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Effect of Alloyed Lu, Hf and Cr on the Oxidation and Spallation Behavior of NiAl

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Abstract

The influences of alloyed Lu, Hf and Cr on the oxidation and spallation behavior of NiAl were investigated. Although Lu has a “block effect” of Al as Hf does, the oxidation rate of Lu-doped NiAl is significantly higher, due to: (1) inhibition of θ - to α -Al₂O₃ transformation in early oxidation stage; (2) stronger scale grain refinement effect and enhanced oxygen transport rate. Segregation of S and C occurs not only at the alloy/scale interface, but also within the scale. Both Lu and Hf can significantly improve the scale adherence. However, This beneficial effect can be easily overcompensated by Cr.

Keywords: Intermetallics, rare earth elements, photoluminescence piezospectroscopy, oxidation, segregation.

1. Introduction

β -NiAl, as a promising candidate for the high temperature protection of superalloys and the bond coat in thermal barrier coating (TBC) system has attracted increasing attention. Compared with conventional MCrAlY (M=Ni, Co or both) alloys, β -NiAl, as a single-phase alloy and a primary alumina former has a number of advantages, such as high strength, high melting point, low density, good isothermal oxidation resistance and low cost [1-4]. The oxidation resistance of β -NiAl is attributed to the exclusive formation of a slow-growing α -Al₂O₃ scale at high temperature. However, the oxide scale formed on NiAl spalls readily during high-temperature thermal cycling, mainly due to its weak adhesion to the underlying alloy. The poor cyclic oxidation performance impedes its further application. To improve the scale adhesion to NiAl alloys or coatings, various elements such as platinum group metals (PGMs) and reactive elements (REs) are alloyed or doped to NiAl.

The most common PGM addition is Pt, its concentration in B2-base structure ranges from 5 to 20 at.%, which in the state-of-the-art Pt-modified Ni-Al coatings is

approximately 7 at.% Pt [5-8]. As a matter of fact, (Ni,Pt)Al, with excellent high temperature oxidation resistance, is one of the most widely adopted bond coat and mainly applied in hot-section components (such as turbine blades) [9-11]. However, the cost of Pt is too high and thus limits its industrial application. As an alternative to Pt, Pd is much less expensive on atom-for-atom basis, which has similar chemical properties with Pt, but its role on the oxidation resistance is still a subject of debate and need further research [12-14]. It is suggested that the lifetimes of Pd-modified coatings are longer than that of unalloyed ones, but less than that of Pt-modified ones. It has been reported extensively that trace addition (0.05~1 at.%) of REs, such as Hf, Zr, Y, could significantly improve the scale adhesion to alloys or coatings. Although these traditional REs, as well as their oxides dispersion in alloys or coatings have been systematically studied [15-20], the RE effect of the lanthanides on the oxidation behavior is relatively less explored [21-24]. It is found that almost all the lanthanides studied have a beneficial effect in Ni-Al alloys or coatings if properly doped. However, previous research suggests that the RE effect of the lanthanides is not as effective as traditional REs (e.g., Zr, Hf, etc). What is more, the RE effect between different lanthanides varies significantly, as a result of the large variety in their physical and chemical properties, such as ionic size, solubility and chemical activity [25]. For example, La, with the largest atomic diameter and highest chemical activity in REs, has little good or even bad effect on the oxidation performance in Ni-Al alloys [23]. In contrast, Lutetium (Lu) is also a typical reactive element, as the last element in the lanthanide has the smallest size and lowest chemical activity. Besides, Lu is the neighboring element of Hf, which is the most widely-doping and effective reactive element in Ni-Al alloys [23, 26, 27]. Therefore, it is worthwhile to investigate the influences of Lu on the oxidation behavior in NiAl and compare with traditional REs. Chromium is the most widely-studied additive in Ni-Al alloys, which could significantly improve the hot-corrosion resistance by more than 1 at.% addition. Moreover, Cr could increase the Al activity, thus promote the α -Al₂O₃ oxide formation [28]. However, Cr is found to be detrimental to the oxidation performance

of Ni-Al alloys, and to some extent, cancel out the beneficial effect of REs [29]. For example, the maximum benefit of Hf was found in NiAl and FeAl materials, but as not as effective as Y in FeCrAl and NiAlCr in improving the scale adherence [29]. It is necessary to examine the co-effect of Cr and Lu on the oxidation behavior of NiAl and to evaluate to what extent Cr can suppress the beneficial effect of Lu.

The objective of this study is as a broader effort to seek a potential doping element which is more effective than the existing system in improving the oxidation performance of NiAl. For this purpose, NiAl alloys with addition of Lu, Hf and Cr, i.e., Ni-50Al, Ni-49.95Al-0.05Lu, Ni-47.95Al-2Cr-0.05Lu, Ni-49.95Al-0.05Hf (in at.%), were prepared by arc-melting. Then their oxidation behavior, including the oxidation rate, scale stress evolution, spallation behavior and chemical distribution were investigated.

2. Experiment

2.1 Sample preparation

The material used for reference was a stoichiometric NiAl (50:50 in atomic ratio), and the other alloys just altered the Al concentration and maintained the content of Ni. The samples were prepared by arc-melting using aluminum (99.99 wt.%), Chromium (99.99 wt.%), Hafnium (99.9% wt.%) and Lutetium (99.9 wt.%) plates and nickel wire (99.99 wt.%), and their compositions are summarized in Table 1. For simplicity, they are defined as NiAl, NiAl-Lu, NiAlCr-Lu, and NiAl-Hf in this study, respectively. To homogenize the composition, the alloys were annealed at 1200 °C for 100 h in argon flow. After annealing, the alloys were cut into 10×6×4 mm plates. The plates were then ground and polished to 0.25 μm finish, using the standard metallographic approaches, followed by ultrasonically cleaning in alcohol and acetone for 10 min, respectively. The oxidation test was performed at 1150 °C in a laboratory chamber furnace, using 12-hour thermal cycles which consisted of a 10-minute heating-up to 1150 °C, 11.5-hour dwelling at 1150 °C and followed by a 20-minute air-cooling to room temperature.

Table 1 The chemical compositions of the NiAl alloys (in at.%).

Samples	Ni	Al	Cr	Lu	Hf
NiAl	50	50	/	/	/
NiAl-Lu	49.95	50	/	0.05	/
NiAlCr-Lu	47.95	50	2	0.05	/
NiAl-Hf	49.95	50	/	/	0.05

2.2 Characterization

The morphologies and microstructures of the samples were analyzed using an optical microscope (BX51M, Olympus) and scanning electron microscope (SEM, Inspect F50, FEI). The phases of the scale were determined by X-ray diffraction (Ultima IV, Rigaku) with Cu K α radiation (wavelength 1.5406 nm). The chemical composition of the alloys and scale was evaluated using energy-dispersive spectroscopy (EDS, Rontech).

Thermal-gravimetric (SETARAM, K/SETEVO16-1A) tests were carried out to measure the mass change during isothermal oxidation at 1150 °C for 100 h. The samples were cut out to 2×6×12 mm plates, grounded and polished to 0.25 μ m finish and then placed in an alumina crucible hanging up in the hot zone of the TG chamber. The heating and cooling rate are all 20 °C/min, and the recorded data began from the dwelling time.

The oxide scale spallation degree (the ratio of the spalled area to the total area of the scale) as a function of cyclic oxidation time at 1150 °C was examined. After cooling to room temperature, almost the entire area of the scale surface (6×10 mm) was taken by the optical microscope with a 5× objective lens. Therefore, for each sample, six images were taken with a individual area of 2.6×3.4 mm. Then the spallation degree was evaluated from these images based on the contrast between the oxide scale and the exposed alloy surface, using the image processing software (ImageJ, NIH) [30-32].

Cr^{3+} luminescence spectra were collected using a LabRAM HR Evolution (Horiba, France) Raman microprobe system coupled with a 532 nm YAG laser by a $10\times$ (NA=0.25) objective lens. For measurement, at least 30 random positions were selected, which were far away from the spalled area. All the spectra were fitted by a mixed Lorentzian-Gaussian function using the Labspec 6 software to obtain the peak position and areas.

The qualitative depth profiles were examined by a radiofrequency glow discharge optical emission spectroscopy (GD-OES, GD Profiler 2, Horiba Jobin Yvon, France). The measurements were performed using argon gas plasma with a power and pressure of 35 W and 700 Pa, respectively. In order to minimize the influence of contamination of the glow discharge source, a sacrificial monocrystalline silicon wafer was sputtered prior to measurements.

3. Result

3.1 Microstructures of the NiAl alloys

Fig. 1 shows the microstructures and alloyed element distributions after melting and homogenizing annealing. The alloys contain a columnar grain structure with different grain sizes. Based on the EDS analysis, the grey scales in the optical images are β phases, and the bright points in the back scattered electron (BSE) images indicate the distribution of RE-rich precipitates.

The effect of Lu/Hf on the grain sizes is negligible because of the low alloying concentration. For NiAlCr-Lu, since Cr is not soluble in β -NiAl at this composition [3], the grain size was significantly decreased by α -Cr precipitates. Examination of the BSE images indicates that the distributions of Lu and Hf were different. In NiAl-Lu and NiAlCr-Lu, Lu primarily distributed within grains as granular precipitates, while in NiAl-Hf, Hf mainly existed in the form of strip precipitates. It seems that the distribution of Lu in NiAl is more uniform and dispersive than Hf at this doping level.

Fig. 1 The optical and backscattered SEM micrographs showing the microstructures of the alloys after etching: (a, b) NiAl, (c, d) NiAl-Lu, (e, f) NiAlCr-Lu, and (g, h) NiAl-Hf. The samples were etched using a mixture of 50 vol.% HCl, 50 vol.% ethanol with 5 wt.% CuCl_2 dissolved.

3.2 Effect of alloyed elements on isothermal oxidation

Fig. 2a shows mass gains of the samples after isothermal oxidation for 100 h at 1150 °C, and the results within 1 h are extracted and plotted in Fig. 2b to identify the

effect of alloyed elements on the early stage oxidation. After 100 h oxidation, the NiAl-Lu exhibited a mass gain of 1.04 mg/cm², lower than that of NiAl, while NiAlCr-Lu had the highest mass gain of 1.41 mg/cm². The NiAl-Hf exhibited the lowest mass gain of 0.25 mg/cm², only one fifth of that of NiAl. It has been well accepted that RE additions can reduce the oxidation rate by “block effect” on Al outward diffusion [23, 33]. During oxidation, REs ions, with relatively larger sizes and extremely low solubility, segregate to Al₂O₃ grain boundaries. Because of their lower diffusibility than Al ions, the outward diffusion of Al is suppressed, and the slower inward diffusion of oxygen becomes predominant, resulting in a decrease of the oxidation rate.

Fig. 2 The mass gains of the alloys during isothermal oxidation at 1150 °C in: (a) 100 h, (b) 1.0 h.

It should be noted that the mass gains were obtained by weighting both the sample and the spalled oxides.

To investigate the “block effect” of REs, surface morphologies after isothermal oxidation were examined. As shown in Fig. 3a, typical scale ridges still existed at the scale/gas interface in NiAl, which were attributed to the growth mechanism by outward Al diffusion [23]. With the proceeding of oxidation, the deep recesses between these ridges were consequently sealed off and incorporated to the growing scale, resulting in a porous structure [23, 30]. For NiAl-Lu and NiAl-Hf, close-packed Al₂O₃ grains were formed and both Lu- and Hf-rich oxides (bright particles) were observed at the surfaces. While Hf oxides existed primarily along grain boundaries, it seems that Lu was incorporated to the Al₂O₃ grains. Compared with NiAl-Hf, the

scale grown on NiAl-Lu and NiAlCr-Lu showed a smaller grain size. It has been reported that the segregation of RE ions at Al_2O_3 grain boundaries lead to grain refinement by solute drag effect and promotion of non-spontaneous nucleation [34, 35]. The fine-grained structure of Lu-doped scale, which means more nucleation sites for Al_2O_3 and/or stronger solute drag effect, indicated a higher concentration of Lu in the scale than Hf. For NiAlCr-Lu, it seemed that Cr inhibited the outward growth of Lu-rich oxides to some extent and made Al_2O_3 grains more clear-cut. In addition, intergranular gaps appeared at scale/gas interface in NiAlCr-Lu, while in NiAl-Lu the gaps were totally sealed.

Fig. 3 The secondary SEM plan-view micrographs of the scale formed on (a) NiAl, (b) NiAl-Lu, (c) NiAlCr-Lu and (d) NiAl-Hf after isothermal oxidation at 1150 °C for 100 h.

Fig. 4 shows the scale fracture section morphologies after isothermal oxidation for 100 h. A double-layer scale structure consisting of a layer of equiaxed grains and a layer of columnar grains beneath was formed on NiAl-Lu and NiAl-Hf, as a result of

the dominant growth mechanism by inward oxygen transport. The scale formed on NiAlCr-Lu revealed a mixture of equiaxed and columnar structure, suggesting its growth was by both inward oxygen transport and outward Al transport. Additionally, interfacial pores were observed at the alloy/scale interface on NiAl and NiAlCr-Lu, which were hardly found in NiAl-Lu and NiAl-Hf. Based on the fractural and cross-section micrographs (not given in this paper), the scale average grain sizes and thickness are given in Table 2. It is evident that both RE and Cr have a scale grain refinement effect.

Fig. 4 The SEM fracture section morphologies of the scale formed on: (a) NiAl, (b) NiAl-Lu, (c) NiAlCr-Lu and (d) NiAl-Hf after isothermal oxidation at 1150 °C for 100 h.

Table 2 The oxide scale grain sizes and thicknesses.

Samples	Scale thickness , μm	Scale grain size, μm
NiAl	7.6 ± 1.7	1.92 ± 0.53
NiAl-Lu	7.2 ± 0.9	0.81 ± 0.26
NiAlCr-Lu	7.9 ± 2.0	0.55 ± 0.23
NiAl-Hf	1.9 ± 0.3	1.03 ± 0.34

Though RE can suppress the scale growth by the “block effect” on Al diffusion during long time oxidation, a different effect on oxidation was observed in the early stage. As shown in Fig. 2b, the oxidation rates within 1.0 h were in the order: NiAl-Lu>NiAl>NiAlCr-Lu>NiAl-Hf, totally different from that in long time oxidation. During oxidation, β -NiAl primarily forms α -Al₂O₃, but transient alumina, particularly θ -Al₂O₃, can be found at low oxidation temperature or in early time [36]. RE additions, such as Hf, Zr, present in Ni-Al alloys, can inhibit the transformation from θ -Al₂O₃ to α -Al₂O₃ by entering the relatively open θ -Al₂O₃ [37]. It is suggested that the fast growth of transient alumina has a great contribution to the overall mass gain, especially when the θ - α transformation is suppressed by REs [37, 38]. To find out the effect of alloyed elements on the transient oxidation, luminescence spectra were collected to characterize the types and evolution of transient alumina. Fig. 5 presents the luminescence spectra and the evolution of θ -Al₂O₃ content with oxidation time. The spectral doublet near the nominal frequencies of ~ 14402 cm⁻¹ and ~ 14432 cm⁻¹ indicates α -Al₂O₃, and the doublet near the frequencies of ~ 14575 cm⁻¹ and ~ 14645 cm⁻¹ stands for θ -Al₂O₃ [3, 39]. The θ -Al₂O₃ content C_θ was estimated using the following equation [40]:

$$C_\theta = \frac{A_{14575} + A_{14645}}{A_{14402} + A_{14432} + A_{14575} + A_{14645}} \quad (1)$$

where A_{14402} , A_{14432} and A_{14575} , A_{14645} represent the peak areas at the actually detected positions of α -Al₂O₃ and θ -Al₂O₃ (fitted by a mixed Lorentzian-Gaussian function), respectively, rather than that of the nominal positions of 14402, 14432, 14575 and 14645 cm⁻¹.

After oxidation for 10 min, both α -Al₂O₃ and θ -Al₂O₃ were formed on NiAl and NiAlCr-Lu, while in NiAl-Lu and NiAl-Hf, there was almost no α -Al₂O₃. As the oxidation time increased, the content of α -Al₂O₃ increased and that of θ -Al₂O₃ decreased for all samples. After oxidation for 50 min, θ -Al₂O₃ was still the dominant phase in NiAl-Lu, while that in the other three alloys was hardly detected. It is

suggested that Lu is more effective than Hf on the transformation inhibition, which might be attributed to the larger ion radius of Lu (84.8 pm) than Hf (71pm) [37] and/or its more uniform distribution in NiAl. Due to the stronger inhibiting effect of Lu, the growth of θ - Al_2O_3 was greatly promoted, resulting in a higher oxidation rate. However, it is very interesting that NiAl-Hf exhibited the lowest oxidation rate, even though Hf has an inhibiting effect too. As for NiAlCr-Lu, since Cr favored the θ - to α - Al_2O_3 transformation [41], the inhibiting effect of Lu was overcompensated, resulting in an even lower growth rate than NiAl in the early time.

Fig. 5 The photo-stimulated luminescence spectra of the oxide scale and the changes of θ - Al_2O_3 concentration after oxidation at 1150 °C for 10 min, 20 min and 50 min.

3.3 Effect of alloyed elements on cyclic oxidation

The oxide scale surfaces of the alloys after cyclic oxidation and the evaluated scale spallation degree as a function of oxidation time are shown in Fig. 6. The NiAl sample suffered the most serious spallation, after 48 h, a 24.7% spallation was observed. However, only 1.56% and 1.84% area in NiAl-Lu and NiAl-Hf spalled even after 996 h, indicating their excellent oxidation resistance. As for NiAlCr-Lu, 35.4%

area spalled after 192 h, suggesting the harmful effect of Cr on scale adherence.

Fig. 6 The optical plan-view images of the oxide scale on the alloys after cyclic oxidation: (a) NiAl, (b) NiAl-Lu, (c) NiAlCr-Lu and (d) NiAl-Hf. (e) and (f) show the scale spallation degree of the alloys as a function of cyclic oxidation time at 1150 °C, and the error bars show the standard deviation of the spallation degree observed at different regions on the surfaces of the samples.

3.4 Effect of alloyed elements on impurities segregation

It has been reported extensively that intrinsic impurities in alloys, such as S and C, can segregate to the alloy/scale interface during oxidation, leading to interfacial degradation. REs can effectively suppress this phenomenon by actively reacting with and tying up impurities [16, 42]. To examine this effect, the elemental profile across the scale thickness was evaluated using GD-OES, which is a powerful tool for elemental depth profile analysis of multilayer materials [43].

The chemical depth profiles of the samples after 100 h isothermal oxidation are shown in Fig. 7, the sputtering times at the alloy/scale interface varied significantly

which roughly corresponded to the scale thicknesses. It is clearly shown that S and C could aggregate in the scale formed on all the samples even alloyed with Lu/Hf. In NiAl and NiAlCr-Lu, S and C segregated not only at the alloy/scale interface, but also within the scale from the alloy/scale interface to some depth. TEM study by Molins et al. [44] has clearly shown that the alloy/scale interface can accommodate only finite amount of sulfur, when the interface is saturated, sulfur passes it and becomes incorporated into the growing scale. Sulfur is usually detected in the inner layer of the scale, which preferentially segregates at: (1) Al_2O_3 grain boundaries, and (2) surfaces of the voids at the alloy/scale interface [33, 44, 45]. Conversely, when the co-segregation of S and C happened, the concentration of O maintained a relatively lower level. However, this phenomenon was not observed in NiAl-Lu and NiAl-Hf, where the concentration of S and C increased from the alloy/scale interface to the scale/gas interface, rather than segregating at alloy/scale interface. While the enrichment of S and C in scale is inevitable, both Lu and Hf could effectively suppress their segregation to the alloy/scale interface, which was responsible for the interfacial degradation.

Fig. 7 The qualitative depth profiles of the alloys after isothermal oxidation at 1150 °C for 100 h:

(a) NiAl, (b) NiAl-Lu, (c) NiAlCr-Lu and (d) NiAl-Hf. Each element is pointed out with the corresponding scaling factor, e.g. Lu*120 means that the Ni intensity displayed in the graph is 120-times the actual intensity detected.

3.5 Effect of alloyed elements on the scale stress

During thermal cycling, spallation is driven by the stress in the oxide scale. The scale residual stress at room temperature mainly comes from two contributions: mismatch stress induced by the mismatch of the coefficient of thermal expansion (CTE) between the scale and substrate upon cooling and the scale growth stress at high temperature, accompanied by stress relaxation processes. Assuming that the alloy/scale interface is flat, the residual stress σ_{ox} in the scale refers to the biaxial stress, which can be calculated by the following equation [42, 46, 47]:

$$\Delta\nu=5.07\sigma_{ox} \quad (2)$$

where $\Delta\nu$ is the peak shift of R2 line, and σ_{ox} is the residual stress in the scale. Since the R-line frequencies are known to be dependent on the Cr concentration (0.83 cm^{-1} per 1% Cr by weight [24]), spectra were also recorded from the oxide detached from the underlying alloy which is assumed to be the stress-free.

In evaluating the residual stress induced by the CTE mismatch alone, the following equation is used [46]:

$$\sigma_{CTE} = \frac{E_{ox}}{(1-\nu_{ox})}(\alpha_{ox} - \alpha_m)\Delta T \quad (3)$$

where σ_{CTE} is the residual stress caused by the CTE mismatch. E_{ox} and ν_{ox} represent the elastic modulus and Poisson's ratio of alumina at room temperature, respectively. α_{ox} and α_m are the thermal expansion coefficients of alumina and substrate, respectively. ΔT is the temperature drop from the exposure temperature to room temperature. By applying the values in Table 3 to Eq. (3), the thermal mismatch stress can be estimated as 3.7 GPa. In this study, because of the small addition of Lu/Hf (0.05 at.%) and Cr (2 at.%), the differences of CTE and elastic modulus of the

four alloys can be neglected.

Table 3 The material properties of alumina and Ni-50Al [31].

Material	Poisson' ratio, ν	Elastic modulus at room temperature, E (GPa)	Elastic modulus at 1150 °C, E (GPa)	CTE, α ($10^{-6}/\text{k}$)
alumina	0.2	380	340	8
Ni-50Al	0.3	190	/	15

Assuming there is no stress relaxation due to the rapid cooling after oxidation, the growth stress can be evaluated based on the residual stress at room temperature [31, 48, 49]:

$$\sigma_{\text{growth}} = \frac{E_{\text{ox}}^T}{1 - \nu_{\text{ox}}} \left[\frac{\sigma_{\text{ox}} (1 - \nu_{\text{ox}})}{E_{\text{ox}}} - \frac{(\alpha_{\text{ox}} - \alpha_{\text{m}}) \Delta T}{1 + R} \right] \quad (4-3a)$$

$$R = \frac{E_{\text{ox}} (1 - \nu_{\text{m}}) h_{\text{ox}}}{E_{\text{m}} (1 - \nu_{\text{ox}}) h_{\text{m}}} \quad (4-3b)$$

where σ_{growth} and σ_{ox} represent the growth stress and residual stress in the scale at room temperature, respectively. α_{ox} and α_{m} , ν_{ox} and ν_{m} , and h_{ox} and h_{m} refer to the thermal expansion coefficient, Poisson's ratio and thickness of the alumina and substrate, respectively. E_{ox}^T and E_{ox} denote the elastic modulus of alumina at oxidation temperature and room temperature, respectively, and E_{m} is the elastic modulus of the substrate at room temperature.

Based on above equations, both the residual stress, σ_{ox} and growth stress, σ_{growth} in the scale after oxidation are presented in Fig. 8. After oxidation for 50 min, the average residual stress in the scale on NiAl was up to -5 GPa, about 1.2 GPa higher than the estimated thermal mismatch stress. While for the other three alloys, the residual stress were just about -3 GPa and roughly the same. In addition, a large compressive growth stress (-1.1 GPa) was generated in NiAl. In comparison, the

growth stress on other alloys were tensile, around 0.3~0.6 GPa. After 108 h cyclic oxidation, the scale residual stress in NiAl decreased from -5 to -3.8 GPa, while that in other samples increased and exceeded the thermal mismatch stress. The evolutions of the residual stress are consistent with the changes of the growth stress, that in NiAl the residual stress had decreased from -1.1 to -0.1 GPa, while in other alloys the residual stress had transformed from tensile to compressive. The reasons for this difference will be discussed later.

Fig. 8 The residual stress and growth stress in the scale after: (a) oxidation for 50 min, (b) thermal cycling for 108 h at 1150 °C. The dash lines represent the CTE mismatch stress and the error bars are the standard deviation of 30 measurements.

4. Discussion

4.1 Effect of alloyed elements on the oxidation rate

In Section 3.2, it was found that both Lu and Hf had a “block effect” on the outward diffusion of Al. However, the oxidation rate of NiAl-Lu was almost four times that of NiAl-Hf. Considering the very similar chemical and physical properties between Lu and Hf, such a difference is surprising. As mentioned above, the oxidation rates of the samples in early stage were largely different from that in long time oxidation, due to the different effect of alloyed elements on the θ - α Al_2O_3 transformation. The higher oxidation rate of NiAl-Lu in early stage was mainly attributed to the promoted growth of θ - Al_2O_3 , which was associated with the strong inhibiting effect of Lu in θ - α Al_2O_3 transformation.

Once the transient oxidation stage is over and a complete $\alpha\text{-Al}_2\text{O}_3$ layer is formed, the “block effect” of RE begins to work [34]. For NiAl-Lu and NiAl-Hf, since the major growth mechanism of the oxide is the inward diffusion of oxygen along the scale grain boundaries, the parabolic rate constant k_p is proportional to the effective diffusion coefficient, D_{eff} [19, 48],

$$k_p \sim D_{\text{eff}} \quad (5)$$

The effective diffusion coefficient, D_{eff} , can be related to the grain boundary diffusion coefficient, D_{gb} , grain size, GS , and grain boundary width, δ , by [48]

$$D_{\text{eff}} \approx 2\delta D_{\text{gb}} / GS \quad (6)$$

Since the grain boundary width δ is almost a constant, D_{eff} is directly related to both GS and D_{gb} . As mentioned previously, the average grain size of the scale formed on NiAl-Lu (0.81 μm) is smaller than that in NiAl-Hf (1.03 μm). Since GS is inversely proportional to D_{eff} , the smaller grain size means the larger effective diffusion rate of oxygen. The fitted k_p by the parabolic law using TG data of NiAl-Lu and NiAl-Hf are 0.109 and 0.024 $\text{mg}/\text{cm}^2 \text{ h}^{1/2}$, respectively. The ratio of the k_p between NiAl-Lu and NiAl-Hf is 4.5, while the ratio of the scale grain size between NiAl-Hf (1.03 μm) and NiAl-Lu (0.81 μm) is just 1.3. Apparently, the difference in the grain size is not enough to cause such a difference in oxidation rate, other reasons could be attributed to the difference in the grain boundary diffusion coefficient, D_{gb} .

The effect of impurities, such as REs, on the diffusion rates of ions in Al_2O_3 is still a subject of discussion [34, 50]. It has been reported by Zhao et al. [48] that the incorporation of Zr and Y promotes alumina growth. REs, which incorporate into the growing scale during transient oxidation, could segregate to the grain boundaries depending on their sizes and solubility. As mentioned previously, Lu is more effective

than Hf in promoting the growth of θ - Al_2O_3 . Therefore, it could be speculated that Lu is more easily to be incorporated into θ - Al_2O_3 than Hf, resulting in a higher concentration of Lu in α - Al_2O_3 grain boundaries. Additionally, as the scale thickening, REs ions are dynamically diffusing from the alloys to the alloy/scale interface due to their strong oxygen affinity [34]. The GD-OES results show different concentration profiles of Lu and Hf in the scale, where in NiAl-Lu the concentration of Lu decreased from the scale/gas interface to the alloy/scale interface, while in NiAl-Hf the trend was opposite. This suggests that Lu is more tend to diffuse outward than Hf, which might be associated with its higher chemical activity. In brief, the higher concentration of Lu in the scale contributed to the enhancement of oxygen transport rate, which could be the primary reason for the higher oxidation rate of NiAl-Lu.

For NiAlCr-Lu, the mass gain after 100 h oxidation was larger even than that of NiAl. The alloyed of Cr could promote the θ - α transformation, thus decreased the oxidation rate in early stage. However, compared with other alloys, the oxidation of NiAlCr-Lu did not follow the parabolic law and still maintained a relatively higher rate during long time oxidation. There are three possible reasons: (a) the scale formed on NiAlCr-Lu had the smallest grain size (0.55 μm); (b) the presence of Lu in the scale could enhance the oxygen transport rate; (c) the scale formed on NiAlCr-Lu revealed a mix of equiaxed and columnar structure (Fig. 4c), indicating that the “block effect” of Lu on Al transport was suppressed. As evidenced in Fig. 7c, the distribution of Lu in the scale was undulant, suggesting an detrimental influence of Cr on the RE effect of Lu. Reason (a) and (b) promoted the inward diffusion of oxygen, and (c) enhanced the outward diffusion of Al, resulting in a high oxidation rate of NiAlCr-Lu.

4.2 Effect of alloyed elements on the scale stress

In Section 3.5, it was found that RE could influence the residual stress in scale, mainly by affecting the growth stress. While CTE mismatch stress is always compressive and determined by the difference in CTE between the substrate and scale,

the growth stress is still poor understood. Residual stress measured in the scale varies significantly, depending on not only the main constituents of the substrate alloy [51], but also on the small amounts of alloyed elements. For example, tensile growth stress has been detected in the scale formed on RE-containing alloys [24, 52, 53].

In this study, after oxidation for only 50 min, a large residual stress (-5 GPa) was developed in NiAl, which mainly came from the CTE mismatch stress and was significantly augmented by the large compressive growth stress. By contrast, the residual stress in NiAl-Lu and NiAl-Hf were just -3 GPa. In situ analysis of growth strains by Veal et al. [54] has demonstrated that REs could modify the growth stress by changing the scale growth mechanism. For RE-free alloys, during oxidation, the counterflow of oxygen and aluminum ions may merge and combine within the scale, forming new oxide at grain boundaries, leading to an in-plane compressive stress [54]. For RE-containing alloys, the presence of RE could inhibit the outdiffusion of Al, thus suppressing the formation of Al_2O_3 at grain boundaries. In addition, the θ - to α - Al_2O_3 phase transformation could contribute to the growth stress. Due to the volume shrinkage, a large tensile strain ($\sim 3.5\%$) can be generated [24]. However, while the content of θ - Al_2O_3 in NiAl-Lu and NiAl-Hf was significantly different after 50 min oxidation (Fig. 5d), the growth stress was almost the same, suggesting that the θ - to α - Al_2O_3 transformation was not the primary reason for the generation of the growth stress. The alloyed 2 at.% Cr to NiAl-Lu decreased the growth stress from 0.58 GPa to 0.35 GPa, but not changed the tensile stress state.

After cyclic oxidation for 108 h, in Lu/Hf-alloyed samples, as the growth stress turned compressive, the residual stress increased and exceeded the estimated CTE mismatch stress. However, the residual stress in NiAl was relatively lower, which in the early stage was the highest. During thermal cycling, since the growth stress are compressive, the observed change of the residual stress are attributed to the stress relaxation both on the scale and alloy at high temperature [6]. Compared with NiAl, the scale formed on RE-doped alloys have higher creep resistance due to being more columnar and/or the grain boundaries being strengthened by RE doping [46], leading

to less stress relief. The largest scale stress of NiAlCr-Lu might be associated with the strengthening effect of Cr, which made NiAlCr-Lu substrate more difficult to creep [55]. In short, Lu/Hf does decrease the residual stress in scale at the beginning of oxidation, but makes it more compressive after long time oxidation.

4.3 Effect of alloyed elements on the scale spallation behavior

During thermal cycling, the spallation behavior of the scale formed on the alloys was significantly different. For any spontaneous spallation of an oxide from a substrate, a pre-existing separation, such as a crack or pore at the alloy/scale interface is needed, and when the stored elastic strain energy in the system exceeds the interfacial toughness, scale spallation occurs [42]. Therefore, to explain this, both the scale stress and interfacial adherence of the alloys should be considered.

As described previously, the stress evolution in NiAl was different from that of the other three alloys. At the beginning of oxidation, the NiAl sample quickly build a larger residual stress in the scale, which might be an important reason for its premature failure behavior. During long time thermal cycling, though NiAl-Lu and NiAl-Hf exhibited excellent oxidation resistance, the scale residual stress were relatively higher than that of NiAl. Moreover, the scale stress state in NiAlCr-Lu was very close to that in NiAl-Lu and NiAl-Hf, while its oxidation resistance was much worse, only slightly better than that of NiAl. It can be inferred that though the scale stress could be modified by REs, the effect is not the determining factor for the spallation behavior.

In Fig. 4, large interfacial voids were formed in NiAl and NiAlCr-Lu, which in NiAl-Lu and NiAl-Hf were hardly observed. Interfacial voids, which are driven from Kirkendall effect, can grow rapidly at high temperature by the presence of nonmetallic impurities, such as S and C. The existence of such interfacial defect reduces the actual contact area between the scale and substrate, leading to a lower interfacial toughness, which is responsible for the higher spallation degree after oxidation. On the other hand, the interface would also be degraded by the impurity segregation (e.g. S and C).

As evidenced in Fig. 7, the GD-OES results clearly show S and C segregated at the alloy/scale interface in NiAl and NiAlCr-Lu, while this phenomenon was not observed in NiAl-Lu and NiAl-Hf. In addition, both Hf and Lu segregated at the interface, especially Lu, which maintained a relatively higher concentration in the whole scale. According to Evans et al. [56, 57], the presence of RE at the interface could improve the adhesion. As a result, the scale spallation resistance of NiAl-Lu and NiAl-Hf are much better than NiAl and NiAlCr-Lu.

In this study, though Lu could significantly improve the oxidation performance of NiAl, this beneficial effect could be easily overcompensated by Cr. In Fig. 7c, Cr was also detected in the scale near the alloy/scale interface, suggesting the S-Cr co-segregation. It has been reported that the segregation of S can be promoted by presence of Cr, while REs, such as Hf, could inhibit this segregation only when present with Y or Pt [29, 58]. The interaction between Cr and REs and how it affects impurities segregation are unknown yet and need further investigation.

5 Conclusions

The influences of Lu and Hf as reactive elements and Cr as the most widely applied additive element, on the oxidation and spallation behavior of NiAl were investigated. The main conclusions can be drawn as follows:

(1) Both Lu and Hf could decrease the oxidation rate, while the parabolic constant of NiAl-Lu was almost four times that of NiAl-Hf, which was attributed to: (a) inhibition of θ - α -Al₂O₃ transformation in the early stage; (b) stronger grain refinement effect and (c) most importantly, enhanced oxygen transport rate.

(2) Lu and Hf did decrease the scale residual stress in the early stage, but makes it more compressive after long time oxidation.

(3) Segregation of S and C occurred not only at the alloy/scale interface, but also within the scale from the interface to some depth. Both Lu and Hf could significantly improve the interfacial adherence by suppressing this phenomenon.

(4) The effect of Lu in enhancing the scale adherence can be easily

overcompensated by Cr, suggesting the necessity of a co-doping element, such as Y or Pt, in Cr-containing alloys.

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