Performance of MCrAlX Coatings

Oxidation, Hot Corrosion and Interdiffusion

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Abstract

MCrAlY coatings (M=Ni and/or Co) are widely used for the protection of super-alloy components against oxidation and hot corrosion in the hot sections of gas turbines. The drive for coating systems to bestow adequate oxidation and corrosion resistance upon the components becomes urgent as an inevitable result of the necessary improvement in engine combustion efficiency and service lifetime. Through careful design of the composition, MCrAlY coating performance can be optimized to meet the needs under different service conditions and component materials, therefore, "MCrAlX", with "X" standing for the minor alloying elements, is used to highlight the effect. In the present thesis, the performance of new MCrAlX coatings is investigated with respect to oxidation, hot corrosion and interactions between coating-superalloy substrates.

Coating performance can be affected by many factors, where their impacts may vary at different oxidation stages, therefore experiments are designed by targeting each stage. Investigation on the initial stage oxidation behavior of MCrAlY coatings with post-deposition surface treatments reveals the different growth mechanisms of alumina scales. Results showed that surface treatments significantly reduce the alumina growth rate by suppressing transient alumina development and aiding the early formation of α -Al₂O₃, which improves the long-term oxidation performance of the coating. Similarly, the modification of minor alloy elements in MCrAlX coatings also yields a similar effect. Subsequently, study on the oxidation behavior of new MCrAlX coatings is carried out at the steady oxidation stage, followed by the microstructure observation, and thermodynamic and kinetic simulations. As an alternative reactive element to Y, Ce shows a negative effect on the formation of columnar alumina scales of high strain tolerance. In comparison, Fe or Ru addition shows no influence on alumina growth, rather than strengthening the phase stability in the coating and reducing the interdiffusion between coating-substrate through different mechanisms. As the oxidation proceeds to the close-to-end stage, a reliable criterion to estimate the capability of coating to form α -Al₂O₃ is of great importance to accurately evaluate coating lifetime. A

temperature-dependent critical Al-activity criterion is proposed to better predict the formation of a continuous α -Al₂O₃ scale based on correction of the elemental activity using commercial thermodynamic databases to replace the empirical Al-concentration based criterion.

Severe interdiffusion occurs between coating-substrate during high temperature oxidation, accelerating the degradation of the system. Interdiffusion behavior of diffusion couples of superalloys-MCrAlX coatings are examined. It is highlighted that the recrystallization of superficial layer of the substrate contributes to the secondary reaction zone formation and element interdiffusion controls subsequent zone thickening.

Study on Type I hot corrosion behavior of new MCrAlX coatings shows that the addition of Fe has no influence on basic fluxing reactions before severe Al depletion from the coating occurs. Instead, it boosts the "effective" Al supply of coating by shifting the equilibrium concentration of Al in the γ phase to a low Al level. Besides, the pre-mature coating degradation at the coating-substrate interface is due to the fast growth of corrosion products from substrate induced large local volume expansions, resulting in early coating spallation.

Populärvetenskaplig sammanfattning

MCrAlY ytbeläggningar (M=Ni och/eller Co) används ofta för att skydda komponenter tillverkade av superlegeringar mot oxidation samt högtemperaturkorrosion i de heta gasturbindelarna. Förbättrad förbränningseffektivitet och livslängd hos gasturbiner, gör att ytbeläggningssystemen måste besitta adekvata oxidations- och korrosionsmotstånd. Genom att omsorgsfullt utforma den kemiska sammansättningen hos MCrAlY ytbeläggningar kan deras prestanda optimeras för att möta kraven från olika driftförhållanden samt olika substratmaterial, därför används beteckningen "MCrAlX" för att belysa förändringar av den kemiska kompositionen, där "X" står för reaktiva legeringsämnen som tillsätts i mindre mängder. I denna avhandling undersöks prestandan hos en ny MCrAlX ytbeläggning med hänsyn till oxidation, högtemperaturkorrosion och interaktionen mellan ytbeläggningen och superlegeringssubstratet.

Oxidation av MCrAlX ytbeläggningar kan generellt kategoriseras i tre faser; initiala, stabila och nära-slutet fasen. Ytbeläggningens prestanda kan påverkas av olika faktorer vid de olika faserna, därför utformades olika experiment för att undersöka de olika oxidationsfaserna. Undersökningen av den initiala fasen av oxidationsbeteendet hos MCrAlX ytbeläggningar som genomgått ytbehandlingar efter ytbeläggningsdeponeringen avslöjade olika tillväxtmekanismer hos aluminiumoxidskikten. Aluminiumoxidens tillväxthastighet reducerades signifikant av ytbehandlingarna, detta genom att undertrycka utvecklingen av övergående aluminiumoxid och bistå den tidiga tillväxten av α -Al₂O₃, vilket förbättrar ytbeläggningens oxidationsprestanda långsiktigt. De reaktiva legeringsämnena som tillsätts i mindre mängder påverkar ytbeläggningens oxidationsprestanda på liknande sätt. Oxidationsbeteendet hos de nya MCrAlX ytbeläggningarna i den stabila fasen följdes av mikrostrukturundersökning, termodynamiska och kinetiska simuleringar. Det framkom att Ce visar en negativ effekt på bildandet av kolumnära aluminiumoxidskikt med hög töjningstolerans som alternativt reaktivt legeringsämne till Y. Jämförelsevis ger Fe- eller Ru-tillsatser ingen påverkan på aluminiumoxidtillväxten, förutom att det förstärker fasstabiliteten i ytbeläggningen samt genom olika

mekanismer reducerar interdiffusionen mellan ytbeläggningen och substratet. När oxidationsprocessen kommit till nära-slutet fasen, är det viktigt att uppskatta kapaciteten hos en ytbeläggning att bilda $\alpha\text{-Al}_2\text{O}_3$, detta då det är ett tillförlitligt kriterium för att noggrant kunna utvärdera ytbeläggningens livslängd. Därför föreslogs ett temperaturberoende kriterium för kritisk Al-aktivitet för att bättre kunna förutsäga bildandet av ett kontinuerligt $\alpha\text{-Al}_2\text{O}_3$ -skikt. Kriteriet baserades på korrigering av legeringsämnens aktivitet genom att använda en termodynamisk databas, detta för att ersätta det empiriska Al-koncentrations baserade kriteriet.

Vid högtemperaturoxidation sker en omfattande interdiffusion mellan ytbeläggningen och substratet, vilket accelererar degraderingen av ytbeläggningssystemet. Därför har interdiffusionsbeteendet mellan superlegeringssubstratet och MCrAlX ytbeläggningen undersökts i denna avhandling. Det framkom att rekristallisationen av ytliga skikt av substratet bidrar till formationen av den sekundära reaktionszonen och att interdiffusion kontrollerar zonens efterföljande tjocklekstillväxt.

Undersökningen av Typ I högtemperaturskorrosionsbeteendet hos en ny MCrAlX ytbeläggning visar att legeringstillägg av Fe inte påverkar de grundläggande flödesreaktionerna innan en kritisk Al utarmning sker i ytbeläggningen. Istället stimulerar det tillförseln av Al genom att skifta jämviktskoncentrationen av Al i γ fasen till en låg nivå av Al. Det framkom också att den tidiga degraderingen av ytbeläggningen vid gränsskiktet mellan ytbeläggningen och substratet kommer av att den snabba tillväxten av korrosionsprodukter från substratet inducerade en stor lokal volymsutvidgning, vilket ledde till tidig ytbeläggningsspallation.

Preface

Cover page images: IPF image of a MCrAlY coating and CMSX-4 interface.
Designed by Wanjun Chu.

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Linköping, September 2019

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Abbreviations

BC	B ond C oat
BLZ	β - L eft Z one
CALPHAD	C ALculation of P HAase D iagrams
CTE	C oefficient of T hermal E xpension
EBS	E lectron B ack S catter D iffraction
EB-PVD	E lectron- B eam P hysical V apor D eposition
EDS	E lectron D ispersive X -ray S pectroscopy
GPZ	G amma- P rim- D epletion Z one
HVAF	H igh V elocity A ir- F uel
HVOF	H igh V elocity O xygen- F uel
IBDZ	I nn- β - D epletion Z one
ODZ	O ut- β - D epletion Z one
PSLS	P hoto- S timated L uminesce S pectroscopy
RE	R eactive E lement
SEM	S canning E lectron M icroscopy
SRZ	S econdary R eaction Z one
TBC	T hermal B arrier C oating
TGO	T hermally G rown O xide
VPS	V acuum P lasma S pray
WDS	W avelength D ispersive S pectroscopy
XRD	X - R ay D iffraction

List of Papers

The following papers have been included in this thesis following a chronological orders of their publication:

Paper I

P. Zhang, K. Yuan, R. Lin Peng, X.-H. Li, and S. Johansson. Long-term oxidation of MCrAlY coatings at 1000 °C and an Al-activity based coating life criterion. *Surface and Coating Technology*, 332C (2017) 12-21.

Paper II

P. Zhang, R. Lin Peng, X.-H. Li, and S. Johansson. Investigation of Element Effect on High-Temperature Oxidation of HVOF NiCoCrAlX Coatings. *Coatings*, 8 (2018) 129.

Paper III

P. Zhang, X.-H. Li, J. Moverare, and R. Lin Peng. The iron effect on oxidation and interdiffusion behaviour in MCrAlX coated Ni-base superalloys. *Materials and Design*, 166 (2019) 107599.

Paper IV

P. Zhang, R. Lin Peng, and X.-H. Li. Failure mechanism of MCrAlY coating at the coating-substrate interface under type I hot corrosion. *Materials and Corrosion*, 70(9) (2019) 1593-1600.

Paper V

P. Zhang, E. Sadeghimeresht, S. Chen, X.-H. Li, N. Markocsan, S. Joshi, W. Chen, I.A. Buyanova, and R. Lin Peng. Effects of surface finish on the initial oxidation of HVAF-sprayed NiCoCrAlY coatings. *Surface and Coating Technology*,

364 (2019) 43-56.

Paper VI

P. Zhang, X.-H. Li, J. Moverare, and R. Lin Peng. The iron effect on hot corrosion behaviour of MCrAlX coating in the presence of NaCl at 900 °C. *Journal of Alloys and Compounds*, 815 (2020) 152381.

Paper VII

K. P. Jonnalagada, **P. Zhang**, M. Gupta, X.-H. Li., and R. Lin Peng. Hot Gas Corrosion and its Influence on the Thermal Cycling performance of Suspension Plasma Spray TBCs. *Proceeding of ASME Turbo Expo 2019*, (2019).

Contribution to the papers included:

For above papers (I-VI), I performed all of the experimental, modelling and analytical work and was the main contributor of the manuscript writing. For paper VII, I performed the corrosion characterization and mechanism analysis. In addition, Kang Yuan conducted oxidation tests in Paper I.

Papers not included in this thesis:

Paper VIII

P. Zhang, R. Lin Peng, X.-H. Li, and S. Johansson. Influence of Ce and Ru on the behaviour of HVOF NiCoCrAlX Coatings in High Temperature Oxidation. *Proceedings of International Thermal Sprayed Conference (ITSC)*, May 10-12, China, (2016) 635-640.

Paper IX

P. Zhang, E. Sadeghimeresht, R. Lin Peng, X.-H. Li, N. Markocsan, S. Joshi, and S. Johansson. Isothermal oxidation behavior of HVOF-sprayed NiCoCrAlY coatings: Effect of surface treatment. *Proceedings of International Thermal Sprayed Conference (ITSC)*, May 7-9, Germany, (2017) 456-461.

Paper X

K. P. Jonnalagada, S. Mahade, S. Kramer, **P. Zhang**, N. Curry, X.-H. Li., and R. Lin Peng. Failure of Multilayer Suspension Plasma Sprayed Thermal Barrier Coatings in the Presence of Na₂SO₄ and NaCl at 900 °C. *Journal of Thermal Spray Technology*, 28 (2019) 212-222.

Part I

Background & Theory

CHAPTER 1

Introduction

1.1 Background

With the increasing of population and industrial development worldwide, the demand for electricity is expanding and will continue to grow. Among many energy resources to generate electricity, such as fossil fuel power plants, nuclear power plant and other renewable energy options, over 80% of the electricity is derived from heat sources [1]. Although the proportion of energy generation of renewable energy options are increasing, more than 65% of energy generation is still relied on the combustion of fossil fuel by turbines, like coal, oil and gas. It is reported that a high efficiency can be achieved by the modern fossil fuel power plant [1, 2]. Industrial gas turbine, since it has been firstly applied in power generation back to 1939, has been the most widely used to produce electricity from heat resources [3]. With the increasing demand of electricity, air pollution and CO₂ emissions induced by the fossil fuel combustion draw much attention, it is urgent to improve the efficiency of gas turbines and reduce fuel consumption. The goal of industry is to improve fuel efficiency and reduce CO₂ emissions of gas turbines through a good gas turbine design and the development of durable materials which provide better performances at elevated temperature including superalloys and functional coating systems [3–6].

A brief introduction on gas turbine system and description of project will be given in the section below. Part I in this thesis book is adapted from the author's licentiate thesis "Oxidation behaviour of MCrAlX coatings-effect of surface treatment and an Al-activity based life criterion" [7].

1.2 Gas turbines

Despite the different applications of gas turbine in power generation or aircraft propulsion, the overall design might vary but the operation principle remains the same, as illustrated in Fig. 1.1. During operation of the gas turbines, air is taken through the INTAKE and compressed by COMPRESSOR in order to increase the temperature of inlet gases. Then the compressed air is mixed with fuels when enters the COMBUSTOR chamber. By igniting the mixture, hot gases with high-temperature and high-pressure are produced, which impact the blades and vanes in the TURBINE section to drive the shaft to generate power. The gas flow achieves the highest temperature, ranging from 927-1593 °C [6], when passing through the first stage of TURBINE next to COMBUSTOR. Afterwards, the gases leave the gas turbine though the EXHAUST with pressure drop and temperature reduction. A gas turbine, such as SGT-800 as shown in Fig. 1.1, can achieve a high energy efficiency up to 40% [8].

Figure 1.1. Section of stationary gas turbines SGT-800 from Siemens. Courtesy of Siemens.

Considering service conditions in different sections of gas turbine, various materials are chosen based on their mechanical properties and the temperature limitation. As illustrated in Fig. 1.1, the INTAKE and COMPRESSOR generally maintain the temperature below 600 °C, Fe-based alloys are commonly used to manufacture these parts. The temperature of gas increases dramatically in the COMBUSTOR and TURBINE sections. Therefore, Ni- and Co-based superalloys are needed as the base materials for the turbine blades and vanes where service temperature up to about 1000 °C is sustained [3, 4]. Due to the aggressive operation condition of these sections, protective coatings are required to provide oxidation and hot corrosion resistance for superalloy-base components. The protective coatings are usually alumina-former as the formation of dense and adhesive thermally grown alumina scale at the coating-gas interface shields the components

from the harsh working environment. In some parts of the gas turbine where the service temperature is even higher, thermal barrier coatings (TBCs) are applied on the components to provide thermal insulation, cooperated with internal cooling systems in the metallic components [9].

1.3 Importance of MCrAlX coatings

MCrAlX (M: Ni and/or Co; X: minor elements) coatings have been largely used on hot components of gas turbines to provide protection against high temperature oxidation and hot corrosion for the base materials. MCrAlX coatings are utilized as overlays on blades and vanes after outlet of the COMBUSTOR; blades and vanes in the low-temperature part of the TURBINE; or as bond coats in TBC systems in the COMBUSTOR section and in high-temperature part of the TURBINE section. The reasons and benefits to use MCrAlX coatings in gas turbines can be summarized as follows:

- To provide protection for base materials from high-temperature oxidation and hot corrosion by forming a protective oxide scale;
- Coating composition can be tailored to meet various application needs and to match various base materials of different components in order to maximize their compatibility and service life;
- Coating thickness can easily be controlled according to the demands;
- Flexible coating deposition methods can be chosen for different applications;
- A good combination of durability and mechanical properties, such as strength and ductility at high temperature, can be achieved;
- To increase bonding between ceramic TBC layer and metallic base materials.

1.4 Scope of the project

The work presented in this thesis is part of a joint project between Linköping University and Siemens Industrial Turbomachinery AB. The project aims at the optimization of durable MCrAlX coatings for the operation conditions in land based gas turbines of medium size (10-60 MW). Such gas turbines used for both static load (long loading duration at high temperatures but few cycles) and peak load (frequent cycles) operations, require protective coatings with both long-term oxidation and thermal cycling resistance. Interdiffusion behaviour between coatings and Ni-base superalloys is also investigated through experiment and thermodynamic-kinetic modelling. This thesis work mainly focuses on three correlated issues: high-temperate oxidation, hot corrosion and interdiffusion between the coating-substrate.

Characterizations using different experimental techniques and thermodynamic-kinetic modelling are applied to investigate the coating performance during oxidation and hot corrosion. The main research goal is to improve the performance of MCrAlX coatings, approaches can be generally summarized below:

1. to investigate surface treatment effect at different oxidation stages;

2. to study the development of oxide scales and degradation of coating microstructure at different oxidation stages;
3. to develop a reliable coating life criterion for the long-term oxidation through modelling;
4. to explore element effect on the oxidation and hot corrosion behaviour of MCrAlX coatings and optimization of the coating chemical composition;
5. to inspect the interdiffusion behaviour between MCrAlX coating and Ni-base superalloy substrate.

CHAPTER 2

High Temperature Oxidation

2.1 Oxidation theory

From a thermodynamic point of view, metals in engineering applications are considered unstable due to their great tendency to interact with the surrounding environment. When a clean metal M is exposed to an oxidizing environment, it reacts with oxygen gas, forming an oxide scale, which can be expressed as:

The growth rate and properties of the oxide scales determine its protectiveness. In general, a protective oxide should be thin, dense, slow-grown, adhesive to the metal, and thermodynamically stable within the working temperature range. The spontaneous formation of oxide depends on the free energy of formation of the oxides, ΔG , where the reaction with negative ΔG can occur spontaneously [10], as presented in Fig. 2.6b.

The initial stage of oxidation reaction between metal and oxygen can basically be described in the following steps: adsorption of oxygen at the metal surface, dissolution of oxygen in metal and separated oxide islands nucleation on the surface, and lateral growth of oxide islands to form a continuous oxide film of M_xO_y form. The oxide film formed can be dense and defect-free which serves as diffusion barrier between metal and reactants, i.e., the oxidation can only proceed with solid-state diffusion through oxide film. However, the formation of porous oxides is frequently observed, in which pores provide fast diffusion paths for the transportation of metal and oxygen ions. Due to the high mobility of oxygen ions, the oxidation is much faster; it cannot be slowed down unless a new barrier is built-up forming a dense and stable oxide layer.

2.2 Solid-state diffusion mechanism

The growth of thick oxide scales at elevated temperatures is in principle governed by diffusion of ions and electrons through the scale, which depends on the defects in the oxides. Based on the defect types, the diffusion mechanisms can be sorted into bulk diffusion (lattice diffusion) and short-circuit diffusion. Among three groups of defects, including point defects, line defects and plane defects, point defects are responsible for lattice diffusion and the rest for short-circuit diffusion. However, the relative contributions to the scale growth by bulk or grain-boundary diffusion depend on the oxidation temperature and scale thickness [11]. Wagner refined Tammann's mechanisms on the oxidation of metals and proposed famous Wagner's model, as shown in Fig. 2.1, where deviation from the model is commonly observed in real systems if all the assumptions are not satisfied. The charged species can either diffuse through the lattice of oxides, or along short-circuit paths.

Figure 2.1. Diagram of scale formation according to Wagner's model [11].

Aluminium is one of the two common metals that form nearly stoichiometric oxides. Schottky and Frenkel defects are two common existed defects in stoichiometric crystals. A Schottky defect is formed by equivalent concentrations of anion and cation vacancies in the structure. On the other hand, Frenkel defect forms when a metal ions moves from the cation lattice to an interstitial site, leaving a metal vacancy on the regular site.

The non-stoichiometric oxides are more common in metal oxides, which are classified as oxygen or cation defects (deficit or excess). More specifically, metal excess compensated by metal interstitial or oxygen deficit compensated by oxygen vacancies are n-type, metal deficit compensated by metal vacancies or oxygen

excess compensated by oxygen interstitial are p-type.

Other than point defects, reaction species also diffuse through grain boundaries, dislocation clusters, continuous pores or cracks as short-circuit, which requires only 50-70% of the activation energy of the lattice diffusion. In addition, the diffusion coefficients are 10^4 - 10^6 times larger than lattice diffusion coefficients [12]. Short-circuit diffusion is a main diffusion mechanism in Al_2O_3 at the high temperature range for the rather low point defect concentrations [13]. For instance, the oxide grain boundaries lead to a thickening of the oxide above and below the oxide on either side of the boundary, as shown in Fig. 2.2.

Figure 2.2. Illustration of alumina formed on polished surface. Schematic of the counter-diffusion of O and Al along the oxide grain boundaries leading to a thickening of the oxide above and below the oxide on either side of the boundary. In between grain boundaries, the oxide is significantly thinner as indicated by the arrows. [14]

2.3 Basic oxidation kinetics

The oxidation kinetics can be quantified by mass gain or oxide thickness increment. Generally, three oxidation behaviours have been observed: parabolic, logarithmic and linear, as illustrated in Fig. 2.3.

At high oxidation temperature, the growth rate of most metal oxides follows the parabolic kinetic law, where the oxide growth is controlled by the diffusion of reaction species through relatively thick oxide scale. Such an oxidation behaviour indicates a direct proportion to time t :

$$x^2 = k_p t, \quad (2.2)$$

where x can be mass gain or oxide thickness, k_p is the parabolic rate constant, and t is the oxidation time [15]. Some assumptions should be considered to interpret the parabolic law: the oxide scale is compact and good adherent; transportation of ions through oxide scale is rate controlled; thermodynamic equilibrium is established at both the gas-oxide and the oxide-metal interfaces.

Figure 2.3. Mass gain or oxide thickness for the kinetic rate of oxidation [15].

When metals are oxidized at low temperatures up to about 400 °C, the initial oxide formation, up to the 1000 Å range, is characterized by an initial rapid reaction that quickly reduces to a very low rate of reaction [11]. Such behaviour follows the logarithmic kinetic law:

$$x = k_{log} \log(t + t_0), \quad (2.3)$$

where x is the oxide thickness, k_{log} is the logarithmic rate constant, t is the oxidation time, and t_0 is a constant. As the oxide scale grows thicker, the parabolic kinetic usually takes over. Besides, it was reported by Lipkin et al. [16] that the lateral growth of α -Al₂O₃ on NiAl at 1100 °C also obeyed the logarithmic law, as presented in Fig. 2.4. It indicates that the α -Al₂O₃ nucleates within the θ -Al₂O₃ and grows laterally by the radial migration of the transformation front until impingement.

Under certain conditions the oxidation rate of a metal can proceed at a constant rate and is proportional to the oxidation time following a linear rate law:

$$x = k_l t, \quad (2.4)$$

where x is the oxide thickness or mass grain, k_l is linear rate constant, and t is the oxidation time. It could happen at early stage of oxidation when the scale is thin and a phase-boundary process is the rate determining step for the reaction [11]. In addition, the existence of micro crack or porosity in oxide scale could transform the oxide growth from parabolic to linear. Such behaviour is commonly observed when a protective scale breaks down at a continuously increasing number of sites, resulting in an accelerated oxidation rate, which is called "breakaway" [15].

Figure 2.4. The measured mean radius of α - Al_2O_3 islands plotted as a function of oxidation time. As the least squares fit demonstrates, the θ -to- α transformation follows logarithmic kinetics. [16]

2.4 High temperature of alumina-forming alloys

In general, the applications for alumina-forming alloys are only for high temperatures ($>900^\circ\text{C}$) or most aggressive environments. For alumina-forming alloys, the general interest is the behaviour of M-Al and M-Cr-Al, where M is the major element (Ni for Ni-base alloys). Most commercial alumina-forming alloys are designed based on MCrAl rather than M-Al since the addition of Cr (typically 10-25 wt%) enables alloys with much lower Al content to form a continuous alumina-scale than observed in M-Al compositions, which is described as third element effect [17]. Small additions of reactive elements, Yttrium (0.3-0.5 wt%), is widely used in overlay-MCrAlY coatings for a better control of scale formation and growth [5]. MCrAlY coatings commonly consist of two phases: Al-rich BCC β phase and Al-poor FCC γ phase. The oxidation of MCrAlY coatings can be divided into three stages, as introduced in Fig. 2.6a. This section addresses the oxidation related issues regarding MCrAlY coatings in general.

2.5 Oxide species

In the case of MCrAlY, most of the alloying elements can be oxidized, forming various oxide species. These oxides include transient and stable Al_2O_3 , Y-oxides, Cr_2O_3 and/or NiO mixed with Al_2O_3 spinel type oxides, and their formation depends on many factors, including the oxidation temperature, alloying composition, coating microstructure, surface condition and so on.

2.5.1 Alumina phases

During oxidation of MCrAlY coatings, Al_2O_3 can be formed in different crystallographic phases. At lower temperatures or in the early stage of oxidation, the formation of metastable γ - Al_2O_3 , δ - Al_2O_3 and θ - Al_2O_3 are often observed, which contain high concentrations of cation vacancies. These metastable oxides show

distinctive morphological features and have a higher growth rate compared with $\alpha\text{-Al}_2\text{O}_3$, and their transformation to $\alpha\text{-Al}_2\text{O}_3$ may take a long time, allowing the preservation of their features [18]. Unlike metastable alumina, the concentrations of ionic and electronic defects in $\alpha\text{-Al}_2\text{O}_3$ are extremely small due to the large band gap and high lattice energy [12]. $\alpha\text{-Al}_2\text{O}_3$ exhibits low diffusivity for cations and anions as well as low oxide growth rate as a result of nearly perfect stoichiometry. Hence, the formation of stable $\alpha\text{-Al}_2\text{O}_3$ scale is desired for its low oxide growth rate and the defect-free stoichiometric structure enable it to serve as protective oxide scales for high temperature application.

The metastable alumina formed on MCrAlY coatings is not widely reported since these phases appear only after short exposure times at relatively low temperatures, which eventually transform to stable $\alpha\text{-Al}_2\text{O}_3$ with prolonged oxidation time. Transient alumina contains high concentrations of vacancies and lattice defects, resulting in a fast outward growth behaviour by outward diffusion of aluminum cations. For instance, the growth rate of $\theta\text{-Al}_2\text{O}_3$ is about an order of magnitude higher than $\alpha\text{-Al}_2\text{O}_3$ [19]. $\alpha\text{-Al}_2\text{O}_3$, has a corundum structure, is the most stable alumina phase. Apart from its nucleation and growth, $\alpha\text{-Al}_2\text{O}_3$ can be transformed from the metastable phases, and the transformation rate depends on various factors, see details in Section 3.3.5. The transformation sequence of alumina phases, depending on temperature, can be expressed as [20–22]:

2.5.2 Other oxides

Due to a high affinity to oxygen, Y in MCrAlY coatings can be easily oxidized. Y-oxide pegs are commonly observed in TGO, where oxide-coating interface and oxide grain boundaries are preferential segregation sites [23]. The positive effect of Y addition can be explained by reactive element (RE) theory, i.e., Y scavenges impurities like sulfur for its segregation to the coating-oxide interface causing a significant decrease in scale adhesion [24–26]. Besides, the presence of Y-oxide can also significantly suppress the formation of voids at the oxide-coating interface, modify the growth rate of $\alpha\text{-Al}_2\text{O}_3$, and increase oxide-coating adhesion due to the formation of inward-grown oxide protrusions (also called pegs) [27]. Fig. 2.5 shows Y-oxide segregates at grain boundaries of $\alpha\text{-Al}_2\text{O}_3$ formed in a HVOF sprayed MCrAlY coating. Recently, Martazavi et al. [28] reported a different alumina growth mechanisms due to RE effect. Results showed an inward growth behaviour of transient alumina on Y doped FeCrAl(RE) alloy oxidized in N_2+H_2 with 35 ppm H_2O at 900°C . A transformation of RE-decorated nanogranular Al_2O_3 to $\alpha\text{-Al}_2\text{O}_3$ and $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) particles was observed. They concluded that RE doping is responsible for the altering of the outward growth into predominated inward growth of alumina scale, which improves the oxide scale adhesion by avoiding the porous oxide/alloy interface typically for outward grown oxides.

The formation of spinel type oxides, $(\text{Ni},\text{Co})(\text{Al},\text{Cr})_2\text{O}_4$, above the alumina scales is commonly observed during oxidation of MCrAlY coatings. The structure of spinel depends on oxidation temperature: spinel tends to have a Cr-

Figure 2.5. Y-oxide segregation at the grain boundary of columnar α - Al_2O_3 .

dominate $(\text{Ni},\text{Co})\text{Cr}_2\text{O}_4$ structure at lower oxidation temperature, but a Al- dominate $(\text{Ni},\text{Co})\text{-Al}_2\text{O}_4$ structure at higher oxidation temperature [29]. The transition from $(\text{Ni},\text{Co})\text{-Cr}_2\text{O}_4$ to $(\text{Ni},\text{Co})\text{Al}_2\text{O}_4$ when increasing temperature is caused by an evaporation of Cr at the higher temperatures [30].

2.6 Three oxidation stage

The oxidation process of coating can be divided into three stages: initial stage, steady stage and close-to-end stage, as schematically shown in Fig. 2.6a. However, the formation of other oxide species are also thermodynamically feasible as suggested by the Ellingham diagram in Fig. 2.6b. These oxides, including Cr_2O_3 and/or spinel type oxides are non-protective and may promote the crack nucleation during thermal exposure of TBC [31–33]. Details of oxidation related issues will be further discussed in next chapter.

2.6.1 Initial stage

Prior to the formation of stable α - Al_2O_3 , metastable alumina oxides, such as γ and θ - Al_2O_3 , develop rapidly showing distinctive morphological features. Considering their higher growth rate compared with α - Al_2O_3 , the rate of transient-to- α - Al_2O_3 phase transformation has a significant impact on the developed oxide scale microstructure. By the nucleation of α - Al_2O_3 at the oxide-coating interface, α - Al_2O_3 grows outward by consuming transient oxides, in this way completing the transient-to- α - Al_2O_3 transformation [18]. In the meantime, the lateral growth of α - Al_2O_3 nucleate islands also occurs till the impingement, forming a continuous α - Al_2O_3 scale layer. A two-layer alumina scale consisting of a dense inward-grown inner α - Al_2O_3 layer and a porous outer layer transformed from outward-grown transient alumina is formed, as shown in Fig. 2.7.

Figure 2.6. (a) Schematic illustration of coating degradation related to the three oxidation stages based on Ref [34], (b) Ellingham diagram showing the Standard Free Energy of formation of oxides [35].

Figure 2.7. BSE image of TGO cross-section showing a two-layer structure, dash line marks the interface [18].

2.6.2 Steady stage

After the initial oxidation stage, a dense layer of $\alpha\text{-Al}_2\text{O}_3$ scales has been developed. The inward diffusion of oxygen ions dominates the growth, resulted in the thickening of elongated columnar $\alpha\text{-Al}_2\text{O}_3$ inner layer, as shown in Fig. 2.5. With further oxidation at steady stage, the inward-growth of alumina scales continues. Once the TGO thickness reaches a critical level, the "breakaway" oxidation initiates due to the thermal stress build-up. After each breakaway, parabolic growth proceeds, eventually leads to complete spallation and a linear growth profile [36], as illustrated in Fig. 2.6a.

2.6.3 Close-to-end stage

Internal oxidation

The complete transformation from β to γ of coating occurs after long-term oxidation, as described in Eq. 3.5. Upon the further oxidation, the Al content in γ phase continues to decrease until it reaches a critically low level when the outward transportation of Al from coating to the oxide-coating interface is insufficient. Internal oxidation occurs, as shown in Fig. 2.8, indicating the end of coating life.

Figure 2.8. Internal oxidation of a MCrAlY coating after long-term oxidation. [37]

A coating life criterion

The depletion rate of β phase in MCrAlY coatings has been frequently used in industry as a criterion to evaluate the end of coating lifetime. However, the complete depletion of β phase doesn't necessarily imply the end of coating life. It was indeed observed that some Ni-Al and Ni-Cr-Al alloy systems with no β phase presence maintain the ability to provide protection. Some researchers found from empirical studies that the concentration of Al in a range of 4–6 wt% is often sufficient to maintain α -Al₂O₃ scales and thus can be used to estimate the coating life. In such cases, the complete depletion of β phase is obviously not an adequate coating life criterion. Nonetheless, the empirical Al concentration criterion also has its limitation: the minimal Al concentration required by a continuous α -Al₂O₃ scale varies with coating composition and oxidation temperature [37].

To address the issue, an Al-activity based coating life criterion is therefore proposed by the authors [37] to predict coating life. In thermodynamic theory, activity is a measure of the "effective" concentration of a species in the system which can be used to define equilibrium constant [38]. It takes into account the fact that a solute in solution does not behave ideally at finite concentrations; only at infinite dilution, will activity a_i be equal to the concentration of solute ions c_i .

numerically. The calculation of element activity in equilibrium is identical to evaluating partial derivatives of total Gibbs energy, ΔG_{total} , with respect to variables at thermodynamic equilibrium as described in Ref [39]. This is performed by solving Lagrangian multipliers of the equilibrium calculation optimization problem in Thermo-Calc software [38]. And it is worthy to mention that ΔG_{total} is a function of all elements in the system, indicating that Al activity is intrinsically a function of all elements in the defined system. The work-flow of activity calculation is described in Ref [37]. Based on Eq. 2.1, the oxidation of Al can be represented by

and the Gibbs free energy of formation of alumina can be expanded consistent with the Van't Hoff isotherm [11] according to

$$\Delta G = \Delta G_0 - RT * \ln \left(\frac{a_{Al_2O_3}^{2/3}}{a_{Al}^{4/3} * \frac{p_{O_2}}{p_{O_2}^0}} \right) = \Delta G_0 + RT * \ln \left(a_{Al}^{4/3} * \frac{p_{O_2}}{p_{O_2}^0} \right), \quad (2.7)$$

where ΔG is Gibbs energy change of the reaction in kJ/mol, ΔG_0 is standard Gibbs energy of formation of alumina in equilibrium reaction, R is gas constant, T is temperature in Kelvin, a_{Al} is Al activity, $a_{Al_2O_3}$ is Al_2O_3 activity (commonly taken to be unity), p_{O_2} is oxygen partial pressure of oxidizing atmosphere, and $p_{O_2}^0$ is the standard pressure, equals to 1 bar. Eq. 2.7 can be transformed into a simplified Arrhenius type equation to calculate the critical Al activity of alumina formation

$$a_{Al} = A * \exp \left(- \frac{\Delta G}{RT} \right), \quad (2.8)$$

where A is a mathematic constant. Based on the experiment results of Ni-Cr-Al, Ni-Al-Si and Ni-Al alloy systems from literature, the critical Al activity of continuous alumina formation for MCrAlY coating in Eq. 2.8 can be expressed as a function of oxidation temperature:

$$a_{Al,cri} = \exp(-10,235/T - 11.1). \quad (2.9)$$

3.1 Coating development in historical perspective

Generally, Ni-based superalloys containing low chromium and aluminum content are less resistant to high temperature oxidation and corrosion in the service environment. Therefore, high chromium and aluminum content diffusion coatings or MCrAlX coatings are applied to improve oxidation and corrosion properties of the alloys. They can be utilized as protective overlay coatings or as bond coats in TBC systems to prolong the service life of coated turbine blades [3, 10, 40, 41]. Typical morphologies of the cross-sections of coatings are shown in Fig. 3.1.

Figure 3.1. Cross sections of high-temperature coatings: (a) NiAl diffusion coating deposited by CVD, (b) MCrAlY overlay sprayed by HVOF, and (c) TBC deposited by EB-PVD. [42]

At the early stage of coating development in the late 1950s, diffusion coatings, i.e., aluminide coatings, are widely explored and still actively used today [43, 44], as a result of the low cost and various well-developed process techniques,

such as slurry cementation, powder pack cementation and chemical vapour deposition (CVD). Typically, aluminide coatings contain in excess of 30% of Al and are deposited in thickness between 30-100 μm depending on the type of aluminide formed, as shown in Fig. 3.1a. Aluminide coatings are produced by enriching the surface with several elements at a substrate surface [36]. For instance, it can be produced by the reaction between the surface Al source and superalloy substrates followed by inward Al diffusion and outward Ni diffusion depending on the aluminium activity during the aluminization process. When Al content at the substrate surface is low and aluminization temperature is high ($>1000\text{ }^{\circ}\text{C}$), the outward diffusion of Ni prevails, creating an outward diffusion coating. On the contrary, an inward diffusion coating is produced when Al content is high and temperature is low ($<950\text{ }^{\circ}\text{C}$) [36]. Therefore, the microstructure of aluminide coatings is highly depended on substrates by the nature of their formation. Besides, aluminide coatings offer only limited protection under hot corrosion conditions or at temperature exceeded $1050\text{ }^{\circ}\text{C}$ [43]. To address these issues, MCrAlY coatings are developed to meet the demands of increasing operation temperature of modern gas turbines.

MCrAlY coatings, with a good balance between oxidation, hot corrosion and ductility compared with aluminide coatings, draw much attentions since the early 1970s. Traditionally, MCrAlY coatings are alloys based on Ni and/or Co containing 15-22 wt% Cr additions and 7.5-12 wt% Al additions and Y levels around 0.5 wt%, which provide good resistance against both oxidation and hot corrosion. Recently, the term "MCrAlX" has also been used to represent the same coating system, since other alloying elements are also added to improve coating performance. By fine tuning the minor additions of oxygen-active elements like Y, Si, Hf or Ta [36, 45–47], or a precious metal, such as Pt, Ru or Re [48–50], a good balance between oxidation, corrosion resistance and ductility of MCrAlX coatings can be achieved. Thus, it's reasonable to name the coating system as "MCrAlX" with "X" representing all minor alloying element additions, which has been used by other researchers [51, 52]. Considering the origin and history of coating development, the use of "MCrAlY" is still adapted in the following chapters.

Thermal barrier coatings (TBCs) have been used to provide thermal insulation for the intermediate bond coat (MCrAlY) and base materials against hot gas in hot sections of gas turbine, such as combustor, turbine blades and vanes. TBCs can provide a temperature decrease in a range of $200\text{--}300\text{ }^{\circ}\text{C}$ at the component surface depending on the thickness and thermal conductivity of the TBCs [36, 53]. Yttria partially stabilized zirconia is the most commonly applied TBC materials in industrial gas turbines, due to its low thermal conductivity, relative large thermal expansion, and advisable price [36, 54, 55]. The microstructure of TBC can be modified to achieve a better thermal insulation, i.e., a lower thermal conductivity, and a better strain tolerance, i.e., columnar structure as shown in Fig. 3.1c [36, 53]. A critical failure mode of TBCs is the spallation of top coat from bond coat, therefore, the surface roughness of the bond coat and quality of TGO are important [54].

3.2 Deposition techniques

Various deposition techniques can be utilized to produce MCrAlY coatings, such as 1) plasma deposition: atmospheric plasma spraying (APS), low-pressure plasma spraying (LPPS), vacuum plasma spraying (VPS); 2) vapor deposition: sputtering, electron-beam physical vapor deposition (EB-PVD); 3) flame spraying: high velocity oxy-fuel spraying (HVOF), high velocity air-fuel spraying (HVOF), 4) cold spraying and so on [56–60]. Flame spraying techniques can produce dense coatings with a proper selection of the process parameter. Due to its low restriction of process, i.e., conduct in atmosphere instead of vacuum, production costs of thermal spraying are considerably lower [58]. In this project, the MCrAlY coatings were manufactured by HVOF and HVOF. The process of HVOF/AF is schematically described in Fig. 3.2. Injecting the feeding powders in carrier gas which consists of oxygen (or air) and fuel in the combustion chamber, and spraying the powders with high velocity on the target. The high speed and temperature of gas flow cause the powder particles to be semi-melted when impacting the target surface, and the continuous spraying process leads to the formation of a typical "splat-on-splat" structure, as presented in Fig. 3.3. The moving of spraying nozzle or the rotation of target eventually guarantees an even layer of compact coating with desired thickness on target materials.

Figure 3.2. Schematic illustration of HVOF spraying process, courtesy of METHU.

3.3 Improving coating oxidation resistance

The drive to improve engine combustion efficiency while reducing emissions by increasing the operation temperature brings a big challenge for coating design. As a result, the need for better oxidation resistance of MCrAlY coating is essential. The ability of a MCrAlY coating to form and maintain a protective α -Al₂O₃ scale depends on many factors and synergistic effects have been reported among these factors. Although the influence of these factors are sometimes reported with substantial divergence, they usually rationalize in regard to the specific conditions

Figure 3.3. Cross sectional microstructure of an as-sprayed MCrAlY coating by HVOF, showing "splat-on-splat" structure and cracks, voids between splats.

and the mechanisms should follow certain general principles. The primary goal of this PhD study is to improve MCrAlY coating oxidation performance, thus, these principles are of interest. In this section, different approaches, including alloys elements, coating microstructure, surface treatment, and deposition method, which applied in the current project or reported by other researchers are firstly described, and the synergistic effect among these four factors are discussed later.

3.3.1 Role of alloying elements

The development of modern sophisticated MCrAlX systems ripened with trials and errors, i.e., to achieve functional coating systems to fulfil requirements of better performance and adapt in the target material systems heavily relied on alloy design. From the alloy design point of view, early research focused on the optimization of the main element contents: Ni/Co ratio and Cr and Al contents [61, 62]. As one of the major elements in MCrAlY coatings, the addition of Cr is essential for oxidation performance and hot corrosion resistance. It reduces the requirement on Al content from 17 wt% to as low as 5 wt% in the Ni-Al system to form a continuous Al_2O_3 scale through gathering effect [36] or third element effect [17]. Most Cr in MCrAlY coatings partitions in γ matrix due to a low solubility of Cr in β phase. Thermally-grown Cr_2O_3 islands from readily due to a sufficient Cr supply from γ phase. The formation of Cr_2O_3 islands share the same epitaxial template as $\alpha\text{-Al}_2\text{O}_3$, thereby catalyze the nucleation of $\alpha\text{-Al}_2\text{O}_3$ facilitating fast $\alpha\text{-Al}_2\text{O}_3$ formation during early stage oxidation [63].

Later the focus was shifted to modification of the minor element to explore the mechanisms of RE (reactive element) effect [64–68]. REs usually have high affinity to oxygen, forming RE-oxides in alumina scales which modify the alumina growth mechanism, as mentioned in Section 2.5.2. Large RE ions in open cubic lattice would inhibit the martensitic transformation from cubic $\theta\text{-Al}_2\text{O}_3$ to hexagonal $\alpha\text{-Al}_2\text{O}_3$ [69]. Co-doping of two or more REs is a practical solution to combine benefits of different elements for better coating performance. However, the level of RE dopant(s) should be always under-controlled to avoid aggravation

of oxidation rate, known as over-doping effect. In terms of multi-element dopants, the controlled level of dopants should be carefully evaluated due to complicated interactions between these alloying elements. The investigations on such interactions between dopants have been reported in many systems, it is a quite relevant and interesting topic in light of the current research scope, unfortunately, space limitations do not permit further discussions of the details.

Recent research trend shows some promising results of alloying element effect, some less reactive elements show different impact on the oxidation performance. For instance, the addition of Re [70] or Ta [71] enhances coating oxidation performance by lowering the oxidation rate and Al diffusivity. Ru addition in MCrAlY coating improves long-term oxidation performance by reducing substrate interdiffusion [72]. It's well-known that Pt addition reduces voids formation near oxide-coating interface, improving cyclic oxidation resistance [73].

It's worth to mention that the doping effect of Dysprosium (Dy) in NiAl coating has been investigated thoroughly by Guo's group [74–77]. It's reported that the presence of Dy at the coating-oxide interface effectively reduces the local sulfur level, suppressing the interfacial voids formation/coalescence and improving oxide scale adhesion. The mechanisms dominated includes: a similar S-gathering effect as RE effect and Dy improves oxide-coating adhesion by participating in bonding across the interface. Consequently, an excellent cyclic oxidation resistance of coating are achieved by Dy doping. Through combining theoretical first-principle calculation and targeted experimental design, the effect of Dy doping on coating oxidation performance can be truly revealed.

Despite the positive effect of RE, element, such as Ti, shows negative influence. Due to the difference in the valence state, $\text{Ti}^{4+}/\text{Al}^{3+}$, the formation and transportation of $\text{Ti}_{\text{Al}}^{\bullet}$ in alumina scales lead to the formation of TiO_2 , accelerating the overall scale growth rate [78]. Additionally, the diffusion of Ti from Ti-containing substrate could be pinned by formation of Ti-rich carbides near the coating-substrate interface.

3.3.2 Role of coating microstructure

By modification of coating microstructure, oxidation resistance of MCrAlY coating can be improved. For instance, a gradient coating with increasing Al content from coating-substrate interface to coating surface increases the surface β phase fraction in MCrAlY coatings promoting oxidation performance [79]. To decrease the Al consumption by the substrate interdiffusion, deposition of a diffusion barrier (DB) layer at the coating-substrate interface is proved to be feasible. Choice of diffusion barrier layer contains several material categories, for instance, a YSZ layer was deposited as a diffusion barrier layer between MCrAlY and René N5 which proved to be effective to suppress the interdiffusion between coating-substrate [80]. Besides, the nano-oxide (Al_2O_3) dispersion in coatings reduces elements diffusion from substrate to coating surface which increases coating oxidation resistance [81], known as oxide dispersed strengthened (ODS) alloys.

3.3.3 Role of post-deposition treatments

A promising route to decrease the oxidation rate of MCrAlY coatings is post-deposition surface modification by facilitating formation of a uniform alumina scale with a considerably low growth rate. Commonly used surface treatment methods include mechanical polishing [82], shot-peening [83, 84], electron beam surface remelting [85–88], laser surface remelting [89, 90] and so on. The benefits can be summarized as follows:

- decreasing coating surface roughness and reducing surface/bulk ratio giving a lower overall oxide growth rate of coating;
- inducing surface defects at the superficial coating layer to create short-circuit diffusion paths to enhance Al diffusion at early oxidation stage;
- suppressing fast growth of transient oxides and aiding the transient-to- α - Al_2O_3 phase transformation;
- providing more nucleation sites of α - Al_2O_3 and enabling the fast development of dense α - Al_2O_3 ;
- suppressing the formation of spinels and improving coating spallation resistance during thermal cycling in TBC system;
- reducing the overall oxide growth rate and the tendency of TGO spallation.

Another effective post-deposition treatment method is vacuum treatment, it promotes the formation of a dense and uniform oxide layer on a HVOF sprayed coatings compared with as-sprayed counterpart [87]. SPS (spark plasma sintering) treatment on HVOF sprayed MCrAlY improves the coating spallation resistance of TGO by suppressing spinel formation and internal oxidation [91].

3.3.4 Role of deposition techniques

A number of deposition techniques can be chosen to produce the MCrAlY coatings. Due to the work principle of deposition techniques, different as-deposited coating microstructures are expected, including grain size, grain orientation, phase species, porosity, element distribution, coating surface roughness, oxidation rate of powder during spraying, the impact on substrate and so on. One or several reasons mentioned above can contribute to such differences. For instance, cold sprayed MCrAlY coatings show a lower β phase depletion rate during oxidation compared with LPPS sprayed coatings due to different element distribution and surface roughness [92]. Besides, spraying parameters of coating deposition can be tuned to optimize the coating performance. For instance, spraying distance, powder flow, gas flow, and powder size of HVOF process have a significant influence on microstructure of coating, giving different coating oxidation performance [93]. Due to the high flame temperature during thermal spraying in the atmosphere, powder particles easily oxidize and alumina oxides strings are commonly observed at the deformed splat boundaries accompanied by the enrichment of RE elements. It's actually quite similar to the ODS microstructure design, slightly differs in the oxide distribution. Moreover, the impact of surface treatment on coatings oxidation resistance differs depended on the deposition techniques.

Among different deposition techniques, the utilization of EB-PVD method for TBCs deposition in industrial gas turbine application has been well established. In terms of EB-PVD bond coat, the microstructure shows distinctive feature. Nijdam and Sloof [94] reported a strong texture with γ and β grains preferably oriented with the (111) and (110) planes parallel to MCrAlY coating surface after coating deposition. Large columnar grains containing both γ and β phases formed in the middle and at the surface of coating. Phase separation inside the columnar grains resulted in a local microstructure consisting of a periodic arrangement of γ and β lamella, related to each other according to the Kurdjumov–Sachs orientation relationship, i.e., $\{111\}_{\gamma} // \{110\}_{\beta} <110>_{\gamma} // <111>_{\beta}$. Upon annealing at 1100 °C, equiaxed grains formed at the expense of the large columnar grains and coarsened by a short range diffusion or interface-controlled growth.

3.3.5 Synergistic effect

At initial oxidation stage

As aforementioned in Section 2.6.1, the development of α -Al₂O₃ originated from two sources: phase transformation from the metastable Al₂O₃ precursors, and direct nucleation of α -Al₂O₃ and subsequently grain growth. The formation of a two-layer structure of alumina scales is intrinsically a competitive growth process between metastable/stable Al₂O₃ depending on the rate of their phase transformation and the availability of nucleation site of α -Al₂O₃. If the transformation to α -Al₂O₃ is fast, the time for the outward growth of transient Al₂O₃ is limited, giving a much thinner outer-layer. For instance, the outer-layer of scale formed on polished coating surface is much thinner than the as-sprayed reference due to an early transformation to α -Al₂O₃, as shown in Fig. 3.4. It's not very clear at this stage how the microstructure affects the former, however, introducing defects to the metal through grain refinement or cold work could provide more heterogeneous nucleation sites for oxides [18, 67, 95]. In the case of HVOF/AF spraying process, powder particles undergo "cold deformation" upon the impact on the previous deposited layers/substrate [96], as evidenced by the elongated diffraction spots of β phase on a as-sprayed HVOF coating in Fig. 3.5. To exaggerate the extent of cold work, shot-peening treatment on a HVOF coating can induce more "defects" to the metal surface. The rapidly developed α -Al₂O₃ scale displays a relatively transient oxide-free "clean" structure on a shot-peened HVOF sprayed coating [18] in contrast to the as-sprayed counterpart, as a result of peening induced high density of heterogeneous nucleation sites for early α -Al₂O₃ development.

The dual phase structure of MCrAlY results in a local "inhomogeneity" between β/γ phase: multi-layer oxides consisting of spinel, Cr-rich and Al-rich layers developed on γ phase; in contrast, only Al₂O₃ on β phase [97]. Interestingly, the Al₂O₃ scales developed on β phase is intrinsically inhomogeneous due to the nature of the outward growth mechanism of θ -Al₂O₃. Besides, θ -Al₂O₃ grows a magnitude faster than α -Al₂O₃ and its development is highly sensitive to local condition. All three factors contribute to a distinctive blade/plate-like feature of θ -Al₂O₃, as observed on polished MCrAlY coating (Fig. 3.6). The grain boundary of the coating also plays an important role in alumina growth, for it is a fast diffu-

Figure 3.4. BSE images of cross-sections of oxide scale formed on a–c) as-sprayed, d–f) polished, g–i) shot-peened coatings; a, d, g) oxidation for 1 h; b, e, h) oxidation for 50 h. Red dash lines in b) and d) mark the inner and outer oxide layer interface. [18]

Figure 3.5. TEM analysis of an as-sprayed HVOF coating: a) bright-field image showing the larger number of dislocations, b) diffraction pattern of the β -grain marked with "D" in (a). The diffraction spots are elongated and diffuse. [97]

sion path for the oxidized species in comparison to lattice diffusion. The diffusion coefficient of Al can be written as:

$$D_{\gamma}^{Al} = (1 - f)D_L^{Al} + fD_{GB}^{Al}, \quad (3.1)$$

where D_L^{Al} and D_{GB}^{Al} are diffusion coefficient of aluminum through lattice and along grain boundary, respectively. f is the ratio of the area of the grain boundary, given by $f = 2\delta a/b$, where δ is the grain boundary thickness and d is the grain size. It is clear that the reduction of grain size, i.e., increasing grain boundary density, significantly increases the Al flux reaching the coating surface to form

Figure 3.6. Evolution of distinctive blade-like feature of θ - Al_2O_3 developed on β phase at the initial oxidation stage, adapted from [98].

exclusive Al_2O_3 scale [97]. This is evidenced by the comparison between coating microstructure prepared by different deposition methods: LPPS coating with a larger average grain size than HVOF sprayed coating gives a much lower Al flux [97]; or design through cryomilling the powder for size reduction before deposition. The cryomilled coating also shows a reduced overall oxidation rate due to an earlier transition of the metastable alumina phases [99]. In a low Al containing Pt-diffused γ/γ' bond coat, the formation of exclusive Al_2O_3 scale is difficult for a very low (8.2 at%) Al content. However, due to the Pt-diffusion induced recrystallization of the coating surface and subsequent precipitation process during coating fabrication [100], a nanostructured grain layer is established on the coating surface. It assisted the formation of a pure alumina scale while spinel formed on the counterpart bulk alloys with coarsened grains. This further demonstrates the great influence of grain boundary diffusion. It's worth to mention that both D_L^{Al} and D_{GB}^{Al} are intrinsically a function of temperature, the benefit of grain size effect tends to be weakened at even higher temperature since the ratio of $D_{GB}^{\text{Al}}/D_L^{\text{Al}}$ drops with the increase of temperature.

Effects of RE addition on coating oxidation performance have been partially covered in the previous chapters, the distribution of RE elements also draws attention for its great impact on the oxide development. In general, Y can form Ni-Y enriched precipitates at the grain boundaries in coating due to a low solubility in the coating and uneven distribution. The formation of Ni-Y precipitates is often observed on the coating deposited in controlled environment or vacuum to inhibit the possible oxidation during production, like LPPS and EB-PVD. In contrast, other deposition methods which operated in ambient environment usually lead to the formation of Y-oxide partitioned at the powder surface, whose

content is controlled by the deposition temperature, time and so on. A homogeneous Y distribution is desired for several reasons: the enrichment of Y could lead to a local fast alumina scale growth, which induces a early TGO spallation; it could also contribute to the formation of large YAlO_3 intrusions, which act as nucleation sites for initial interface delamination of TGO [28, 101]. In terms of long-term coating performance, such Y-enrichment could deplete and quickly exhaust the effective usage of Y. The mobility and reservoir of Y are also essential. With the prolonged oxidation time, the thickening of TGO will inevitably reach a critical thickness when TGO spallation initiates. Once the TGO spallation occurs, those "effective" Y_2O_3 /YAG incorporation in TGO are peeled off along with TGO. Therefore, "new" Y supply which is mobile enough to diffuse to the new metal/gas interface is important to form a new adhesive TGO to reduce further "break-away" oxidation.

The distribution of Y in MCrAlY coatings could be quite different according to the deposition methods. For instance, large Ni_5Y precipitates identified on cast MCrAlY specimen results in an accelerated local oxide growth rate, compared to the EB-PVD coating counterpart with much smaller Y-precipitates [102]. In the case of SPS (spark plasma sintering) method, the fast sintering time limits the grain growth, reducing the extent of Y local enrichment. In a recent published work by Lu et al. [103], ball milling MCrAlY powder gives a nano-size Y_2O_3 particles uniformly dispersed at γ/β grain boundaries and in β phase in SPS coating. The segregation of S at the oxide-coating interface is effectively inhibited, and the spallation tendency is therefore greatly reduced.

The formation of interfacial voids significantly deteriorates oxide scale adhesion to the metal surface. Most of the explanations are based on the theory of Kirkendall effect, vacancy injection or combination of these. As presented in Fig. 3.4, the fast growth of $\theta\text{-Al}_2\text{O}_3$ on as-sprayed coating relies on the outward diffusion of cations in the $\theta\text{-Al}_2\text{O}_3$, which accompanied by the counter-flux of vacancy injection. The injected vacancies later coalesced at the oxide-coating interface to form large interfacial voids. Moreover, the difference in multicomponent intrinsic diffusivity between species also contributes to Kirkendall porosity formation: outward transport of Al to the oxide and coating interface causes the simultaneous counter-flux of Ni diffusion to bulk, a faster diffusion of Ni than Al in γ -phase, which further promotes the voids coalescence [18]. Besides, the possible volatilization of newly formed CrO_3 or even pure Cr from coating could also facilitate the voids formation during initial oxidation stage. The formation of such voids should be always suppressed to reduce the oxide scales spallation, other than the surface treatment mentioned above, to apply a Pt layer on coating surface can also successfully suppress the interfacial voids formation [104]. The presence of Pt modifies the interdiffusion coefficient D_{AlAl} to diminish the unbalance in Al and Ni flux, assisting the "healing" of the created cavities with the oxide.

It's well accepted that S segregation weakens the oxide-coating bonding strength and one of the key benefits of Y addition is to gather S from breaking oxide-coating bond. The strong tendency for S to segregate at the oxide-coating interface is driven by a decrease of surface-interface energy through saturation of free bonds and decrease in elastic energy by release of stresses in the lattice caused by dis-

solved atoms [105–107]. It's reported that the segregation of sulfur at the oxide-coating interface is always lower than that on void surfaces, due to the fact that segregation to free surface is often more favourable than to the grain boundaries or to interfaces [108]. The sulfur segregation behaviour was investigated by Hou [109] using AES (Auger electron spectroscopy), results show that the severe segregation of S at the oxide-coating interface is significantly enhanced when co-segregated with Cr, and Y is a more effective candidate to gather S than Hf unless Hf is co-doped with Pt. It is interesting to point out that the S source is substrate, which again highlights the importance of RE addition in coating for the application in low purity Ni-base superalloy substrate. A recent study on EB-PVD Pt-(NiAl) coating system by Bai et al. [107] reported a new theory on S segregation. Results show that it is the formation of residual sulfide beneath the oxide scales with weaker ionic bonding strength to alloy cations instead of a segregation of sulfur atoms, and it is assumed that S in TBCs could also contribute to the failure of TBCs among other extrinsic factors. What's more, a strong S gathering effect of the dispersed oxide particles (introduced prior to Pt electroplating by surface treatment) in coating was observed, which further demonstrates the potential of ODS (oxide dispersion strengthened) alloys.

Residual stress in coating

The stress development in coating system is important since it's tightly related to the TGO spallation during cyclic oxidation. The roughening of the interface between TGO/bond coat can initiate the cracking and later failure of TBCs, which is also known as "rumpling", "ratcheting" or "scalloping" [110]. Most of related researches focused on commercial supplied (Ni,Pt)Al coatings for a relatively thin coating thickness of 40–50 μm , and the correlation of rumpling with coating thickness was established [111]. Although, the application of MCrAlY coatings usually requires a much thicker thickness in industrial application, where the rumpling is less significant, to understand stress evolution in coating still helps to explain the TGO spallation. Yang et al. [112] developed a new approach to investigate the coating high temperature stress, results showed that the volume shrinkage of β - γ phase transformation is responsible for the stress build-up in coating, and the grain sliding in response to the high temperature stress in coating is the dominant factor for the surface rumpling.

From a mechanistic point of view, the strain energy stored in the intact TGO is one of the main driving forces for crack propagation in the oxide layer. The investigation on stress development of TGO can shine light on the failure mechanisms of TBCs. The residual stress development in TGO originates from two sources: (i) growth or intrinsic strains, which are mainly caused by the lateral growth of TGO constrained by the underlying metal during oxidation, and (ii) thermal mismatch strains, which are induced by the thermal-expansion mismatch between the oxide scales and the metal during cooling [113]. By using piezospectroscopy of the fluorescence from the small Cr^{3+} content, the residual stress can be measured in sintered Al_2O_3 . Details of piezospectroscopy are given in Section 4.4. It's found that the residual stress in sintered Al_2O_3 is mainly originated from the

thermal-mismatch strains during cooling, while the initial intrinsic growth stress is quickly modified by the phase transformation in the underlying coating, as illustrated in Fig. 3.7. The maintenance of a high compressive stress level of TGO is sensitive to local condition of oxide-coating, i.e., the stress can be quickly relaxed due to cracking or interfacial voids formation, therefore it is a sign of the integrity of the TGO.

Figure 3.7. In situ strain analysis in the TGO formed on NiCrAlY at 1100 °C. The temperature was abruptly decreased to 1000 °C and the strains monitored at 1000 °C for 2 hrs. The temperature was raised again to 1100 °C accompanied by cooling. [113]

3.4 Hot corrosion

Hot corrosion of metals or alloys is an accelerated oxidation process due to the deposition of a thin film of molten salts, sulphates, on the material surface at temperature between 650-1000 °C [114–116]. There are two types of hot corrosion depending on the mechanism induced by corrosive salt: Type I at "high" temperature 850-1000 °C [114, 115] and Type II at "low" temperature below 800 °C [117, 118], as illustrated in Fig. 3.8. Type I hot corrosion occurs at temperature above the eutectic melting point of (Na,K)₂SO₄ salt mixture to dissolve oxide scale. This process usually produces a porous oxide scale leaving the underlying alloy/coating with sulfidation penetration [119]. Type II hot corrosion commonly presents a pitting attack with less sulfidation [36]. The damage induced by hot corrosion depends on factors such as coating composition, thermomechanical condition, contaminant species, flux rate, temperature, salt deposition rate, gas composition, gas flow rate and erosion [114]. For example, the mixture of different corrosive salts may reduce the eutectic melting point, which expands the temperature range of the hot corrosion attack. The presence of NaCl-V₂O₅ with sulfates further reduces

the eutectic melting point of salt mixture [114, 119, 120], leading to a severe attack at a lower temperature.

Figure 3.8. Schematic illustration of hot corrosion type I and II superimposed on contribution of pure oxidation at different temperature regime [36, 119].

Even though the true mechanism of hot corrosion is not well understood yet, a commonly accepted mechanism is explained by fluxing of the oxides in molten salts due to the gradient of their solubility through the salt film thickness [36, 116, 119]. The most commonly observed corrosive salt in gas turbines is Na_2SO_4 [121–123], and the fluxing can be driven in two conditions based on the acidity or basicity of the molten salts, which can be described in Eqs. 3.2 and 3.3. The acidity or basicity of the molten salts is controlled by the temperature and gas composition (SO_3) of service condition [36, 116].

Although attempt has been made to investigate type II hot corrosion on MCrAlY coating [124] in the first stage of the research project, the corrosion attack on coating was very weak. Therefore, the current research focuses on the coating performance under type I hot corrosion. Pre-mature failure of the coating-substrate interface under type I hot corrosion is observed on a single-side coated specimen [125]. Results show a fast growth of corrosion products from substrate quickly penetrate into the coating-substrate interface from the edge of the specimen. Local large volume expansion at the interface due to corrosion products growth causes the above coating deformation and cracking. Also, the addition of Fe in MCrAlY coating shows a promising hot corrosion resistance due to an increase of "effective" Al content for the basic fluxing with high Fe content.

Besides, pure gas phase corrosion attack on a TBC system is investigated

[126], the calculated (Ni,Cr)-S-O stability diagram at 780 °C successfully explains the formation of various corrosion products at different locations, as shown in Fig. 3.9.

Figure 3.9. (Ni,Cr)-S-O stability diagram at 780 °C, arrow indicates the formation path for various corrosion products. [126]

3.5 Coating-superalloy interdiffusion

3.5.1 Superalloys

Many components in gas turbines need to withstand both extreme loads and temperature during service. Ni-based superalloys show good mechanical and chemical properties at the temperatures above 0.6 times its melting point, including high strength, creep and moderate oxidation resistance at high temperature [127]. Ni is stable, since there's no phase transformation of its face centered cubic (FCC) structure from room temperature to melting point at 1455 °C, and has a high solubility for the alloying elements. The FCC matrix of Ni-based superalloy can be strengthened by dissolution of alloying elements to form strengthening precipitates γ' phase and/or carbides or dispersive oxide-particles like Y_2O_3 [3]. Turbine disc alloys are commonly wrought in polycrystal form, while DS (directionally solidified) or single-crystal form is often used in turbine blades. DS turbine blades have longitudinal grains oriented parallel to the axial direction of the blade, while single-crystal blades consist of one grain.

In this project, a Ni-base polycrystalline superalloy, Inconel 792, is used as substrate, see details listed in Table. 3.1. Possible phases include disordered FCC- γ phase matrix, ordered FCC- γ' , carbides (MC or $M_{23}C_7$) depending on the carbon contents and TCP phases (σ , μ etc.), which should be controlled to a limited content for the consideration of material ductility.

Table 3.1. The composition (wt%) of Inconel 792 and heat treatment process.

Compositions	Ni	Cr	Co	W	Ta	Ti	Al	Mo	C	Zr	B
(wt%)	Bal.	12.5	9.0	4.2	4.2	4.0	3.4	1.9	0.08	0.018	0.015
Heat treatment	Solution annealing (1120±10) °C for 2 hours in vacuum;										
processes	Ageing: (845±10) °C for 24 hours [128].										

3.5.2 Interdiffusion between coating and superalloy

Interdiffusion inevitably occurs between MCrAlY coating and Ni-base superalloy due to the alloying element gradient existed between two alloy systems. The interdiffusion causes the loss of Al from coating to substrate, and the formation of a secondary reaction zone (SRZ) or gamma-prime depletion zone (GPDZ) (Fig. 3.10) beneath the coating in the substrate. Both reactions are undesired for the reduction of coating oxidation performance, and the formation of SRZ leads to the degradation of the creep properties of the bulk superalloy substrate by reducing its effective cross-section.

In general, MCrAlY coating is designed with a much higher Al and Cr content compared with Ni-base superalloy substrate for a better oxidation and hot corrosion resistance. The severe uphill inward diffusion of Cr from MCrAlY coating to substrate quickly shifts the local γ/γ' structure of the substrate to a single γ microstructure accompanied by the formation of TCP phase and/or carbides due to the abrupt change of local chemistry. The design of diffusion barrier aims to reduce such interdiffusion as mentioned in Section 3.3.2. It was observed that high Fe addition in MCrAlY coatings promoted the formation of an "in-situ" discontinuous σ phase layer in SRZ, the phase transformation is described as:

where "c" is carbide. The formation of such σ phase layer can effectively suppresses the Al inward diffusion to substrate at 900 °C, and therefore improves the coating long-term oxidation performance [129].

3.5.3 Stability of coating

To improve the long-term oxidation performance, the stability of MCrAlY coating is essential, i.e., the depletion rate of β phase should be controlled for a better long-term Al supply. Aluminum in MCrAlY coatings is mainly consumed by two reactions: formation of alumina scales at coating-gas interface and inward diffusion of Al from coating to substrate. Due to the consumption of Al in coating during oxidation, the β phase (high Al content) transforms into γ' (medium Al content) or γ (low Al content) following the route:

The stability of γ' phase in coatings depends on the local composition and temperature, as illustrated by the calculated isothermal phase diagram in Fig. 3.11. The depletion of β phase leads to the formation of an outer β phase depletion zone (OBDZ) and an inner β phase depletion zone (IBDZ) as shown in Fig. 3.10.

Figure 3.10. Microstructure of MCrAlY coating after oxidation, showing different reaction zones.

Figure 3.11. Calculated isothermal section for a MCrAlY system at 1000 °C, dash lines denote shifted phase boundaries at 1100 °C (purple) or 900 °C (green). The long arrows indicate phase transformation following two different paths. [129]

The positive effect of post-deposition surface treatment to reduce oxidation rate has been discussed in previous sections. Another approach in this project is to extend the $\beta+\gamma$ phase region to a broader Al range through alloying with β phase stabilizing elements. As illustrated in Fig. 3.11, the increase of Fe content in C2 coating could successfully extend the $\beta+\gamma$ region to a lower Al composition range [129]. By extending the $\beta+\gamma$ region with the increase of Fe content, the partition level of Al to β phase is raised, i.e., the equilibrium Al content in γ phase is therefore reduced, as shown in Fig. 3.12. It is beneficial under type I hot corrosion to provide a higher "effective" Al content to take part in fluxing reaction,

which suppresses the extent of internal oxidation in coating. The addition of Ru in MCrAlY also achieves a similar effect as reported in Ref [130].

Figure 3.12. Isothermal section at 900 °C for a NiCoCrAlFe system, equilibrium γ phase composition are marked by star, iso-content of Al is marked by a red dashed line.

3.5.4 Modelling of coating-superalloy diffusion couple

For MCrAlY coating-superalloy diffusion couple modelling, two reactions are essential to simulate the phase evolution of the system: oxidation induced Al depletion at the coating-gas interface and the multi-alloy interdiffusion in coating-superalloy system. It's of great interest and practical to predict the phase degradation of $\beta+\gamma$ dual phase coating system in industrial application for coating life evaluation, and the principle implemented is the diffusion controlled phase transformation process. In general, a one-dimensional multicomponent model is sufficient to represent the whole process due to the planar nature of interfaces of the coating-substrate.

Oxidation model

To predict the Al loss by oxidation, the general approach can be treated as a continuous process to simulate the evolution of a non-conservative system:

1. to apply a proper oxidation model to simulate the oxide scale (Al_2O_3) thickness growth,
2. to convert the thickness of Al_2O_3 into Al loss using volume-to-molar mass conversion,
3. to incorporate the molar mass loss of Al into the boundary condition set-up as a function of time in a non-conservative system,
4. to calculate the phase equilibrium of the non-conservative system.

To simulate a continuous process can be tricky, i.e., the establishment of a reasonable boundary condition is difficult, therefore, an alternative approach is to

break the continuous long process into small isolated loops (Δt) of a conservative system, and then stitch loops to restore the whole non-conservative system. In order to connect each loops, the strategy is to change the system based on the Al loss which is derived from the oxidation model and reconstruct a new initial condition as the input for the next simulation loop. The benefit to break down a continuous process is obvious: adjustment can be made in the "new" system by a user-defined function to achieve different purposes. However, special attentions are required to test on the parameters to avoid the break-down of simulation due to the possible variables beyond the limits of the physics of the model. For instance, the loop can break down as a result of a too fast Al depletion in the surface oxidation where the flux cannot be balanced by a low diffusion coefficient. Anyhow, the design of the work-flow highly relies on the bottom hierarchy of the physical model.

For the available oxidation models developed, the experimental data are required to obtain the constants, including growth rate coefficient, exponential constant and so on. For example, the classic parabolic law (Eq.2.2) and its variations are applicable in the model developed by Kang et al. [131, 132]. Concerning the possible kinetic transformation from initial to steady oxidation stages, it is also recommended by Bataillou et al. [133] to perform a longer experiment until the steady regime is reached, and to extrapolate with the "parabolic law" method using the stationary k_p and the complete law. An alternative method in using an analytical or numerical model that includes grain growth kinetics, where the evolution of local k_p is assumed to be due to the oxide grain size evolution. The effect of grain boundary density (grain coarsening) of oxide scale on its growth was discussed by Geer's et al [134] by considering two scenario: rate of grain boundary density loss to be independent of the rate of oxide growth and two instantaneous rates to be equal. Results showed that there's a transition from early superparabolic ($x \propto t^{2/3}$) or parabolic to late cubic or logarithmic for the degree of synchronization between rates of scale growth and oxide grains coarsening, highlighting the effect of grain coarsening during oxide growth. Such effect was also reported by Zhang et al. [135] that a deviation from parabolic oxidation kinetic due to the oxide grain coarsening, where a correction factor of grain boundary density was used to correct the kinetic.

A scheme proposed by Meier at al. [136] can be described as follows:

$$\delta = \left[\exp \left\{ Q \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\} t \right]^n \quad (3.6)$$

where the thickness of oxide scale is δ , Q , T_0 and n are constants equal to 27777.4, 2423.7 K and 0.332, respectively; T is the temperature in K and t is the time in seconds.

In the case of cyclic oxidation, where oxide spallation should be considered, the DICOSM model [137] shows a reasonable fit by introducing a prescribed spallation area fraction, F_A (or $1/n_0$, n_0 denotes number of oxide segments). It is assumed that the oxide region is divided into $1/F_A$, one of which spalls each cycle and the spalling occurs interfacially at the thickest region of the scale [138]. The

Good-Smialek approximation [137] applies an expansion to make a continuous and differentiable expressions, where the flux of the metal elements, J_m , of the interface can be described as:

$$J_m = \begin{cases} (S_c - 1) F_A \sqrt{k_p} \left\{ n_0 t^{-1/2} + \frac{1}{2\Delta t} t^{1/2} \right\} & \text{for } t \leq \Delta t n_0 \\ (S_c - 1) F_A \sqrt{k_p} \left\{ n_0^{1/2} \right\} & \text{for } t > \Delta t n_0 \end{cases} \quad (3.7)$$

where S_c is the stoichiometric constant and is calculated by weight fraction of oxide/oxygen.

Diffusion model

With the help of diffusion-controlled transformation (DICTRA) module in Thermo-Calc software package, the interdiffusion between the coating-substrate can be simulated. The diffusion problem is solved in a lattice frame of reference and it is based on the assumption that the local fraction of vacancies always corresponds to equilibrium and that no pores are formed as a result of vacancy annihilation [139]. The flux expression in the lattice-fixed frame of reference for a moving phase boundary problem can be described as:

$$J_k = -\frac{M_k RT}{V_m \Delta \tilde{z}} \sqrt{x_k^1 x_k^2} \sinh\left(\frac{\Delta \mu_k}{2RT}\right), \quad (3.8)$$

where x_k^1 and x_k^2 denote the mole fraction of species k on plane 1 and 2, respectively, $\tilde{z}$ is a time-dependent spatial coordinate, M_k is the mobility of species k , $\Delta \tilde{z}$ is the distance between the centres of the two planes and $\Delta \mu_k$ is the difference in chemical potential.

The homogenization model is applied to the multiphase mixtures by assuming locally minimized Gibbs energy and locally averaged kinetic properties. The Eq. 3.8 is modified by introducing a locally averaged kinetic properties, M_k^{eff} , using a Global minimization function, and x_k^1 and x_k^2 denote the local overall mole fraction regardless of the number of phases present locally.

Based on Onsager's reciprocity theorem, it is supposed that the fluxes J_k have been determined in such a way that they are independent for the forces X_k of different forms. Suppose further that they are independent, which yields the corrected entropy product σ , $\sigma = \sum_i J_i X_i$, then gives:

$$J_k = -\sum_i L_{ik} X_i, \quad (3.9)$$

with L_{ik} the phenomenological coefficients and J_k and X_k obtained from the expression of entropy production σ , which is the form of a sum of products of conjugated fluxes and thermodynamic forces. These relations can be used in the conservation laws which can be solved numerically to calculate the evolution of the system in time. For these phenomena a variety of combination rules exist for determining "effective" transport properties in multiphase mixture, it is possible to find a suitable combining rule which allows the M_k^{eff} to be calculated from the

M_k of individual phases. For example, the combining rule for fluxes described by a diagonal L matrix can reduce M to a scalar, and M can be further simplified to a diagonal matrix by ignoring the correlation effects.

It is useful to derive suitable bounds to modify diffusion flux according to the "geometry" of the system. The simplest examples are the Wiener bounds [140]: the lower bound (inverse rule of mixtures) defined from assuming a spatially uniform flux through each volume elements $M_k^{eff} = [\sum f^i / M_k^i]^{-1}$; the upper bounds (rule of mixtures) defined from the assumption of a uniform force, $M_k^{eff} = \sum f^i M_k^i$. As for Hashin and Shtrikman bounds [141], the geometry attained is the "composite sphere assemblage", which takes the main contribution of the radii or composite sphere into consideration as upper or lower bounds.

Experimentals and computational methods

In this chapter, the methods employed are described. For brevity, details can be found in the corresponding research papers in Part II.

4.1 Coating systems

In this project, most of the material systems consist of MCrAlX coating and IN792 superalloy substrate (composition see Table 3.1). MCrAlX coatings are designed with minor element additions including Fe, Ru, Ce, and Ta, details of the doping level of minor elements can be found in the appended papers. Other systems like (Ni,Pt)Al diffusion coating on single-crystal alloy, like CMSX-4 or PWA1483, were also investigated, and results were partially covered in the thesis.

4.2 Oxidation testing

Oxidation tests were performed in lab air at isothermal condition (900, 1000 and 1100 °C) or at thermal cycling condition with 1 h heating at 1100 °C and 10 min compressive-air cooling to 100 °C. Most oxidation tests were performed in muffle furnaces, except that the short-term oxidation test was conducted in a small-scale tube furnace for a better control of temperature.

4.3 Hot corrosion testing

Type I hot corrosion tests were conducted in this work. Specimens were coated with a thin film of salt mixture and then tested at 900 °C using salt combinations,

$(0.8\text{Na}, 0.2\text{K})_2\text{SO}_4$ or $0.8\text{Na}_2\text{SO}_4 + 0.2\text{NaCl}$. During the test, specimens were removed from furnaces and cooled down to room temperature after holding period for new salt deposition. In some tests, specimens were cleaned in distilled water before salts redeposition, for the removal of residual reaction products. Mixed-gas corrosion tests were conducted at RISE KIMAB, Sweden. Description of hot corrosion set-up can be found in Ref [126].

4.4 Photo-stimulated luminescence spectroscopy

Photo-stimulated luminescence spectroscopy (PSLS) is used in materials science for the detection of "photo-emitted" light from the materials, due to its high sensitivity and non-destructive character. In a photoluminescence process, an incoming high energy light at a constant wavelength is used to illuminate the specimen to be analyzed. The incoming photos are focused on samples, and the incident energy can be absorbed when photo energy is greater than the band gap of the materials ($E > E_g$), leading to a photo-excited process. The electrons within the samples are excited to higher states, and return to a lower energy state accompanied by the emission of a photo [142].

The experiments were carried out using a Horiba Jobin Yvon integrated micro-Raman setup. The photo-stimulated luminescence was excited by a diode laser at wavelength (λ) of 532 nm, the laser was focused using a 50x objective lens with NA=0.5 on the sample. The signal was collected using the same lens, and dispersed on a 300 mm^{-1} grating and collected with a Horiba Synapse Peltier-cooled charge-coupled device (CCD). The recorded spectra were analyzed and fitted using commercial Origin software. The fitting of spectral peaks with a combination of peaks are based on Levenberg-Marquardt non-linear peak method [143].

4.4.1 Identification of alumina phases

Due to the doping of Cr^{3+} in $\alpha\text{-Al}_2\text{O}_3$, Cr^{3+} ions substitute Al^{3+} site in the octahedral coordination giving a strong luminescence [144], which can be identified by PSLS. The origin of the luminescence is the photo-stimulation and subsequent radiative decay of excited d^3 electrons in substitutinal Cr^{3+} ions located on octahedral sites [145, 146]. And Cr^{3+} ions substitution of Al^{3+} site in octahedral ($\theta\text{-Al}_2\text{O}_3$) and tetrahedral sites ($\gamma\text{-Al}_2\text{O}_3$) can also generate characteristic luminescence [147].

4.4.2 Piezospectroscopic Effect

The characteristic lines resulted from the electronic transitions of the dopant ions are extremely sensitive to the local ionic environment in the host crystal as described by Ligand field theory. As a result, deformation which alters the interionic distances can cause shifts in the characteristic luminescence lines. Also, deformation which reduces the symmetry of the crystal will remove the existing degeneracy of the energy states and thereby lead to splitting as well as shifting of lines in the

spectra [148]. The relation between strain (equivalently stress) and the change in energy of the electronic states is the piezospectroscopic effect, as first described by Grabner [149]. The relationship between the fluorescence frequency shift, $\Delta\nu$, and the local stress can be expressed to a first-order approximation, as

$$\Delta\nu_{stress} = \prod_{ij} \sigma_{ij}^c = \prod_{ij} a_{ki} a_{lj} \sigma_{kl}, \quad (4.1)$$

where $\prod_{ij}$ is the ij th component of the piezospectroscopic tensor and σ_{ij}^c is the stress state in the crystallographic basis of the host crystal. In a general coordinate system, the stress state, σ_{ij} , is related to σ_{ij}^c by the transformation matrix, a_{ij} . The piezospectroscopic tensor is a material-specific parameter that reflects the point symmetry of the fluorescing ion in the host lattice. The coefficients of the piezospectroscopic tensor were redetermined with greater accuracy from a series of calibrations, wherein appropriately oriented ruby single crystals were stressed along the respective principal axes and the corresponding piezospectroscopic shifts recorded, with details described in Ref [150].

When Cr-doped Al_2O_3 is strained, the frequency of the Cr^{3+} luminescence shifts from its stress-free value. By assuming a flat alumina scale, the stress is presumed to be in a biaxial compression, i.e., $\sigma_{xx}=\sigma_{yy}=\sigma$ and $\sigma_{zz}=0$, therefore, Eq. 4.1 can be reduced to

$$\overline{\Delta\nu} = \frac{2}{3} \prod_{ii} \sigma, \quad (4.2)$$

where the value of the trace of the piezospectroscopic tensor, $\prod_{ii}$ equals to 7.6 $\text{cm}^{-1}/\text{GPa}$.

4.5 X-ray diffraction

X-ray diffraction (XRD) provides information about compounds and crystalline phases which are present in materials. In this work, an XPERT-PRO X-ray diffractometer was used to identify the oxides species and corrosion products. The analyses were made in grazing incident mode. Characteristic Cu-K α radiation ($\lambda=1.54178 \text{ \AA}$) was generated from a copper anode X-ray tube. When the sample surface is hit by X-rays at the incident angle θ , the radiation is diffracted at an angle θ from the crystal planes (hkl) if the Bragg law, $2d_{hkl}\sin\theta = n\lambda$ ($n=1, 2, 3, \dots$), is satisfied, where d_{hkl} is the inter-planer spacing, λ the wavelength of radiation and n is order of diffraction [151]. The crystal structure and the phase composition can be identified by retrieving the diffraction angle and the intensity of the diffracted beams.

4.6 Scanning electron microscopy

Standard metallographic cross-section and surface morphology of the coatings were studied by Scanning electron microscope (SEM). Two modes are commonly used, namely secondary electron (SE) mode and back scattered electron (BSE) mode.

SE mode was applied to capture the morphology of sample surface due to its high spatial resolution; BSE mode, on the contrary, has a low depth resolution but high contrast to the chemical variation (elemental contrast), grain orientation and plastic deformation. Microanalysis of chemical compositions was performed in SEM by energy or wavelength dispersive spectroscopes (EDS or WDS). With the interaction between electron beam and samples, characteristic X-rays of corresponding elements can be identified. The quantitative measurement of chemical composition of interested area was performed by EDS with the correction of ZAF parameter from a pure Co standard. Electron back scatter diffraction (EBSD) was utilized for microstructure characterization and the data were processed and analyzed using the HKL Channel 5 software package (Oxford instrument).

4.7 Thermodynamic and kinetic modelling

In this work, most of the coating degradation processes can be intrinsically interpreted as phase transformation in a kinetic process. Thermo-Calc software is a useful tool to perform thermodynamic and kinetic modelling based on CALPHAD method. A powerful feature of the software is the possibility to obtain analytical derivatives of thermodynamic quantities with respect to equilibrium conditions by employing suitable databases. Combined with experimental observation, it is possible to make use of calculated phase diagram to explain research questions, such as how Fe addition alters the phase equilibrium [129] or calculate the aluminium activity for coating lifetime evaluation [37]. Diffusion module of Thermo-Calc software package, DICTRA, is quite handy to investigate the short-range and long-range diffusion behaviour. For instance, it demonstrated the positive effect of Ru on stabilizing β phase [130].

CHAPTER 5

Summary of Appended Papers

The objects of the present work cover three intrinsically correlated aspects: oxidation, hot corrosion and interdiffusion. In principle, hot corrosion can be interpreted as an accelerated oxidation which is enhanced by the fluxing mechanism; interdiffusion between the coating-substrate during oxidation or hot corrosion displays a great impact on the coating degradation. Therefore, most of the appended research works are inevitably dealing with one or combination of two objects. Nevertheless, the primary goal of the thesis work is to improve the coating performance through different approaches based on the understanding of the mechanisms.

Paper I: Long-term oxidation of MCrAlY coatings at 1000 °C and an Al-activity based coating life criterion

A reliable criterion to estimate the capability of MCrAlY coating to form α - Al_2O_3 is of great importance for the accurate evaluation of the coating lifetime, however, the use of empirical Al-concentration based criterion generates erroneous conclusion in some industrial applications. In this paper, a reliable Al-activity based criterion to estimate the capability of coating to form α - Al_2O_3 was proposed to for a more reliable evaluation. Survey of published results of critical Al-concentration to form α - Al_2O_3 on binary Ni-Al and ternary Ni-Cr-Al systems were collected, which can be categorized into three groups, including: 1) alloys are able to form a single scale of alumina, 2) alloys are able to form an alumina scale with other oxides outside, 3) alloys are unable to form a continuous alumina, the formation of severe internal alumina occurs. The use of the empirical Al-concentration based criterion is inadequate to mark the boundaries. By calculating the corresponding Al-activity using Thermo-Calc software, several boundaries were derived to differentiate three groups. The lower boundaries (the minimal Al activity) for the formation of a continuous alumina scale, can be used as a criterion to predict the formation of a continuous alumina layer. To support the criterion,

long-term oxidation tests at 1000 °C were performed on five different MCrAlY coatings for various periods of time up to 10,000 h. The new critical Al-activity criterion has been successfully adopted in α -Al₂O₃ formation prediction, showing a good agreement with experiment results. Therefore, it can be concluded that the extrapolation of new criterion from binary and ternary systems to multi-alloyed MCrAlY system is reasonable. Furthermore, the partial pressure of oxygen (p_{O_2}) in atmosphere has been taken into consideration by combination with Al-activity to calculate the critical chemical reaction constant (K) of α -Al₂O₃ formation. The criterion developed in this paper could be useful for the prediction of MCrAlY lifetime in industrial application, also provide a tool for MCrAlY coating composition design. In addition, experimental results showed complicated interdiffusion behaviour near the coating-substrate interface. The inward diffusion of Co and Cr from coating to substrate destabilized γ' in substrate and the outward diffusion of Ti and Ta from substrate to coating stabilized γ' in both the coating and substrate.

Paper II: Investigation of Element Effect on High-Temperature Oxidation of HVOF NiCoCrAlX Coatings

The investigation of element effect on MCrAlX coating performance is one of the primary goal of the project. In this paper, the effect of Ce and Ru additions in MCrAlX oxidation performance was evaluated. Two MCrAlX coatings were designed with RE addition: C1 coating with Ru and C2 with Ce in replace of Y. Isothermal and cyclic oxidation tests were performed at different temperatures to study the oxidation kinetics. Results showed a different oxidation activation energy between two coatings at 900-1100 °C range due to a significant rapid development of transient alumina of C2 coating at 900 °C. In the case of C1 with Y addition, the dominate mechanism of oxide growth shifted from outward growth of transient α -Al₂O₃ to inward growth of columnar α -Al₂O₃ with the prolonged oxidation time, while the continuous outward growth of transient α -Al₂O₃ dominated upto 5000 h accompanied by a weak inward growth of α -Al₂O₃ in C2 coating at 900 °C. From the observation of cross-sectional microstructure of TGO, Y addition in MCrAlY coating contributed to the development of a fine columnar α -Al₂O₃ inner layer, while an equiaxed inner α -Al₂O₃ layer was observed on C2 coating. The oxidation kinetic was modified by the microstructure of the oxide scale, giving a different oxidation activation energy. Besides, a reduction of cyclic oxidation resistance in C2 coating indicated that Ce is not as effective as Y in respect to improving the oxide adhesion.

Although no obvious effect of Ru addition on coating oxidation was observed, its positive influence mainly lied on the coating stability. Experimental results showed that Ru preferably partitioned in β phase and significantly stabilized it, which was further demonstrated by thermodynamic calculation on NiCoCrAlRu alloy system. The observation on the interdiffusion behaviour between the coating-substrate showed a retardation of inward diffusion of Al from C1 coating to substrate, which improved the long-term oxidation performance of the C1 coating. Short-range and long-range kinetic modelling were performed to validate the element effect, modelling results showed that the addition of Ru in MCrAlY coating suppressed the long-range interdiffusion between coating-substrate and reduced

the growth rate of β grain in C1 coating by short-range diffusion.

Paper III: The iron effect on oxidation and interdiffusion behaviour in MCrAlX coated Ni-base superalloys

Continued with the research on element effect, the positive effect of iron addition on improving coating performance was examined in this paper. Two MCrAlX powders with different Fe content (1.6 and 9.6%) were deposited on an IN792 superalloy by HVOF, isothermal oxidation and interdiffusion behaviour of coating was studied at 900-1100 °C range. Experimental results showed a minor effect of Fe on coating oxidation performance, while a significant effect was observed on the phase equilibrium of coating. High Fe addition in MCrAlX coating increased the β phase fraction and stabilized the β phase by extending the $\beta+\gamma$ phase region, which was validated by thermodynamic calculation.

A significant reduction of the Al depletion was observed in high Fe-containing coating, therefore, element composition profiles were measured by EDS to explore the interdiffusion behaviour. The diffusion coefficients of Al, D_{Al} , in substrate near the interface were calculated based on the element profiles at three temperatures. It's found that the presence of Fe composition gradient showed a minor impact on D_{Al} and the activation energy of D_{Al} is independent of the Fe gradient. High Fe additions modified the Cr interdiffusion and altered the local phase equilibrium at the coating-substrate interface. A discontinuous σ phase diffusion barrier layer formed at the coating-substrate interface due to the high Fe addition, suppressing Al inward diffusion at 900 °C. Besides, grain coarsening of the coating was retarded by high Fe addition during oxidation, which was demonstrated by experimental observation and kinetic modelling.

Paper IV: Failure mechanism of MCrAlY coating at the coating-substrate interface under type I hot corrosion

MCrAlY type coatings provide excellent hot corrosion resistance for superalloy component in gas turbine engines, however, the coating-substrate interface, where the substrate is only partially covered by the coatings, is vulnerable to the hot corrosion attack. In this paper, the failure mechanism of MCrAlY coating at the coating-substrate interface under type I hot corrosion was examined. IN792 disks were one-side coated with MCrAlY coating using HVOF, and type I cyclic hot corrosion test was carried out at 900 °C in a (0.8Na,0.2K)₂SO₄ molten salt condition. Results showed a minor corrosion attack at the coating center, while an accelerated degradation at the coating-substrate interface caused early failure of MCrAlY coating. Through the investigation on the microstructure of severe attacked region at the edge of the specimen, it is observed that the corrosion products grew rapidly from the substrate which later penetrated into the coating-substrate interface. With the continuous development of corrosion products, large local volume expansions at the coating-substrate interface occurred mitigating cracking of the coating bulk above. The cracks allowed the penetration of molten salts, creating new interfaces for basic fluxing reaction, where the corrosion products species formed presented a transition from Cr₂S₃ (near corrosion front) to (Al,Cr)₂S₃ (far end of corrosion front). In addition, the severe deformation of corroded coating

region also ruptured newly formed protective alumina scales on the coating surface, which further accelerated the attack. Eventually, an early coating spallation initiated from the edge of the specimen.

Paper V: Effects of surface finish on the initial oxidation of HVOF-sprayed NiCoCrAlY coatings

To improve the oxidation performance of MCrAlY coatings, post-deposition surface treatment has been widely used in the industrial application, however, its mechanism remains unclear. In this paper, the effect of post-deposition surface treatment on MCrAlY coatings was investigated focusing on the initial oxidation stage. HVOF sprayed MCrAlY coatings were surface-treated after deposition using mechanical polishing and shot-peening process in comparison with the as-sprayed condition. Three groups of MCrAlY coatings, including: as-sprayed, polished and shot-peened, were oxidized at 1000 °C for various time, and the weight gain of oxidized samples were recorded. After oxidation test, the evolution of the scale microstructure, morphology, phase composition, preferential scale nucleation site, residual stress, oxidation kinetics and cross-sectional microstructure were investigated using several experimental techniques, such as scanning electron microscopy (SEM), photo-stimulated luminescence spectroscopy (PSLS), and weight gain method. Results showed that both polished and shot-peened coatings exhibited superior performance due to the rapid formation of α -Al₂O₃ fully covering the coating and the suppression of the transient alumina growth, assisted by high density of α -Al₂O₃ nuclei on surface treatment induced defects. The fast growth rate of transient alumina is one magnitude higher than α -Al₂O₃, therefore, the suppression of transient alumina development effectively reduced the overall oxide scale growth rate on surface-treated coatings. On the contrary, the early development of a two-layer alumina scale on as-sprayed coating consisted of an inward-grown inner α -Al₂O₃ layer and an outer layer transformed from outward-grown transient alumina. The fast growth of transient alumina outer layer contributed to a higher overall oxide growth rate of the as-sprayed coating. Despite the oxide growth, the fast development of transient alumina scale led to the microvoids injection to the coating-scale interface, which later coalesced into large interfacial voids and therefore weakened the scale adhesion. To sum up, schematic illustrations of phase constitutions, transformation and growth of oxide scale formed on as-sprayed, polished and shot-peened coating at different oxidation stages were proposed for a better description of the influence of surface treatment.

Paper VI: The iron effect on hot corrosion behaviour of MCrAlX coating in the presence of NaCl at 900 °C

As a continuation of Paper III, cyclic hot corrosion tests of two MCrAlX coatings with different Fe contents were carried out in a molten salt (75 wt% Na₂SO₄+25 wt% NaCl) environment at 900 °C under type I hot corrosion. Results showed that the main corrosion reaction is the basic fluxing of Al at the coating surface, while Fe is relatively inert. To evaluate the extent of corrosion attack, the corrosion depth was defined as the depth of internal oxidation measured from the coating surface, where high Fe containing coating showed a less corrosion

depth development compared with the low Fe-containing counterpart. Based on the element composition profile measured by EDS, it is clear that the β phase near the coating surface was greatly stabilized due to the presence of local high Fe content. Thermodynamic calculation on isothermal phase diagram of NiCoCrAlFe system revealed that a high Fe addition in MCrAlX coatings shifts the equilibrium Al content of the γ phase towards a low level. Besides, the loss of Al due to interdiffusion between the coating-substrate was retarded by the formation of σ phase diffusion barrier as also reported in Paper III, moreover, it also reduces the loss of Cr from coating to the substrate. In summary, both effects contributed to a higher "effective" Al supply of the coating to resist basic fluxing and thereby enhanced the coating resistance to hot corrosion by reducing the rate of advancing of corrosion front.

Paper VII: Hot Gas Corrosion and its Influence on the Thermal Cycling performance of Suspension Plasma Spray TBCs

A case study of a high sulphur containing mix-gas, 1SO₂-0.1CO-20CO₂-N₂ (bal.) in vol%, cyclic hot corrosion behaviour of a suspension plasma spray (SPS) YSZ TBCs was investigated at 780 °C for a period of 186 h. Results showed a minor corrosion attack in the specimen center but rapid growth of Ni_xS_y corrosion product from the side of the specimen covering the sample surface. The formation and presence of various corrosion products at different locations were identified and analysed by a (Ni,Cr)-S-O stability phase diagram. The pre-corroded samples were later exposed to thermal cyclic (TCF) tests between 100-1100 °C with 1 h holding at 1100 °C. In comparison with the reference sample without any pre-treatment, pre-corroded samples showed a significant TCF life reduction (~61%) as a result of the infiltration of chromia scale in columnar gaps. Such oxide infiltration reduced the train tolerance of columnar structure. Moreover, the fast corrosion product growth at the bond coat and top coat interface promoted CTE mismatch stress build-up.

Concluding Remarks

The present research focuses on MCrAlX coatings behaviour with respect to oxidation, hot corrosion and interdiffusion, aiming to improve the coating performance through different approaches. A better understanding of coating degradation mechanisms can be achieved through the investigation on coating behaviour under different conditions supported by CALPHAD method. The outcomes of the research can provide guidance for the design and production of MCrAlX coatings and also are applicable for optimization of coating performance under various industrial applications.

1. The flexibility of MCrAlX coating design has been well recognized. In terms of composition design, more than one criterion should be considered, and the balance must be achieved between oxidation, hot corrosion and ductility. The existence of a universal good MCrAlY coating is questionable.
2. The essence of coating alloy development is the choice of doping element(s) and the optimization of the doping level: too few additions lead to a less significant effect, while over-doping could create unexpected side-effect.
3. The development of oxide scale at the initial oxidation stage is critical, which significantly affects the long-term performance. It is generally recommended to apply post-deposition surface treatment on thermal sprayed MCrAlX coatings for a better long-term oxidation performance. However, the parameters of treatment process should be carefully optimized.
4. The protection of MCrAlX coatings for superalloy is substantial under oxidation or hot corrosion. However, the interdiffusion between coating and superalloy could quickly degrade the system, which requires extra attention. The great impacts of superalloy on coating performance further demonstrates the fact that coating design should be application-oriented.

5. The standard for coating performance evaluation should be flexible and targeting the application.
6. The design principle of MCrAlX coatings could be well adapted in the scope of integrated computational materials engineering (ICME). CALPHAD method is quite profitable in alloy design, consequently, the reliability of the databases is essential.
7. Although the history of MCrAlX coating development is long, there's still a great potential to explore. For instance, its close correlation with high entropy alloys (HEA) is worthy to be mentioned. A bright future awaits.

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Part II

Papers Included

Papers

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