>$E_{ox}^T$</td>
<td>elastic modulus of the oxide at 1150°C</td>
</tr>
<tr>
<td>$E_\gamma$</td>
<td>elastic modulus of the (\gamma)-phase</td>
</tr>
<tr>
<td>$F_{hkl}^\beta$</td>
<td>structure factor of a ({hkl}) family in the (\beta)-phase unit cell</td>
</tr>
<tr>
<td>$h_{BC}$</td>
<td>thickness of the bond coat</td>
</tr>
<tr>
<td>$h_{ox}$</td>
<td>oxide thickness</td>
</tr>
<tr>
<td>$h_\gamma$</td>
<td>thickness of the (\gamma)-phase layer</td>
</tr>
<tr>
<td>$I_i$</td>
<td>calculated intensity at the frequency $i$</td>
</tr>
<tr>
<td>$I_{\text{max}}$</td>
<td>maximum intensity</td>
</tr>
<tr>
<td>$I_\Psi$</td>
<td>peak intensity in a direction at an angle $\Psi$ to the surface normal</td>
</tr>
<tr>
<td>$m_i$</td>
<td>atomic mass of the element $i$</td>
</tr>
<tr>
<td>$n$</td>
<td>number of total data points</td>
</tr>
<tr>
<td>$Q_{\text{creep}}$</td>
<td>activation energy for creep</td>
</tr>
<tr>
<td>$R_q$</td>
<td>root mean square roughness</td>
</tr>
<tr>
<td>$V_i$</td>
<td>volume of the unit cell $i$</td>
</tr>
<tr>
<td>$V_2$</td>
<td>volume fraction of phase 2</td>
</tr>
<tr>
<td>$W$</td>
<td>characteristic wavelength</td>
</tr>
</tbody>
</table>
NOMENCLATURE

\[ \bar{Z} \] average height over the surface

\[ \alpha_{m} \] coefficient of thermal expansion of the metal

\[ \alpha_{S} \] coefficient of thermal expansion of the substrate

\[ \gamma_{F} \] energy required per unit area to produce interfacial fracture

\[ \Delta T \] temperature drop

\[ \Delta \alpha \] different in coefficients of thermal expansion

\[ \Delta v \] frequency shift of the R2 line and

\[ 2\theta \] Bragg angle

\[ \mu \] linear attenuation coefficient

\[ \nu_{hkl} \] Poisson's ratio of a (hkl) family

\[ \nu_{\text{ox}} \] Poisson's ratio of the oxide

\[ \nu_{\gamma} \] Poisson's ratio of the \( \gamma \)-phase

\[ \rho_{\gamma} \] density of the \( \gamma \)-phase

\[ \sigma_{\text{ox}} \] growth stress in the oxide

\[ \sigma_{BC} \] thermal misfit stress in the bond coat

\[ \chi^{2} \] reduced chi-square

\[ \alpha_{BC} \] coefficient of thermal expansion of the bond coat

\[ \alpha_{\text{ox}} \] coefficient of thermal expansion of the oxide

\[ \alpha_{\gamma} \] coefficient of thermal expansion of the \( \gamma \)-phase

\[ \Delta^{2} \] variance of measurements

\[ \Delta \nu \] frequency shift of the R2 line and

\[ \dot{\varepsilon}_{\text{ creep}} \] creep strain rate

\[ 2\theta_{\psi} \] Bragg angle in a direction at an angle of \( \psi \) to the surface normal

\[ \nu_{BC} \] Poisson's ratio of the bond coat

\[ \nu_{m} \] the frequency at the maximum intensity

\[ \nu_{S} \] Poisson's ratio of the substrate

\[ \rho_{\beta} \] density of the \( \beta \)-phase

\[ \sigma \] residual stress

\[ \sigma_{\text{ox}}^{T} \] thermal misfit stress in the oxide

\[ \sigma_{\gamma} \] residuals stress in the \( \gamma \)-phase layer

\[ \psi \] angle between the surface normal and the bisector of the incident and diffracted beam
List of Publications


M. Bai, E. Sarakinou, Y. Chen, A. Chandio, X. Zhao, M. Preuss, P. Xiao, Microtecture analysis of the alumina scale in thermal barrier coatings. Journal of the American Ceramic Society, 2015;1-4


Abstract

Study of Bond Coats for Thermal Barrier Coating Applications

Ying Chen

The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Engineering and Physical Sciences

2015

Bond coats used in thermal barrier coatings (TBCs) for gas-turbine engine applications are studied in this thesis, with a focus on oxidation behaviour, surface rumpling and stress evolution.

Bond coats made of γ/γ' Ni-Al-Pt alloys have been widely used in TBCs and it has been found that addition of platinum greatly improves the oxidation resistance of the coatings. The mechanisms behind this benefit, however, are not well understood. For this reason, the oxidation behaviour of four γ/γ' Ni-20Al-xPt (x= 0, 5, 10 and 15 at. %) alloys at 1150 °C is studied and compared in terms of oxide spallation, oxide microstructure and growth, residual stress in the oxide scale and oxide/alloy interface morphology. The progressive increase of platinum addition into the alloys results in (1) greater resistance to oxide spallation, (2) reduction in oxidation of nickel, (3) lower stresses in the α-Al₂O₃ scale and (4) more planar oxide/alloy interfaces. It is found that the selective oxidation of aluminium promoted by platinum plays a central role in the evolution of the oxidation behaviour of the alloys.

Surface rumpling of a NiCoCrAlY bond coat deposited on a Ni-base superalloy during cyclic oxidation at 1150 °C is studied. The extent of rumpling is found to depend on thermal history, coating thickness and exposure atmosphere. While the coating surface progressively roughens with cyclic oxidation, bulk NiCoCrAlY alloys with the same nominal composition show a much less tendency to rumple under the same thermal cycling condition. The coatings, especially the thin ones, experience substantial degradation (e.g. β to γ phase transformation and exhaustion of yttrium) induced by oxidation and coating/substrate interdiffusion during thermal exposure. The observations together suggest that rumpling is driven by the lateral growth of the thermally grown oxide (TGO) and the coating deforms in compliance with the TGO. While the dependence of rumpling development on experimental conditions is generally in agreement with the prediction of the existing model, it is suggested that the degradation of the NiCoCrAlY coating and its dependence on coating thickness need to be taken into consideration when predicting the rumpling development of NiCoCrAlY coatings.

The residual stresses in a NiCoCrAlY bond coat deposited on a Ni-base superalloy are studied by X-ray diffraction using the sin²Ψ technique. The stresses at room temperature are found to be tensile; they first increase and then decrease with oxidation time. The stress develops and builds up upon cooling, predominantly within the temperature range from 1150 °C to 600 °C. Due to the limited penetration depth into the bond coat, the X-ray only probes the stress in a thin surface layer consisting of a single γ-phase formed through aluminium depletion during oxidation. Above 600 °C, the volume fraction of the β-phase in the bond coat increases with decreasing temperature. The mechanisms of stress generation in the coating are examined and discussed based on experiments designed to isolate the contribution of possible stress generation factors. It is found that the measured bond coat stresses are mainly induced by the volume change of the bond coat associated with the precipitation of the β-phase upon cooling.
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Chapter 1

Introduction

1.1 Development of gas-turbine engine materials

Gas-turbine engines used for aircraft propulsion and electricity generation are Carnot engines which convert chemical energy from burning fuels (e.g. natural gas or other liquid fuels) into mechanical energy [1]. In order to maximise their operating efficiency, turbines should work at temperatures as high as possible [1, 2]. To withstand loading and maintain structural integrity as well as long-term durability, however, the upper limit of the operating temperature is restricted by the high-temperature capability of the turbine blade materials. For these reasons, Ni-base superalloys, which possess a combination of high melting point (~ 1300 °C) and superior mechanical properties (e.g. creep resistance) at high temperatures are exclusively used [3]. Until approximately 25 years ago, relentless increases in operating temperatures were mainly achieved through three advances in materials technology: substantial progress in alloy design to produce alloy compositions that were both more creep resistant and oxidation resistant; development of directionally solidified and subsequently single crystal turbine blades; and state-of-art internal cooling by air flow through intricate internal channels cast into the component [4, 5]. Fig.1.1 shows the increase in maximum allowable temperatures (the brown line) in gas-turbine engines afforded by the development of the Ni-base superalloys and cooling technologies over decades[6].

Further improvements in efficiency of gas-turbine engines, both to increase the electricity output and for jet engines, the thrust-to-weight ratio, require even higher operating temperatures. This requirement seems unlikely to be achieved through further development of superalloys alone since the hot gas temperatures in today’s engines exceed the melting point of the Ni-base superalloys by hundreds of degrees [7]. The only way that the turbines
can survive in such an extremely harsh environment is by excessive internal and external cooling, which is, nevertheless, detrimental to the overall engine efficiency. To address these challenges an alternative engineering concept, which is to apply advanced thermal barrier coatings (TBCs) on Ni-base superalloys, has been introduced and developed over the last decades [4, 6, 8-16]. The application of TBCs leads to significant increases in engine temperature (Fig.1.1), much bigger than any earlier materials development including application of single crystal superalloy, thereby increasing engine efficiency.

![Fig.1.1 Progression of temperature capability of Ni-base superalloys and thermal-barrier coating (TBC) materials over the past five decades. The red line indicates progression of maximum allowable gas temperatures in engines, with the large increase gained from employing TBCs [6].](image_url)
1.2 Introduction of thermal barrier coatings

TBCs are multifunctional, complex films (typically 100 μm to 3 mm thick) made of low thermal conductivity materials that reduce heat transfer from the hot gas to the surface of the underlying alloys [13]. Modern TBCs typically comprise a yttria-stabilised zirconia (YSZ) coating deposited onto an oxidation-resistant metallic bond coat that is first applied onto a Ni-base superalloy substrate (Fig.1.2 [11]). The use of TBCs together with state-of-art cooling technology has enabled modern gas-turbine engines to operate at significantly higher temperatures (hundreds of degrees above the melting point of the superalloys) than their predecessors [6, 7]. The reduced alloy temperature benefited from the protection of
TBCs in turn prolong the life of the highly loaded turbine blades, whether from environmental attack, creep rupture, or fatigue [17].

While dramatic improvements in power output and efficiency have been achieved by the use of TBCs, further demands for better engine efficiency, reliability and durability raise new problems and challenges to the existing TBCs. First, TBCs are currently not considered “prime reliant” to the extent that they can be used with assurance that spallation failure will not occur [10, 17]. The failure of TBCs can endanger the engine because it exposes the underlying load-bearing alloy to temperatures above its melting point. Therefore it is extremely important to develop a solid lifetime prediction model for TBCs. To achieve this, it is essential to gain a more comprehensive understanding of the failure mechanisms of TBCs, as well as better modeling of the evolution of TBCs with a better description of compositions, microstructures, geometries, stresses and properties. Since a number of thermally induced phenomena, such as oxidation, diffusion, sintering and mechanical interactions between the constituent layers, occur concurrently in TBCs during service, it is of great challenge to understand their failure mechanisms and predict their lifetimes. This requires great modeling efforts incorporating extensive parameters, as well as substantial experimental validation. The problem is further complicated by the fact that the failure modes of the TBCs could vary depending on the coating deposition techniques and engine operating conditions. For example, TBCs deposited by electron-beam physical deposition vapour deposition (EBPVD) and air plasma spraying (APS) are so disparate in their morphology, microstructure and thermal physical properties that they generally have different failure mechanisms [10, 11, 15]. Second, the reproducibility of the coating deposition needs to be improved so that the potential temperature capabilities of existing TBCs can be fully exploited and utilised with greater confidence. A seemingly minor change of deposition parameters may cause a large scatter in lifetimes of TBCs [4]. In fact, only about half of the possible increase in operating temperature given by the TBCs is
considered in current engine design due to a lack of confidence in coating processing reproducibility [6]. Primary reliant TBCs with predictable life-time performance are required to implement TBCs as designed-in components and in this way to fully exploit their potential for significant performance improvements. Third, the increasing engine temperature poses new challenges that TBCs need to not only reflect or scatter heat transport through the coating but also resist attack of molten salts like calcium-magnesium-alumino-silicate (CMAS)[18]. This will require the development of both new engineering designs and new TBC materials.

1.3 Objective and structure of the thesis

As a key component in TBCs, the bond coat plays a crucial role in controlling the durability of TBCs. The ultimate goal of this thesis is to provide a better understanding of the bond coats in terms of oxidation behaviour, surface rumpling, stress evolution and as well as how these phenomena are correlated with compositional and microstructural evolution.

The structure of the thesis is organised as follows:

In Chapter 2, the constituents of the multilayer TBC system are reviewed in terms of material requirements, material selections and material properties. Degradation and failure mechanisms of TBCs identified to date are also reviewed.

In Chapter 3, the effect of platinum addition on oxidation behaviour of γ/γ΄Ni-Al alloys is studied. Bond coats made of Pt-diffused γ/γ΄Ni-Al alloys have been an accepted industrial standard used in TBCs and it has been found that addition of platinum greatly improves the oxidation resistance of the coatings. However, the mechanisms behind this benefit are not well understood. In this study, the oxidation behaviour of four ternary Ni-20Al-xPt (x= 0, 5, 10 and 15 at. %) alloys is studied and compared in terms of oxide spallation, oxide microstructure and growth, residual stress in the oxide scale and oxide/alloy interface
morphology. The effect of platinum addition on oxidation behaviour of \( \gamma/\gamma' \)Ni-Al alloys is then summarised and discussed.

Chapter 4 presents a series of experimental observations and analyses on surface rumpling of a NiCoCrAlY bond coat deposited on a Ni-base superalloy after cyclic oxidation. Rumpling is one of the most important degradation phenomena of TBCs because it gives rise to tensile stress normal to the metal/ceramic interface and motivates delamination. Therefore, it is of great importance to characterise how rumpling progresses with thermal cycling and how rumpling is affected by various experimental factors. Moreover, while surface rumpling of \( \beta \)-Ni (Pt, Al) coatings has been extensively investigated, few studies have been carried out to systematically investigate rumpling of NiCoCrAlY coatings so far to the best of our knowledge. The work here studies rumpling of a NiCoCrAlY coating under different experimental conditions and then compares the observations with the existing rumpling models. Factors that affect rumpling growth but have not been considered in the existing rumpling models are discussed.

In Chapter 5, the residual stresses in a NiCoCrAlY bond coat deposited on a Ni-base superalloy substrate are characterised and interpreted. Bond coat stress is important because it promotes creep of the coating and degrades the metal/ceramic interface. Although stress measurements on the bond coat have been reported in previous publications, they have been exclusively focusing on a study of the \( \beta \)-Ni (Pt, Al) and Pt-diffused \( \gamma/\gamma' \) bond coats. Measurements of residual stresses in the NiCoCrAlY bond coat have been hardly reported so far to the best of our knowledge. On the other hand, extensive characterisations have been done on the microstructure and phase compositions of the NiCoCrAlY coatings at room temperature. However, little is known about the evolution of the phase compositions with temperature and how the change of the phase composition would affect the stress in the bond coat. In this study, the residual stresses in the coating are measured as a function of thermal exposure time and temperature by X-ray
diffraction using the $\sin^2\psi$ technique. The mechanisms of stress generation in the bond coat are then examined and discussed based on a series of experiments designed to isolate the contribution of possible stress generation factors.

In Chapter 6, the main conclusions are summarised, along with outlook for future work.
Chapter 2

Literature Review

2.1 Thermal barrier coating system

The development of TBCs started in the 1950s with the manufacture of the first enamel coatings for military engine components [19]. The first flame sprayed ceramic coatings were introduced and used in commercial jet engines in the 1960s [20]. Subsequent decades witnessed continuous progress in TBC materials and coating technology. It was however in the 1980s when the TBCs were significantly improved [19]. Modern TBCs typically consist of four primary constituents (Fig.2.1), and each has specific functions and properties. They are (i) a ceramic topcoat with a low thermal conductivity and high strain compliance, (ii) a load-bearing superalloy substrate, (iii) an aluminium containing metallic bond coat between the topcoat and the substrate and (iv) a thermally grown oxide (TGO), predominately $\alpha$-$\text{Al}_2\text{O}_3$, that forms between the topcoat and the bond coat as a result of bond coat oxidation during high temperature exposure. Fig.2.1 illustrates the multilayer structure of a typical TBC system where the main functions and properties of each layer are briefly described. Due to the coupled mechanical and diffusional interactions between the ceramic coating and the underlying metal, it is necessary to consider TBCs as a complex, integrated, and evolving multimaterial system rather than simply a thermal insulating ceramic coating. The whole system is dynamic and all components interact with each other to control the performance and durability [10, 11].
Fig. 2.1 Schematic illustration of the multilayer, multifunctional nature of the thermal barrier coating system. Properties/functions and approximate thickness of different layers are indicated [6].

2.2 Ceramic topcoat

2.2.1 Requirements

The primary function of the topcoat is to provide thermal insulation for the underlying metallic components. Therefore, the coating material must have a low thermal conductivity and sufficient high temperature capability. Besides this major requirement, the extremely aggressive thermomechanical environment imposes additional constraints on the topcoat material [13]. First, the material must be “strain compliant” so as to be capable of withstanding the thermal misfit strains between the coating and the superalloy substrate during thermal cycling. Second, the material must not undergo phase transformations upon thermal cycling because such phase transformations usually result in disruptive volume change and compromise the strain compatibility and reversibility of the coating. Third, the material must be stable (e.g. high resistance to decomposition and sintering) during the long-term exposure at high temperature in an oxidising atmosphere. Another requirement
is that the coating material must be mechanically robust to resist fracture, erosion and impact damage from airborne particles, which requires high resistance to deformation and fracture. In addition, the coating material must be thermodynamically compatible with the TGO (they do not form interphases and their mutual solubility is very limited) in order to maintain interfacial bonding and structural integrity. These requirements have established some basic guidelines for searching and developing potential topcoat materials in the past decades and should still be valid in future provided that TBCs are still the choice of engineering design.

2.2.2 Topcoat materials

Today, the topcoat is typically made of ~ 7 wt. % yttria-stabilised zirconia (YSZ) because of its desirable comprehensive properties that make it the material of choice. Fully dense YSZ has one of the lowest thermal conductivities of all known ceramics (Fig.2.2), especially at elevated temperatures (~ 2.3 W·m⁻¹·K⁻¹ at 1000 °C [21]) because of its high concentrations of point defects (substitutional solute atoms and oxygen vacancies), which scatter lattice vibration [22]. As a ceramic, YSZ has a relatively high coefficient of thermal expansion (CTE, ~ 10 × 10⁻⁶ °C⁻¹, Fig.2.2), which is comparable to that of Ni-base superalloys (~15 × 10⁻⁶ °C⁻¹, Fig.2.2) and therefore helps alleviate stresses induced by the thermal expansion mismatch between the topcoat and the superalloy substrate. To further reduce these stresses, pores and cracks are deliberately incorporated into the topcoat during manufacture processing to lower its in-plane modulus, thereby making the coating “strain tolerant” and highly compliant. These microstructural defects also effectively reduce the thermal conductivity of the coating by decreasing the net-section area through which heat can be transported. As a refractory oxide, YSZ has a high melting temperature (~ 2700 °C [11]) and long-term stability (e.g. resistance to decomposition and sintering) in a high-temperature, oxidising atmosphere. YSZ is also phase compatible with α-Al₂O₃ (the predominant form of TGO), which ensures long-term thermodynamic stability of the
coating [23]. In addition, the high hardness (~ 14 GPa at room temperature) of YSZ enables the coating to resist erosion and foreign object damage [11]. Finally, YSZ has a demonstrated manufacturing capability for depositing it with a constant composition [6, 7, 24, 25].

![Diagram of thermal expansion coefficient and thermal conductivity](image)

**Fig. 2.2** Coefficients of thermal expansion and thermal conductivities of a range of engineering materials [4, 10]

As mentioned above, one of the requirements of the topcoat material is that it must not undergo phase transformations upon thermal cycling because the volume change associated with such transformations will cause a disruptive effect to the coating coupled with a rigid alloy substrate. This is also an important reason for the choice of stabilised zirconia as the topcoat material. Depending on temperatures, pure zirconia exists as three different crystallographic phases: monoclinic up to 1170 °C, tetragonal from 1170 °C to 2370 °C, and cubic from 2370 °C to its melting point [26]. The tetragonal to monoclinic transformation during cooling is martensitic in nature and can lead to undesirable cracking
and failure of the material as a result of a 4-5% volume change [27]. One way to suppress this transformation is to stabilise zirconia by doping a host of different oxides (e.g. $Y_2O_3$, $MgO$, $CaO$, $CeO_2$, $In_2O_3$, $Sc_2O_3$) [28]. Although all these oxides tend to stabilise zirconia to some extent, numerous studies have shown that zirconia doped with 7 wt. % yttria (7YSZ) exhibits the longest thermal cycling life and therefore is most suitable for TBC applications [11]. For yttria at this level, a tetragonal phase YSZ is stabilised above 1050°C under equilibrium conditions [29]. Unless mechanically constrained, the equilibrium tetragonal YSZ transforms to a mixture of monoclinic and cubic YSZ upon cooling. However, since the coating deposition techniques, such as electron-beam physical vapour deposition and air plasma spraying, are rapid, nonequilibrium processes, the deposited YSZ coatings typically have a metastable tetragonal-prime structure rather than an equilibrium tetragonal structure [30]. Although these two structures are closely related, a key difference between them is that the tetragonal-prime structure does not undergo any phase transformation upon cooling, even after a prolonged exposure at high temperature ($\leq$1200 °C) [31]. The non-transformable tetragonal prime 7YSZ makes it the most desirable phase for TBC applications. Besides, tetragonal prime 7YSZ has remarkably high fracture toughness due to ferroelastic toughening in which reorientation of ferroelastic domains occurs when the stress applied exceeds a critical value [32]. This toughening mechanism is different from that in some other zirconia-based ceramics where toughening arises from martensitic transformation from the tetragonal to monoclinic phase [26, 27]. Also, while the contribution of transformation toughening is expected to decay with increasing temperature and eventually disappear above $\sim$ 900 °C, ferroelastic toughening is insensitive to temperature and therefore have potential to retain high toughness at much higher temperatures, typical of those in gas-turbine engines. The high fracture toughness of the topcoat resulting from the ferroelastic toughening enables the coating to resist fracture and spallation induced by stresses, thereby extending the lifetime of TBCs.
2.2.3 Deposition techniques and coating attributes

As a refractory oxide with a melting point close to 2700 °C, YSZ requires ultrahigh temperature materials processing capabilities to deposit the material. Hence, air plasma spraying (APS) and electron-beam physical vapour deposition (EBPVD), which can generate extremely high temperature, have become primary and preferred choices [33]. The former involves propelling molten powder particles, while the latter relies on evaporation and vapour deposition from ceramic ingots in a vacuum chamber [33]. Although these two deposition techniques are vastly different, they are both designed to bond the ceramic coating with the metallic substrate and engineer microstructural defects to the coating in order to impart strain compliance and reduce thermal conductivity.

TBCs deposited by APS are about several hundred microns to several millimeters thick, and are characterised by splat grain morphology with a network of crack-like inter-splat boundaries and voids parallel to the alloy/coating interface (Fig.2.3a and b). The porosity (15-25% [11]) incorporated in the coating during the manufacturing process reduces the in-plane modulus and thermal conductivity through the coating. However, because the orientation of the microstructural defects are normal to the ceramic/metal interface, APS TBCs are less strain compliant than EB-PVD TBCs and have shorter thermal-cycling lives. Therefore, APS TBCs are mainly used on stationary components such as combustor cans, fuel vapourisers, vanes and shrouds.

TBCs deposited by EBPVD (~ 120-150 μm thick) are featured by highly textured columnar grain structure with multiscale porosity [33, 34], as illustrated in Fig.2.4. The columnar structure of the coating is due to the atomistic nature of the deposition process in which nucleation and growth of the grains are governed by condensation from the vapour of the ceramic ingot [33, 34]. The gaps between the disconnected columns can separate or converge to accommodate thermal misfit stress between the coating and the
substrate during thermal cycling, thereby conferring high strain tolerance and a long thermal-cycling life. The porosity helps reduce the through-thickness thermal conductivity as well, but to a less extent than that in APS TBCs, because the channels are parallel to the direction of heat flow [35]. TBCs deposited by EBPVD are more expensive, but more durable, than those deposited by APS, and are primarily used in most demanding applications, such as high thermo-mechanically loaded turbine blades and vanes in jet engines.

Fig.2.3 Microstructures of an atmospheric plasma sprayed TBC: (a) polished cross-section [36] and (b) fractured cross-section [37]. Defect components are highlighted.

Fig.2.4 Microstructures of an electron-beam physical vapour deposition TBC: (a) polished cross-section [38] and (b) fractured cross-section [31]. Multiscale defects are highlighted.
2.2.4 New topcoat materials

Since TBCs made of YSZ have been demonstrated to be highly durable, it is likely that YSZ remains the primary material of choice for gas-turbine engines with current operating temperature. However, at even higher operating temperatures, which are envisaged in pursuit of further improvement in engine efficiency and performance, YSZ topcoats undergo two detrimental compositional and microstructure changes: phase transformation and sintering. On long-term exposure at elevated temperatures, the supersaturated metastable tetragonal prime phase partitions into a mixture of two equilibrium phases: a low-yttria tetragonal phase and a high-yttria cubic phase [39-41]. The former then undergoes a tetragonal to monoclinic phase transformation during subsequent cooling, causing a disruptive volume change associated with the phase transformation. On the other hand, sintering of the topcoat upon high temperature exposure leads to a reduction of strain tolerance and hence early failure [42-44]. In addition, CMAS penetration and the increment of radiative heat transfer through the topcoat penetration associated with higher temperatures require a further reduction in thermal conductivity and a higher resistance to CMAS attack [6, 18]. Therefore, new TBC materials with lower thermal conductivities, higher thermal stabilities, lower sintering tendencies and greater resistance to CMAS attack are being searched and developed.

Among the interesting candidates, materials with pyrochlore structures ($A_2^{3+}B_2^{3+}O_7$) such as La$_2$Zr$_2$O$_7$, Gd$_2$Zr$_2$O$_7$ and Nd$_2$Zr$_2$O$_7$, have shown promising thermo-physical properties. Compared to YSZ, these pyrochlore materials exhibit lower thermal conductivities, higher thermal stabilities, a lower tendency to sinter and a higher resistance to CMAS attack [15, 16, 45, 46]. However, the CTEs of these pyrochlores are lower than that of YSZ, which would lead to higher thermal stresses in the topcoats made of pyrochlores upon cooling [16, 46]. Also, the materials have been reported to have relatively low fracture toughness due to the absence of toughening mechanisms [16, 46]. In addition, some pyrochlores are not
thermo-chemically compatible with the underlying TGO \[47\]. For example, Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} has been reported to react with the TGO to form a porous GdAlO\textsubscript{3} interphase, leading to degradation of the TGO protective function and likely loss of adhesion \[47\]. As a result, TBCs made of pyrochlores tend to have a short lifetime. A way to maximise the benefits of these materials and overcome their disadvantageous properties is the use of a so-called double-layer system, with a first layer of YSZ and a top layer made of pyrochlore materials \[16, 48, 49\]. The YSZ is a diffusion barrier to preclude deleterious reaction between the TGO and the pyrochlore, and also gives a CTE close to that of the substrate as well as a high toughness to hinder the propagation of cracks originating near and above the TGO. These double-layer TBC systems have shown excellent high-temperature capability significantly better than the single-layer YSZ TBC system and they are expected to improve the thermal capability of gas-turbine engines during application \[46\].

2.3 Bond coat

2.3.1 Requirements

Since YSZ is a fast-ion oxygen conductor (oxygen transparent \[28\]) and the interconnected porosity in the TBC allows easy ingress of oxygen, oxidation of the underlying metallic substrates becomes a major concern during service at high temperature. While the design and development of superalloys are dictated by the demand to improve their high temperature mechanical properties (e.g. creep resistance), the alloys generally do not have intrinsic resistance to oxidation required for long-term durability. At high temperature, the surface of the bare Ni-base superalloy rapidly forms complex, porous, multilayer Ni-rich oxides (e.g. NiO and Ni(Cr, Co, Al, Ti, Ta)\textsubscript{2}O\textsubscript{4}) \[50\], which are disruptive and thermodynamically incompatible with the YSZ layer above. This leads to rapid build-up of strain energy in the oxides and poor oxide/metal interface bonding, which causes early failure of TBCs. To overcome these problems, coatings with sufficient high melting point
and oxidation resistance are applied onto the superalloy components prior to TBC deposition to achieve the desired performance and required service lifetimes [9]. These coatings are generally referred to as “bond coats”, so called because it was initially found that the superalloy needed to be first covered with a metallic bond coat to ensure that the YSZ topcoat, especially the topcoat deposited by APS, remained adherent upon oxidation [4].

The primary function of the bond coat is to provide adequate oxidation resistance for the underlying superalloy substrate by forming a slow-growing, protective TGO scale on the surface of the bond coat as a result of bond-coat oxidation at high temperature. Today, the bond coat is typically made of alloys enriched with aluminium — a composition carefully engineered to result in a high melting point and formation of a TGO composed principally of \( \alpha\)-Al\(_2\)O\(_3\) — a stable, mechanically robust and effective barrier to oxygen diffusion [51], which prevent oxidation and resultant deterioration of the substrate alloy. Another reason that \( \alpha\)-Al\(_2\)O\(_3\) is favoured is that it is thermodynamically compatible with the YSZ topcoat, which is essential to maintain their interfacial adhesion upon high temperature exposure. Apart from being oxidation resistant, the coupled diffusional and mechanical interactions between the bond coat and the adjacent layers (TGO and superalloy substrate) during thermal exposure require that the coating also meet other constraints. The bond coat should maintain a high adhesion to the TGO to prevent spallation failure induced by the thermal stress in the TGO and degradation of interfacial bonding through migration of deleterious impurities (e.g. sulphur and carbon [52-54]) to the TGO/bond coat interface. Also, the bond coat should be resistant to chemical degradation, especially aluminium depletion, induced by coating/substrate interdiffusion, because continuous aluminium loss would eventually reduce its content in the coating to a level that \( \alpha\)-Al\(_2\)O\(_3\) is no longer the thermodynamically preferred phase and other non-protective oxides may form, particularly in the event of localised detachment or microcracking [55]. In addition, the bond coat
should be morphologically stable to minimise plastic deformation (e.g. surface distortion) induced by thermal stresses or phase transformations, because the distortion can introduce geometrical incompatibilities that cause interfacial debonding [10]. In summary, the bond coat is complex, multifunctional with a composition optimised to obtain a set of desirable thermochemical and thermomechanical properties. In reality, it is extremely difficult to satisfy the full range of these desirable properties and the selection of bond-coat materials is largely a compromise of these properties with a priority on oxidation resistance.

2.3.2 Bond coat materials

Based on deposition techniques and formation mechanisms, bond coats can be roughly divided into two categories: diffusion coatings and overlay coatings [4, 5, 8-10]. The former is based on intermetallic compound $\beta$-NiAl or $\gamma$-Ni/$\gamma'$-Ni$_3$Al and the latter is made of M-Cr-Al-X (M=Ni, Co, Ni-Co, Co-Ni; X=reactive element (e.g. Y) alloys. Although these two types of coatings are greatly different in terms of microstructure and chemistry, both of them are designed and developed to form a protective, adherent and durable $\alpha$-Al$_2$O$_3$ scale at high temperature through selective oxidation of aluminium contained in the coatings.

2.3.2.1 Diffusion coatings based on $\beta$-NiAl

Diffusion coatings based on nickel aluminide ($\beta$-NiAl) are reaction products of interdiffusion between a Ni-base superalloy substrate and an external aluminium source (donor) at elevated temperature. In this process, aluminium from the vapour source diffuses into the alloy while nickel from the substrate diffuses out where they react to form a coating mainly consisting of a $\beta$-NiAl phase (typically about 40-60 $\mu$m thick) at the surface. The $\beta$-NiAl phase has an ordered body centered cubic (b.c.c) or B2 (CsCl, space group Pm3m) crystal structure and exists over wide composition ranges [56-58], as shown from the equilibrium Ni-Al binary phase diagram in Fig.2.5 (The composition of the $\beta$-NiAl in the bond coat may slightly deviate from that predicted by the Ni-Al phase diagram
due to the presence of small amounts of other alloying elements such as Cr from the substrate). This phase acts as an aluminium reservoir that ensures the formation and sustenance of a protective \( \alpha\)-\( \text{Al}_2\text{O}_3 \) scale on the coating surface during thermal exposure, thereby providing long-term oxidation resistance to the underlying superalloy component. Also, the fact that \( \beta\)-NiAl phase can exist over a wide range of compositions suggests that diffusion coatings have resistance to undesirable phase transformation induced by aluminium depletion through coating/substrate interdiffusion, although a martensitic transformation can occur upon cooling as the compositions of the coatings shift to Al-rich side after prolonged thermal exposure [59, 60]. However, a drawback of the \( \beta\)-NiAl phase is its relatively low yield strength at high temperature, which makes the coating susceptible to thermo-mechanical fatigue degradation [4, 10, 15]. Micro-tensile testing based on free-standing diffusion aluminide coatings has shown that they exhibit a ductile to brittle transition temperature at approximately 600°C, and above this temperature the yield strength rapidly decrease with increasing temperature, reaching a value of 25 MPa at 1150 °C [61, 62]. Although thermal cycling could improve the intermediate temperature yield and creep strengths, it shows little effect on high temperature mechanical properties [61].

A number of methods such as pack cementation, slurry coating and chemical vapour deposition (CVD) have been used to fabricate \( \beta\)-NiAl bond coats [8, 9, 63-66]. Among all these methods, however, the pack cementation has been widely used due to its simplicity, flexibility and cost effectiveness [65]. During pack-cementation, the superalloy components are embedded in a powder mixture of aluminium source, a halide salt activator (e.g. \( \text{AlF}_3 \) or \( \text{NH}_4\text{F} \)) and an inert filler material such as \( \alpha\)-\( \text{Al}_2\text{O}_3 \) that prevents the pack from sintering. Depending on temperature and aluminium activity during deposition, \( \beta\)-NiAl bond coats are categorised into either low-activity (also referred to “outward-grown”), in which temperature is above \( \sim \) 1050 °C and formation of the coatings are dominated by
outward diffusion of nickel, or high-activity (also referred to as “inward-grown”), in which temperature is below ~1000 °C and coatings are formed by predominant inward diffusion of aluminium [63, 66, 67]. Fig.2.6 shows the microstructure of two β-NiAl coatings deposited on a Ni-base superalloy using low-activity (a) and high activity (b) pack cementation, respectively. While both types of coating consist of an outer β-NiAl layer and an inner interdiffusion zone (IDZ), the outer layer shows slight difference in terms of composition and microstructure. First, since a lot more aluminium diffuses into a high-activity coating than that into a low-activity coating during the aluminisation process, the outer β-NiAl phase of the high-activity coating is mostly hyperstochiometric (Al-rich) while that of the low-activity coating is hypostoichiometric (Ni-rich) in nature [63, 67]. Second, a high-activity coating usually contains numerous complex precipitates in the outer β-NiAl matrix, while there is virtually no precipitate in the outer layer of the low-activity coating. The reason for this microstructural difference is that during the formation of the high-activity coating, the slow diffusing alloying elements originally present in the superalloy substrate become trapped in the newly formed β-NiAl matrix and then precipitate out due to their limited solubility in the β-NiAl [68].

![Fig.2.5 Binary phase diagram of Ni-Al](image)
The effectiveness of β-NiAl bond coats greatly depends on their resistance to spalling of the protective α-Al$_2$O$_3$ scale during thermal exposure, especially under cyclic oxidation conditions that are commonly encountered in a gas-turbine engine. Repeated spallation of the TGO during cyclic oxidation causes accelerated aluminium depletion from the bond coat and a loss in its oxidation resistance. More importantly, spallation of the scale debonds the coating/TGO interface and can eventually lead to failure of TBCs. To improve TGO adhesion, modification of the β-NiAl coatings by alloying elements such as platinum, yttrium, hafnium and zirconium has been extensively studied [52, 64, 70-77]. Among these elements, platinum has been consistently found to be very effective in reducing TGO spallation. Today, Pt-modified nickel aluminide bond coats (β-(Ni,Pt)Al) have been established as a widely accepted industrial standard, outperforming their un-modified counterparts. The β-(Ni,Pt)Al bond coats are typically single-phase (β) with platinum solid solution. This coating is fabricated by first electroplating a thin platinum layer (~5-7 μm)
onto the surface of the superalloy component and then aluminising by either pack cementation or CVD [63]. The microstructure of $\beta$-(Ni,Pt)Al bond coats depends on processing conditions (e.g. platinum thickness, temperature and time), but are fundamentally similar to those observed in $\beta$-NiAl coatings, both of which consist of an outer $\beta$-phase layer and an inner interdiffusion layer, as shown in Fig.2.7.

![Cross-sectional microstructure of an as-deposited platinum modified nickel aluminide bond coat fabricated by chemical vapour deposition](image)

Fig.2.7 Cross-sectional microstructure of an as-deposited platinum modified nickel aluminide bond coat fabricated by chemical vapour deposition [78].

Although it is now well established that platinum addition greatly improves the oxidation resistance of $\beta$-Ni,Pt)Al bond coats and such improvement is primarily achieved through the enhanced resistance to TGO spallation, the mechanisms of this beneficial effect are still not fully understood. Density-functional theory (DFT) calculations have indicated that platinum actually decreases $\text{Al}_2\text{O}_3$ (0001)/NiAl (110) or $\text{Al}_2\text{O}_3$ (0001)/NiAl (111) interfacial bonding, which rules out a direct role for platinum improving adhesion of the metal/oxide interface [79]. This suggests that there should be other mechanisms responsible for the
observed improvements in lifetimes of the TGO resulting from platinum addition. Oxidation studies based on bulk $\beta$-(Ni,Pt)Al alloys and $\beta$-(Ni,Pt)Al bond coats have shown that platinum addition reduces the formation of voids at the TGO/metal interface [80, 81], which increases the contact area between the TGO and the metal, and therefore raises the effective overall energy needed to separate the TGO from the coating surface. DFT calculations have shown that platinum decreases the formation energies of point defects and defect clusters in $\beta$-NiAl, which leads to a decrease in diffusion activation energy and an increase in the diffusivity of aluminium in $\beta$-NiAl. [82]. The enhancement in the diffusivity of aluminium resulted from platinum addition is postulated to have several benefits to oxidation resistance such as promoting selective oxidation of aluminium by forming a comparatively pure, slower-growing $\alpha$-$\text{Al}_2\text{O}_3$ scale [83, 84], preventing the formation of disruptive Ni-rich oxide even after long-time oxidation by maintaining a relatively high concentration of aluminium at TGO/bond coat interface, and retarding the undesirable $\beta$ to $\gamma'$ or $\gamma$ phase transformation due to the aluminium depletion caused by oxidation and interdiffusion between the coating and substrate [85]. It has also been proposed that the presence of platinum prevents the segregation of deleterious impurities (e.g. sulphur) to the $\alpha$-$\text{Al}_2\text{O}_3$/$\beta$-NiAl interface and, therefore, suppresses embrittlement of the interface [81, 86]. Besides, platinum present in $\beta$-NiAl alloys has been reported to slow down the phase transformation from transient $\theta$-$\text{Al}_2\text{O}_3$ to stable $\alpha$-$\text{Al}_2\text{O}_3$ during oxidation, which in turn is beneficial to the relaxation of stresses generated by the growth of $\alpha$-$\text{Al}_2\text{O}_3$ [87].

2.3.2.2 Diffusion coatings based on Pt-diffused $\gamma$-$\text{Ni}/\gamma'$-$\text{Ni}_3\text{Al}$

An alternative type of diffusion coating, generally referred to as Pt-diffused $\gamma/\gamma'$ bond coat, has recently been developed [88, 89]. Typical fabrication method of this coating involves electroplating a thin platinum layer ($\sim$ 7-12 $\mu$m) onto the surface of an aluminium-containing, single-crystal superalloy substrate, followed by a diffusion treatment at high
temperature in vacuum. The aluminising process used for depositing the $\beta$-NiAl and $\beta$-(Ni,Pt)Al coatings is eliminated in the fabrication of the Pt-diffused $\gamma/\gamma'$ bond coat, thereby lowering the fabrication cost. The Pt-diffused $\gamma/\gamma'$ coating is a direct reaction product of interdiffusion between a Ni-base superalloy and the platinum layer. During this process, platinum diffuses into the $\gamma/\gamma'$ lattices of the alloy and expands the unit cells due to its larger atomic radius \[90\]. The lattice strain induced by platinum solid solution leads to recrystallisation near the alloy surface and subsequent precipitation of Pt-enriched f.c.c $\gamma$-Ni and L1\textsubscript{2} $\gamma'$-Ni\textsubscript{3}Al phases \[90\] (Fig. 2.8), which forms the Pt-diffused $\gamma/\gamma'$ bond coat.

![Fig. 2.8 Cross-sectional microstructure of an as-deposited Pt-diffused $\gamma/\gamma'$ bond coat. The $\gamma'$-phase in the coating exhibits a brighter contrast due to the segregation of platinum \[91\].](image)

Platinum plays an essential role in oxidation resistance of the Pt-diffused $\gamma/\gamma'$ bond coat. Due to the lack of the external aluminium source, the aluminium required to form a protective $\alpha$-Al\textsubscript{2}O\textsubscript{3} scale at the coating surface is exclusively from the superalloy substrate in which the aluminium content is generally not high enough to inhibit the rapid growth of the disruptive Ni-rich oxides \[50\]. Nevertheless, the solid-solution platinum in $\gamma$ and $\gamma'$ phases reduces the chemical activity of the aluminium at the alloy surface, causing an uphill
diffusion of aluminium from the inner part of the alloy to the surface and a subsequent increase in the aluminium content in the coating [92, 93]. As a noble metal, platinum does not form any stable oxide under normal oxidation conditions. However, platinum shows a strong tendency to replace the nickel sites in $\gamma'$ and $\gamma$ lattices, resulting in an increase in the atomic ratio of aluminium to nickel [93]. These properties of platinum lead to an increase in the effective aluminium content in the coating, thereby promoting selective oxidation of aluminium. In addition, recent studies have shown that platinum in Pt-diffused $\gamma/\gamma'$ bond coat inhibits segregation of sulphur into the TGO/bond coat interface [53]. However, the relatively low aluminium content (~ 25 at. %) in the Pt-diffused $\gamma/\gamma'$ bond coat raises the concern for the long-term oxidation resistance of the coating. Previous study has shown that aluminium depletion results in the formation of brittle spinel phases between the bond coat and the $\alpha$-$\text{Al}_2\text{O}_3$ under unfavoured conditions, thereby compromising the interfacial toughness [94]. Further studies are required to have a complete understanding of the effect of platinum on oxidation behaviour of $\gamma/\gamma'$ bond coats.

Pt-diffused $\gamma/\gamma'$ bond coat offers a couple of performance advantages over the conventional $\beta$-(Ni,Pt)Al bond coat. Because of its lower aluminium content, Pt-diffused $\gamma/\gamma'$ bond coat is more compositionally compatible with the underlying Ni-base superalloy than $\beta$-(Ni,Pt)Al bond coat. Furthermore, the superalloy-like structure offers the Pt-diffused $\gamma/\gamma'$ bond coat a high creep resistance, which gives the coating a greater resistance to morphology instability degradation (e.g. rumpling) than the $\beta$-(Ni,Pt)Al bond coat upon thermal cycling. Indeed, the Pt-diffused $\gamma/\gamma'$ bond coat exhibits negligible surface rumpling even after extensive thermal cycling [14, 95, 96]. High temperature stress measurement by X-ray diffraction has shown that the Pt-diffused $\gamma/\gamma'$ bond coat shows negligible creep from room temperature to as high as 1000 °C [90]. A drawback of the Pt-diffused $\gamma/\gamma'$ bond coat in terms of processing is that this type of coating can only be applied onto Al-
containing superalloys (e.g. CMSX-4 and Rene N5) due to the absence of aluminising during the fabrication, which limits the application range of the coating.

### 2.3.2.3 Overlay coatings

Diffusion coatings, by the nature of their formation, suggest that the compositions, microstructures, thicknesses and properties of the coatings are dictated by thermodynamic and kinetic constraints inherent to the interdiffusion process between the superalloy substrates and platinum/aluminium. Unlike the diffusion coatings, overlay coatings are applied onto superalloy substrates by physical deposition techniques in which coating materials are directly sprayed or grown onto the alloy surface without chemical reactions (e.g. diffusion) with the substrate [8, 9, 66, 97-99]. Typical deposition methods of overlay coatings include APS, low-pressure plasma spraying (LPPS), high velocity oxygen fuel spraying (HVOF) and EBPVD [64, 97, 99]. The composition of an overlay coating is only dictated by the coating source, and therefore, can be tailored and controlled with great flexibility for specific applications. Also, the deposition methods enable the thickness of overlay coatings to be varied by simply changing the deposition time or rate, which is another advantage over the diffusion coatings.

Typical overlay coatings are made of MCrAlY (M=Ni, Co or a mixture of the two) alloys, which usually contain (in wt. %) 15-25 % chromium, 10-15 % aluminium and 0.2-1 % yttrium [9, 66, 98, 99]. The coatings are generally composed of a two-phase structure (Fig.2.9) a brittle β-phase embedded in a ductile γ-phase matrix. The β-phase acts as an aluminium reservoir and provides oxidation resistance; the γ-phase improves ductility of the coating thereby reducing its susceptibility to brittle cracking induced by thermomechanical fatigue. A commercial NiCoCrAlY coating has been reported to exhibit a very high tensile strength (~1.4 GPa) and substantial plasticity (>2%) at room temperature, but its elevated temperature strength is dramatically reduced [100]. Chromium is added to
promote the formation of $\alpha$-$\text{Al}_2\text{O}_3$, as well as improving the hot corrosion resistance of the coatings [66]. Trace amounts (<1 wt. %) of reactive earth element dopants (e.g. yttrium) are added to improve TGO scale adhesion to the coating, although the principles behind this benefit are still in debate. Mechanisms that have been proposed in the literature include mechanically keying the TGO by forming oxide pegs [101, 102], reducing oxide growth rate [102], inhibiting metal-scale interfacial void growth [103], alleviating sulphur segregation to the interface [73, 104-106], and forming strong bonds with the oxygen in $\alpha$-$\text{Al}_2\text{O}_3$ [107]. Future work is needed to clarify the effect of reactive elements.

![Cross-sectional microstructure of a NiCoCrAlY bond coat deposited by HVOF](image)

Fig.2.9 Cross-sectional microstructure of a NiCoCrAlY bond coat deposited by HVOF [108]: (a) optical image and (b) high-magnification backscattered electron (BSE) image showing that the bond coat consists of $\beta$-phase (grey contrast), $\gamma$-phase (white contrast) and interfacial pores (dark contrast) between the metal particles

### 2.3.3 Bond coat stress

As the bond coat and the superalloy are intrinsically different in chemistry and microstructure, their CTEs are generally different. As a result, a thermal misfit stress develops in the bond coat upon cooling. The nature of this stress depends on the sign of the CTE misfit (tension in the coating with higher CTE than that of the superalloy and compression in the coating with a lower CTE than that of the superalloy). Zhao et al. have used both curvature and X-ray diffraction methods to measure the residual stress as-
deposited Pt-diffused $\gamma/\gamma'$ bond coat on CMSX-4 superalloy and reported a compressive stress of about 180 MPa [90], while Watanabe et al. have used a curvature method to measure the residual stress in an as-deposited $\beta$-(Ni,Pt)Al bond coat deposited on Rene N5 superalloy and have reported a tensile stress of about 140 MPa [109]. The nature and magnitude of these stresses are in agreement with those predicted based on the bond coat/substrate CTE misfit. Furthermore, the $\beta$-NiAl and $\beta$-(Ni,Pt)Al bond coats can undergo a martensitic transformation (from B2 to L10) upon cooling from a sufficiently high temperature (above 1000 °C) when the coatings have been subject to extensive aluminium depletion [59-61]. The martensitic transformation gives rise to stress in the bond coat as well due to the volume shrinkage (~ 2%) from the parent phase to martensite [60]. Bond coat stress plays an important role in degradation of TBCs because it promotes creep of metal and degrades the metal/ceramic interface during thermal cycling [110]. One of the dominant degradation mechanisms of TBCs, rumpling, as will be described and discussed later, has been shown to be accelerated by the periodic generation and decay of bond coat stress during thermal cycling [110]. Therefore, determining the bond coat stress and its evolution is essential to a better understanding of failure mechanisms of TBCs and development of a reliable life prediction model.

2.4 Thermally grown oxide

2.4.1 Requirements and material of choice

The thermally grown oxide (TGO) is a reaction product resulting from the oxidation of the bond coat. The TGO should be protective, slow-growing, stable, mechanically robust and thermodynamically compatible with the YSZ in order to be an effective oxygen diffusion barrier while maintaining adhesion with the topcoat without reacting with it. Since $\alpha$-$\text{Al}_2\text{O}_3$ meets all the requirements above, the composition of the bond coat is engineered to form a TGO scale predominately consisting of $\alpha$-$\text{Al}_2\text{O}_3$. The TGO scale is polycrystalline, with an
outer portion composed of equiaxed grains and an inner portion columnar grains (Fig. 2.10). The columnar shape is a consequence of inward growth of the grains controlled by the inward diffusion of oxygen along the TGO grain boundaries [111], particularly in the event that reactive elements are doped into the bond coat [112]. The columnar grains may or may not show a fiber texture along the normal of the interface, depending on the composition of the bond coat and the processing of the ceramic topcoat [113]. Previous studies on oxidation of bond coats have shown that the growth of the TGO is either parabolic or sub-parabolic [114-116], depending on the types of the underlying bond coat and the oxidation temperature.

![Figure 2.10](image)

Fig. 2.10 SEM in-lens image of TGO grown in an APS-TBC-system with a NiCoCrAlY bond coat after 400 h cyclic air oxidation at 1050 °C [117]

### 2.4.2 TGO stress

Large compressive stresses (~ 2-6 GPa) are developed in the TGO, as the coupled metal-oxide system cools to ambient, primarily due to the thermal misfit between the TGO and the superalloy substrate. Stresses also arise during TGO growth, but are smaller (≤1 GPa) [118-120]. The contribution to the TGO growth stress is associated with its growth strain.
consisting of a simple thickening component and another lateral growth component [121, 122]. While the thickening of the TGO could be accommodated by a rigid body displacement (provided that the TGO/bond coat is flat), the lateral elongation of the TGO is constrained by the underlying alloy thereby generating a lateral compressive growth stress in the growing oxide. In the event of a curved interface, both the thickening and the lateral growth strains of the TGO contribute to the growth stress because the thickening strain cannot be fully accommodated by a rigid body displacement [121, 122]. The magnitude of the growth stress depends on the dynamic competition between the stress generation and concurrent TGO creep. Addition of minor reactive elements into the bond coat significantly increases the magnitude the TGO growth stress [123-125], which is generally ascribed to the enhanced creep resistance of the TGO induced by segregation of these elements at the TGO grain boundaries. The existence of an in-plane compressive stress in a growing oxide has been known for many years and manifested in a few ways. For instance, thin sheets and wires made of alloys elongate during oxidation [126, 127], which are attributed to a tensile stress in the alloy generated in response to the compressive stress in the growing oxide. The origin of lateral growth strain is not fully understood but is generally attributed to the formation of new TGO grains at the existing grain boundaries perpendicularly oriented to the interface [121, 122], caused by the counter-diffusion of outward diffusing Al\(^{3+}\) and outward diffusing O\(^2-\). High-energy synchrotron X-ray diffraction has been used to measure the growth strains in the TGO formed on some \(\alpha\)-\(\text{Al}_2\text{O}_3\)-forming materials, such as FeCrAlY and NiAl, and found that the TGO growth stresses range from several hundred MPa on NiAl to about 1 GPa on FeCrAlY [118, 119, 128].

The formation and growth of the TGO exert a central role in governing the durability of a TBC system since the build-up of the strain energy associated with TGO stress development and thickening motivates delamination at the metal/ceramic interface [10, 15].
The fundamental mechanics of this form of fracture is similar to the loss of coherence of epitaxial thin films to a thick, rigid substrate, namely when the release rate of strain energy in the growing films exceeds the interfacial fracture toughness. Therefore, knowledge of the magnitude and spatial distribution of the TGO stress is essential to understanding the failure of TBCs and developing a reliable life prediction model of TBCs. However, since the TGO in the TBC system is buried underneath a thick YSZ topcoat, determination of the TGO stress by conventional techniques has been intractable. For example, the laboratory X-rays can hardly reach the TGO due to the limited penetration depth [129]. High-energy synchrotron X-rays that can penetrate through the TBC have been shown to be a powerful and novel technique, but the availability is limited. Furthermore, the X-ray diffraction does not provide sufficient spatial resolution of the stress distribution since this technique typically probes the average strain over an area (in the magnitude of millimeters) that are an order-of-magnitude larger than the characteristic areas of interest (in the magnitude of microns) in TBCs. An alternative and more revealing method is one that takes advantage of the transparence of YSZ and utilises photoluminescence piezospectroscopy (PLPS) to measure the TGO strains through the YSZ topcoat [130-132]. In this technique, a focused laser beam with an appropriate wavelength (e.g. an argon laser with a wavelength of 512 nm) is illuminated through the ceramic topcoat, which is transparent in the visible, and excites the R-line luminescence from trace Cr$^{3+}$ ions which are invariably present in the TGO as it grows. The mean stress in the region probed by the laser is proportional to the frequency shifts of the R-lines with respect to stress-free R-lines, and the shape of the PLPS lines is correlated with the stress distribution within the region (Fig.2.11). Since the diameter of the region sampled by the laser generally ranges from tens of microns to hundreds of microns (depending on the spot size of the focused laser and the scattering of the laser through the topcoat) [133, 134], the PLPS technique can provide a high-resolution spatial distribution of stresses. As a local damage is usually accompanied with relaxation of the stress, the PLPS technique has enabled correlations to be non-
destructively mapped between the luminescence shifts and the development of local damage during the service of TBCs [135-137].

![Graph showing photostimulated R-line luminescence from a spalled piece of alumina and the alumina TGO in an EBPVD TBC sample after one-cycle oxidation at 1200°C](image)

Fig. 2.11 Photostimulated R-line luminescence from a spalled piece of alumina (dotted line) and the alumina TGO in an EBPVD TBC sample after one-cycle oxidation at 1200°C (solid line); the lower intensity of the spectrum from the TBC sample is a result of absorption and scattering within the TBC coating. Sharp line at ~ 14 355 cm⁻¹ is an Ar emission line used to calibrate the frequency [130].

### 2.5 Failure mechanisms of TBCs

The effectiveness of the TBC system depends on the integrity of the ceramic topcoat and the thermal insulation provided by the coating. In the event that part of the coating is eroded away or the coating spalls off underlying metallic component, the thermal protection is lost and the bare metal is exposed to dangerously hot gases with temperatures over its melting point. The concern of failure has retarded the use of TBCs, and even
where used, the full temperature capability, and hence energy efficiency and operating lifetime, offered by TBCs have not been realised [11]. Therefore, knowledge of TBC lifetimes is of extreme importance from the perspective of engine safety. A thorough understanding of the failure mechanisms is essential to the development of both reliable life-prediction models and future prime-reliant TBCs.

Superficially, failure of TBCs is manifested by ceramic topcoat spalling away from the engine part, exposing the underlying metal to rapid oxidation and even melting. Spallation generally occurs at or closed to the bond coat/topcoat interface upon cooling from high temperature to ambient. A consensus view is that the growth of the TGO resulting from bond coat oxidation is a major factor controlling the degradation and failure process [138]. Indeed, substantial previous work aimed at identifying failure mechanisms of TBCs has mainly focused on oxidation of bond coat, which promotes interfacial debonding by forming a brittle and highly stressed $\alpha$-$\text{Al}_2\text{O}_3$ scale. A proposed failure criterion associated with these studies is the combination of temperature and time to form a critical thickness of TGO [139]. However, while there is a degree of correlation between the thickness of the TGO and the propensity of spallation, the concept that failure occurs when the TGO reaches a critical thickness is oversimplified and does not constitute a thoroughly satisfactory lifetime prediction methodology. Recent studies have shown that a number of other mechanisms, which are linked to complex interactions between the four constitutive layers and their evolution with time and temperature, is also responsible for the observed failure of TBCs besides bond coat oxidation [10, 11, 15]. Based on the nature of the failure mechanisms, however, they can be categorised into intrinsic and extrinsic mechanisms. The former is associated with thermally induced processes such as oxidation-induced TGO growth, stress development, bond coat deformation and bond coat/substrate interdiffusion; the latter is associated with environmental degradation such as foreign object damage and
CMAS attack. The following part will mainly review the intrinsic failure mechanisms with the extrinsic ones briefly described and discussed in the end.

2.5.1 General failure modes and principles

A prevalent failure mode of TBCs is one in which part of the ceramic topcoat buckles and spalls off the metallic substrate upon cooling down to ambient temperature, as schematically illustrated in Fig.2.12. Fig.2.13 shows a typical example of a buckling driven failure occurred near the edge of an EBPVD TBC. Such buckling and following spallation is a common failure mode of coatings and thin films subject to lateral compressive stresses induced by the CTE misfit between the coating and the underlying substrate upon cooling. The mechanics of buckling of a thin film compressively stressed on a flat surface have been well understood, provided that a flaw size, \( L \), is present at the film/substrate interface. For a given film thickness, \( h \), and lateral residual stress, \( \sigma_0 \), the flaw size, \( L_b \), at the onset of axisymmetric buckling is given by [140]:

\[
L_b/h = 2.21\sqrt{E/\sigma_0}
\]  \hspace{1cm} (2.1)

Fig.2.12 Schematic illustration of buckling of a compressively stressed film above a pre-existing flaw of size \( L \) [140]
Where $\bar{E}$ is in-plane modulus of the film. The $L_b$ represents the smallest interface separation required to give rise to buckling and subsequent failure in absence of any interface imperfections. Eq. (2.1) indicates that $L_b$ depends linearly on $h$, and for typical moduli of TBCs and their compression stresses, $L_b$ is about 20 times of $b$ or even more.

Since a typical TBC is over 100 um thick, the critical separation size to activate buckling is in the magnitude of millimetres. As interface separations as large as this size are generally not present after coating deposition, one unsolved question is that how interface separations initiate first and then grow to a critical size. Progressive failure following a sequence of crack nucleation, propagation and coalescence has indeed been observed before [130, 141]. Recent calculations based on fracture mechanics have shown that interface imperfections (e.g. interface undulations) can decrease the critical separation size at which buckling can initiate [140]. Nevertheless, localised flaws must first form and then grow for buckling and spallation to occur.
In summary, the eventual failure of TBCs is a chronic phenomenon that occurs through a progressive degradation process consisting of crack nucleation, propagation and coalescence events. Understanding this degradation process is essential to identifying the specific failure mechanisms and developing realistic lifetime prediction models. Recent studies on failure mechanisms of TBCs have shown that nucleation and propagation of interface separation are governed by two prototypical imperfections [10, 140]: interface undulations and morphological heterogeneity (Fig.2.14). Both imperfections locally redistribute the residual stress such that out-of-plane tensions develop normal to metal/ceramic interface, as illustrated in Fig.2.14. These tensile stresses motivate interface cracking and translate into stress intensity factors around the crack tips to drive crack propagation. Since TBCs deposited by APS and EBPVD are so disparate in morphology, microstructure and thermal physical properties, the detailed failure mechanisms in these two types of TBCs are different and are discussed separately below.
2.5.2 Failure mechanisms of APS TBCs

APS TBCs are typically deposited onto MCrAlY bond coats with their surfaces deliberately roughened (the peak-to-trough roughness amplitude can be tens of micron$^{[142]}$) prior to topcoat deposition for better topcoat adhesion by mechanical keying. However, the highly undulated metal/ceramic interface gives rise to local tensile stresses normal to the interface $^{[10, 17]}$, thereby motivating crack nucleation and propagation around the undulations. A typical cross-section of a failed APS TBC is shown in Fig.2.1a. A substantial proportion of the delamination traverses the base of the topcoat, with local segments entering the TGO as well as the interface with the bond coat. The proposed cracking mechanisms based on experimental observations are schematically illustrated in Fig.2.1b. Due to thermal misfit between the TGO and the bond coat, stresses are generated at the bond coat/TGO interface upon cooling: the stresses are tensile at the undulation crests and compressive at the troughs $^{[143, 144]}$. The tensile stress increases as the TGO thickens, causing cracking at the bond coat/TGO interface at crests (type I cracking in Fig.2.1b). Similarly, the undulations also result in out-of-plane stresses in the vicinity of the TGO/topcoat interface: tension at the crests and compression at the troughs. The tensile stress causes cracking along the TGO/bond coat interface (type II cracking in Fig.2.1b) at the crests and within the brittle topcoat in the vicinity of the crests (type III cracking in Fig.2.1b).

The mechanism behind type IV cracking in Fig.2.1b is still currently in debate and remains to be clarified. Evans et al. have proposed that geometric misfit due to TGO growth around the undulations induces a normal tensile stress in the surrounding topcoat and leads to subsequent cracking in the undulation trough regions $^{[10]}$. Specifically, as the volume expansion strain associated with the TGO growth around the undulations cannot be fully accommodated by a rigid body displacement, the following dilation induces out-of-plane tensile stress within the surrounding topcoat and leads to subsequent radial cracking in the valleys between the crests. Schlichting et al. have proposed a different formation
mechanism of the type IV cracking, in which the cracking is induced by the thermal misfit between the topcoat and the bond coat/TGO “composite” [36]. The thickening of TGO gradually consumes the metallic bond coat, and the TGO can constitute a good fraction of the bond coat asperity after a certain period of time. Therefore, the thermal stresses upon cooling are locally dictated by the CTE misfit between the topcoat and the bond coat/TGO “composite” asperity, rather than just the bond coat. Beyond a critical TGO thickness, the CTE of the bond coat/TGO becomes lower than that of the topcoat, which reverses the stress in the topcoat undulation troughs from compression to tension. This reversal causes transverse cracking within the topcoat in the troughs.

Fig.2.15 (a) cross-sectional SEM micrograph of topcoat side of a failed APS TBC [36] and (b) schematic diagram showing four cracking mechanisms in APS TBC [11]
2.5.3 Failure mechanisms of EBPVD TBCs

Unlike APS TBCs, EBPVD TBCs are deposited on flat bond coats with peak-to-trough amplitudes up to only a few microns [141]. However, the TGO that forms on the surfaces of bond coats, especially those made of $\beta$-(Ni,Pt)Al and MCrAlY alloys, progressively displaces into the bond coats with thermal cycling [145-148], as illustrated in Fig.2.16. This morphology instability of the TGO during cyclic oxidation has been referred to as “rumpling” or “ratcheting”. The inward displacements of the TGO induce tensile strains at the TGO/TBC interface and cause cracking. On the other hand, the development of the undulations resulting from TGO rumpling induces and enlarges the tensile stress at the TGO/bond coat interface at the undulation crests upon cooling and leads to subsequent...

Fig.2.16 TGO rumpling on (a) a $\beta$-(Ni,Pt)Al bond coat [145] and (b) a NiCoCrAlY bond coat after thermal cycling [146]
interface cracking [10, 11, 140, 141]. The cracks extend laterally as rumpling grows and eventually link together to trigger buckling and spallation.

The underlying mechanisms responsible for rumpling have been subject to extensive studies in the past decades. Experimental observations of TGO rumpling on β-(Ni,Pt)Al coatings have shown that the rumpling magnitude depends on oxidation time, oxidation temperature, oxidation modes (cyclic or isothermal), oxidation atmospheres (in air or vacuum), sample configurations (bulk alloys or coatings), coating thicknesses, contents of reactive elements (REs, such as yttrium and hafnium) in the coatings and external loads [78, 149-153]. A comprehensive analytical model (Balint-Hutchinson model) based on continuum mechanics has been recently developed to simulate rumpling evolution under a variety of different experimental conditions [110]. The basic concept of the model is that rumpling is driven by the lateral growth strain in the TGO and assisted by concurrent creep of the bond coat to accommodate the deformation of the TGO. At high temperature, the TGO undergoes thickening as well as lateral growth. Due to the constraint from the underlying bond coat, the lateral growth of the TGO produces a compressive strain in the scale. As with any type of compressively stressed films, the TGO attempts to alleviate the stress and associated strain energy by lengthening itself through out-of-plane displacements (rumpling). The geometry compatibility also requires the bond coat to deform in compliance with the TGO, provided that they remain bonded to each other. Theoretically, the TGO could move both upward and downward with respect to original surface to form a sinusoidal surface profile during rumpling, and this has been widely observed on bond coats without topcoats [150, 151]. In the event that the topcoat is present, which is also the case in EBPVD TBC systems, however, rumpling occurs exclusively through the downward displacement into the bond coat because the superimposed topcoat imposes considerable mechanical constraint on the upward movement of the TGO [138]. The growth of the rumpling amplitude is governed by many factors, including creep of the
bond coat and plastic yielding of the TGO. The predictions of the Balint-Hutchinson model have been found to agree with many observations reported in the literature, although the correspondence between the experiments and simulations remains to be validated.

Unlike the idea that rumpling is driven by the lateral growth strain in the TGO, some researchers have proposed that rumpling is motivated by distortion of the bond coat surface and the TGO deforms in compliance with the coating surface. Tolpygo and Clarke have suggested that the volume shrinkage associated with the localised $\beta$ to $\gamma'$ phase transformation in the $\beta$-NiPtAl bond coat could lead to out-of-plane distortion of the coating and subsequent rumpling [150]. However, while this mechanism may have an effect after prolonged cycling, it is not responsible for the initiation and early growth of undulations. The reason is that rumpling occurs from very beginning of thermal cycling, long before any substantial amount of $\gamma'$ has formed [151]. Panat et al. have proposed that rumpling is driven by surface diffusion induced by the thermal misfit stress in the bond coat [154]. One implication of their analysis is that rumpling increment would be effectively shut off as soon as the stress is fully relaxed at the maximum temperature (once the stress is fully released, the bond coat remains stress-free during the rest dwell period and there will be no driving force for surface diffusion). In another word, the rumpling would be independent on the dwelling time at peak temperature as long as the dwell time is sufficient for relaxation of the stress in the bond coat. However, this is not in agreement with the experimental observations showing a longer dwell time at peak temperature produces a higher rumpling magnitude for a given cycle number and the same ramp rates [150, 151].

For the EBPVD TBCs deposited on MCrAlY bond coats, another type of imperfection, TGO thickness heterogeneity (often referred to as “pegs”), could develop besides TGO rumpling upon oxidation [146, 155]. The thickness heterogeneity forms and enlarges in regions where the $O^2-$ diffusion through the TGO is exceptionally fast. This occurs at
locations where the TGO contains yttrium aluminium garnet (YAG) [155] (Fig.2.17), an oxide with a much higher $O^2-$ diffusivity than $\alpha$-$Al_2O_3$. When the thickness imperfection reaches a critical size, the tensile stresses around this imperfection can nucleate bond coat/TGO interface separations [10, 17].

For EBPVD TBCs deposited on Pt-diffusion $\gamma/\gamma'$ bond coats, the failure mechanisms are not clearly understood. This type of bond coats neither shows rumpling nor develops TGO thickness heterogeneity after thermal cycling [14, 95, 96]. However, it has been known that failure mainly occurs at the bond coat/TGO interface and it is believed that the bond coat/TGO interface undulation due to the initial non-planarity of the bond coat surface plays a major role in damage development. Previous studies using PLPS and cross-sectional observations have concluded that the local interface damage nucleates at the crests of the undulations due to the normal tensile stress across the interface [96]. These damaged regions gradually link up into larger areas of delamination.

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**Fig.2.17** A thickness imperfection in the TGO grown on a NiCoCrAlY bond coat [155]
2.5.4 Environmental degradation

One type of environmental degradation is related to the ingestion of particulates into the combustion gas steam and subsequent impact on the rotating airfoils, which leads to loss of the TBCs by erosion and foreign object damage (FOD) [38]. Erosion generally describes the progressive removal of the material from the TBC surface while still maintaining the integrity of the characteristic microstructure (e.g. columnar microstructure for EBPVD TBCs and splat microstructure for APS TBCs). This occurs under small particle conditions where the near surface regions of the individual columns are cracked and lost due to continuous impact [156]. A typical example of erosion is shown in Fig.2.18a where the top region of the coating has been removed. FOD, on the other hand, is caused by large particles travelling at low velocities or smaller particles at higher velocities [156]. FOD is characterised by severe local plastic deformation and densification around the impact site, as well as formation of shear bands and extensive cracking [157, 158] (Fig.2.18b). Within the shear bands, the individual columns are usually cracked at the boundaries, and therefore the structural integrity of the material has been compromised, rendering them preferential sites for material removal upon subsequent impact. Simulations based on properties of EBPVD TBCs have indicated that the erosion and FOD thresholds are elevated by enhancing the toughness of topcoat materials and by lowering its hot hardness [159]. However, models that provide explicit relations between the impact and the extent of the cracking have yet to be developed.

Another type of environmental degradation of TBCs is related to molten calcium-magnesium-alumino-silicate (CMAS) deposits at the working temperature, formed by the ingestion of fine particles from the environment (e.g. volcanic ash and sand) and the subsequent melting [18]. The molten CMAS not only wets and dissolves the surface regions of the YSZ topcoat, but also penetrates into the coating and infiltrates open void space [160]. The CMAS attack changes the properties of the infiltrated regions of the
topcoat and enhancing its susceptibility to cold shock delamination upon cooling [14, 160, 161], mainly due to the formation of a fully dense stiff domain with a high elastic modulus as the CMAS penetrated layer solidifies upon cooling (The spatially configured voids, which offer the topcoat a low elastic modulus and high strain tolerance, are no longer existing.). Fig. 2.19 shows an actual example of degradation caused by CMAS infiltration into an EBPVD topcoat found in an engine-tested airfoil. Tentative models on mechanisms of cracking and delamination subject to CMAS penetration have been developed [160-162], yet there has been no independent validation of these models. Degradation caused by CMAS deposits will likely affect more engines as the operating temperatures are anticipated to increase in pursuit of greater engine efficiencies [6]. Tailoring of TBC compositions and microstructures and developing new TBC materials for greater resistance against CMAS attack are now becoming important areas of TBC research.

Fig. 2.18 Cross-sectional microstructure of (a) an eroded EBPVD TBC [156] and (b) an EBPVD TBC subject to FOD [159]

Fig. 2.19 Delaminations in a CMAS infiltrated topcoat layer found in an engine-tested airfoil [160]
2.6 Summary

The constituents of the multilayer TBC system have been reviewed in terms of material requirements, material selections and material properties. Degradation and failure mechanisms identified to date have been also reviewed. The sheer complexity of the interaction between the four layers — ceramic topcoat, TGO, bond coat and superalloy substrate, and their evolution with time at high temperature — make it essential that synergistic progress be made in all areas to enable TBCs to operate reliably at still higher temperatures in the future.
Chapter 3

Effect of platinum addition on oxidation behaviour of γ/γ’Ni-Al alloys

3.1 Introduction

Bond coats based on β-NiAl have been widely used in TBCs to provide oxidation resistance due to their ability to form a continuous and stable TGO (mainly α-Al₂O₃) scale during high temperature exposure [64]. The failure of TBCs deposited by EBPVD usually occurs at the TGO/bond coat interface, driven by the TGO strain energy which builds up as the oxide thickens during service at high temperature. Therefore, an improved TGO/bond coat bonding has been considered as one of the key factors to control the durability of the TBCs. The Pt-modified nickel aluminide bond coats, β-(Ni,Pt)Al, demonstrate significant improvement in resistance to oxide spallation than their unmodified counterparts, which has been identified by extensive research [70-73, 163, 164]. However, this type of bond coat is prone to undesirable surface rumpling after cyclic oxidation due to its low creep resistance [110, 150]. The undulated TGO/bond coat interface initiates crack formation and eventually leads to spallations of TBCs [10].

In the last decades, a Pt-diffused γ/γ’ bond coat has attracted great interest due to its good chemical compatibility with the γ/γ’-based superalloy substrate [64, 88, 89]. Furthermore, this coating exhibits negligible rumpling after thermal cycling due to its high creep resistance at elevated temperature [14, 95, 96], which retards degradation of the TGO/bond coat interface. However, the oxidation resistance of this bond coat has been a potential concern due to its relatively low aluminium content (~27 at. %) compared to that in β-NiAl-based bond coat (40-45 at. %) [63]. For instance, Zhao et al. [94] have shown that aluminium depletion in Pt-diffused γ/γ’ bond coat results in the formation of spinel
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under unfavourable conditions, which compromises the interface toughness due to the brittleness of spinel.

In general, the spallation of an oxide scale occurs when the strain energy within the layer exceeds the energy required to produce decohesion from the underlying metal substrate. For a thin, biaxially strained oxide scale after cooling from high temperature, this critical strain energy criterion can be expressed through the energy balance [138]:

\[
\frac{\left(\sigma^G_{ox} + E_{ox} (\Delta T)(\Delta \alpha)\right)^2 (1 - v_{ox})h}{E_{ox}} = \gamma_F
\]  

(3.1)

Where \( \sigma^G \) is the growth stress; \( \Delta T \) is the temperature drop, \( E_{ox} \) is the Young’s modulus, \( v_{ox} \) is the Poisson’s ratio; \( \Delta \alpha (= \alpha_m - \alpha_{ox}) \) is the difference in CTEs between metal and oxide, \( b \) is the thickness and \( \gamma_F \) the energy required per unit area to produce interfacial fracture. For a given metallic system oxidised at a certain temperature, reduced \( \sigma^G \) and \( b \) or an increased \( \gamma_F \) are preferred because they either decrease strain energy within the oxide or increase the interfacial toughness based on Eq. (3.1). Zhao and Xiao have shown that platinum in the \( \gamma/\gamma’ \) bond coat inhibits the segregation of the impurities, such as sulphur and carbon, into the TGO/bond coat interface, and thereby increases \( \gamma_F \) [53]. Previous publications have also manifested that platinum addition to the bulk \( \gamma/\gamma’ \) Ni-Al alloys promotes the establishment of a protective, slow-growing \( \alpha-Al_2O_3 \) scale [92, 165, 166], which leads to a reduced oxide thickness throughout the oxidation. However, little work has been done on the influence of platinum on the growth stress (\( \sigma^G \)) of the oxide on the \( \gamma/\gamma’ \)-based coatings or alloys. The only related work from Fountain et al. [167] pointed out that platinum reduces growth stress through the formation of volatile PtO\(_2\) incorporated in the oxide scale at the oxidation temperature. However, platinum was in the presence of pure element hung alongside the alloy in their research, which is different from the scenario in the Pt-modified bond coat where platinum is a non-reactive solid-solution atom. Besides, there
was no stress measurement or calculation in their work, which makes the conclusion less convincing.

Apart from the stress generation in the oxide, the oxide/metal interfacial geometry has been widely known to play an important role in oxide adhesion [144]. An undulated interface gives rise to out-of-plane tensile stress and initiates interfacial decohesion, where the oxide is compressively stressed in the lateral direction. This eventually leads to oxide buckling and spallation [10]. Nevertheless, few attempts have been carried out to investigate the impact of platinum on this aspect to the best of our knowledge.

In this study, the effect of platinum on the oxidation behaviour of Ni-Al alloys was investigated. Bulk model alloys, denoted as Ni-20Al-xPt (x=0, 5, 10 and 15 at. %), with γ/γ' microstructure were used throughout the study. The reason for using these alloys instead of the commercial bond coat is that the latter contains several alloying elements which could probably interfere with the effect of platinum. The results from this study are expected to provide more comprehensive understanding of the role of platinum in the oxidation behaviour of the γ/γ' Ni-Al alloys.

### 3.2 Materials and methods

Ni-20Al-xPt (x=0, 5, 10 and 15 at. %) alloys were fabricated by arc melting pure nickel, aluminium and platinum metals with designed chemistry in vacuum, and then casting in inert atmosphere, followed by annealing at 1200 °C for 200 h in vacuum. Samples were cut into 3 mm thick discs using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 5, Struers). The surfaces of the samples were ground and polished to a 0.25 µm finish.

Oxidation was performed at 1150 °C in laboratory air. The samples were isothermally oxidised for different periods of time up to 100 hours, followed by air cooling.
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Thermogravimetric (TG; SETARAM, K/SETEVO16-1A) tests were also carried out to measure the mass change throughout the oxidation. The samples were placed in an alumina crucible hung up by a platinum wire and oxidised at 1150 °C for 100 hours in the hot zone of the TG chamber.

The microstructures of the alloys and oxides were examined using optical microscope (Olympus BH2-UMA), optical profilometer (MicroXAM) and scanning electron microscope (SEM; FEI, Quanta 250) coupled with a focus ion beam system (FIB; FEI Quanta 3D). The chemical compositions of the alloys were determined by energy dispersive X-ray spectroscopy (EDS, Oxford Instruments, X-Max). The phases present in the alloys and oxides were analysed by X-ray diffraction (XRD; Philips PANalytical X’Pert diffractometer). The residual stresses in the α-Al₂O₃ scale after oxidation were measured at room temperature using photoluminescence piezospectroscopy (PLPS) on a Renishaw Ramanscope 1000 (Renishaw™, Gloucestershire, UK) with an argon laser source (λ =514 nm). The laser was focused to a spot size of ~ 5 μm on the sample surface. Although the α-Al₂O₃ layer was buried underneath the Ni-based transient oxide according to the subsequent results in this work, the laser could penetrate through it and fluorescent signals from Cr³⁺ in α-Al₂O₃ were collected.

To determine the peak positions of R1 and R2 lines, spectra were deconvoluted in GRAMS 32 software with an automatic fitting program by two mixed Gaussian-Lorentzian functions [130, 131]:

\[
\Phi(\nu) = (1 - M)I_{\text{max}} \exp \left[-\left(\frac{\nu - \nu_m}{w}\right)^2 (4ln2)\right] + M \left[\frac{I_{\text{max}}}{1 + 4\left(\frac{\nu - \nu_m}{w}\right)^2}\right] \quad (3.2)
\]

The first term is the Gaussian component and the second term the Lorentzian component. \(M\) is the relative proportion of Lorentzian component, \(\nu_m\) the frequency at the maximum

68
intensity ($I_{\text{max}}$) and $\omega$ the full width at half maximum. The goodness of fit was evaluated by a factor named reduced $\chi^2$ described by the equation:

$$\chi^2_{\text{Red}} = \frac{1}{f} \sum_{i=1}^{n} \frac{(I_i - I_{i,\text{exp}})^2}{\Delta^2}$$  \hspace{1cm} (3.3)

Here $f$ is the degree of freedom (125) obtained by subtracting the number of fitting coefficients (eight for a single doublet fitted by Eq.(3.2)) from the total number of data points (133); $I_i$ is the calculated intensity for a given frequency; $I_{i,\text{exp}}$ the measured intensity at this frequency and $\Delta^2$ the variance of the measurement. Theoretically, $\chi^2_{\text{Red}} = 1$ means a perfect fit. In reality, the software considers the fitting to have converged when $0 < \chi^2_{\text{Red}} < 3$. Since the R2 line has a linear dependence on stress, the stress was estimated from the peak shift of the R2 line with respect to that of the unstrained sapphire by assuming a state of equibiaxial plane stress and a random distribution of the crystallographic texture in the $\alpha$-$\text{Al}_2\text{O}_3$ scale through the following equation [131, 132]:

$$\Delta\nu = 5.07(\text{cm}^{-1}\text{GPa}^{-1})\sigma$$  \hspace{1cm} (3.4)

Where $\Delta\nu$ is the frequency shift of the R2 line and $\sigma$ is the residual stress.

3.3 Results

3.3.1 Microstructure of as-fabricated alloys

XRD analysis in Fig.3.1a shows that all samples consist of two phases: $\gamma$ and $\gamma'$. The $\gamma'$-phase has an ordered face-centred cubic (f.c.c.) crystal structure (L1$_2$ superlattice), and the $\gamma$-phase is a disordered f.c.c. solid solution. The diffraction peaks of $\gamma$ and $\gamma'$ locate very close to each other, apart from those additional peaks from $\gamma'$. All peaks shift to smaller $2\theta$ positions as the platinum content increases in the alloy, which suggests a continuous lattice expansion of both phases resulting from solid solution of platinum. The variation of the
relative peak intensity of each lattice plane amongst the alloys is due to the large grain size (hundreds of microns, shown in Fig.3.2) of the alloys which limits the numbers of the grains sampled by XRD.

Fig.3.1 (a) X-ray diffraction (XRD) patterns and (b) lattice parameters of as-fabricated alloys. The XRD pattern of each peak contains fundamental diffraction peaks from \( \gamma \) and \( \gamma' \) and the superlattice peak from \( \gamma' \). The crystal orientation corresponding to each peak has been assigned.

To determine the lattice parameter and its evolution with the platinum content, Rietveld refinement was carried out on the diffraction patterns in TOPAS software (Bruker 2005). Space groups of Fm-3m and Pm-3m were assigned to describe the unit cells of \( \gamma \) and \( \gamma' \), respectively. The texture in the XRD patterns was also considered in the fitting process. Fig.3.1b shows the lattice parameters of \( \gamma \) (\( a_\gamma \)) and \( \gamma' \) (\( a_{\gamma'} \)) plotted as functions of the platinum content. For a given platinum content \( a_{\gamma'} \) is larger than \( a_\gamma \). Both \( a_\gamma \) and \( a_{\gamma'} \) are proportional to the platinum content and can be described by the following relationships:

\[
a_{\gamma'} = 3.563 + 0.00174C_{Pt} \\
a_\gamma = 3.545 + 0.000882C_{Pt}
\] (3.5)  (3.6)
where $C_{Pt}$ represents the platinum content (at. %). According to the functions above, $a_{\gamma'}$ increases faster than $a_\gamma$ with the increase in the platinum content, which is due to the fact that platinum prefers to segregate in $\gamma'$ than in $\gamma$ [166].

Fig. 3.2 shows the microstructure of the as-fabricated alloys where the bright areas in Fig. 3.2a-d represent $\gamma'$ and the dark dendritic areas consist of network-structure $\gamma$ with $\gamma'$ blocks embedded within the channels (Fig. 3.2c). The dendrites become finer with increasing platinum content. To quantify the relative amounts of $\gamma$ and $\gamma'$ in the alloys, the optical images were further processed with use of Image J software wherein $\gamma$ and $\gamma'$ were highlighted by white and dark colours (Fig. 3.3a and b). The relative portions of these two phases were worked out based on the area ratio of the two colours, as plotted in Fig. 3.3c. The fraction of $\gamma'$ is almost proportional to the platinum content in the alloy, whereas the relative amount of $\gamma$ shows an opposite trend. Extrapolation based on Fig. 3.3c shows that the alloy becomes single $\gamma'$ when the platinum content extends to $\sim$ 19.at. %. Table 3.1 shows the chemical compositions of $\gamma$ and $\gamma'$ in each alloy determined by EDS. The narrow $\gamma$ channels were pinpointed under SEM using a high magnification (e.g. the inset in Fig. 3.2e). A total of 25 random locations on each phase were selected and the results were averaged. For a given alloy composition, aluminium and platinum are found to segregate in $\gamma'$. The aluminium content in each phase slightly decreases with increasing platinum content. It should be noted that due to the limited cooling rate in the vacuum furnace, precipitation of $\gamma'$ from $\gamma$ tended to occur upon cooling, which could deviate the chemical compositions and the ratio of the two phases from those predicted by the Ni-Al-Pt ternary phase diagram reported by Hayashi et al. [168].
Fig. 3.2 Microstructure of as-fabricated Ni-20Al (a), Ni-20Al-5Pt (b), Ni-20Al-10Pt (c and e), and Ni-20Al-15Pt (d and f). The inset in Fig. 3.2e shows a magnified morphology of the $\gamma/\gamma'$ region used to pinpoint the narrow $\gamma$ channel for EDS analysis. The EBSD map (f) with color-coded inverse pole figure (IPF) shows that the alloy has a grain size of hundreds of micrometers.
### Table 3.1 Chemical compositions (at. %) of $\gamma$ and $\gamma'$ in each alloy

<table>
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<tr>
<th></th>
<th>Ni-20Al</th>
<th>Ni-20Al-5Pt</th>
<th>Ni-20Al-10Pt</th>
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<tr>
<td></td>
<td>$\gamma'$</td>
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<td>$\gamma$</td>
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<td>68.2</td>
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<tr>
<td>Pt</td>
<td>/</td>
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<td>5.74</td>
<td>15.89</td>
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Fig. 3.3 Procedures to determine the relative amount of $\gamma$ and $\gamma'$ in the alloys. (a) optical images of Ni-20Al-5Pt; (b) threshold image of two phases in white and black; (c) evolution of the relative amount of $\gamma$ and $\gamma'$ with the platinum content. Calculations are based on the area ratio of the two colors.
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3.3.2 Oxide spallation

Compared to the Pt-containing alloys, Ni-20Al is more susceptible to oxide spallation. Fig.3.4 gives an example of this performance difference. Exposed metal surface (the bright areas marked by white arrows in Fig.3.4a) left by detached oxide is observed on Ni-20Al after 4 hour oxidation, but no such spallation is found on Ni-20Al-15Pt (Fig.3.4b). For Ni-20Al, spallation occurs at both the oxide/alloy interface and the interface between the transient oxide and α-Al₂O₃ (the areas marked by the dark arrows in Fig.3.4a). After 100 hour oxidation, spallation occurs all over the surface of Ni-20Al (Fig.3.4c). However, spallation is significantly reduced on Ni-20Al-10Pt (Fig.3.4d) and the oxide scale is almost intact on Ni-20Al-15Pt (Fig.3.4e). Therefore, the addition of platinum improves the resistance of the Ni-20Al alloy to oxide spallation and this improvement becomes more significant as the content of platinum increases.

Fig.3.4 Optical images of (a) Ni-Al and (b) Ni-20Al-15Pt after oxidation at 1150 °C for 4 hours; surface appearances of (c) Ni-20Al (b) Ni-20Al-10Pt and (c) Ni-20Al-15Pt after oxidation at 1150°C for 100 h. The white and black arrows in (a) mark the spallation between the oxide and the metal, and the spallation at the interface between the oxide layers, respectively.
3.3.3 Oxide microstructure and growth kinetics

Fig. 3.5 shows phase compositions in the oxides grown on Ni-20Al and Ni-20Al-15Pt after isothermal oxidation for 100 h, where both $\alpha$-$\text{Al}_2\text{O}_3$ and spinel (NiAl$_2$O$_4$) are found on both alloys. However, NiO (peaks denoted as “3”) is only identified in the oxide on Ni-20Al. This demonstrates that growth of NiO on the alloy with a high platinum content is inhibited.

![XRD patterns](image)

**Fig. 3.5** Glancing angle (3°) XRD patterns of the oxide on Ni-20Al and Ni-20Al-15Pt

Fig. 3.6 shows the microstructure of the oxides on Ni-20Al, Ni-20Al-10Pt and Ni-20Al-15Pt after isothermal oxidation for 100 hours. Oxide scales are essentially duplex in structure, with outer transient oxide (NiO and NiAl$_2$O$_4$) and inner $\alpha$-$\text{Al}_2\text{O}_3$. The main body of the oxide on Ni-20Al is NiO and NiAl$_2$O$_4$, whereas $\alpha$-$\text{Al}_2\text{O}_3$ with column-shape grains dominates the compositions of the oxides on Ni-20Al-10Pt and Ni-20Al-15Pt. This confirms that platinum promotes the growth of $\alpha$-$\text{Al}_2\text{O}_3$. NiO is not observed on Ni-20Al-
15Pt, which is in agreement with the GAXRD results (Fig. 3.5) where no NiO is detected on Ni-20Al-15Pt. Fig. 3.6d shows a representative spallation area at the $\alpha$-$\text{Al}_2\text{O}_3$/NiAl$_2$O$_4$ interface where a large number of pores is present. The formation of those interfacial voids is probably due to a solid-state reaction between $\alpha$-$\text{Al}_2\text{O}_3$ and NiO. When the reaction occurs, a volume contraction arises, leading to the formation of those pores [10].

Fig. 3.6 Fracture cross-sections of the TGO on (a) Ni-20Al, (b) Ni-20Al-10Pt and (c) Ni-20Al-15Pt after oxidation at 1150 °C for 100 hours; (d) spallation at the interface between the Ni-based transient oxide and the $\alpha$-$\text{Al}_2\text{O}_3$ on Ni-20Al-10Pt after oxidation at 1150 °C for 100 hours. M, A and O denote alloy, $\alpha$-$\text{Al}_2\text{O}_3$ and Ni-based transient oxide, respectively. Images were captured at a 60° tilt.

Fig. 3.7a shows the TG results of Ni-20Al and Ni-20Al-15Pt after 100 hour isothermal oxidation. Both curves of mass gain against time are continuous and smooth, indicating that there were no cracks or spallation during the oxidation process. A larger mass gain per
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unit area is obtained on the Ni-20Al alloy than that on the Ni-20Al-15Pt alloy for a given oxidation time. This is especially salient within the initial period of oxidation (≤ 1 hour) during which a fast mass build-up occurred on Ni-20Al. This supports the SEM results wherein Ni-20Al has a thicker oxide than Ni-20Al-15Pt (Fig. 3.6).

In order to work out the oxidation rate throughout the 100 h oxidation, the mass gain curve of each sample is first fitted with a Logistic function (which gives the best fit among various functions tried) below:

\begin{align*}
m_{\text{Ni-20Al}} &= 21.5329 + \frac{-20.2207}{1 + \left(\frac{t}{310359.3717}\right)^{0.35843}} \quad (R^2 = 0.99743) \\
m_{\text{Ni-20Al-15Pt}} &= 4.32972 + \frac{-3.70738}{1 + \left(\frac{t}{311.49545}\right)^{0.56974}} \quad (R^2 = 0.99997)
\end{align*}

Where $m$ (mg·cm$^{-2}$) is the mass gain per unit area at time $t$ (h). The instant oxidation rates are then obtained by differentiating $m$ against $t$, as shown in Fig.3.7b-d.

Both Ni-20Al and Ni-20Al-15Pt start with a high mass gain rate (Fig.3.7b), corresponding to the initially fast growth of NiO on both samples, followed by a rapid drop with oxidation time. For a given oxidation time, especially at the first half an hour, however, the mass gain rate of Ni-20Al is higher than that of Ni-20Al-15Pt, suggesting a faster growth of NiO on Ni-20Al. As the thickness of NiO builds up, the relative content of nickel and the oxygen partial pressure at the oxide/alloy interface decreases, thereby significantly retarding the growth of NiO. In this case, the most thermodynamically stable $\alpha$-Al$_2$O$_3$ nucleates underneath the NiO layer, which further blocks the outward diffusion of Ni$^{2+}$. Therefore, the oxidation rates of both samples rapidly drop with oxidation time as the oxidation is then dominated by the growth of protective $\alpha$-Al$_2$O$_3$. After about 1 hour oxidation, the oxidation rate of Ni-20Al drops to a level that is even lower than that of Ni-
20Al-15Pt (Fig. 3.7c) and this difference in oxidation rate is maintained during further oxidation up to 100 hours (Fig. 3.7c). The results here indicate that while platinum substantially promotes the selective oxidation of aluminium at the very initial stage of oxidation, it slightly increases the growth rate of $\alpha$-$\text{Al}_2\text{O}_3$ once the growth of $\alpha$-$\text{Al}_2\text{O}_3$ takes over the oxidation process.

Fig. 3.7 (a) Mass gain of Ni–20Al and Ni–20Al–15Pt during 100 hour oxidation at 1150 °C; corresponding mass gain rates from (b) 0 to 1 h, (c) 0.5 to 1.5 h and (d) 1.5 to 100 h. Each mass grain curve is fitted with a Logistic function, which is then differentiated to obtain the instant oxidation rates.
3.3.4 Oxide stress

3.3.4.1 Stress evolution during the initial oxidation stage

The surface morphology of the oxides on the γ’ and γ/γ’ areas is different after a short-time oxidation and this distinction is remarkably obvious on the alloy with a higher platinum content, which is exemplified by Fig.3.8a and b. It is also observed that the height of the surface after oxidation shows little dependence on the orientation of the alloy grain, but depends on the region (whether γ/γ’ or pure γ’) in which the oxide grows (Fig.3.8c). Similar phenomena are also observed on other areas as well as other alloys after oxidation. This implies that the crystallographic orientation plays a negligible role in oxidation kinetics of the alloys. The result is similar with the previous study on oxidation of the single-crystal Fe-Cr-Al alloy which has shown that the oxide scales growing on (0 0 1) (1 0 1) and (1 1 1) orientations have almost identical oxidation kinetics [124]. The different oxide morphologies on γ’ and γ/γ’ lead to the necessity to separately measure the stresses within the oxides above those two areas. This can be achieved by the PLPS method due to the different contrast between the oxide above γ’ and γ/γ’ areas under the optical microscope: the former appears brighter and the latter darker (Fig.3.8b). On the other hand, to avoid the effect of grain orientation on stress all measurements were confined on the same grain. This is also available because of the large grain size shown in Fig.3.2f.

Fig.3.8d shows the stress evolution at room temperature in the α-Al₂O₃ scales on the γ’ and γ/γ’ areas during the initial 1 hour oxidation. The scale on the γ/γ’ area shows a compressive stress with a magnitude of ~ 4.5 GPa throughout the oxidation. The corresponding value in the α-Al₂O₃ scale on the γ’ area is ~ 0.8 GPa lower, yet the difference gradually narrows down as the oxidation proceeds. This clearly shows that there is a dependence of stress magnitude on the phases out of which the oxide grows.
Fig. 3.8 SEM (a) and optical (b) images of surface morphology of Ni-20Al-15Pt after 15 min oxidation; (c) topographic profilometer image of grains after 30 min oxidation. The image was recorded by an optical profilometer scanning through the sample surface. The inset shows that the area before oxidation is part of Fig. 3.2f where the grain orientations are shown and (d) evolution of residual stresses in the $\alpha$-Al$_2$O$_3$ scales grown on $\gamma'$ and $\gamma'/\gamma'$ areas of the Ni-20Al-15Pt alloy with oxidation time during the first 60 min oxidation.

3.3.4.2 Stress evolution during further oxidation

After 4 hour oxidation, the stresses are fairly uniform all over the surface, although large variation still exists occasionally. The stresses were measured until oxide spallation occurred (except at the edge).
Fig. 3.9 Typical spectrum of the $\alpha$-$\text{Al}_2\text{O}_3$ scale on Ni-20Al after 4 hour oxidation

Fig. 3.9 shows a typical spectrum from the oxide on Ni-20Al after oxidation for 4 hour. The presence of multiple doublets in the spectrum arises from inhomogeneous stress distribution within the probe volume. The spectrum was deconvoluted by a constrained fitting with two doublets. The solid arrows mark the peaks from the intact $\alpha$-$\text{Al}_2\text{O}_3$ while the dashed arrows represent the peaks from the detached areas. Since this spectrum is detected all over the surface, it suggests that there are numerous local interfacial defects between the substrate and the oxide, besides those visible spallation sites shown in Fig. 3.4a.

Fig. 3.10 shows the evolution of stresses at room temperature in the $\alpha$-$\text{Al}_2\text{O}_3$ scale with oxidation time for both the Ni-20Al-5Pt and Ni-20Al-15Pt samples. In general, the stress in the oxide on Ni-20Al-5Pt is higher than that on Ni-20Al-15Pt. The stress on Ni-20Al-5Pt decreases significantly (from 5.4 GPa to 4.5 GPa) with oxidation time until oxide spalls after 16 hours (Fig. 3.11d), whereas the stress in the oxide on Ni-20Al-15Pt increases slightly (from 4.3 to 4.5 GPa) with the oxidation up to 100 hours. The decrease in the
stress on the Ni-20Al-5Pt sample might be caused by creep or generation of interfacial imperfection upon cooling. To conclude, the magnitude of the residual stresses in α-Al₂O₃ reduces with increasing platinum content in the alloys.

Fig.3.10 Evolution of residual stresses in the α-Al₂O₃ scales on Ni-20Al-5Pt and Ni-20Al-15Pt with oxidation time. The inset shows the fractured cross-section of the oxide formed on Ni-20Al-5Pt after spallation.

3.3.5 Oxide/alloy interfacial morphology

Oxide grooves, as shown in Fig.3.11a, formed along the grain boundaries of the Ni-20Al after 15 minute oxidation. Fig.3.11b shows the cross-section produced by a FIB across one of the grooves. The oxide consists of NiO, NiAl₂O₄ and α-Al₂O₃ layers from outside to inside. Particularly, the oxide has the smallest thickness right on top of the grain boundary of the alloy substrate. This leads to the formation of a ridge-like oxide/substrate interface
underneath the grooved oxide. The reason for the inhomogeneous oxide thickness is unclear at the moment. No obvious difference in elemental composition is detected between the grain boundary of the alloy and its inner part of the grain. One possible reason is the fast diffusion of aluminium along the grain boundary during oxidation, which leads to a quicker formation of the $\alpha$-$\text{Al}_2\text{O}_3$ scale, and thereby inhibits the growth of the nickel oxide more significantly than that on the inner part of the grain. Further study is needed to confirm this explanation.

Fig.3.11 SEM images of (a-c) Ni-20Al and (d) Ni-20Al-15Pt after oxidation, showing the formation of a ridge at the oxide/alloy interface and the oxide spallation that preferentially occurs at those ridges. The black frame shown in (a) denotes the grain boundary at which a section was cut using a FIB.

It is widely accepted that an undulated interface is detrimental to the adhesion of oxide, where the oxide is subjected to compressive stress laterally. For example, when a ridged interfacial morphology forms, as shown in Fig.3.11, the stress in the oxide redistributes around the ridge and a tensile stress normal to the interface is generated at the crest of the
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ridge. This tensile stress could initiate crack nucleation and propagation. Fig.3.11c and d shows the typical oxide spallation sites on Ni-20Al and Ni-20Al-5Pt. Most of the oxide failure on Ni-20Al occurs along the ridge-like grain boundary of the substrate after 4 hour oxidation, as shown in Fig.3.11c. On Ni-20Al-5Pt, oxide spalls (Fig.3.11d) after 16 hour oxidation and the spallation is also found to preferentially occur along the protruded grain boundaries of the alloy. However, no such spallation is found on Ni-20Al-10Pt or Ni-20Al-15Pt. Instead, the oxide/metal interface is flat without formation of local ridges (Fig.3.12).

Fig.3.12 Optical image of the cross-section of Ni-20Al-15Pt after 100 hour oxidation. Pores are marked by white arrows.

3.4 Discussion

Overall, the spallation of an oxide scale from an alloy is driven by the residual stress in the oxide and resisted by the interfacial toughness. The study shows that the addition of platinum to the Ni-20Al alloy promotes the formation of a protective α-Al₂O₃ scale and reduces the residual stress in the oxide, which lowers the driving force for the spallation of the oxide according to Eq. (3.1). On the other hand, the addition of platinum prevents the formation of interfacial ridges along the grain boundaries of the alloys, which reduces the
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out-of-plane tensile stress across the oxide/alloy interface, therefore improving the adhesion to the alloy. This effect can be also attributed to the fact that platinum inhibits the initial oxidation of nickel and therefore eliminates the formation of a ridged oxide/alloy interface. The following sessions discuss the mechanisms by which platinum promotes the selective oxidation of aluminium and reduces the residual stress in the oxide.

3.4.1 Effect of platinum addition on oxidation

The study above shows that the addition of platinum improves the oxidation resistance of the Ni-20Al alloys by promoting the formation of a protective $\alpha$-$\text{Al}_2\text{O}_3$ scale. This is consistent with oxidation behaviour of Ni-Al-Pt alloys reported in the literature [63, 92, 165, 166]. This benefit of platinum, as already discussed in previous publications, can be mainly ascribed to the two following aspects. First, as a noble element, platinum is non-reactive and does not form stable oxides under normal oxidation conditions. However, previous experimental results confirm that platinum strongly prefers to replace nickel sites in the lattices of $\gamma'$ and $\gamma$ [166], resulting in an increase in the atom number ratio of aluminium to nickel. This effective aluminium enrichment in the alloy kinetically favours the formation of $\alpha$-$\text{Al}_2\text{O}_3$ relative to NiO. Second, platinum tends to segregate in the subsurface of the Pt-containing alloys during the early stage of oxidation [166, 169]. The enrichment of the platinum in the alloy subsurface reduces the activity of aluminium at the oxide/alloy interface [169], which facilitates the diffusion flux of aluminium from the inner part to the alloy/oxide interface, and therefore provides an aluminium reservoir at the interface. Both of these contribute to the formation of an oxidation-resistant $\alpha$-$\text{Al}_2\text{O}_3$ scale.

The early establishment of the protective $\alpha$-$\text{Al}_2\text{O}_3$ scale inhibits the initially competitive oxidation of nickel and therefore eliminates the formation of a ridged oxide/alloy interface, as shown in Fig.3.11. As long as the aluminium content underneath is enough for the continuous growth of $\alpha$-$\text{Al}_2\text{O}_3$, the growth of any transient oxide will be inhibited. The
absence of the transient oxide also eliminates the opportunities for spallation to occur at the $\text{Al}_2\text{O}_3$/transient oxide interface. Indeed, previous observations on PWA 1480 superalloy after oxidation have shown that the spallation occurs between the spinel and the $\alpha$-$\text{Al}_2\text{O}_3$. Figs. 3.4 and 3.6 in this work also show similar results.

Fig. 3.13 Elemental map of (a) nickel, (b) platinum and (c) aluminium in as-deposited Pt-diffused $\gamma/\gamma'$ bond coat. The thin and Al-rich layer at the top of the bond coat is the TGO scale formed during the deposition process of the thermal barrier coating.

For the commercial Pt-diffused $\gamma/\gamma'$ bond coat, platinum enhances its oxidation resistance in a similar way as it does on the bulk $\gamma/\gamma'$ Ni-Al alloys. Fig. 3.13 shows a representative elemental map of the as-deposited Pt-diffused $\gamma/\gamma'$ bond coat on CMSX-4 superalloy. Fabrication of this coating involves in electroplating of a thin platinum layer (~7-12 $\mu$m) and diffusion treatment in vacuum afterwards [88, 89]. During interdiffusion, platinum first dissolves in the superalloy substrate and then precipitates as Pt-enriched $\gamma'$ and $\gamma$ in which platinum occupies a large amount of the sites originally positioned by nickel. Therefore, the nickel content in the bond coat is lower compared to that in the substrate (Fig. 3.13a). On the other hand, the segregated platinum in the bond coat, especially in $\gamma'$, picks up aluminium from the substrate to the bond coat due to the strong affinity between platinum and aluminium [93] (Fig. 3.13c). The enrichment of aluminium in the bond coat facilitates the formation of the $\text{Al}_2\text{O}_3$ scale and therefore improves the oxidation resistance of the coating.
3.4.2 Effect of platinum addition on oxide stress

The result in Fig.3.8d shows that residual stress in the $\alpha$-$\text{Al}_2\text{O}_3$ scale above pure $\gamma'$ is $\sim 0.8$ GPa lower than that above $\gamma/\gamma'$ mixed area during the first hour oxidation. Basically, residual stresses measured by PLPS at room temperature include the thermal misfit stress ($\sigma_{\text{Tox}}^T$) upon cooling and growth stress ($\sigma_{\text{Gox}}^T$) during oxidation. In order to work them out individually, a couple of assumptions are made as follows:

1. No creep relaxation occurs upon cooling. This assumption is believed to be reasonable based on three aspects. First, the fast cooling rate (air quenching) used in the oxidation experiments is expected to prohibit creep relaxation of both the alloy and the oxide during cooling. Second, high-temperature stress measurements by Zhao et al. have shown that no creep of the Pt-diffused $\gamma/\gamma'$ bond coat occurs at a temperature as high as 1000 °C [90]. Extrapolation of the results based on CTE misfit implies little creep between 1000 °C and 1150°C as well. Third, the thickness of the $\alpha$-$\text{Al}_2\text{O}_3$ scale at the beginning of the oxidation is believed to be too thin (compared to the thickness of the substrate (3 mm)) to cause any plastic deformation of the alloy upon cooling.

2. There is no stress-induced interfacial imperfection which leads to stress relaxation upon cooling. This is also true as shown in Fig.3.15.

Under this circumstance, $\sigma_{\text{Tox}}^T$ and $\sigma_{\text{Gox}}^T$ are calculated using the following formula:

\[
\sigma = \sigma_{\text{Tox}}^T + \frac{E_{\text{ox}}}{E_{\text{ox}}^T} \sigma_{\text{Gox}}^T
\]

\[
\sigma_{\text{Tox}}^T = \frac{E_{\text{ox}}(\alpha_{\text{ox}} - \alpha_m)\Delta T}{(1 - v_{\text{ox}}) + (1 - v_m)h_{\text{ox}}E_{\text{ox}}/h_mE_m}
\]

$E_{\text{ox}}^T$ denotes the elastic modulus of $\alpha$-$\text{Al}_2\text{O}_3$ at oxidation temperature of 1150°C. As the oxide scale is three order of magnitude thinner than the alloy, Eq.(3.10) can be simplified as:
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\[ \sigma_{ox} = \frac{E_{ox}(\alpha_{ox} - \alpha_{m})\Delta T}{(1 - v_{ox})} \]  

(3.11)

Using the only available CTE data of Pt-enriched γ and γ’ [90], the CTE of γ’ is set to be 14.32 and the CTE of γ/γ’ mixed area is calculated to be 14.49 based on the mixed role (the relative ratio of γ’ to γ is about 3:1 according to image analysis on the γ/γ’ mixed area). All other values used in calculation are listed in Table 3.2. \( \sigma_{ox} \) and \( \sigma_{Gox} \) on both γ’ and γ/γ’ areas were then obtained by Eq.(3.9) and (3.11) and plotted in Fig.3.14. While the difference between the \( \sigma_{ox} \) on both areas is almost negligible (~0.1GPa), there is significant gap between \( \sigma_{Gox} \) on γ’ and that on γ/γ’. Specifically, while \( \sigma_{Gox} \) on the γ/γ’ area is ~0.7 - 0.8 GPa throughout the first hour oxidation, \( \sigma_{Gox} \) on the γ area is much lower (0 - 0.3 GPa).

<table>
<thead>
<tr>
<th></th>
<th>E(GPa)</th>
<th>E’(GPa)</th>
<th>( \alpha \times 10^6 / ^\circ \text{C} )</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ’</td>
<td>/</td>
<td>/</td>
<td>14.32 [90]</td>
<td>/</td>
</tr>
<tr>
<td>γ/γ’</td>
<td>/</td>
<td>/</td>
<td>14.49</td>
<td>/</td>
</tr>
<tr>
<td>( \alpha )-( \text{Al}_2\text{O}_3 )</td>
<td>380</td>
<td>340 [170]</td>
<td>8.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In searching of reasons for the difference between the growth stresses on γ’ and γ/γ’, FIB was used to reveal the cross-sectional microstructure of the oxide after 1 hour oxidation, as shown in Fig.3.15. The oxides on both γ’ and γ/γ’ show a layer sequence from top Ni-based transient oxide to bottom \( \alpha \)-\( \text{Al}_2\text{O}_3 \), but the transient oxide above γ/γ’ is thicker than that on γ’. No cracking is observed along the oxide/alloy interfaces. Moreover, while the thickness of the \( \alpha \)-\( \text{Al}_2\text{O}_3 \) scales above both areas is almost the same (~500 nm), the oxide/alloy interfaces show different profiles. The oxide/interface scale on γ’ is almost flat, whereas the interface on γ/γ’ becomes slightly wavy.
Fig. 3.14 Growth stresses in the $\alpha$-$\text{Al}_2\text{O}_3$ scales formed on $\gamma'$ and $\gamma/\gamma'$ areas of the Ni-20Al-15Pt alloy as a function of oxidation time during the first hour oxidation. The thermal misfit stresses in the scales on both areas are also shown.

It should be noted that the non-planar interface between the oxide and $\gamma/\gamma'$ invalidates the assumption of biaxial stress, and therefore the calculation based on Eqs. (3.4), (3.9) and (3.11) is no longer valid. However, since there is a direct correspondence between the frequency shift of the R2 line and elastic strain energy in the oxide, the frequency shift still directly reflects the average stress magnitude in the scale. For this reason, the stresses on $\gamma/\gamma'$ in Fig. 3.14 are regarded as equivalent biaxial stresses.
Fig.3.15 Backscattered electron images of the oxide/alloy interfaces on $\gamma'$ (top) and $\gamma/\gamma'$ (bottom) on Ni-20Al-15Pt after 60 min oxidation. The bright spots within the oxide are platinum particles precipitating from the alloy when nickel has been consumed during the oxidation.

In general, the growth stress of an oxide at high temperature is a dynamic competition between the stress generation due to the lateral growth of the oxide and concurrent relaxation through creep. In reality, the growth stress usually maintains under a certain level, irrespective of the oxidation time. For example, the growth stress on FeCrAlY alloy at 1200 °C has been found to be $\sim$ 1 GPa throughout 300 hour oxidation [120]. This suggests that the magnitude of the growth stress is mainly determined by the creep relaxation of the oxide. For a duplex oxide system consisting of outer transient oxide and inner $\alpha-Al_2O_3$, creep of the $\alpha-Al_2O_3$ scale involves in concurrent deformation of the coupled transient
Therefore, compared to a single $\alpha$-$\text{Al}_2\text{O}_3$ layer system (the same thickness and grain size), the relaxation of the $\alpha$-$\text{Al}_2\text{O}_3$ scales on $\gamma/\gamma'$ and $\gamma'$ is retarded due to the additional constrain from the attached transient oxide. Since the transient oxide on $\gamma/\gamma'$ is about four times as thick as that on $\gamma'$ (Fig. 3.15), the relaxation of the $\alpha$-$\text{Al}_2\text{O}_3$ scale on $\gamma/\gamma'$ is more significantly inhibited than that on $\gamma'$, leading to a higher growth stress on $\gamma/\gamma'$. As the relative amount of $\gamma'$ in the alloy is in proportion to the platinum content according to Fig. 3.3, it is believed that an increase in the platinum content would lower the residual stress in the oxide at the early stage of the oxidation.

A plausible explanation of the undulated oxide/alloy interface on $\gamma/\gamma'$ is the uneven growth of NiO over the surface due to chemistry difference between $\gamma$ and $\gamma'$ as well as composition fluctuation in $\gamma$ and $\gamma'$. Indeed, the locations where thicker NiO is present correspond to the concaved profiles of the oxide/alloy interface (Fig. 3.15). On pure $\gamma'$ area, however, oxidation of nickel is significantly suppressed because of its higher platinum and aluminium contents which promote the initial selective oxidation of aluminium, resulting in a flat oxide/alloy interface and a reduced total oxide thickness. The NiO formed in the $\gamma/\gamma'$ regions of Ni-20Al-15Pt after 60 min oxidation, however, is expected to be gradually converted to NiAl$_2$O$_4$ through the solid state reaction between NiO and Al$_2$O$_3$ during the subsequent oxidation, which is confirmed by the results in Fig. 3.5, wherein the NiO peak is not found on Ni-20Al-15Pt after 100 hour oxidation (It is still possible some NiO exists at the surface of Ni-20Al-15Pt after 100 hour oxidation, but the amount may be too low to be detected by XRD). The reaction between NiO and Al$_2$O$_3$ occurs on Ni-20Al during oxidation as well. However, since the NiO layer on Ni-20Al is much thicker than that on Ni-20Al-15Pt (Fig. 3.5 and Fig. 3.11b), the NiO layer is still present on Ni-20Al after 100 h oxidation.

It should be noted that although undulations occur at the oxide/alloy interface in the $\gamma/\gamma'$ region of Ni-20Al-15Pt (Fig. 3.15), the spallation is largely inhibited from this region even
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after prolonged oxidation. This could be explained from several aspects. First, compared to Ni-20Al or Ni-20Al-5Pt on which oxide spallation occurs after oxidation, the $\gamma/\gamma'$ region of Ni-20Al-15Pt has lower stresses in the $\Al_2O_3$ scale (Fig.3.10) and a thinner oxide scale, especially the thickness of the Ni-rich oxide layer. Therefore, the total strain energy in the oxide scale on the $\gamma/\gamma'$ region of Ni-20Al-15Pt is reduced and thereby reduces propensity of spallation. Second, the undulation profile at the interface between the oxide and the $\gamma/\gamma'$ region of Ni-20Al-15Pt is different from that on Ni-20Al or Ni-20Al-5Pt (Fig.3.11b-d). According to the models (either spherical or cylindrical) developed by Gong and Clarke [144], for an undulated oxide scale attached to a metallic substrate, the local tensile stress at the crest of the undulated area increases with increasing curvature. The ridge-like oxide/alloy interface at the grain boundary of Ni-20Al or Ni-20Al-5Pt introduces a large local curvature at the crest of the undulation, which could lead to a large local tensile stress and subsequent spallation at this area. In contrast, such ridge-like oxide/alloy interface is not observed in the $\gamma/\gamma'$ region of Ni-20Al-15Pt. In fact, the undulation at the oxide/alloy interface in the $\gamma/\gamma'$ region of Ni-20Al-15Pt is generally gradual, which lowers the local curvature as well as the tensile stress at the interface. In addition, as the NiO layer in the $\gamma/\gamma'$ region of Ni-20Al-15Pt is gradually converted to spinel through solid state reaction between NiO and $\Al_2O_3$, as confirmed by XRD results in Fig.3.5 and SEM observation in Fig.3.6d, the interface between the NiO layer and the oxide scale underneath disappears eventually. This also eliminates the possibility for the spallation of the NiO layer after long-time oxidation.

The variation of the stress levels on alloys with different platinum contents after long time oxidation can be explained in a similar way. The alloy with less platinum addition tends to form a thicker oxide and undulated oxide/alloy interface for a given oxidation time, which leads to a higher growth stress in the $\alpha$-$\Al_2O_3$ scale and therefore a higher residual stress at room temperature. However, the growth stress calculation based on the Eqs.(3.8) and (3.9)
are not applicable for long time oxidation because creep relaxation or interfacial
imperfection occurred upon cooling. The oxide thickens as oxidation proceeds, which
probably causes the alloy to creep upon cooling. On the other hand, imperfections emerge
along the oxide/alloy interface and eventually lead to oxide spallation (Figs. 3.10 and 3.11).
The rapid stress drop on Ni-20Al-5Pt and oxide spallation shown in Figs. 3.10 and 3.11
suggests creep relaxation and interfacial cracking during cooling.

3.5 Conclusions

Platinum addition into bulk $\gamma/\gamma'$ Ni-20Al alloys improves their resistance to oxide
spallation. This is due to several reasons: (i) platinum facilitates the formation of a
protective $\alpha$-$\text{Al}_2\text{O}_3$ scale; (ii) platinum reduces the growth stress in $\alpha$-$\text{Al}_2\text{O}_3$ scale and (iii)
suppresses formation of a ridge-like oxide/alloy interface. All these benefits from platinum
are attributed to the fact that platinum promotes the selective oxidation of aluminium.
Chapter 4

Rumpling of a NiCoCrAlY bond coat for thermal barrier coating applications

4.1 Introduction

One of the most important origins of the initial flaws at the topcoat/bond coat interface is associated with progressively roughening, also termed rumpling or ratcheting, of the bond coat surface along with the TGO scale during the course of cyclic oxidation [10, 137, 171, 172]. The out-of-plane displacement accompanying rumpling gives rise to a tensile stress across the TGO/bond coat interface, where the TGO scale is compressively stressed in the lateral direction. The tensile stress can initiate interfacial cracking and eventually leads to failure of the TBC. Surface rumpling of $\beta$-(Ni,Pt)Al coatings induced by cyclic oxidation has been extensively investigated by experiments and simulations in the past decades. These studies have shown that the evolution of rumpling depends on oxidation time, oxidation temperature, oxidation mode (cyclic or isothermal), oxidation atmosphere (in air or vacuum), sample configuration (bulk alloys or coatings), coating thickness, content of reactive elements (REs, such as yttrium and hafnium) in the coatings and external load [78, 149-153, 173]. Recently, a comprehensive analytical model (Balint-Hutchinson model) has been developed to simulate rumpling development of the $\beta$-(Ni,Pt)Al bond coat during thermal exposure [110]. The model has incorporated extensive parameters (e.g. TGO growth strain, TGO yielding strength, bond coat stress and bond coat yielding strength) about the properties of the materials and explored the rumpling development under a number of distinct experimental conditions. The predictions of the model have been found to be in agreement with most of the experimental observations reported in the literature, although the correspondence between the experiments and simulations remains to be validated.
Another type of bond coat, made of NiCoCrAlY alloys, also shows a propensity to rumple after oxidation [147, 148, 174, 175], although the coating also shows other concomitant degradation mechanisms apart from rumpling (e.g. thickness heterogeneities (often referred to as “pegs”) accompanied by localised TGO cracks [147, 155, 176-179]). However, few experimental studies have been carried out to systematically investigate rumpling of NiCoCrAlY coatings and how their rumpling could be affected by experimental variables so far to the best our knowledge. On the other hand, since the Balint-Hutchinson model is developed based on continuum mechanics, it is expected that the model is generic and therefore system-independent. Nevertheless, the model has been primarily used to simulate rumpling of the β-(Ni,Pt)Al coating system so far. At this stage, there is still a lack of experimental data to testify whether the model is applicable to predicting rumpling development of the NiCoCrAlY coating. In this work, surface rumpling of a NiCoCrAlY bond coat deposited on a Hastelloy® X superalloy substrate was studied under a variety of experimental conditions. The intent of this work is to present the experimental observations and assessments on rumpling of NiCoCrAlY coatings and to compare the observations with the existing rumpling models. Factors that affect rumpling growth but have not been considered in the existing rumpling models are discussed.

4.2 Materials and methods

4.2.1 Sample preparation

The NiCoCrAlY overlay bond coat was sprayed on one side of Hastelloy® X polycrystalline superalloy strips (55 × 8 × 1.6 mm³) using high velocity oxygen fuel (HVOF) spraying. Table 1 shows the nominal compositions of the as-sprayed NiCoCrAlY coating and the Hastelloy® X superalloy substrate. The thickness of the as-deposited bond coat varies between 200 to 230 μm from place to place (Fig.4.1a), owing to the extensive surface roughness formed during the spraying process. The coating consists of two phases,
generally identified as the $\beta$-phase (grey contrast) and the $\gamma$-phase (light contrast) (Fig. 4.1c).

Table 4.1 Chemical compositions (wt. %) of Hastelloy® X superalloy and NiCoCrAlY coating

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Al</th>
<th>Y</th>
<th>Fe</th>
<th>Mo</th>
<th>W</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy® X</td>
<td>Bal</td>
<td>22</td>
<td>1.5</td>
<td>/</td>
<td>/</td>
<td>18</td>
<td>9</td>
<td>0.6</td>
<td>0.1</td>
<td>1*</td>
<td>1*</td>
<td>0.008*</td>
</tr>
<tr>
<td>NiCoCrAlY</td>
<td>Bal</td>
<td>17</td>
<td>23</td>
<td>12.5</td>
<td>0.45</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
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<td>/</td>
</tr>
</tbody>
</table>

* Maximum

Fig. 4.1 Microstructure of the NiCoCrAlY bond coat: (a) optical image of the cross-section of the as-deposited bond coat; (b) optical image of the cross-section of the bond coat after the removal of the surface asperities through grinding and polishing and (c) bond coat high-magnification backscattered electron (BSE) image showing that the bond coat consists of $\beta$-phase (grey contrast), $\gamma$-phase (white contrast) and interfacial pores (dark contrast) between the NiCoCrAlY particles.
The bulk NiCoCrAlY alloy with the same nominal composition as the as-sprayed NiCoCrAlY coating was fabricated using spark plasma sintering (SPS). Briefly, the powder was packed in a column graphite die with an internal diameter of 28 mm, and densified at 1050 °C using a SPS system (FCT-HP D25/4-SD) in vacuum (< 1 mbar) at a load of 31 KN for 10 minutes. The as-sintered NiCoCrAlY alloy is fully dense (Fig. 4.2a) and consists of the β-phase (dark contrast) and the γ-phase (light contrast). The presence of these two phases is further confirmed by the EBSD phase contrast map shown in Fig. 4.2b where the areas with red color are indexed as the γ-phase and the areas with the blue color the β-phase.

Fig. 4.2 Microstructure of the as-sintered Bulk NiCoCrAlY alloy; (a) BSE image and (b) EBSD phase contrast map. The red color represents the γ-phase and blue color the β-phase.

Rectangular (15 × 8 mm²) and disc (28 mm in diameter and 2 mm thick) samples were cut from the bond-coated superalloy plates and the bulk NiCoCrAlY alloy bar, respectively, using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 5, Struers, Denmark). The surfaces of the coatings and the alloy were progressively ground and polished to a 1 μm finish to remove the existing surface asperities and a macroscopic flat surface was thereby obtained (Fig. 4.1b). This step produced a similar initial root-mean-square roughness (~ 0.05 μm) on all samples. Some coatings were mechanically thinned to
several thicknesses in order to assess the effect of the coating thickness on rumpling development. A micrometer was used to monitor the thickness during the thinning process and an optical microscope was used to double-check the final thickness of the cross-section of the coating edge. Subsequent oxidation experiments showed that coatings with thicknesses less than 50 μm tended to have TGO cracking and spallation after cyclic oxidation for a period of time (e.g. 50 1-hour cycles at 1150°C), and therefore were not used in this study. In addition, Vickers micro-hardness indentations were placed into the surfaces of several samples as markers so that the rumpling evolution of the identical surface areas with increasing numbers of thermal cycles could be tracked.

4.2.2 Thermal treatment

Cyclic oxidation was performed in laboratory air between room temperature and 1150 ºC in a furnace with a stage automatically moving in and out of the heating chamber. Each cycle consisted of 10-minute ramping, 1 hour “hot time” at 1150 ºC and 15-minute cooling. Some additional sets of cyclic oxidation experiments were performed with a shorter “hot time” (10 min) at 1150 ºC in each cycle, while other cycling parameters remained unchanged. A few oxidation experiments were also carried out isothermally at 1150 ºC. The use of different oxidation regimes is to assess the effect of thermal history on rumpling development. Apart from thermal exposure in air, several coating samples were cycled at 1150 ºC in vacuum where the partial pressure of oxygen was significantly reduced (~ 1 × 10^2 mbar) compared to that in air. This was achieved by wrapping the samples in FeCrAlY foils (Goodfellow, UK) and then sealing them in quartz tubes in vacuum. Due to its great resistance to thermal shock, the quartz tube was intact throughout thermal exposure and therefore the vacuum was maintained.

4.2.3 Characterisation methods

The morphology and microstructure of the samples were examined using scanning
electron microscope (SEM, Quanta 650, FEI) coupled with electron backscatter diffraction (EBSD, NordlysNano, Oxford Instruments). SEM images of surface morphology after oxidation were captured at the same tilt angle (60°), so the extent of rumpling could be directly compared. Chemical analysis of the TGO was carried out using scanning transmission electron microscope (STEM, Tecnai™ G², 300kV, FEI) equipped with energy-dispersive X-ray spectroscopy (EDS, X-MaxN 80T SDD, Oxford Instruments). The STEM samples were prepared by a focused ion beam (FIB, Quanta 3D, FEI) cutting through the TGO scale combined with an in-situ life-out technique. The EBSD data were processed and analysed using the HKL Channel 5 software package (Oxford Instruments).

The surface topography and roughness of the samples were characterised using a non-contact optical profilometer (MicroXAM). During thermal cycling, samples were removed from the rig at specific intervals for roughness measurement and then returned for further cycling. The profilometer provided digital images in the form of surface height, \( z_i \), as a function of lateral position, \( x \) and \( y \). The rumpling magnitude is characterised by the root mean square roughness, \( R_q \), given by:

\[
R_q = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (Z_i - \bar{Z})^2}
\]  

(4.1)

Where \( n \) is the number of total data points, \( Z_i \) the height of each point and \( \bar{Z} \) the average height for the entire measured area. The obtained images were leveled to eliminate the effect of any macroscopic slope on the roughness calculation. Since the rumpling patterns show substantial periodicity, the wavelength, \( \lambda \), of rumpling was characterised by the average distance between the adjacent undulation peaks or valleys. At least 10 locations were recorded for each sample.
4.3 Results

4.3.1 Effect of thermal history and coating thickness on rumpling

Fig. 4.3 Surface morphology of (a) a thick coating (~180 μm), (b) a coating with an intermediate thickness (~120 μm) and (c) a thin coating (~60 μm) after 50 1-hour cycles; (d) Surface morphology of a coating (~60 μm thick) after 50 hours isothermal oxidation.

Fig. 4.3a-c shows the surface morphologies of three NiCoCrAlY coatings after 50 1-hour cycles. No TGO spallation (except at the edge of the sample) on the coating surfaces is observed throughout the oxidation experiments. The initially planar coating surfaces rumple after 50 1-hour cycles and the extent of rumpling shows a dependence on the thickness of the coating: the rumpling becomes more pronounced as the thickness of the coating decreases from 180 to 60 μm. The observation is further illustrated by the profilometer images in Fig. 4.4 in which the surface topographies (Fig. 4.4a and b) and typical surface profiles of the line segments along the lateral direction (Fig. 4.4d), together
with the corresponding $R_q$ and $W$ values, of a thin (~ 60 μm) and a thick (~ 180 μm) coating after 50 1-hour cycles are shown. The roughness on the thin coating is significantly higher than that on the thick coating, yet the wavelengths (~ 63-66 μm) of the rumpling on both coatings are more or less the same. The rumpling amplitudes, wavelengths and their ranges for the different coating thicknesses and thermal cycles are listed in Table 4.2. For comparison, the coating surfaces, irrespective of the coating thickness, show far less rumpling after 50 hour isothermal oxidation (e.g. Fig.4.3d). This indicates that for the same cumulative exposure time at 1150°C, at least for the oxidation time used in this study, the bond coat is more susceptible to rumpling under cyclic oxidation.

![Fig.4.4 Profilometer images of three coatings after cyclic oxidation: (a) a thin coating (~ 60 μm) after 50 1-hour cycles; (b) a thick coating (~ 180 μm) after 50 1-hour cycles; (c) a thin coating (~ 60 μm) after 50 10-minute cycles; (d) surface profiles of the white lines in a-c](image-url)
Table 4.2 Roughness ($R_q$) and wavelength ($\lambda$) of coatings after thermal cycling

<table>
<thead>
<tr>
<th>Coatings (≈ 180 μm thick) after 50 1-hour cycles</th>
<th>$R_q$ (μm)</th>
<th>$\lambda$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.71±0.07</td>
<td>65.13±4.56</td>
<td></td>
</tr>
<tr>
<td>Coatings (≈ 60 μm thick) after 50 1-hour cycles</td>
<td>1.26±0.11</td>
<td>64.39±3.52</td>
</tr>
<tr>
<td>Coatings (≈ 60 μm thick) after 50 10-minute cycles</td>
<td>0.85±0.08</td>
<td>52.02±4.19</td>
</tr>
</tbody>
</table>

Fig. 4.5a shows the surface morphology of the coating (≈ 60 μm thick) after 50 10-minute cycles. While the coating surface rumple as well after 50 10-minute cycles, the extent of rumpling is less pronounced compared with that after 50 1-hour cycles (Fig. 4.3c). This observation could be further illustrated by the profilometer images (Fig. 4.4a and c) where surface roughness and profiles of line interceptions (Fig. 4.4d) after 50 1-hour and 10-minute cycles are compared. The characteristic wavelength of rumpling (≈ 50 μm) after 50 10-minute cycles is smaller than that after 50 1-hour cycles (≈ 66 μm) as well. In short, the observation suggests that for a given cycle number the exposure time at peak temperature plays an important role in rumpling growth.

Fig. 4.5 Surface morphology of (a) a NiCoCrAlY coating (≈ 60 μm thick) and (b) a bulk NiCoCrAlY alloy after 50 10-minute cycles

4.3.2 Rumpling of bulk NiCoCrAlY alloys

In contrast to the coating deposited on the superalloy substrate, the surface of the bulk
NiCoCrAlY alloy shows a much less propensity to rumple after cyclic oxidation. This is illustrated in Fig. 4.5b which shows the surface morphology of the alloy after 50 10-minute cycles. The magnitude of rumpling is greatly reduced compared with that on the coating surface (Fig. 4.5a). This demonstrates that the presence of the superalloy substrate is essential to rumpling development. Observations on rumpling of the bulk NiCoCrAlY alloys after 50 1-hour cycles are not shown since the samples have been through catastrophic TGO spallation and reoxidation, and thereby impeding the application of the profilometer for quantitative assessment of roughness.

4.3.3 Evolution of rumpling with cyclic oxidation

Fig. 4.6a-e presents a series of profilometer images recorded from the identical regions of a coating surface (~ 60 μm thick) to illustrate the evolution of rumpling with increasing number of 10-minute cycles. The initially flat surface gradually roughens with increasing number of thermal cycles. Comparison of these images reveals that once rumpling is initiated, the areas above the average surface plane continue to bow up while the areas below the average surface plane continue to depress during the subsequent cyclic oxidation. This observation is similar to the phenomenon described in the ratcheting mechanism of the TGO proposed by He et al. [172]. Fig. 4.6f shows the evolution of the height profile of a line segment (the white line in Fig. 4.6a) across the area probed during cyclic oxidation. The height profiles clearly show that the coating surface progressively moves either up or down with respect to the average surface plane. The surface roughness $R_q$, calculated based on the cross-sectional height profile using Eq (4.1), increases from 0.21 μm after 5 cycles to 0.87 μm after 50 cycles.

Compared to the coating samples, rumpling increment on bulk NiCoCrAlY alloy samples is almost indistinguishable with increasing cycle number, as shown in Fig. 4.7a-d where profilometer images recorded from identical regions are presented. The surface topography
after 10 10-minute cycles is almost the same as that after 50 10-minute cycles. This is further confirmed by the evolution of the height profile of the line segment (the white line in Fig.4.7a) with cyclic oxidation, as shown in Fig.4.7e where the roughness only slightly increases from 0.17 after 10 cycles to 0.3 μm after 50 cycles.

Fig.4.6 Profilometer images of a NiCoCrAlY coating surface after (a) 5 10-minute cycles, (b) 10 10-minute cycles, (c) 20 10-minute cycles, (d) 35 10-minute cycles and (e) 50 10-minute cycles recorded at identical regions, as illustrated by the indentation marks. (f) The evolution of the surface profile and corresponding $R_q$ of the line interception shown in a
Fig. 4.7 Profilometer images of a bulk NiCoCrAlY alloy surface after (a) 10 10-minute cycles, (b) 20 10-minute cycles, (c) 35 10-minute cycles and (d) 50 10-minute cycles and recorded at identical regions, as illustrated by the indentation mark. (e) The evolution of the surface profile and corresponding $R_q$ of the line interception shown in d.
4.3.4 Microstructure examination

Fig. 4.8 Microstructure of (a) a thick coating (~180 μm) and (b) a thin coating (~60 μm) after 50 1-hour cycles; (c-d) fractured cross-sections of the TGO on the thick and thin coating, respectively, at the edges of the surfaces. The inset in Fig. 4.8a is an EBSD phase contrast map where the red color represents the γ-phase and the blue color the β-phase.

Fig. 4.8a and b shows the cross-sectional microstructure of a thick (~180 μm) and a thin coating (~60 μm) after 50 cycles. A TGO scale with a thickness of about 3.5 μm forms on both coatings. The white contrast in the TGO is Y-rich alumina garnet (YAG). The thickness of the TGO is fairly uniform all over the coating surface, suggesting that
rumpling could not be induced by oxide intrusions or variation of the oxide growth rate from place to place. Due to the selective oxidation of aluminium and the interdiffusion between the coating and the substrate, the β-phase near the TGO/coating interface and the coating/substrate interface decomposes to the γ-phase, leading to the formation of a layered structure through the coating thickness: an Al-depleted γ-phase layer at the top, a γ/β mixed layer in the middle and a γ-phase layer at the bottom. As a matter of fact, for the thin coating the aluminium depletion becomes so extensive that only a small amount of the β-phase could be observed. The fractured cross-sections of the TGO scales captured at the edges of both coatings show negligible difference in terms of thickness and microstructure (Fig.4.8c and d). The average grain size of both γ- and β-phase is less than 10 μm (the inset in Fig.4.8a), which is significantly smaller than the characteristic wavelengths of the rumpling patterns. This feature is different from the rumpling behaviour of the β-(Ni,Pt)Al bond coat on which the wavelength of rumpling is generally comparable with the average grain size of the coating [116, 145].

Two orientation maps of the TGO grains on a thick bond coat after 50 1-hour cycles are given in Fig.4.9a and d. As previous studies have demonstrated that the TGO scale may or may not exhibit a (0001) fiber texture parallel to the bond coat/TGO interface normal, depending on the composition of the bond coat and the processing of the ceramic topcoat [113], the colors in Fig.4.9a and d are coded based on the degrees away from the (0001) fiber component. It can be observed from the corresponding distribution plots (Fig.4.9b and e) that most of the (0001) basal normals are substantially misaligned with the interface normal and there is no dominant frequency of the deviation angle, which implies that the TGO grains show no significant basal texture along the interface normal. This is further confirmed by the pole figures in Fig.4.9c and f where the poles of (0001) planes are distributed all over the projection plane without a segregated zone. Fig.4.10 presents the orientation maps (Fig.4.10a and d) and the corresponding frequency plots (Fig.4.10b and e)
as well as pole figures (Fig. 4.10c and f) of the TGO grains on a thin coating after 50 1-hour cycles. These figures demonstrate similar features with those in Fig. 4.9, suggesting that the TGO grains on the thin coating show no significant basal texture as well. These results are similar to previous texture analysis of the TGO grains by X-ray diffraction on a FeCrAlY alloy where the columnar $\alpha$-Al$_2$O$_3$ grains on FeCrAlY show no significant fiber texture along the surface normal [180].

Fig. 4.9 Analysis of microtexture of the TGO grains on a thick (~ 180 μm) bond coat after 50 1-hour cycles. (a, d) orientation maps combined with band contrast; (b, e) colour legend shows deviation of (0001) basal normal away from the surface normal as well as relative frequency of the deviation; (c, f) pole figures. Colors represent degrees away from the surface normal as shown in legend in b and e.
Fig. 4.10 Analysis of microtexture of the TGO grains on a thin (~ 60 μm) bond coat after 50 1-hour cycles. (a, d) orientation maps combined with band contrast; (b, e) colour legend shows deviation of (0001) basal normal away from the surface normal as well as relative frequency of the deviation; (c, f) pole figures projected in X-Z planes. Colors represent degrees away from the surface normal as shown in the legend in b and e.

Fig. 4.11 shows the STEM-EDS mapping across a TGO grain boundary on a thick coating (~ 180 μm) after 50 1-hour cycles. Signal from yttrium (Fig. 4.11e) is extremely weak and no segregation of yttrium is found at the boundary. Considering the sensitivity of the STEM-EDS, the content of yttrium should be so low that we believe that there is essentially no yttrium at the TGO grain boundary. Examination of other TGO grain boundaries and the TGO on the thin coating shows no detectable segregation of yttrium at TGO grain
boundaries as well. Instead, chromium is found to segregate at the TGO grain boundaries (Fig.4.11d). One possible reason for this chromium enrichment at the TGO grain boundaries is the incorporation of the Cr-rich oxide, which forms at the very initial stage of the oxidation, into the later-formed α-Al₂O₃ during subsequent high temperature oxidation [181]. However, it is expected that the segregation of chromium at TGO grain boundaries has negligible effect on the growth rate of the TGO due to the following two reasons. First, Cr³⁺ has the same valence as Al³⁺ and therefore does not introduce defects (e.g. vacancies) into the oxide. Second, the radium of Cr³⁺ is comparable to that of Al³⁺ and therefore does not efficiently block the diffusion flux of Al³⁺ [104]. The effect of the segregation of chromium on the creep resistance of the TGO is not yet clear.

![STEM EDS map across a TGO grain boundary on a NiCoCrAlY coating (~ 180 μm thick) after 50 1-hour cycles](image)

- (a) electron image, (b) oxygen, (c) aluminium, (d) chromium and (e) yttrium
4.3.5 Rumpling of coatings after cycling in vacuum

Fig. 4.12 Microstructure of a NiCoCrAlY coating (~ 60 μm thick) after 50 1-hour cycles in vacuum: (a) general view of the cross-section, (b) surface morphology (c) higher magnification of the cross-section showing TGO cracking and separation at the TGO/bond coat interface, (d) fractured cross-section of the TGO at the edge of surface and (e) profilometer image showing the surface roughness and characteristic wavelength.

Fig. 4.12 shows the surface and cross-sectional morphologies of the bond coat (~ 60 μm thick) after 50 1-hour cycles in vacuum. The coating surface rumpling as well, yet the roughness (~ 1.09 μm, Fig. 4.12b and d) and wavelength (~ 45 μm, Fig. 4.12b and d) are both slightly lower than those after cycling in air (Rq ≈ 1.23 μm and W ≈ 66 μm, Fig. 4.3c and Fig.4.4a). The thickness of the TGO scale is about 1.6 μm (Fig.4.12d), approximately 2 times thinner in comparison with that after the same exposure time in the air (~ 3.5 μm, Fig.4.8). Cracking is observed through the TGO scale and along the TGO/coating interface around the crest part of the rumpling (Fig.4.12c), which is believed to be associated with the shear and tensile stress at the interface induced by the undulated geometry. Since the microstructure of the coating (with the same thickness) after thermal cycling in vacuum is more or less the same as that after cycling in air (Fig.4.8b and Fig.4.12a, both coatings are susceptible to severe aluminium depletion and subsequent β to γ phase transformation due to coating/substrate interdiffusion) and the thermo-mechanical history...
of both coatings are therefore expected to be the same as well, the lower surface roughness after cycling in vacuum suggests that the TGO growth rate, or the TGO thickness, is also an important factor for rumpling development.

4.4 Discussion

4.4.1 Fundamental rumpling mechanism

In terms of geometric profile, surface rumpling indicates overall lateral lengthening of the TGO relative to that on a flat surface. The lengthening of the TGO could be associated with either of the following two mechanisms. One is the lateral growth strain of the TGO and concurrent creep of the coating in compliance with the TGO. The other is the out-of-plane distortion of the coating surface (induced by the volume change of phase transformations of the coating [150], for instance) and concomitant TGO creep to accommodate the deformation of the coating surface. While these two mechanisms may lead to the same experimental observations, they represent two rather contrasting rumpling processes. The former suggests that the fundamental driving force for rumpling development is TGO lateral growth strain, while the latter implies that rumpling growth is driven by deformation of the coating surface and the growth strain of the TGO only plays a secondary role. Another intrinsic difference between these two mechanisms is that the latter does not necessarily require lateral growth strain of the TGO; the TGO simply bends to accommodate the distortion of the coating surface for geometry compatibility.

However, the concept that rumpling is driven by deformation of the coating surface and the TGO deforms in compliance with the coating is inconsistent with some observations in this work. As suggested by Tolpygo and Clarke [150], distortion of a β-(Ni,Pt)Al coating surface could be induced by volume reduction accompanying a localised phase transformation from the low-density β-phase to the high-density γ′- or γ-phase. Nevertheless, this mechanism is unlikely to be applicable to the scenario in this study since
the $\beta$ to $\gamma$ transformation in the NiCoCrAlY coating is rather uniform over the entire lateral direction of the coating during the cyclic oxidation, as indicated by the uniform thickness of the $\gamma$-phase layers at the top and bottom of the coating (Fig.4.8). Furthermore, if rumpling were induced by the $\beta$ to $\gamma$ transformation, it would be expected that there is a pattern of transformation locations corresponding to the periodicity of rumpling. However, no such correlation has been observed in this study either. Panat et al. [154] have proposed that rumpling could be possibly induced by surface diffusion driven by stress in the bond coat. One implication of their analysis is that rumpling increment would be effectively shut off as soon as the stress is fully relaxed at the maximum temperature (once the stress is fully released, the bond coat remains stress-free during the rest dwell period and there will be no driving force for surface diffusion). In another word, the rumpling would be independent on the dwelling time at peak temperature as long as the dwell time is sufficient for relaxation of the stress in the bond coat. However, this is not in agreement with the observation in this study which shows that the rumpling magnitude increases with increasing dwell time at the peak for a given cycle number and the same ramp rates. Furthermore, if rumpling is caused by surface diffusion driven by bond coat stress, cycling in vacuum would be expected to produce a larger, at least an equivalent, rumpling magnitude than cycling in air (both coatings undergo same strain/stress history for a given cycle number). This is because the TGO scale in vacuum is thinner than that in air and therefore has a lower bending stiffness which makes it easier to deform to accommodate the distortion of the coating surface. However, this is contradictory to the experimental observation in this study where the rumpling magnitude of the coating after cycling in air is larger than that after cycling in vacuum. Therefore, we believe that the lateral expansion strain in the TGO is the driving force for rumpling, and creep of the bond coat is the accommodation mechanism.
4.4.2 Correlation of rumpling development with the existing model

The observations presented in this work show that the rumpling development on the NiCoCrAlY coating is generally similar to that of the $\beta$-(Ni,Pt)Al coating reported in the literature, both depending on thermal history, sample configuration, coating thickness, and oxidation atmosphere. Therefore, before discussing the effect of these experimental conditions on rumpling development of the NiCoCrAlY bond coat, it is necessary to briefly summarise some key features in the Balint-Hutchinson model that works well on prediction of rumpling growth on the $\beta$-(Ni,Pt)Al bond coat [110]. In this model, rumpling is driven by the lateral growth strain in the TGO and the bond coat deforms in compliance with the TGO. Due to the constraint of the thick, rigid superalloy substrate, coating/substrate thermal misfit and phase transformation (e.g. B2 to martensite) produce an equibiaxial stress in the bond coat upon temperature change. This stress promotes the creep of the bond coat and therefore enhances undulation growth through the interaction between the stress in the bond coat and the stress applied at the bond coat surface by the TGO, before the bond coat stress decays by creep.

One major distinction between isothermal and cyclic oxidation is the stress history in the bond coat. During cyclic oxidation the bond coat undergoes periodic stress relaxation and generation (due to coating/substrate thermal misfit or phase transformations) as the coating is repeatedly cycled between the oxidation temperature and the ambient temperature. The evolution of this stress imposes a profound effect on the creep of the coating. In general, the bond coat can be modelled as a power-law creep material, and its temperature dependence can be described by the following phenomenological equation for steady-state creep:

$$
\dot{\epsilon}_{\text{creep}} = C \left( \frac{\sigma}{E} \right)^n \exp \left( \frac{-Q_{\text{creep}}}{RT} \right)
$$

(4.2)
Where $\varepsilon$ is creep strain and the dot above denoting its time rate of change; $C$ is a constant; $E$ is the temperature dependent Young’s modulus; $\sigma$ is the temperature dependent equiaxial stress in the bond coat; $Q_{\text{creep}}$ is the activation energy for creep; $R$ is gas constant and $T$ is absolute temperature.

At high temperature when bond coat stress is relaxing and the creep resistance of the bond coat is relatively low, the coating is susceptible to undulation growth driven by the normal stress applied on the rumpled coating surface by the laterally compressed TGO layer. As soon as the stress in the bond coat decays completely by creep, the undulation growth is shut off effectively. Further elongation of the TGO during the rest of the dwell period is prohibited: the TGO formed at existing grain boundaries is mainly redistributed as thickening [182]. Since cyclic oxidation periodically renews the stress in the bond coat, rumpling therefore grows on a cycle-by-cycle basis. During isothermal oxidation once the stress in the bond coat relaxes completely, it renders the coating stress-free for the remainder of the isothermal period. The absence of the stress in the coating significantly reduces its creep strain, and therefore no appreciable rumpling is observed. This reason is also applicable to explain the negligible rumpling growth with cyclic oxidation on the NiCoCrAlY alloy where the equibiaxial stress is not present due to the absence of the constraint of the superalloy substrate.

The fact that 50 1-hour cycles produce a larger rumpling magnitude than that after 50 10-minute cycles suggests that the dwell time at 1150 °C is important for rumpling development. However, the lack of substantial rumpling after 50 hours isothermal oxidation suggests that the dwell time at the peak temperature does not play a decisive role in rumpling growth. The key to this dilemma is that although a longer dwell period at peak temperature is not directly correlated to rumpling development, it produces a thicker TGO and therefore an increased compressive force per unit length[110]. The increased force encourages rumpling growth when stress in the bond coat is relaxing during cyclic
oxidation, although the advantage is compromised by the incremental bending stiffness of the thicker TGO. Therefore, for a given cycle number rumpling growth is more pronounced with increasing dwell time at peak temperature. This effect is also applicable to explain the observation that thermal cycling in air produces a larger rumpling magnitude than cycling in vacuum. The former leads to the formation of a thicker TGO, which promotes rumpling growth.

4.4.3 Effect of coating thickness on rumpling development

4.4.3.1 Degradation of coatings and its dependence on thickness

The observation in this work also demonstrates that the rumpling magnitude of the NiCoCrAlY bond coat increases with decreasing coating thickness. This dependence of the extent of rumpling on the coating thickness is similar to the observations by Deb et al. who have studied surface rumpling of \( \beta \)-(Ni,Pt)Al coatings deposited on IN-738 superalloy substrates after cyclic oxidation at 1100°C and found that a thicker coating shows a smaller propensity to rumple [173]. However, in contrast to these observations, Tolpygo and Clarke have studied surface rumpling of NiAl-based overlay coatings deposited on René N5 single crystal superalloy substrates after cyclic oxidation at 1150 °C and found that the coatings with intermediate thicknesses have the maximum rumpling magnitude [152]. To account for the effect of coating thickness on rumpling growth, Balint et al. have extended the existing rumpling model (Balint-Hutchinson model) to include a finite substrate thickness [183]. The revised model reveals that when the coating is thin, it lacks the ability to deform to the extent needed to accommodate the TGO undulations; conversely, when the thickness of the coating increases to a certain level, the strains induced in the substrate reduce the constraint imposed on the coating, again reducing its ability to accommodate the undulations. The interplay of these two opposite effects thus produces a maximum rumpling magnitude on coatings with intermediate thicknesses. The prediction of the
revised model is consistent with the experimental observations by Tolpygo and Clarke [152].

As the model is established on continuum mechanics, it is expected to be generic and valid to any coating system subject to rumpling, including the NiCoCrAlY/Hastelloy system used in this study. It is also expected that with a thorough understanding of the material properties of the NiCoCrAlY coating and subsequent simulations based on those parameters, it would be able to predict how the rumpling magnitude is related to coating thickness. However, the significant degradation of the NiCoCrAlY coatings (Fig.4.8) and its dependence on the coating thickness make the simulations of rumpling of NiCoCrAlY even more complicated.

In the simulations conducted by Balint et al.[183], the thermomechanical properties of the coating (e.g. CTE and yielding strength) are taken to be time- and thickness-independent over the entire thermal cycling process. This assumption is believed to be reasonable for the materials used by Tolpygo and Clarke [152] since their observations show that the coatings undergo little degradation during cyclic oxidation (no data of phase transformations are given in reference, but their cross-sectional images show few phase transformations). Therefore, the dependence of rumpling magnitudes on coating thicknesses is simply caused by the change of the constraint imposed on the coating associated with the variation of the coating thicknesses. However, in case of the NiCoCrAlY/Hastelloy system used in this study, the coatings, especially the thin ones, are subject to extensive aluminium depletion and substantial $\beta$ to $\gamma$ phase transformation after 50 1-hour cycles (Fig.4.8). This degradation could lead to significant changes of the thermomechanical properties of the coatings and compromise the prediction of the simulations using time- and thickness-independent material properties. Specifically, the degradation of the coatings affects the thermomechanical properties and subsequent rumpling development through following two mechanisms. First, it reduces the coating
strength (e.g. yielding strength) at high temperature [100], thereby promoting rumpling growth. This effect becomes more pronounced as the thickness of the coating decreases since a thin coating undergoes more extensive aluminium depletion than a thick coating after oxidation (Fig.4.8). Second, the degradation of the coating induced by coating/substrate interdiffusion assimilates their mutual compositions, leading to a decrease of the coating/substrate thermal misfit strain and thereby retarding rumpling development. This effect, again, is more significant for a thinner coating. The contributions of these two effects to rumpling development are opposite and the net contribution needs to be quantitatively assessed by future modelling. However, the observations in this work have shown that the rumpling magnitude of the NiCoCrAlY coatings increase substantially as the coating thickness reduces from ~ 180 μm to ~ 60 μm. This suggests that the relatively rapid loss of the strength of the thin coating caused by the degradation may make it more susceptible to rumpling growth and therefore play an important role in rumpling development. In short, for the NiCoCrAlY/Hastelloy system where the coating appreciably degrades with thermal exposure, the thermomechanical properties of the coating evolve with time and depend on the coating thickness. The dynamic nature of these properties and their dependence on coating thickness needs to be incorporated into future simulations for rumpling development of NiCoCrAlY coatings.

4.4.3.2 Dynamic segregation of yttrium and its dependence on coating thickness

Previous studies have revealed that addition of minor (usually below 1 wt. %) reactive elements (REs, e.g. yttrium and hafnium) into FeCrAl alloys or β-(Ni,Pt)Al bond coats reduces surface undulation after oxidation [78, 124]. This effect is generally believed to be associated with an increase in creep resistance of the TGO due to segregation of REs at TGO grain boundaries. In other words, the TGO acts as a “wet blanket” to suppress significant changes of the surface geometry of the coating. During oxidation yttrium diffuses outwards to the scale-gas interface along the TGO grain boundaries as a result of
the oxygen potential gradient in the metal-scale-gas system [104]. When a supersaturation is reached, Y-rich oxide particles (e.g. YAG) are nucleated and ripen as yttrium ions continue to diffuse outward. Therefore, a diffusion flux of yttrium along the TGO grain boundaries, where the concentration of yttrium is below its solubility limit, is established. However, the STEM EDS mapping in this study (Fig.4.11) reveals that there is hardly any yttrium segregation at the TGO grain boundary. The plausible explanation of this phenomenon is that the temperature (1150°C) and oxidation time (50 hours) used in this study is sufficient to exhaust yttrium from all the coatings irrespective of their thicknesses. If the depletion rate of yttrium in the NiCoCrAlY coatings is controlled by oxygen partial pressure gradient across the TGO, the time needed to exhaust the yttrium from the coating will depend on yttrium reservoir in the coating and thus on the coating thickness. In another word, it will be expected that a thicker coating is able to keep the yttrium diffusion flux, therefore segregation of yttrium at grain boundaries, for a longer time because the amount of yttrium available in the coating increases with increasing thickness. Indeed, previous study on FeCrAlYZr has suggested that exhaustion of the reservoir of the reactive elements occurs earlier on an alloy sample with a smaller thickness [184]. The relatively earlier exhaustion of the dynamic yttrium segregation at the TGO grain boundaries on the thinner coating would make it more susceptible to rumpling due to the decrease of the TGO creep resistance at an earlier time. In short, the central point is that under the same oxidation conditions, a thick coating needs more time to get yttrium exhausted from the coating due to a large yttrium reservoir. Therefore, the time yttrium segregates at the TGO grain boundaries on a thick coating will be longer (which increases the creep resistance of the TGO), and therefore reduce rumpling.

4.4.4 Initiation of rumpling

Rumpling models proposed in the literatures require an initial, pre-existing surface undulation above a critical magnitude for rumpling to evolve with subsequent thermal
cycling. The observations in this study show that rumpling of NiCoCrAlY coatings occurred despite the fact that the surfaces of the coatings were polished before thermal cycling \((R_q=0.05 \text{ um})\). This implies that either the initial surface roughness produced by polishing is large enough for rumpling to develop, or otherwise there is microstructural evolution of the coating during the thermal exposure to initiate rumpling. At this stage, it is unknown whether the former argument is true or not since the critical roughness \((\text{above which rumpling could progress with thermal cycling})\) proposed by the models highly depends on selection of the parameters used in the simulations.

In terms of microstructure evolution to initiate the onset of rumpling, Dryepondt et al. have tracked rumpling evolution of identical regions of a \(\beta\)-(Ni,Pt)Al coating surface during cyclic oxidation and found that surfaces of grains with six or more sides bowed up whereas surfaces of grains with fewer than six sides depressed \([185]\). This out-of-plane movement of grains initiates the onset of rumpling and this phenomenon is ascribed to surface diffusion associated with grain growth of the coating and TGO growth stress. Once initiated, the rumpling evolves in accord with the existing rumpling models. Since NiCoCrAlY coatings undergo grain growth and oxidation during thermal cycling as well, it is expected that the grains would follow the same movement pattern as that on the \(\beta\)-(Ni,Pt)Al coating. However, it is difficult to experimentally verify this prediction due to a few reasons. First, the grain size of the as-deposited NiCoCrAlY coating is extremely small \((\sim 1 \text{ um})\), which makes the sides of grains almost indistinguishable. Second, unlike the large, columnar grains spanning the entire thickness of the \(\beta\)-(Ni,Pt)Al coating (therefore the lateral grain growth is constrained by the underlying interdiffusion zone and superalloy substrate), the equiaxed grains of the NiCoCrAlY coating grow in both in-plane and normal directions. The constant growth or shrinkage of the grains in three dimensions gives even more difficulty in tracking the movement of the grains. In addition, besides grain growth and oxidation, the two-phase NiCoCrAlY is also subject to a \(\beta\) to \(\gamma\) phase
transformation and perhaps elemental diffusion between the two phases upon thermal exposure. The diffusion associated with these two processes may intervene with the atomic flow caused by grain growth, resulting in a more complex diffusion scenario in the NiCoCrAlY coating.

4.5 Conclusions

The surface of a NiCoCrAlY coating deposited on a Ni-base superalloy progressively roughens during cyclic oxidation. The rumpling magnitude depends on thermal history, coating thickness and oxidation atmosphere. Compared to the coating, bulk NiCoCrAlY alloys with the same nominal composition show a much smaller tendency to rumple after thermal cycling. The coatings, especially the thin ones, experience substantial degradation (e.g. $\beta$ to $\gamma$ transformation and exhaustion of yttrium) induced by selective oxidation of aluminium and coating/substrate interdiffusion after thermal exposure. The TGO scales on thick and thin coatings show little difference in terms of thickness, grain size and microtexture. The observations together suggest that rumpling is driven by the lateral growth of the TGO and the coating deforms in compliance with the TGO. The dependence of rumpling development on experimental conditions is generally in agreement with the prediction of the existing model. It is suggested that the degradation of the NiCoCrAlY coatings and its dependence on coating thickness need to be taken into consideration when predicting rumpling development of NiCoCrAlY coatings.
Chapter 5

Characterisation and understanding of residual stresses in a NiCoCrAlY bond coat for thermal barrier coating applications

5.1 Introduction

Due to the intrinsic difference in chemistry and thermal-elastic properties between the bond coat and the superalloy substrate, a thermal misfit stress is generated in the coating upon cooling from high temperature. Watanabe et al. have reported a tensile stress of about 140 MPa in an as-deposited β-(Ni,Pt)Al bond coat deposited on Rene N5 superalloy [109]; Zhao et al. have reported a compressive stress of about 180 MPa in an as-deposited Pt-diffused γ/γ’ bond coat on CMSX-4 superalloy [90]. These stresses are in agreement with those predicted based on the coating/substrate thermal misfit. Furthermore, for the bond coat containing the B2-structure nickel aluminide, a martensitic transformation (from B2 to L1₀) could occur when cooling from a sufficiently high temperature above 1000 °C [59-61, 186]. This phase transformation also gives rise to stress in the bond coat because of the volume shrinkage (~2%) from the parent phase to martensite [60]. Previous experimental assessments and numerical simulations have revealed that the stress in the bond coat, combined with the stress in the TGO scale, drives cyclic undulation of the bond coat/TGO interface [110]. The roughened geometry initiates crack formation at the interface between the bond coat and the TGO scale. The cracks grow on a cycle-by-cycle basis and eventually coalesce to induce spallation failure of the TBCs [10]. The stress in the bond coat, therefore, plays an important role in the degradation of TBCs, and determining this stress and its evolution with thermal exposure is essential to establish a reliable life prediction model of the TBCs.

Although stress measurements on the bond coat have been reported in previous
publications, they have been exclusively focusing on a study of the β-Ni (Pt, Al) and Pt-diffused γ/γ’ bond coats. Measurements of residual stresses in the NiCoCrAlY bond coat have been hardly reported so far to the best of my knowledge. On the other hand, extensive characterisations have been done on the microstructure and phase compositions of the NiCoCrAlY bond coat at room temperature. However, little is known about the evolution of the phase compositions with temperature and how the change of the phase composition would affect the stress in the bond coat. In this study, the sin²Ψ technique was used to study the stress in a NiCoCrAlY bond coat deposited on a Ni-based superalloy substrate [129, 187]. This technique is non-destructive, and therefore allows us to monitor the evolution of the stress with thermal exposure time. The mechanisms responsible for the stress generation were examined and discussed.

5.2. Materials and methods

5.2.1 Sample preparation and thermal treatment

The NiCoCrAlY (Ni–23Co–17Cr–12.5Al–0.45Y (wt. %)) overlay bond coat was deposited on one side of HASTELLOY® X superalloy plates (50 × 30 × 5 mm³) using high velocity oxygen fuel spraying (HVOF). The as-deposited coating is approximately 230 μm thick (Fig.5.1a) with two phases identified as the β-phase (grey contrast) and the γ-phase (white contrast) (Fig.5.1c). Square-shaped samples (15 × 15 mm²) were cut from the coated superalloy plates using a SiC abrasive cutting blade in a precision cut-off machine (Accutom 5, Struers). The surface of the bond coat was ground and polished to a 1 μm finish to remove the surface asperities (Fig.5.1b). The samples were oxidised at 1150 °C for different periods of time up to 50 hours, and then slowly moved out of the hot zone of the furnace using an automatic rig and cooled in air. No spallation of the TGO scale was observed throughout the course of the oxidation.
Fig. 5.1 Microstructure of the NiCoCrAlY bond coat: (a) cross-sectional image of the as-received bond coat showing that the thickness of the coating is about 230 μm. The inset shows the NiCoCrAlY particles on the bond coat surface after deposition; (b) cross-sectional image of the bond coat after the removal of the surface asperities; (c) high-magnification cross-sectional image showing that the bond coat consists of β-phase (grey contrast), γ-phase (white contrast) and interfacial pores (dark contrast) between the NiCoCrAlY particles; (d) highlight of β-phase, γ-phase and pores with red, green and blue contrast, respectively. The area ratio of β to γ is about 3:1.

5.2.2 Bond coat stress measurement

The biaxial stresses in the bond coat were measured using the sin²Ψ method carried out in a portable X-ray diffractometer (Proto iXRD). An X-ray tube and two position sensitive detectors (PSDs) were mounted together in an assembly and tilted around the β angle (the angle between the surface normal and the incident X-ray beam) during the measurement, whereas the sample remained stationary. The twin detectors captured the opposite sides of the diffraction cone, thus enabling two Ψ (the angle between the surface normal and the
bisector of the incident and diffracted beam) offsets to be measured simultaneously. The sample was placed on a motor-driven stage and aligned in the focused geometry with a pointer. The geometry configuration is shown in Fig. 5.2a.

Fig. 5.2 (a) Measurement geometry of the Proto iXRD diffractometer and (b) a typical plot of (311) d-spacing against sin^2Ψ obtained in measuring the bond coat stress after 35 hours oxidation.

Mn Kα radiation (\(\lambda_{Mn} = 2.1031 \, \text{Å}\)) was used to acquire the diffraction peak from the (311) plane of the γ-phase at a 2θ angle around 154° for all measurements. The (311) reflection was selected as it has been shown to be representative of the bulk properties of a polycrystalline Ni-based superalloy without being affected by yielding [188]. The X-rays were illuminated through a brass collimator with an aperture of 2 mm to the sample surface. To remove the instrumental background, a gain measurement was performed on a non-diffracting ferrite material before the measurement. The measurements were performed at eleven ±Ψ angles. A 3° oscillation in the β angle was used at each tilt to improve the sampling statistics. The Bragg angle, \(2\theta_{bs}\), at each tilt was obtained by fitting the profile in XrdWin software with a Gaussian function [187]:
\[ I_\psi = I_{\text{max},\psi} \exp \left[ -\left( \frac{2\theta - 2\theta_\psi}{H_\psi} \right)^2 \left( 4\ln 2 \right) \right] \] (5.1)

where \( I \) is the peak intensity and \( H_\psi \) the full width at half maximum. The acquired \( d_\psi - \sin^2 \Psi \) plot was fitted with a straight line since subsequent measurements showed that the out-of-plane shear stresses were negligible. An example of this fitting is shown in Fig.5.2b. No splitting or oscillation between the data obtained from two tilts (+\( \Psi \) and −\( \Psi \)) can be observed, indicating a negligible out-of-plane shear stress and stress gradient. The slope of the line was used to determine the residual stress (\( \sigma \)) according to the formula [129, 187]:

\[ \sigma = \left( \frac{E}{1 + v} \right)_{(hkl)} \frac{1}{d_n} \frac{\partial (d_\psi)}{\partial (\sin^2 \Psi)} \] (5.2)

where \( E \) and \( v \) are the elastic modulus (200 GPa) and Poisson’s ratio (0.31) of the (311) plane, respectively, and \( d_n \) is the \( d \)-spacing along the surface normal (when \( \Psi = 0 \)). \( d_n \) was estimated based on the (311) diffraction peak of the \( \gamma \)-phase recorded at a 2\( \theta \) angle of about 91° using Cu K\(_\alpha\) radiation \( (\lambda_{\text{Cu}} = 1.5406 \ \text{Å}) \) under the \( \theta/2\theta \) scanning configuration in a powder X-ray diffractometer (Philips PANalytical X’Pert).

25 measurements (a 5 x 5 matrix) were carried out in a grid of a 10 x10 mm\(^2\) area with a step size of 2 mm to map the stress magnitude and distribution in the bond coat. It should be noted that this method is still available even when the TGO scale is present on top of the bond coat after oxidation because the X-rays are capable of penetrating through the scale.

In addition to the stress measurement at room temperature, stress measurements at elevated temperatures were also carried out in the Proto iXRD diffractometer where the sample was heated and held at target temperatures (between room temperature and 1150 °C) using a hot stage (TS1200, Linkam Scientific Instruments) in the course of the measurements. The heating rate between the target temperatures was 20 K·minute\(^{-1}\).
10-minute holds were used to reach a uniform temperature all over the sample before the measurements. The rest procedure of the measurements was similar to that at room temperature. However, since the elastic modulus of the (311) plane of the \( \gamma \)-phase is temperature dependent, the measurement results are, therefore, presented as strains \( \varepsilon \) which are given by:

\[
\varepsilon(T) = \left( \frac{1}{1 + v} \right) \frac{1}{d_n(T)} \frac{\partial [d_\psi(T)]}{\partial (\sin^2 \psi)}
\]  

(5.3)

where \( E \) is not required in the calculation. \( d_n(T) \) was estimated based on the 2\( \theta \) angle of the (311) peak of the \( \gamma \)-phase determined by high temperature X-ray diffraction, as will be described later.

5.2.3 Microstructural and chemical characterisation

The microstructure of the sample was examined using scanning electron microscope (SEM, FEI, Quanta 650) and electron backscatter diffraction (EBSD, Oxford Instruments, NordlysNano). Chemical analysis of the bond coat was executed by energy dispersive X-ray spectroscopy (EDS, Oxford Instruments, X-Max) and X-ray diffraction (XRD, Philips PANalytical X'Pert). To monitor if there was phase transition (e.g. \( \beta \) to \( \gamma \) transformation or otherwise) in the bond coat associated with a temperature change, high temperature X-ray diffraction (HT-XRD) analysis was carried out using a Bruker D8 Advance diffractometer with Cu K\( _{\alpha} \) radiation. The sample was heated up and dwelled at target temperatures in a high temperature chamber (Materials Research Instruments) under a protective atmosphere of pure nitrogen.

Quantitative XRD analysis was performed based on the intensities of the diffraction patterns where texture was not present. The volume fraction of each phase in the two-phase region at a given temperature is given by [187]:

\[
\text{Volume Fraction} = \frac{\text{Intensity of Phase}}{\text{Sum of Intensities of All Phases}}
\]

(5.4)
\[
\frac{V_1}{V_2} = \frac{I_1 R_2}{I_2 R_1}
\]  

(5.4)

where \( I_1 \) and \( I_2 \) are the measured integrated intensity (area) of the phases 1 and 2, respectively. \( R \) is the correction factor defined as [187]:

\[
R_i = \frac{1}{v_i^2} \left[ \left| F_{i,hkl} \right|^2 p_{i,hkl} \left( \frac{1 + \cos^2 \theta_{i,hkl}}{\sin^2 \theta_{i,hkl} \cos \theta_{i,hkl}} \right) \right] e^{-2M_i}
\]  

(5.5)

where \( v \) is the volume of the unit cell (3rd power of the lattice parameter); \( F \) and \( p \) are the structure factor and the multiplicity of the \((hkl)\) reflection, respectively. \( e^{-2M} \) is the temperature factor (a function of the \( \theta \) angle).

The lattice parameter of each phase was determined using the extrapolation against \( \frac{\cos^2 \theta}{\sin \theta} \) method [187]. In this method, the lattice parameter obtained from each peak was plotted against \( \frac{\cos^2 \theta}{\sin \theta} \) and \( \frac{\cos^2 \theta}{\theta} \) and extrapolated to \( \cos^2 \theta = 0 \) to minimise the experimental errors induced by the displacement of the sample surface from the centre of the focusing circle during the HT-XRD measurements.

The structure factor of the disorder f.c.c. \( \gamma \)-phase is given by:

\[
F_{hkl}^\gamma = \left( \sum_{i=1}^{n} f_i c_i \right) (1 + e^{\pi(i h+k)} + e^{\pi(i+k)h} + e^{\pi(i+l)h})
\]  

(5.6)

where \( n \) is the total number of the elements contained in the \( \gamma \)-phase; \( f_i \) is the atomic scattering factor of element \( i \), which is given in the reference [189]; \( c_i \) is the atomic percentage of the element \( i \), determined by EDS. For the ordered B2-structure \( \beta \)-phase, besides the atomic percentage of each element, the atom position of each element in the unit cell needs to be known to calculate the structure factor. This will be specified later.
5.3 Results

5.3.1 Bond coat stress evolution with oxidation time

Fig. 5.3 Bond coat stress maps after oxidation for (a) 2, (b) 5, (c) 10, (d) 20, (e) 35 and (f) 50 hours. (g) Evolution of the bond coat stress with oxidation time.

Fig. 5.3 shows the room temperature stress maps of the bond coat after oxidation for different periods of time. There are a couple of features of the data in Fig. 5.3. One is the time independence of the stress nature and distribution. After any given oxidation time, the stresses are tensile and show fairly uniform distribution over the sampled area. The other feature is the time dependence of the stress magnitude. The average stress in the bond coat...
first grows with the oxidation time and reaches a peak value after 35 hours oxidation. After that, the stress starts to slightly decrease with the oxidation time. Stress data on the as-received bond coat are not available because the diffraction peak from the (311) plane of the γ-phase cannot be detected.

5.3.2 Bond coat stress evolution with temperature

Fig. 5.4 Temperature dependence of the bond coat strain. The sample had been subjected to 50 hours oxidation prior to heating, which produced an average strain of about $1.6 \times 10^{-3}$ (≈312 MPa) in the coating at room temperature.

Fig. 5.4 shows the evolution of the elastic strain in the bond coat with temperature. The sample had been subject to 50 hours oxidation prior to the measurement, which produced an average strain of about $1.6 \times 10^{-3}$ (≈312 MPa) in the coating. The strain is a constant from room temperature to 700 °C, and then drops quickly above 700 °C and onward (when creep starts). The strain in the bond coat at the peak temperature (1150 °C) is close
to 0, no matter whether measured after a dwell time for 10 minutes or 1 hour. This means that no elastic strain is accumulated at 1150 °C. The strain develops and builds up upon cooling from 1150 °C to 600 °C, and then remains constant from 600 °C to room temperature. The ultimate strain at room temperature is approximately half of that before heating. For comparison, a parallel sample, which had been also subject to 50 hours oxidation, was heated up to 1150 °C, and followed by air cooling. The strain is found to be extremely close to the original value before heating, as shown in Fig.5.4. This suggests that the strain in the bond coat depends on the cooling rate. This is reasonable because slow cooling offers more time for creep relaxation, and therefore leads to a lower strain level.

5.3.3 Microstructure evolution of the bond coat

Fig.5.5a and b shows the cross-sections of the bond coat after oxidation for 2 and 50 hours. A thin TGO scale (~500 nm) forms on top of the coating after 2 hours oxidation. Meanwhile, the β-phase near the bond coat/TGO interface and the bond coat/substrate interface decomposes to the γ-phase due to the aluminium depletion induced by TGO growth and bond coat/substrate interdiffusion, leading to the formation of two distinct and continuous γ-phase layers: one (~2 μm thick) next to the TGO scale and the other (the interdiffusion zone, ~13 μm thick) next to the superalloy substrate, as shown in Fig.5.5a. Between the top γ-phase layer and bottom interdiffusion zone is the middle two-phase layer (~185 μm thick) with the γ-phase and the β-phase uniformly distributed within the thickness. After 50 hours oxidation, the TGO scale thickens to approximately 3.5 μm, but remains in contact with the γ-phase layer that has reached a thickness of about 7 μm (Fig.5.5b). The thickness of the γ-phase interdiffusion zone increases to about 35 μm, while the thickness of the middle dual-phase layer shrinks to about 160 μm, but with a coarser γ-phase and β-phase compared to those after oxidation for 2 hours.
Fig. 5.5 SEM images and EDS analysis of the bond coat cross-section: (a) cross-sectional microstructure after oxidation for 2 hours; (b) cross-sectional microstructure after oxidation for 50 hours; (c-g) EDS maps of the area framed within the white rectangular in (b); (h-i) chemical compositions of the $\gamma$-phase and the $\beta$-phase after 50 hours oxidation.

Fig. 5.5c-g illustrates EDS maps taken within the rectangular area framed in Fig. 5.5b. The composition of the TGO scale predominately consists of aluminium and oxygen through the thickness, confirming that the TGO is $\text{Al}_2\text{O}_3$ in nature. A Cr-rich thin layer is detected.
at the top of the TGO scale, indicative of the presence of a Cr-containing oxide (e.g. spinel) that probably forms prior to Al₂O₃ at the initial stage of the oxidation. The γ-phase is enriched with cobalt and chromium, and the β-phase is enriched with aluminium. The chemical compositions of the γ-phase and the β-phase after 50 hours oxidation determined by EDS analysis are shown in Fig.5.5h and i. For the β-phase, the content of nickel (49.8 at.%) is extremely close to that in the stoichiometric β-NiAl. However, the aluminium content in the β-phase (~28%) is significantly lower than the minimum value (~42 at.%) shown in the Ni-Al binary phase diagram. As suggested by previous research, the Al-sublattice in B2 NiAl is always fully occupied [57], and elements such as chromium and cobalt show a stronger preference for the Al-sublattice than nickel does [190]. Therefore, we assume that the alloying elements, chromium and cobalt, occupy the Al-sublattice, and the structure factor of the ordered β-phase is given by:

\[
F_{hkl}^\beta = f_{Ni} + \left( \frac{c_{Al}}{c_{Al} + c_{Co} + c_{Cr}} + f_{Co} \frac{c_{Co}}{c_{Al} + c_{Co} + c_{Cr}} + f_{Cr} \frac{c_{Cr}}{c_{Al} + c_{Co} + c_{Cr}} \right) e^{\pi i (h+k+l)} \]  (5.7)

EDS analysis on both phases after different periods of oxidation time shows little variation of the chemical compositions with oxidation time. Besides the elements that originally exist in the bond coat, trace amounts of alloying elements (iron and molybdenum) that are initially present in the superalloy substrate only, are also found in the γ-phase.

The phase-contrast EBSD maps in Fig.5.6a-c show that, accompanying with aluminium depletion and the subsequent β-phase to γ-phase transformation, the grain size of both phases grows with the oxidation time, yet this remains to be quantified. Substantial annealing twins are found within the γ-phase grains, which are believed to form during the grain growth. Fig.5.6d shows a low-magnification EBSD map of the bond coat near the TGO/bond coat interface after oxidation for 50 hours. The contoured inverse pole figures (Fig.5.6e-g) show the distribution of the transverse direction (TD), normal direction (ND) and rolling direction (RD) with respect to crystallographic axes of the γ-phase in Fig.5.6d.
The maximum pole density is found to be 1.79, indicating that there is little texture present in the \( \gamma \)-phase layer at the top of the bond coat.

Fig. 5.6 EBSD maps of the bond coat cross-section after oxidation for (a) 5 hours, (b) 20 hours and (c-d) 50 hours. The red color represents the \( \gamma \)-phase and blue color the \( \beta \)-phase. The color-contoured inverse pole figures (e-g) show the distribution of the transverse direction (TD), normal direction (ND) and rolling direction (RD) with respect to crystallographic axes of the \( \gamma \)-phase in Fig. 5.6d.

5.3.4 Penetration depth of X-rays

The presence of the \( \gamma \)-phase layer at the top of the bond coat after oxidation introduces the issue of the penetration depth of X-rays in the bond coat. In fact, most metals strongly absorb X-rays, and because of this the intensity of the incident beam is greatly reduced in a very short distance (a few micrometers) below the surface [129, 187]. The diffracted beams therefore originate mainly from a thin surface layer. This could be illustrated by the
evolution of the XRD patterns of the coating with oxidation time, as shown in Fig. 5.7. The peak intensities of the $\beta$-phase drop with the thickening of the $\gamma$-phase layer associated with the oxidation time. As the top $\gamma$-phase layer reaches a thickness of about 7 $\mu$m after 50 hours oxidation, the intensity of the diffracted beam below this thickness becomes so weak that all the peaks of the $\beta$-phase could be hardly observed in the diffraction pattern. Besides, the relative peak intensities of the $\gamma$-phase match greatly with those of the reference $\gamma$-Ni structure, suggesting no texture is present in the $\gamma$-phase layer, which is in agreement with the EBSD result in Fig. 5.6.

Fig. 5.7 Evolution of the X-ray (Cu K$_\alpha$) diffraction patterns of the bond coat with oxidation time. $\alpha$ denotes $\alpha$-$\text{Al}_2\text{O}_3$. The inset is the schematic illustration of the cross-section of the sample.
In case of a flat-plate sample in a diffractometer where the incident angle and diffracted angle are symmetrical with respect to the sample surface ($\Psi = 0$), the fraction, $G_x$, of the total diffracted intensity of a certain reflection from a surface layer of depth, $x$, is given by [187]:

$$G_x = 1 - e^{-\frac{2\mu x}{\sin \theta}}$$  \hspace{1cm} (5.8)

Here $\mu$ is the linear attenuation coefficient of the material, which depends on the energy of the radiation source. $\theta$ is the Bragg angle of the $(hkl)$ reflection. Eq. (5.8) can be put into the following form:

$$x = \frac{\ln \left( \frac{1}{1 - G_x} \right)}{2\mu} \sin \theta$$  \hspace{1cm} (5.9)

$x$ is defined as the penetration depth when $G_x$ reaches a certain value. Therefore, the penetration depth of the X-rays into a given material depends on its linear attenuation coefficient and the diffraction angle of the $(hkl)$ reflection. For Ni-base alloys, the maximum penetration depth of the Mn Kα radiation is around 4 μm [90, 129]. Under the circumstance when a series of non-zero $\Psi$ angles are involved (e.g. Proto diffractometer), the relationship between $x_{\Psi=0}$ and $x_{\Psi\neq0}$ into a given reflection (e.g. (311) plane of the $\gamma$-phase) is given by [129]:

$$x_{\Psi\neq0} = \frac{\ln \left( \frac{1}{1 - G_x} \right)}{\mu \left( \frac{1}{\sin(\theta + \Psi)} + \frac{1}{\sin(\theta - \Psi)} \right)}$$  \hspace{1cm} (5.10)

Combining Eqs. (5.9) and (5.10), we have

$$x_{\Psi=0} = \frac{1}{\sin(\theta + \Psi)} + \frac{1}{\sin(\theta - \Psi)} \frac{1}{2 \sin \theta}$$  \hspace{1cm} (5.11)
The dependence of the penetration depth on the \( \sin^2\Psi \) values used in this study is plotted and shown in Fig. 5.8, provided that \( x_{\Psi=\theta} = 4 \, \mu m \) and \( 2\theta = 154^\circ \). The penetration depth decreases with the increase of \( \sin^2\Psi \). The average penetration depth over the 11 pairs of \( \pm\Psi \) angles is about 3.5 \( \mu m \). Besides, the attenuation effect through the TGO scale on top of the bond coat after oxidation further compromises the penetration depth of the Mn K\( \alpha \) radiation into the bond coat. Therefore, we conclude that the results in Fig. 5.3 only give the stresses in the \( \gamma \)-phase layer at the top of the bond coat.

![Graph showing penetration depth vs. \( \sin^2\Psi \)](image)

**5.3.5 Quantitative XRD analysis**

Fig. 5.9 shows the XRD patterns of the bond coat after different periods of oxidation time. The TGO scale and the \( \gamma \)-phase layer formed during oxidation have been ground and polished off prior to scanning, which exposed the two-phase (\( \beta+\gamma \)) layer to the X-rays, as shown in the inset in Fig. 5.9. No martensite peak is identified in the diffraction patterns throughout the course of the oxidation. This suggests that there is either no martensite in
the bond coat or the amount of the martensite is extremely low and therefore beyond the measurable limit of the XRD. The relative peak intensities of either phase are in good agreement with those of the reference \(\gamma\)-Ni or \(\beta\)-NiAl structure, suggesting no texture is present in the volume probed by the X-ray.

Fig.5.9 X-ray (Cu K\(_\alpha\)) diffraction patterns of the bond coat after different periods of oxidation time. The TGO scale and the \(\gamma\)-phase layer formed during oxidation had been removed by grinding and polishing prior to scanning. The inset is a schematic illustration of the cross-section of the sample.
Fig. 5.10 X-ray (Cu Kα) diffraction patterns of the bond coat upon heating: (a) full range pattern and (b) partial range pattern highlighting evolution of (111) γ and (110) β peaks with temperature. Prior to heating and scanning, the bond coat had been subjected to 50 hours oxidation and the TGO scale and the γ-phase layer formed during oxidation had been removed by grinding and polishing. The inset in Fig. 10a is a schematic illustration of the cross-section of the sample.

Fig. 5.10 shows the HT-XRD patterns of the bond coat after 50 hours oxidation. The TGO scale and the γ-layer were removed prior to heating and scanning, which exposed the two-phase (β+γ) layer to the X-rays, as shown in the inset in Fig. 5.10. The phases identified are β-phase and γ-phase from 40 °C to 900 °C. The lattice parameter of each phase shows almost a linear increase with increasing temperature (Fig. 5.11). The CTE of the γ-phase and β-phase between 40 °C and 900 °C is calculated to be 17×10⁻⁶ and 19.3×10⁻⁶, respectively, by fitting the lattice parameters as linear functions of the temperature.
However, it should be noted that the accuracy of the CTEs obtained by this method might be compromised by two facts. Firstly, since the bond coat is bonded to the substrate with a much greater thickness, the expansion of the coating with increasing temperature is constrained or enhanced (depending on the sign of CTE misfit) by the substrate due to their thermal misfit. Secondly, due to the difference in the thermal-elastic properties between the $\beta$-phase and the $\gamma$-phase, microstrains could be generated in both phases upon the temperature change. These extra strains besides the intrinsic expansion of the coating would introduce errors into the calculation of the CTEs if the strains are reflected in the diffraction patterns. The error is expected to be more pronounced under the temperature when creep can be initiated (e.g. ~600 °C). Otherwise, the strains could be partially relaxed through creep.

Fig.5.11 Temperature dependence of the lattice parameter of (a) $\beta$-phase and (b) $\gamma$-phase

Fig.5.12 shows the volume fractions of the $\beta$-phase and the $\gamma$-phase calculated based on the intensities of (111)$_\gamma$ and (110)$_\beta$ at different temperatures. The temperature factor, $e^{-2M}$, which is a function of the $\theta$ angle, is cancelled during the calculation since the difference in the peak positions between (111)$_\gamma$ and (110)$_\beta$ is less than 1°. As the temperature increases from 600 °C to 900 °C, the volume fraction of the $\gamma$-phase increases from 32% to 49%, while the volume fraction of the $\beta$-phase decreases from 68% to 51%, suggesting that the
β-phase transforms to the γ-phase with increasing temperature. Below 600 °C, the volume fraction of each phase remains constant down to room temperature. Since the γ-phase and the β-phase are uniformly distributed in the middle two-phase layer, as shown in Fig. 5.5a and b, the result in Fig. 5.12 can be regarded as the volume fraction of each phase in the middle two-phase layer at different temperatures.

Fig. 5.12 Temperature dependence of the volume fraction of the β-phase and the γ-phase determined by high temperature X-ray diffraction

It is worth mentioning that the bond coat surface after the HT-XRD experiment remained as shiny as it was before the experiment, which means that surface was hardly oxidised during the heating. This could be important because it rules out the external factor that may lead to the increase of the amount of the γ-phase with increase in temperature (oxidation would induce Al depletion in the coating and subsequent γ precipitation near the surface), especially considering the low penetration depth of the X-rays into the bond coat. We also attempted to carry out the HT-XRD measurements at higher temperatures (1000
and 1150 °C). However, a colored thin film was observed on the bond coat surface when dismounting the sample from the chamber, suggesting that the metal surface was slightly oxidised. Therefore, the data were not used.

The reason for the change of the volume fraction of the β-phase and the γ-phase with temperature change is beyond the scope of this study. However, the variation trend, as shown in Fig.5.12, is in agreement with the result reported by Toscano et al. who used ThermoCalc Software to calculate the molar fraction of the β-phase and the γ-phase in a NiCoCrAlY and a CoNiCrAlY bond coat at high temperature [191]. On the other hand, the Ni-Al binary phase diagram shows that in the two-phase (β + γ') region which spans from approximately 32 at.% to 38 at.% aluminium [69], the amount of the β-phase increases with increasing temperature. However, this result might not be applicable to the NiCoCrAlY bond coat due to its high contents of the alloying elements, chromium and cobalt, which might significantly deviate the thermodynamic properties of the coating from those of the binary Ni-Al alloy. For example, the phase compositions present in the NiCoCrAlY bond coat in the equilibrium state are β plus γ, instead of β plus γ' as shown in Ni-Al phase diagram.

5.4 Discussion

Because diffraction is inherently selective, and therefore biased toward a particular set of grains, the peak shift samples both macrostresses (stresses varying continuously over large distance) and average microstresses (intergranular or interphase stresses varying over the grain scale) for the particular grain set [192]. Since the X-ray only probes the stress in the top γ-phase layer which is single-phase and texture free, and the diameter of the X-ray aperture (2 mm) is orders-of-magnitudes larger than the average grain size (Fig.5.6) of the γ-phase (a sufficient amount of grains with orientations in all directions is therefore assumed to be sampled), it is believed that the microstress in the γ-phase layer averages out
over the length scale of the measurement. Therefore, only the macrostresses are recorded in the results in Fig.5.3. The following part focuses on exploring the possible mechanisms responsible for the measured bond coat stresses in this work.

5.4.1 Effect of TGO/bond coat thermal misfit

It is known that the TGO scale attached to the bond coat is subject to a compressive stress upon cooling from high temperature. For example, the compressive stress in the TGO scale after 50 hours oxidation is about 5 GPa (Fig.5.13f) measured by photoluminescence piezospectroscopy (PLPS) according to the methodology described in the literature [130, 132]. In response to the compressive stress in the TGO scale, a tensile stress should be applied on the bond coat for a force balance. This tensile stress, if distributed uniformly across the cross-section of the whole metallic component, would be negligible at room temperature because the thickness of the TGO scale is orders-of-magnitude smaller than that of the bond coat and the substrate. For instance, a calculation based on simple force balance yields a tensile stress of about 3 MPa applied by the TGO scale on the bond coat and substrate after 50 hours oxidation, provided that the TGO stress is 5 GPa and the thickness of the TGO scale and the metallic substrate are 3.5 μm and 5.2 mm, respectively. However, since the X-rays only probe the stress in a shallow surface layer (the γ-phase layer) which is in direct contact with the TGO scale, the effect of the TGO scale on the stress in the γ-phase layer might be more pronounced than that predicted based on the simple force balance.

In order to understand the contribution of the TGO scale, it would be straightforward to conduct the stress measurements on the bond coat without the TGO scale and compare the result with the stress in the coating with the TGO scale. Therefore, a proper method, which could remove the TGO layer but would not introduce any mechanical or microstructural damage into the bond coat, would be preferred. Out of this consideration,
a sample that has been subject to 50 hours oxidation was immersed into a hot, concentrated NaOH solution (20 mol·L\(^{-1}\)) for up to 24 hours. This method was expected to remove the TGO layer through the following chemical reaction:

\[
Al_2O_3 + 2NaOH + 3H_2O = 2Na[Al(OH)_4]
\]

(5.12)

As the TGO was gradually dissolved, the alkaline solution became accessible to the TGO/bond coat interface. In this case, another possible mechanism that might facilitate decohesion and subsequent spallation of the TGO scale is moisture-induced stress corrosion. For example, the presence of water in the atmosphere has been reported to be detrimental to the bonding between the Al\(_2\)O\(_3\) and the \(\gamma\)-Ni alloys or the \(\beta\)-(Ni,Pt)Al bond coat [193, 194]. In case of the scenario in this study, the aqueous solution was able to penetrate into the TGO/alloy interface and therefore might lead to the spallation of the TGO.

Fig. 5.13a-e shows the surface morphology of the sample after immersion in the NaOH solution for different periods of time. It is observed that the surface area of the bond coat covered by the TGO scale (dark contrast) decreases with increasing immersion time. After 24 hours, almost the entire metal surface (bright contrast) is exposed, although some isolated TGO islands remain in contact with the bond coat. (Fig. 5.13d). Examination of the exposed metal surface reveals numerous imprints of the Al\(_2\)O\(_3\) grains. Retention of this faceted morphology indicates that the microstructure of the metallic coating is preserved. The grain boundaries of the exposed metal are also etched out. A plausible explanation for this phenomenon is the rapid penetration of oxygen along the grain boundaries of the bond coat at high temperature, which leads to intergranular oxidation and subsequent dissolution of the TGO when immersed in the etching solution. Fig. 5.13f shows typical PLPS spectra from the original TGO scale, the residual TGO scale and the stress-free sapphire, respectively. The R lines of the spectrum collected from the isolated TGO island
show little shift relative to those from the stress-free sapphire, implying the stress in the residual TGO has been relieved.

Fig. 5.13 Surface morphology of the bond coat during the removal of the TGO scale: (a) as-oxidised (after 50 hours oxidation); (b) after immersion in NaOH solution for 12 hours; (c-e) after immersion in NaOH solution for 24 hours. Some isolated TGO islands (dark contrast in Fig. 5.13d) remained attached to the metal surface. The exposed metal surface (Fig. 5.13e) exhibits numerous TGO grain imprints. (f) Typical PLPS spectra of the original TGO scale, the residual TGO scale and the stress-free sapphire.
Fig. 5.14 Evolution of the bond coat stress with the removal of the TGO scale: (a) stress map after oxidation for 50 hours; (b) stress map after immersion in NaOH solution for 12 hours; (c) stress map after immersion in NaOH solution for 24 hours; (d) evolution of the bond coat stress with immersion time.

Stress mapping conducted during the course of the TGO removal shows that the tensile stresses in the bond coat decrease as the TGO is continuously removed from the coating (Fig. 5.14). The average stress after immersion in the NaOH solution for 24 hours when the entire metal surface is exposed is 238 MPa, corresponding to a decrease of 75 MPa compared to the stress magnitude in the coating prior to immersion. Therefore, the presence of the TGO scale is by all means a reason for the bond coat stress measured in this study, and the contribution is significantly larger compared to the value (~3 MPa) predicted based on the simple force balance. However, it should be noted that a large proportion of the stress (~238 MPa) still remained in the bond coat even in the absence of
CHAPTER 5  RESIDUAL STRESSES IN A NiCoCrAlY BOND COAT

the TGO scale. Therefore, other mechanisms, perhaps more important, should also account for the development of the stresses in the bond coat.

5.4.2 Effect of bond coat/substrate thermal misfit

Another possible reason for stress generation in the bond coat is the coating/substrate thermal misfit upon cooling. Indeed, results from previous stress measurements on a $\beta$-(Ni,Pt)Al bond coat and a Pt-diffused $\gamma/\gamma'$ bond coat are in agreement with those calculated based on the CTE misfit between the bond coat and the substrate using the equation [90, 109, 120]:

$$\sigma_{BC} = \frac{E_{BC}(\alpha_{BC} - \alpha_S)\Delta T}{(1 - v_{BC}) + (1 - v_S)h_{BC}E_{BC}/(h_SE_S)} \quad (5.13)$$

where $\alpha$ is the CTE; $\Delta T$ the temperature change and $h$ the thickness; the subscripts “BC” and “S” refer to the bond coat and the substrate, respectively. However, direct assessment of the thermal misfit stress in the NiCoCrAlY bond coat after oxidation is difficult since its composition and properties (e.g. CTE) change with thermal exposure. More importantly, the stress calculated based on Eq.(5.13) might not be representative of the stress in the thin $\gamma$-phase layer the X-ray probes, considering the layered structure of the coating induced by oxidation and interdiffusion. If the coating system is taken as a multilayer material with a thick, stiff substrate, the thermal misfit stress in the $\gamma$-phase layer is written as:

$$\sigma_{\gamma} = \frac{E_{\gamma}(\alpha_{\gamma} - \alpha_S)\Delta T}{(1 - v_{\gamma}) + (1 - v_S)h_{\gamma}E_{\gamma}/(h_SE_S)} \quad (5.14)$$

A major implication of Eq.(5.14) is that the thermal misfit stress and strain in the $\gamma$-phase layer would decrease as temperature rises. However, this is apparently no in agreement with the strain evolution presented in Fig.5.4 where the strain almost stays the same upon heating and cooling between room temperature and 600°C. In addition, the thermal misfit
stress would be expected to decrease with thermal exposure time due to the bond coat/substrate interdiffusion which continuously assimilates their microstructure, chemistry as well as CTEs. This is also inconsistent with the variation trend of the stresses in Fig.5.3.

To assess the influence of the superalloy substrate on the measured stresses, a free-standing NiCoCrAlY coating (~0.21 mm thick) was prepared by removing the substrate through grinding and polishing. Due to the internal stress gradient (quenching stress) introduced in the deposition process [195], the free-standing coating surface was slightly curved when the substrate was removed. The coating was annealed in a vacuum furnace (under a pressure of $1 \times 10^{-5}$ mbar) at 1150 °C for 2 hours, which dissipated the stress gradient and resulted in a flat coating surface. After that, the free-standing coating was oxidised for different periods of time and the stresses in the coating were measured by the $\sin^2\Psi$ method. The contribution of the bond coat/substrate thermal misfit can be evaluated by comparing the stresses in the free-standing coating with those in the coating attached to the superalloy substrate.

![Stress maps of the free-standing coating after oxidation for (a) 2 and (b) 5 hours](image)

**Fig.5.15 Stress maps of the free-standing coating after oxidation for (a) 2 and (b) 5 hours**

Fig.5.15 shows the stress maps of the freestanding coating after oxidation for 2 and 5 hours. Stress mapping after a longer oxidation time is not available because warping occurs, which...
inValidates the plane stress state in the coating. Stresses in the freestanding coating after oxidation are tensile as well. Direct comparison with the results in Fig.5.3f shows that, for a given oxidation time, the average stress in the freestanding coating is even higher than that in the coating bonded to the superalloy substrate, which can probably be attributed to the increasing contribution from the TGO scale as the thickness of the metal is significantly reduced. To conclude, the thermal misfit between the coating and the substrate is unlikely the reason for the measured stresses shown in Fig.5.3.

It might be argued that the stresses measured based on free-standing coatings could be the thermal misfit stresses between the top γ-phase layer and the middle two-phase layer. However, as the β-phase generally shows a larger CTE than the γ-phase (the magnitude of the difference depends on their compositions [196]), the thermal misfit stresses in the γ-phase would be compressive, if the stresses are induced by CTE misfit between the γ-phase layer and the middle two-phase layer.

5.4.3 Stress induced by a phase transition

In general, the macrostresses arise from misfits in the natural shapes between different parts (e.g. TGO/bond coat thermal misfit stresses) of the materials [197]. Since the measured stresses in the bond coat cannot be explained, at least cannot be fully explained by either TGO/bond coat thermal misfit or bond coat/substrate thermal misfit, other processes involved with macroscopic shape changes should account for the measured stresses. Tolpygo and Clarke have reported that the phase transformation from the β-phase to γ′-phase results in a significant volume contraction (~38 %) of the bond coat due to the smaller density of the β-phase compared to that of the γ′-phase [150]. Our HT-XRD reveals that, above 600 °C, the volume fraction of β-phase increased with decreasing temperature, while the volume fraction of the γ-phase had the opposite trend within this temperature range. The density difference between these two phases could induce the
volume change in the bond coat upon the phase transition and subsequent stress generation.

The density, $\rho$, of each phase is correlated to their compositions, crystal structures and lattice parameters, which is given by:

$$\rho_y = 4 \frac{\left(\sum m_i c_i\right)}{a_y^3}$$  \hspace{1cm} (5.15)

$$\rho_\beta = \frac{m_{Ni} + \left(\frac{m_{Al}}{c_{Al} + c_{Co} + c_{Cr}} + m_{Co} \frac{c_{Co}}{c_{Al} + c_{Co} + c_{Cr}} + m_{Cr} \frac{c_{Cr}}{c_{Al} + c_{Co} + c_{Cr}}\right)}{a_\beta^3}$$  \hspace{1cm} (5.16)

where $m_i$ is the atomic mass of the element $i$. The densities of the $\beta$-phase and $\gamma$-phase are worked out to be 6.7 g/cm$^3$ and 7.8 g/cm$^3$ respectively, based on the lattice parameters obtained from Fig.5.11 and the chemical compositions based on the EDS results shown in Fig.5.5. Due to the high concentrations of the alloying elements (chromium and cobalt), the calculated densities of the both phases deviates significantly from those of the stoichiometric $\beta$-phase ($\beta$-NiAl, 5.9g/cm$^3$) and $\gamma$-phase ($\gamma$-Ni, 8.9g/cm$^3$) [56].

As is shown in Fig.5.5, the oxidation produces a layered structure in the bond coat: a $\gamma$-phase layer at the top, a middle two-phase ($\beta$ and $\gamma$) layer in the middle and a bottom $\gamma$-phase interdiffusion layer at the bottom. Upon cooling, the low-density $\beta$-phase precipitated out in the middle two-phase layer, leading to the volume increase of this layer. The expansion normal to the surface can be accommodated by the rigid body displacement of the coating, provided that the interface between the layers is flat. The lateral expansion of the middle two-phase layer, however, is constrained by the remaining part of the bond coat. In response to the constraint, a tensile stress is, therefore, applied on the $\gamma$-phase layer at the top of the bond coat. This mechanism is also applicable to the stress generation in the free-standing coating.
The explanation above is in agreement with the result in Fig.5.4, in which the elastic strain in the υ-phase layer increases from the oxidation temperature to 600°C and then remains constant during cooling down to room temperature. Briefly, the precipitation of the β-phase upon cooling leads to the swelling of the middle two-phase layer and induces a tensile strain in the υ-phase layer above. This tensile stress increases with decreasing temperature (still above 600 °C) due to the enhanced creep resistance of the υ-phase layer associated with the decrease of the temperature. The expansion of the middle two-phase layer ends below 600 °C since the volume fraction of the β-phase shows little variation below this temperature, which corresponds to the nearly constant strain in the bond coat.

5.4.4 Evaluation of other possible stress generation mechanisms

As mentioned before, although no martensite peak is identified in the XRD pattern of the bond coat, this does not necessarily mean there is no martensite in the bond coat at all. It is still possible that there is small amount of martensite in the coating, with a volume fraction too low to be detected by XRD. Indeed, Mendis et al. have reported that the martensite is observed in a similar NiCoCrAlY coating by transmission electron microscopy (TEM) [186]. The study has also shown that the martensitic transformation occurs at a temperature around 150 °C. This temperature, however, is significantly lower than the temperature range within which the strain in the bond coat develops, as shown in Fig.5.4. Therefore, the martensitic transformation is not the reason for the measured bond coat stress in this study.

5.4.5 Stress evolution with oxidation time

As the top υ-phase layer thickens with the oxidation time, it becomes increasingly creep resistant upon cooling, which leads to the continuous increase of the bond coat stress during the first 35 hours oxidation (Fig.5.3). The creep resistance of the υ-phase layer could also be improved through two other microstructural changes induced by the oxidation.
One is the increased grain size with oxidation time, which could improve the creep resistance of the γ-phase layer at high temperature. The other is the precipitation of the nano-sized, coherent γ′-phase in the matrix γ-phase upon cooling, as suggested by a previous TEM study [100, 186], which imparts the γ-phase layer superalloy-like creep resistance, although the γ′ precipitates are not observed in this study. An Additional contribution to increased bond coat stress might be from the thickening of the TGO scale with oxidation time.

As aluminium in the bond coat is continuously depleted through oxidation and interdiffusion, the total amount of the β-phase that could precipitate from the γ-phase matrix upon cooling is decreased. Therefore, the volume expansion strain of the middle-two phase layer is expected to decrease correspondingly upon cooling. On the other hand, perhaps more importantly, the thickening of the γ-phase layer could reach to an extent that substantial creep relaxation of the other part of the bond coat (e.g. the middle two-phase layer) is initiated upon cooling. This in return relaxes the stress in γ-phase layer and leads to the decrease of the stress with oxidation time.

In an extreme scenario, in which the aluminium depletion in the bond coat has reached an extent that the entire coating is converted to a single γ-phase and a phase transition from the γ-phase to the β-phase upon cooling is not available, there would be no volume expansion strain in the coating. In this case, the stresses in the bond coat measured by the sin^2Ψ method are expected to be significantly lower than those shown in Fig.5.3. In order to confirm this argument, the bond coat of the as-received sample was mechanically thinned to about 40 μm, and then oxidised for 50 hours at 1150 °C. Fig.5.16 presents a typical plot of the (311) d-spacing against sin^2Ψ in measuring the stress in the thin bond coat after 50 hours oxidation. The stress is found to be about 60 MPa, which is, indeed, significantly lower compared to the stresses shown in Fig.5.3. The β-phase is hardly present in the coating based on the cross-section observation (the inset in Fig.5.16).
Fig. 5.16 A typical plot of the (311) d-spacing against $\sin^2\Psi$ obtained in measuring the stress in a thin bond coat (~ 40 μm) after 50 hours oxidation, showing that the magnitude of the stress is only about 50 MPa. The $\beta$-phase is hardly observed in the bond coat (the inset).

5.5 Conclusions

The residual stresses in the NiCoCrAlY bond coat after oxidation are studied by X-ray diffraction. The stresses at room temperature are found to be tensile; they first increase then decrease with oxidation time. The stress develops upon cooling, mainly within the temperature range from the oxidation temperature to 600 °C. Due to the limited penetration depth, the X-rays only probe a shallow thin surface layer predominantly consisting of the $\gamma$-phase formed during oxidation. It is found that, besides the TGO/bond coat thermal misfit, the development of the measured bond coat stress is mainly induced by the volume expansion of the bond coat associated with the $\gamma$ to $\beta$ transition upon cooling.
Chapter 6

Conclusions and future work

6.1 Conclusions

Oxidation behaviour of $\gamma'$ Ni-20Al-xPt ($x=0, 5, 10$ and $15$ at.%$)$ alloys, surface rumpling and residual stress of NiCoCrAlY bond coats have been studied in this thesis. The main conclusions are:

1. Platinum addition into bulk $\gamma'/\gamma' \text{Ni-20Al}$ alloys improves their resistance to oxide spallation. This is due to several reasons: (i) platinum facilitates the formation of a protective $\alpha$-$\text{Al}_2\text{O}_3$ scale; (ii) platinum reduces the growth stress in $\alpha$-$\text{Al}_2\text{O}_3$ scale and (iii) suppresses formation of a ridged oxide/alloy interface. All these benefits from platinum are attributed to the fact that platinum promotes the selective oxidation of aluminium.

2. The surface of a NiCoCrAlY coating deposited on a Ni-base superalloy progressively roughens during cyclic oxidation. The rumpling magnitude depends on thermal history, coating thickness and oxidation atmosphere. Compared to the coating, bulk NiCoCrAlY alloys with the same nominal composition show a much smaller tendency to rumple after thermal cycling. The coatings, especially the thin ones, experience substantial degradation (e.g. $\beta$ to $\gamma$ transformation and exhaustion of yttrium) induced by selective oxidation of aluminium and coating/substrate interdiffusion after thermal exposure. The TGO scales on thick and thin coatings show little difference in terms of thickness, grain size and microtexture. The observations together suggest that rumpling is driven by the lateral growth of the TGO and the coating deforms in compliance with the TGO. The dependence of rumpling development on experimental conditions is generally in agreement with the prediction of the existing model. It is suggested that the degradation of the NiCoCrAlY coatings and its dependence on coating thickness need
to be taken into consideration when predicting rumpling development of NiCoCrAlY coatings.

(3) The residual stresses in a NiCoCrAlY bond coat after oxidation have been studied by X-ray diffraction using the $\sin^2\Psi$ technique. The stresses at room temperature are found to be tensile; they first increase then decrease with oxidation time. The stress develops upon cooling, mainly within the temperature range from the oxidation temperature to 600 °C. Due to the limited penetration depth, the X-rays only probes a shallow thin surface layer predominantly consisting of the $\gamma$-phase formed during oxidation. It is found that, besides the TGO/bond coat thermal misfit, the development of the measured bond coat stress is mainly induced by the volume expansion of the bond coat associated with the $\gamma$ to $\beta$ transition upon cooling.

(4) The findings in this thesis provide a few design guidelines for the desired attributes of a bond coat. The study has shown that platinum addition into $\gamma/\gamma'$ Ni-Al alloys significantly improves their oxidation resistance. Combined with the findings in the established literature, it is anticipated that alloying platinum into diffusion-based bond coats will still be a primary strategy to improve their performance in future coating design. This guideline is further reinforced by the fact that although some other elements have shown their capability of enhancing the oxidation resistance of diffusion-based coatings to some extent, they are neither as effective nor as consistent as platinum. Another important finding in this study is that a thicker overlay NiCoCrAlY bond coat is more resistant to undesirable surface rumpling during thermal cycling. This phenomenon has an important practical implication to coating design in that rumpling can be minimized by using a coating as thick as possible. A sufficiently thick coating is also desirable for a better oxidation resistance since it creates a large reservoir of aluminum and rare earth elements, which is believed to be necessary for the growth and maintenance of a protective TGO scale. The study has also shown overlay NiCoCrAlY bond coats undergo substantial degradation and periodic phase
transformation between $\gamma$ and $\beta$ during cyclic oxidation. These chemical and microstructural evolutions promote cyclic plastic deformation of the coatings and compromise their oxidation resistance. Further coating design are required to improve the compatibility between the bond coat and the substrate as well as suppress the undesirable phase transformation during temperature change.

6.2 Future work

(1) Study the effect of platinum on the durability of the Pt-diffused $\gamma/\gamma'$ bond coat

In Chapter 3 we have shown that the platinum addition into $\gamma/\gamma'$ Ni-Al alloys improves their resistance to oxide spallation and studied the mechanisms behind this benefit. However, it should be noted that the study is conducted based on bulk Ni-Al-Pt alloys, which are different from the Pt-diffused $\gamma/\gamma'$ bond coats in terms of compositions, microstructures, properties as well as their evolution with thermal exposure. Future study is needed to identify if platinum in the Pt-diffused $\gamma/\gamma'$ bond coats plays the same role as it does in the Pt-alloyed $\gamma/\gamma'$ Ni-Al alloys.

(2) Quantify the evolution of the mechanical properties of the NiCoCrAlY coatings with thermal exposure

Chapter 4 has shown that the NiCoCrAlY coatings experience compositional and microstructural degradation during thermal cycling, which leads to degradation of the mechanical properties (e.g. creep strength) of the coatings and affects their rumpling behaviour. To incorporate this effect into rumpling models, the evolution of the mechanical properties of the coatings with thermal exposure needs to be experimentally determined.

(3) Study the stress profile through the whole thickness of the NiCoCrAlY coatings
The findings in Chapter 5 have indicated that the laboratory X-rays can only probe the stress in a shallow surface layer of the metallic NiCoCrAlY bond coat due to their limited penetration depths. The stress profile through the entire coating thickness is still unknown. As high-energy synchrotron X-rays and neutrons have much greater penetration depth and higher spatial resolution compared to laboratory X-rays, future work based on these techniques is required to have a thorough investigation of the stress profile through the entire bond coat.
References

REFERENCES


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