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Some aspects of elemental behaviour in HVOF MCrAlY coatings in high-temperature oxidation

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Abstract. MCrAlY coatings are widely used to protect superalloys against oxidation and corrosion at high temperature in gas turbine engines. To design a durable MCrAlY coating, the behaviour of alloying elements in coating-superalloy system needs to be better understood. After oxidation tests in temperature range between 900 °C to 1100 °C, the development of the microstructures in the samples was analysed at the coating surface or in areas near the coating-superalloy interface. Some interdiffusion simulations were also done to model the diffusion behaviour of alloying elements in different coating-superalloy couples. The results show that both oxidation at the coatings' surface and the elements' diffusion inside of the materials were temperature- and chemical-composition dependent. The behaviour of some minor elements like Y, Hf, Ru and Ir in the oxidation processes was particularly studied by tracking their position and composition in the materials.

Abbreviations

high-velocity oxy-fuel (HVOF)

coating-substrate interface (CSI)

inner- β -depletion zone (IBDZ)

γ' -depletion zone (GPDZ)

secondary β phase (SBP)

1. Introduction

MCrAlY coatings (M for Ni and/or Co) are widely used to protect the base materials (superalloys) against high-temperature oxidation and hot corrosion in gas turbine engines. Two important issues always capture researchers' attention when the oxidation behaviour of MCrAlY-

coated superalloys is investigated at high temperature: the formation of oxides at coating surface, and the interdiffusion-induced microstructural evolution at the coating-substrate interface (CSI).

MCrAlY coatings are good alumina formers [1,2]. At high temperature, a continuous and protective alumina scale can form at MCrAlY surface, to protect the coating and base material against high-rate oxidation. Dependent on coating composition and temperature, other oxides like Cr_2O_3 , CoO , NiO , and spinels may also form [1-3]. Brandl et al.'s results showed that, besides alumina, Cr_2O_3 formed at 950 °C while NiAl_2O_4 and CoAl_2O_4 spinels formed at higher temperature (1050 °C) on a NiCoCrAlYRe coating. The oxidation behaviour of MCrAlY coatings was also influenced by the surface modification [4,5] and coating spraying technique [3,6,7]. For instance, ground and polished samples performed an accelerated oxidation due to surface deformation [5]. Coatings sprayed by high-velocity oxy-fuel (HVOF) technique may have a slower oxidation rate than coatings sprayed by VPS, due to a probable diffusion-blocking effect by some small alumina formed in the coatings after HVOF spraying [3].

The microstructural evolution near the coating-substrate interface (CSI) was dependent on coating composition, substrate composition, and temperature [8,9]. For instance, due to the diffusion of Co into the substrate, secondary β phase (SBP) may form in the substrate [8]. Taylor et al.'s result [10] further showed that the Al in the SBP could diffuse back to the coating and be used for the oxidation at the coating surface. TCP phases, like σ -CrW, may also form near the CSI due to the interdiffusion of alloying elements in some coating-superalloy systems [11]. In coating side, due to the diffusion of Al into the substrate, there usually formed a β -depletion zone [8]. With development of thermodynamic and kinetic databases in recent decades, the microstructural evolution in coating-superalloy systems can be simulated [9,12,13].

The current work focuses on the behaviour of main elements (Ni, Co, Cr and Al) and some minor elements (Y, Hf, Ru and Ir) in some HVOF MCrAlY coatings during high-temperature oxidation processes at 900 to 1100 °C. The diffusion behaviour of alloying elements was also simulated by using DICTRA software [14]. This paper is aiming at providing knowledge for designing new MCrAlY coatings to be used for the oxidation protection at high temperatures.

2. Experimental and simulation

The MCrAlY coatings were sprayed by using high-velocity oxy-fuel (HVOF) technique. The thickness of the coatings was in a range about 170 to 200 μm . The substrate material to hold the coatings was a Ni based superalloy – Inconel 792. The nominal compositions of the MCrAlY coatings and the substrate are shown in Table I. A0, A1 and A2 were Ni based MCrAlY coatings, and B0, B1, B2 and B3 were Co based ones. The heat treatment on the samples after the HVOF spray included a solution annealing at 1120 °C for 2 hours in vacuum and an ageing treatment at 845 °C for 24 hours in air. Such heat treatment was similar to the practice in industry, aiming at

improving the bonding strength of the CSI and strengthening the substrate by creating γ' precipitates. After the heat treatment, the porosity in the coatings was lower than 1%.

The samples were subjected to oxidation at 900 °C, 1000 °C, or 1100 °C in air. The microstructural development in the materials was studied after different exposure times. The samples were cross-sectioned and polished for the investigations in an optical microscope (OP) and a scanning electron microscope (SEM). In the SEM, there are two modes to image the microstructures in the materials: secondary-electron (SE) mode, and backscattered-electron (BSE) mode. SE images capture surface-sensitive morphologies while BSE images usually give atomic and crystalline contrasts. Chemical compositions were measured by using energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) in the SEM.

To better understand the behaviour of the alloying elements in the materials at such high temperatures, some thermodynamic calculations and diffusion simulations were carried out. For instance, some ternary phase diagrams were calculated by using ThermoCalc, and interdiffusion simulations were performed in a “rule of mixture” homogenization model by DICTRA [9,13,14]. In the interdiffusion simulations in the coating-substrate diffusion couples (150 μm coating and 200 μm substrate), the diffusion behaviour of the alloying elements through the CSI was simulated. Since the simulations were only for diffusion processes when there still reserved a lot of β -NiAl phase in the coating (the β phase can provide Al for the surface oxidation), the surface oxidation was believed to have no significant influence on the microstructural development near the CSI. Therefore, the surface oxidation was not considered in the simulations. The input compositions of the coatings and the substrate in the simulations used the nominal compositions as given in Table I; to avoid a sudden change of the elemental concentrations at the CSI, the input composition profiles for the simulations were gently smoothed at the CSI by using error equations.

3. Results

3.1. Coatings as-received and heat-treated

Fig. 1a shows the morphology of the powders used for the HVOF spray. The average diameter is about 30 μm . The cross section of the powder particles in Fig. 2b (BSE image) shows some dendrite-like morphology; the dark-grey phases are Ni, Al rich, while the light-grey phases are Co, Cr rich.

The cross section of an as-received coating is shown in Fig. 2a. Splat-on-splat structures can be seen with some cracks and pores which mark the splats' interfaces. Among the splats, O and Si are rich along the splats' interfaces, while Y is uniformly distributed (Fig. 2b).

After the solution and ageing heat treatment, a typical $\gamma+\beta$ microstructure forms in coatings, as shown in Fig. 3a (in coating part, dark phases are mainly pores, dark-grey phases are β , and light-

grey phases are γ). Comparing with the as-received coating (Fig. 2a), the amount of cracks and pores is significantly reduced due to a sintering effect during the heat treatment; the porosity of the coatings becomes less than 1%. The quality and the bonding strength of the CSI are also improved. In addition, the distribution of the alloying elements in the coating is also changed (Fig. 3b) from the as-received status (Fig. 2b). For instance, Si is dissolved into the metallic phases in the splats, while Y tends to move to the splats' interfaces.

3.2. Interdiffusion during oxidation

The oxidation tests at high temperatures (900 °C, 1000°C, and 1100 °C) cause the microstructural development near the CSI. The study on the microstructures in the samples shows that A1 and A2 have the same microstructural development as A0, while B1, B2, B3 share the same behaviour as B0, therefore, the microstructural evolution due to the interdiffusion of alloying elements can be focused in A0 and B0.

At 900 °C for 5000 hours (Fig. 4), A0 and B0 show considerably different microstructures at the CSI. In A0, due to the diffusion of Al into the substrate, β phase in the coating is depleted in a certain thickness and γ' phase formed in this β -depletion zone. Such β -depletion zone is termed inner- β -depletion zone (IBDZ). In B0, there is no IBDZ formed in the coating for 5000 hours. Furthermore, β phase forms in the substrate in a γ' -depletion zone (GPDZ); such β phase is termed secondary β phase (SBP). Some Ta-Ti-carbides are also found in the GPDZ, which may form due to the dissolution of the original large Ta-Ti-carbides in the substrate followed by the re-precipitation of the carbides in the GPDZs.

At 1000 °C, an IBDZ forms with a $\beta \rightarrow \gamma$ transition in A0 for 1500 hours (Fig. 5a), but after a longer time (5000 hours) $\beta \rightarrow \gamma'$ transition occurs in the IBDZ (Fig. 5b). In B0 at 1000 °C, the microstructure after 1500 hours (Fig. 5c) is similar to that at 900 °C for 5000 hours (Fig. 4b), i.e. SBP forming in the substrate and no IBDZ forming in the coating. With a longer time at 1000 °C (5000 hours), the SBP disappears and an IBDZ forms in the coating (Fig. 5d).

With another 100 °C increase of the oxidation temperature (at 1100 °C, Fig. 6), IBDZ forms in both coatings (A0 and B0) with similar thicknesses but with ten-time shorter times. In other words, the β -depletion rate in the coatings, due to the interdiffusion, appears to be about ten-time faster with a 100 °C increase of the oxidation temperature, which agrees with the results by diffusion modelling [9]. The γ' -depletion rate in the substrate is also highly accelerated at the higher temperature.

The coating-substrate systems, at the high temperatures, behave as diffusion couples. The diffusion direction of the alloying elements is determined by their thermal activities. As an example, Fig. 7 shows the activity profiles of the alloying elements in the A0-substrate couple at 900 °C for 5000 hours by the interdiffusion simulation; such activity results are corresponded to the composition-profile results in Fig. 8b. The results in Fig. 7 indicate a diffusion process with Co and Al moving from the coating to the substrate and the other elements in the opposite

direction, since only the activities of Co and Al are higher in the coating than that in the substrate. The difference of the microstructural evolution near the CSI between A0-substrate and B0-substrate couples is definitely due to the difference of the coating compositions. Since A0 and B0 have a similar Al content, the difference should be related to the Co and Cr contents in the two coatings.

Fig. 8 and 9 give the simulation results (curves) of microstructure and composition in the A0-substrate and B0-substrate couples, with a comparison with some experimental data (dots). The calculated profiles have somewhat fluctuations due to the numerical instability of the DICTRA simulations, for instance on the phase profiles in Fig 8. Ignoring the numerical fluctuations, the simulated microstructures in the A0-substrate couple are basically comparable with the experimental observations. The composition profiles, especially the profiles of the four main elements (Ni, Co, Cr and Al), are also well predicted by the simulation. According to those results, how the β phase is depleted in the coating seems to be mainly related to the diffusion of Co from the coating to the substrate. For instance, at 1000 °C and 1100 °C, there forms Co-rich zones near the CSI (the Co concentration is about 7% higher than that in the mid of the coating) where Cr is also rich (the Cr concentration is about 6% higher than that in the mid of the coating) but the Ni and Al contents are low (the Ni and Al concentrations are about 8% and 5%, respectively, lower than that in the mid of the coating), which promotes the formation of β -depleted zones, i.e. IBDZ, in the coating, and the formation of GPDZ in the substrate; γ' becomes unstable when the concentrations of Co and Cr are high (e.g. when Co is above 25% or Cr is above 20% at 1000 °C in NiCoCr-5Al-1.5Mo-0.5Si-3Ta-3Ti-3W alloys [9]). At 900 °C, however, Co and Cr concentrations in areas near the CSI (about 20 wt.% Co, 15 wt.% Cr) are not as high as that at 1000 °C (about 28 wt.% Co, 22 wt.% Cr) and 1100 °C (about 25 wt.% Co, 18 wt.% Cr), so γ' phase can form when the coating lose Al into the substrate and β phase is depleted.

For the B0-substrate couple (Fig. 9), the composition profiles predicted are barely satisfactory due to the limitation of the database used. Therefore, the microstructures predicted were imperfect either. By focusing on the experimental data, i.e. the dots in the graphs, one can see that from 900 °C to 1100 °C, Co and Cr peaks form at the CSI where a Ni valley is found. In other words, Co and Cr replace Ni near the CSI, which causes the microstructure changes [8]. SBP forms in the substrate in short time, but gradually disappears with longer time (see Fig. 5c, d or Fig. 6c, d), probably due to a further diffusion of Al in the SBP into the deeper substrate or due to a back diffusion of Al from the SBP to the coating [10].

Fig. 10 presents the results of the compositions of Y, Ru and Ir in coating-substrate couples by EDS measurement. In those graphs, the color bars attaching the CSI stand for the thickness of the GPDZs forming in the substrate. The size of the GPDZs can be taken as a characteristic scale marking the diffusion depths of alloying elements like Co and Al from the coating into the substrate. Since the uncertainty range of the EDS measurement is about 0.2 wt.% mainly due to an overlap of the EDS peaks from different elements, 0.2 wt.% is taken as the detectable level for those minor elements. As shown in Fig. 10a, Y is only detected in the coating part even after

long-term thermal exposure. That could be due to that Y is mainly in oxide form in the HVOF coatings, making Y hardly diffuse into the substrate. Ru and Ir have a different behaviour from Y (Fig. 10b and c); they diffuse from the coating to the substrate with the same diffusion depths as the thickness of the GPDZs. Some literatures [15,16] claimed that Ru and Ir could hardly dissolve in the γ' phase in superalloys, which is probably the reason that Ru and Ir is only detected in the coating or in the GPDZs. Furthermore, our previous results [17] showed that Ru and Ir mainly dissolved in the β phase in MCrAlY (Fig. 11). In addition, Ru and Ir are not detected as oxides at the coating surface, nor to dissolve in alumina scales in this study.

The ability of an element to stabilize a phase can be investigated by studying the effect of the element on the extension of the phase field in phase diagram. For instance, Ochiai et al. [18] analysed the stability of γ' phase in a Ni-Al-X phase diagram. By applying such approach, Ni-Al-X ternary phase diagrams are draw in Fig. 12, by highlighting the extension of γ' and β fields due to the addition of the third element X in Ni₃Al or NiAl alloys. The extended phase field of γ' (Fig. 12a) and β (Fig. 12b) is a collection of many Ni-Al-X phase diagrams in literature and by calculation using ThermoCalc software; the details are shown in Table II. The site preference of the X elements in the FCC Ni₃Al cell or in the BCC NiAl cell is also presented in Fig. 12 with red for strong Al-site preference, blue for strong Ni-site preference, and green for slight site preference or no preference. Note that the site preference is only for the case that a small fraction of an X element is added into Ni_{0.75}Al_{0.25} or Ni_{0.5}Al_{0.5} chemistries by either simulations or experiments. The diagrams in Fig.12 can provide a basic knowledge of how the alloying elements affect the stability of γ' and β phases at high temperatures, even for multi-component MCrAlY coatings and superalloys. For instance, Fig. 12a shows that Ru and Ir can hardly dissolve in the γ' phase (limited size of the γ' -phase field) while the result in Fig. 12b indicates that Ru and Ir can greatly stabilize the β phase by largely extending the β phase field in the phase diagram.

3.3. Oxidation

The MCrAlY coatings in this study are good alumina formers at high temperature in oxidation. Continuous and dense alumina scales can form at the coating surfaces. Besides the alumina, the XRD results (Fig. 13) show that other oxides, typically (Co,Ni)(Cr,Al)₂O₄ spinels, also form. The crystalline structure of the spinels is found to be strongly related to the oxidation temperature. As shown in Fig. 13, the spinels have a CoCr₂O₄ structure at lower temperature (900 °C), but own a CoAl₂O₄ structure at higher temperature (1100 °C), and with both types at the medium temperature (1000 °C). This result is further confirmed by measuring the chemical composition of the spinels (Fig. 14). In both A0 and B0, the spinels at 900 °C have a very low Al content (~ 0 to 5 at.%) and a high Cr content (~ 25 to 30 at.%), coinciding to the CoCr₂O₄ form. However at 1100 °C, the spinels contain a higher Al content (~ 20 at.%) and a lower Cr content (~ 10 at.%) to coincide with the CoAl₂O₄ form.

Fig. 15a shows a cross section of a coating in which Al-rich β phase is highly depleted due to both the surface oxidation and the diffusion of Al into the substrate after an isothermal oxidation

at 1100 °C. The EDS mapping results in Fig. 15b show that Y, as oxides, is preferably distributed along the splats' interfaces and on the coating surface. In addition, in a cyclic oxidation process as shown in Fig. 16, alumina scale can partially spall off and then a new alumina scale forms, which causes the layer-by-layer morphology of alumina at the coating surface; the thermal cycling is a temperature cyclic process with one-hour heating at 1100 °C and ten-minute cooling down to 100 °C by forced air. Since Y can be found on each alumina scale surface, it is believed that during the oxidation process Y can diffuse to the surface to participate in the oxidation.

Besides Y, another oxygen-affinitive element, Hf, also plays a critical role in the growth of alumina scales. As shown in Fig. 17, Hf is mainly segregated at the grain boundaries of alumina. Some Hf and Y rich particles can be found inside the coating, which can be probably Y-Hf-rich oxides (Fig. 18). Fig. 19 shows a comparison of the oxidation behaviour of the coatings without (B0) and with Hf (B3). A much higher oxidation rate occurs in B3 with a typically uneven inward growth of alumina scale (Fig. 19e and f), indicating that the segregation of Hf at the grain boundaries of the alumina accelerated the inward diffusion of oxygen and the inward growth of alumina scale.

4. Discussion

For the MCrAlY coatings, the main elements are Ni, Co, Cr and Al which usually have high concentrations, while other elements like Y and Hf are added with small amounts, being called minor elements. Based on the results obtained above, the following discussion will focus on the role of those elements in the phase stability in MCrAlY coatings, microstructural evolution at CSI, and oxidation performance at the coating surfaces.

4.1. Main elements (Ni, Co, Cr, and Al)

4.1.1. β phase stability

The microstructure of free-standing MCrAlY coatings is mainly dependent on their composition and the operation temperature, usually having a phase combination of $\gamma+\beta$ or $\gamma+\beta$ +others [1,62]. β is a BCC phase and has a NiAl-based chemistry in which other elements like Co and Cr can be dissolved. The results in Fig. 12 have shown that Co prefers to stay in the Ni sites in β phase; Co can even totally replace Ni in the β phase as shown in the Ni-Al-X diagram. Cr shows no special preference on Ni and Al sites in the β phase, but usually occupies the sites on which the element (Ni or Al) is poorer in content [23,28]. The composition limit for Cr induced extension of the β phase field is around 15 at.% in the Ni-Al-X diagram. Because of this, in a $\gamma+\beta$ coating Cr usually has a higher solubility in γ phase than in β phase.

4.1.2. γ' phase stability

Up to around 25 at.%, Co can be dissolved in γ' -Ni₃Al phase by occupying the Ni sites (Fig. 12); keep in mind that the total Ni sites are 75 at.% in the FCC cell. Cr has around 10 at.% solubility in the Ni₃Al to replace Ni and around 5 at.% to replace Al. In multicomponent superalloys where many other alloying elements are also added, Co and Cr usually lose their competitiveness to occupy the Ni or Al sites in the γ' phase, and mostly dissolve in the disordered γ phase. Due to that, increasing the content of Co and/or Cr usually makes γ' unstable at high temperatures. This result is quite important for understanding the microstructure changes in $\gamma+\gamma'$ substrate due to the interdiffusion effect at the CSI, for instance the depletion of γ' in the substrate due to the enrichment of Co and Cr.

4.1.3. Microstructural evolution near CSI

Due to their higher activity on the coating side (Fig. 7), Al and Co diffuse into the substrate, while other elements diffuse towards from the substrate into the coating. The interdiffusion of the alloying elements drives the microstructure changes [9]. Itoh et al.'s research [8] indicated that the microstructures in the substrate were mainly controlled by the diffusion of Co (and Ni) through the CSI, which agrees with the results in this work. The microstructures in the GPDZ are different when the substrate is coated with different coatings (Fig. 4 to 6), which is mainly due to a competition of the diffusion of Al and Co. The inward diffusion of Al can cause enrichment of Al under the GPDZ (see the Al profiles in Fig. 8 and 9). Since Al is usually diffuses faster than Co, the diffusion depth of Al is larger than that of Co; for instance, the diffusivity of Al in the γ phase is around $1\text{E-}14\text{ m}^2/\text{s}$ while Co's is around $6\text{E-}16\text{ m}^2/\text{s}$ at the CSI at 1000 °C after the interdiffusion for 1500 hours (the values are calculated by DICTRA). However, within a short time, as shown by the microstructures in Fig. 4b, 5c and 6c, some Al may be trapped in the GPDZ to form SBP, which occurs only when a large amount of Co diffuses into the substrate (e.g. being coated with the high Co coating – B0) [9]. The GPDZ may not form in the substrate if being coated with a low Co and Cr coating and the temperature is low (Fig. 4a); in this case, Co does not highly diffuse into the substrate (Fig. 8a).

The contents of Co and Cr in the coatings also affect the behaviour of the depletion of β phase in the coatings. The results show that a higher Co and Cr content, or a higher oxidation temperature, promotes the formation of a pure- γ IBDZ in the coating; vice versa the formation of a $\gamma+\gamma'$ IBDZ (Fig. 4, 5 and 6).

4.1.4. Surface oxides

As shown in Fig. 15, a continuous alumina scale can form at the MCrAlY coating surface in the oxidation processes at high temperature in air. The growth of the scale requires the support of Al from the coating. If the scale spalls off, especially in a thermal cyclic oxidation condition (Fig. 16), new alumina can form provided that a sufficient amount of Al exists in the coating.

Besides alumina, CoCr₂O₄ or CoAl₂O₄ spinels also form, typically above the alumina scale. The results in Fig. 13 and 14 show that the spinels tend to have an Al-dominant CoAl₂O₄

structure at higher temperature (e.g. 1100 °C) but a Cr-dominant CoCr_2O_4 structure at lower temperature (e.g. 900 °C). Therefore, the structure of the spinels is temperature dependent. The transition from CoCr_2O_4 to CoAl_2O_4 when increasing temperature can be due to an evaporation of Cr at the higher temperatures [63,64].

4.2. Minor elements (Y, Hf, Ru and Ir)

4.2.1. Phase stability and diffusion behaviour

As shown in Fig. 12a, the solubility of Y, Ru and Ir in γ' is very limited, while Hf has a similar solubility as Nb in γ' . The results in Fig. 10 b and c show that Ru and Ir can hardly diffuse into the area where γ' phase exists. In the β phase, Ru and Ir can expand the phase field largely (Fig. 12b), indicating that Ru and Ir are strong β phase stabilizers. Hf has a similar solubility as Ti in β phase according to the result in Fig. 12b. However, in the HVOF MCrAlY coatings, elements like Y and Hf which are oxygen-affinitive tend to form oxides at splats' interfaces or at coating surfaces (Fig. 3b, 15b, 17 and 18).

4.2.2. Surface oxidation

Y is added in MCrAlY coatings mainly for improving the adhesion of alumina scales [65,66]. Y can also affect the growth rate of alumina scales. According to some published work, if large Y-oxides form in the alumina scale, the growth rate of the alumina scale will increase due to an increase of the inward diffusion of oxygen along grain boundaries [67-69]. However, if no large Y-oxides form, doping some yttrium in the alumina scale can decrease the grain-boundary diffusion of cations, resulting in a slower oxidation rate [70,71].

The results in Fig. 19 clearly show that the segregation of Hf at the alumina grain boundaries accelerates the inward diffusion of oxygen and causes a higher oxidation rate of the coating, agreeing with some other researches [72,73]. Matsudaira et al's results [71] showed that doping some Hf in an alumina layer could increase the inward diffusion of oxygen along grain boundaries. Therefore, the Hf segregation in alumina scales provides fast diffusion paths for oxygen.

Since no Ru and Ir oxides have been found, and those two elements can not be detected in alumina scales or spinels either, it is believed that Ru and Ir have no direct influence on the oxidation of the coating. However, some researches claimed that Ru and Ir can form oxides in some RuAl or IrAl alloys, but they were evaporated away at high temperature [74,75]. More study is needed to investigate the influence of Ru and Ir on the oxidation behaviour of MCrAlY coatings in the future.

5. Conclusions

This paper studies the performance of some HVOF MCrAlY coatings in high-temperature oxidation, with focusing on the behaviour of alloying elements including the main elements (Ni, Co, Cr and Al) and some minor elements (Y, Hf, Ru and Ir). The main remarks can be summarized as follows.

1. The diffusion of Al from the coating to the substrate and the enrichment of Co and Cr at the coating-substrate interface are the key factors causing the microstructure changes near the coating-substrate interface. The main microstructure changes are, like, the formation of β -depletion zone in the coating, the formation of secondary β phase and γ' -depletion zone in the substrate.

2. Spinels formed at the coating surface, above the alumina scales, are temperature dependent. At a lower temperature (e.g. 900 °C), the spinels have a CoCr_2O_4 structure, but become a CoAl_2O_4 structure at a higher temperature (e.g. 1100 °C).

3. The addition of Hf (0.3 wt.%) causes a significantly accelerated inward growth of alumina scales, by segregating at the grain boundaries of alumina to provide fast diffusion paths for oxygen.

4. Ru and Ir mainly dissolve in the β phase in the MCrAlY coatings, and can hardly diffuse into a $\gamma+\gamma'$ area in substrate. In addition, Ru and Ir may be inert in the oxidation at the coating surface.

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Tables and figures.

Table I. Nominal compositions of the HVOF coatings (in weight percent).

Alloys	Ni	Co	Cr	Al	Y	Si	Ta	Ir	Ru	Hf	Mo	Ti	W	C	Zr+B
A0	Bal. (44.85)	28	15	11	0.4	0.25	0.5								
A1	Bal. (43.85)	28	15	11	0.4	0.25	0.5		0.5		0.5				
A2	Bal. (44.35)	28	15	11	0.4	0.25	0.5	0.5							
B0	30	Bal. (38.9)	20	10	0.6	0.5									
B1	30	Bal. (37.9)	20	10	0.6	0.5	0.5		0.5						
B2	30	Bal. (38.4)	20	10	0.6	0.5		0.5							
B3	30	Bal. (37.8)	20	10	0.6	0.5		0.05	0.25	0.3	0.5				
substrate	Bal. (60.69)	9	12.5	3.4			4.2				1.9	4	4.2	0.08	0.03

Figure 1. Powders used for the HVOF spray. (a) SE image showing the morphology of the powders, (b) BSE image showing the cross section of a powder.

Figure 2. (a) BSE image showing the cross section of an as-received coating, (b) EDS mapping of O, Si and Y in the as received coating. The coating is A0.

Figure 3. (a) BSE image showing the cross section of a coating after the heat treatment, (b) EDS mapping of O, Si and Y in the coating. The coating is A0.

Figure 4. Microstructure near the interface (marked by dash curves) between the coating (upper part) and the substrate (lower part) due to the interdiffusion of elements. The oxidation is at 900 °C for 5000 hours in (a) A0 and (b) B0. “c” donates MC-type carbides rich of Ti and Ta.

Figure 5. Microstructure near the interface (marked by dash curves) between the coating (upper part) and the substrate (lower part) due to the interdiffusion of elements. The oxidation is at 1000 °C: (a) for 1500 hours in A0, (b) for 5000 hours in A0, (c) for 1500 hours in B0, and (d) for 5000 hours in B0. “c” denotes MC-type carbides rich of Ti and Ta.

Figure 6. Microstructure near the interface (marked by dash curves) between the coating (upper part) and the substrate (lower part) due to the interdiffusion of elements. The oxidation was at 1100 °C: (a) for 100 hours in A0, (b) for 300 hours in A0, (c) for 100 hours in B0, and (d) for 300 hours in B0. “c” donates MC-type carbides rich of Ti and Ta.

Figure 7. Activity profiles of the alloying elements in the A0-substrate system by the interdiffusion simulation (condition: 1100 °C, 1500 hours), corresponding to the results in Fig. 8b. Distance=0 marks the coating-substrate interface, and the coating is on the right. The activity profiles are only showing their shapes, not exact values.

Figure 8. Profiles of phase fractions and elemental compositions by simulation (curves) and experiment (dots) in the A0-substrate system after the interdiffusion (a) at 900 °C for 5000 hours, (b) at 1000 °C for 1500 hours, and (c) at 1100 °C for 100 hours. Distance=0 marks the coating-substrate interface, and the coating is on the right. The curves and dots in color should be corresponded with the phases or the elements with the same color in each graph. The fluctuations on the profile curves, particularly on the phase-profile curves, are due to the numerical instability of the calculations by DICTRA software.

Figure 9. Profiles of phase fractions and elemental compositions by simulation (curves) and experiment (dots) in B0-substrate system after the interdiffusion (a) at 900 °C for 5000 hours, (b) at 1000 °C for 1500 hours, and (c) at 1100 °C for 100 hours. Distance=0 marks the coating-substrate interface, and the coating is on the right. The curves and dots in color should be corresponded with the phases or the elements with the same color in each graph.

Figure 10. Compositions of Y, Ru and Ir in some samples measured by EDS. The solid bars from the CSI to the substrate stand for the γ' -depletion zone. The colors should be corresponded to the relevant oxidation conditions.

Figure 11. Solid solution content of Ir and Ru in coating A1 and A2 during oxidation processes, showing the dissolution of these two elements in γ and β phases near coating surfaces [17].

Table II. Summary of the site preference of alloying elements X in Ni-Al-X systems for the γ' -Ni₃Al and β -NiAl phases. The calculation (“calc”) or experimental (“exp”) results are mainly for high temperatures at about 800-1300 °C (in some references temperature effect is not considered). The results are mainly for the case when small amount of an X element is added to replace Ni or Al in the chemical formulas of Ni₃Al or NiAl.

Elements	Site preference in γ' -Ni ₃ Al phase	Site preference in β -NiAl phase	Ref. for phase diagrams
Co	(calc) slightly Ni site [19]; (calc) composition dependent [20]; (exp) Ni site [21,22];	(calc) Ni site [23-26]; (exp) Ni site [27,28];	[29]
Pt	(calc) Ni site [20,30];	(calc) Ni site [26]; (exp) Ni site [28];	[31]
Pd	(calc) Ni site [20,30]; (exp) Ni site [32].	(calc) Ni site [26]; (exp) Ni site [33];	-
Ru	(calc) slightly Al site [19]; (calc) Al site [20]; (calc) Ni site [30]; (exp) Al site [15,34];	(calc) slightly Al site [24]; (calc) Ni site [26]; (exp) Ni site [28,33];	[35,36]
Ir	(calc) composition dependent [20];	(calc) Ni site [26,26];	[37]
Re	(calc) Al site [19]; (exp) Al site [15];	(calc) Ni site [26]; (exp) Ni site [38];	[39]
Fe	(calc) Al site [20]; (exp) slightly Al site [22]; (exp) Al site when adding < 3-4 at.% [40]; (exp) composition dependent when adding > 3-4 at.% [40]; (exp) composition dependent [21]	(calc) Ni site [23,41]; (calc) slightly Ni site [26]; (calc) slightly Al site [24,25]; (calc) composition dependent [42]; (exp) composition dependent [27,28,38,43,43-45]; (exp) Al site[45,46];	[47,48]
Cr	(calc) Al site [19]; (exp) Al site [21,49,50];	(calc) composition dependent [23]; (calc) Al site [24,25,41]; (calc) composition dependent [26]; (exp) composition dependent [28]; (exp) Al site [38,51];	[52]
Mn	(calc) Al site [20];	(calc) Ni site [23]; (calc) composition dependent [26]; (exp) Al site [28]; (exp) composition dependent [53];	[54]
Mo	(calc) Al site [19,30];	(calc) composition dependent [23,26]; (calc) Al site [24,41]; (exp) Ni site [28];	-
W	(calc) Al site [19];	(calc) composition dependent [23,26]; (calc) Al site [24];	-
Ti	(calc) Al site [19]; (exp) Al site [49];	(calc) Al site [23-26,41]; (exp.) Al site [28,55,56];	[57]
Ta	(calc) Al site [19]; (exp) Al site [50];	(calc) Al site [23,24,26]; (exp) Ni site [28];	[58]
Si	-	(calc) Al site [23,24];	[59]
Nb	(calc) Al site preference [19];	(calc) Al site [23,24,26]; (exp) Ni site [28];	-
Hf	(calc) Al site [20]; (exp) Al site [22,60];	(calc) Al site [23,24,26];	[61]
Zr	(calc) Al site [20];	(calc) Al site [23,24,26,41];	-
V	(calc) Al site [20];	(calc) Al site [23-26,41]; (exp) Al site [60]; (exp) Ni site [28];	-
Y	(calc) Al site [19];	-	-

Figure 12. The effect of element X on the extension of the fields of γ' phase (figure a) and β phase (figure b) in the Ni-Al-X phase diagrams, showing the preferred site in the Ni_3Al and NiAl cells (red for Al-site preference, blue for Ni-site preference and green for no strong preference). The site preference of the X elements and the phase-field extension are based on the results in Table II and some calculations by using Thermo-Calc software.

Figure 13. XRD spectra showing the spinels with a CoCr_2O_4 structure at lower temperature but with a CoAl_2O_4 structure at higher temperature: (a) for coating A0, (b) for coating B1.

Figure 14. Compositions of spinels measured by quantitative EDS. The results for 900 °C are taken from the sample after oxidation process for 5000 h, while the results for 1100 °C are for 100 h. The EDS measurement is done on the cross section of samples. Figure (c) gives an example of a cross section of coating A0 after oxidation at 900 °C for 5000 h, showing alumina scale and spinels.

Figure 15. (a) BSE image showing the cross section of coating B0 after oxidation at 1100 °C for 500 h, (b) EDS mapping of the area marked by red square in figure (a).

Figure 16. EDS mapping on the layer-by-layer alumina scales on the coating surface. The red arrows mark some Y-rich particles.

Figure 17. EDS mapping on Hf-containing oxide layer in the coating B3 after oxidation at 1000 °C for 1000 hours. The coating surface is to the right.

Figure 18. EDS mapping on a part of cross section of coating B3 after oxidation at 1000 °C for 1000 hours, showing the Y and Hf rich particles.

Figure 19. Comparison of the oxidation behavior between coating B0 and B3 at 1000 °C for 10000 h. Figure (a), (b), (c) are for B0, and (d), (e), (f) for B3. (a) and (d) are showing the overview of the cross sections of the coatings (BSE). (b), (c), (e), (f) are showing the high-resolution morphology of the oxide scales in SE and BSE modes. The brighter phases above the alumina scale in (c) are spinels.