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# Effects of reactive element oxides on the isothermal oxidation of $\beta$ -NiAl coatings fabricated by spark plasma sintering

Wenfu Chen <sup>a</sup>, Limin He <sup>b</sup>, Yi Guo <sup>c</sup>, Xiao Shan <sup>a</sup>, Jianghua Li <sup>d</sup>, Fangwei Guo <sup>a</sup>,  
Xiaofeng Zhao <sup>a\*</sup>, Na Ni <sup>e\*</sup>, Ping Xiao <sup>c</sup>

<sup>a</sup> School of Material Science and Engineering, Shanghai Jiao Tong University,  
Shanghai 200240, China

<sup>b</sup> Beijing Institute of Aeronautical Materials, Beijing, 100095, China

<sup>c</sup> School of Materials, University of Manchester, Grosvenor Street, Manchester M1  
7HS, UK

<sup>d</sup> State Key Laboratory of Metastable Materials Science and Technology, Yanshan  
University, Qinhuangdao, Hebei 066004, China

<sup>e</sup> Gas Turbine Research Institute, Shanghai Jiao Tong University, Shanghai, China

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\* Corresponding author: Xiaofeng Zhao

Tel./fax: +86-021-54742561

E-mail: [xiaofengzhao@sjtu.edu.cn](mailto:xiaofengzhao@sjtu.edu.cn)

\* Corresponding author: Na Ni

Tel./fax: +86-021-54742561

E-mail: [na.ni@sjtu.edu.cn](mailto:na.ni@sjtu.edu.cn)

**Abstract**

The CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> doped  $\beta$ -NiAl coatings with controlled concentrations were fabricated on Hastelloy substrates using spark plasma sintering. The effects of reactive element oxide (REO) species and concentrations on the isothermal oxidation of the  $\beta$ -NiAl coatings were investigated. It was found that the addition of Y<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> improved the oxidation performance of  $\beta$ -NiAl coatings, but CeO<sub>2</sub> with high concentrations (0.5 at.%) had a detrimental effect. At low concentration (0.05 at.% and 0.1 at.%), HfO<sub>2</sub> was less effective in improving the oxidation resistance of  $\beta$ -NiAl compared with Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>, while HfO<sub>2</sub> at higher concentration of 0.5 at.% was the most effective among the three. The effects of REO species and concentrations on the NiAl oxidation behavior were further discussed in related to the intrinsic properties of the REOs and the chemical compositions of the substrate.

**Keywords:** NiAl; Coatings; Reactive element oxide; Oxidation; Spallation

## 1. Introduction

NiAl and its derivatives have been widely used as high-temperature coatings for decades due to their excellent oxidation resistance and hot-corrosion resistance [1]. Recently,  $\beta$ -NiAl has been considered as a potential bond coat used in thermal barrier coating (TBC) systems [2, 3]. It has primary alumina formation with virtually no nickel oxide at high temperature, which could favor the oxidation resistance. In addition, it has high melting point, low density and low cost compared with bond coats of Ni(Co)CrAlY or (Ni, Pt)Al. However, the use of  $\beta$ -NiAl alloys or coatings has been hindered by insufficient adhesion resulted from excessive voids between the scale/metal interfaces at high temperature and low ductility at room temperature [4-7]. Many studies have shown that reactive elements (REs) such as Hf, Y, Zr or Ce could significantly improve the scale adhesion of  $\beta$ -NiAl alloys by casting or ion implantation [2, 8-10]. Techniques such as diffusion-aluminizing, magnetron sputtering (MS) or electron-beam physical-vapor deposition (EB-PVD), also have been employed to prepare  $\beta$ -NiAl coatings doping with REs [7, 11-13]. However, the addition of REs to  $\beta$ -NiAl is difficult, and the concentration or distribution of REs varies with the preparation methods. For example, ion implantation is generally not effective in improving the scale adhesion of alumina-formers due to the shallow distribution of REs [10]. In MS, EB-PVD or casting process, the formation of second phases, such as  $\text{NiY}_x$ , may actually be detrimental to the oxidation behavior due to

non-uniform distribution of the REs in the alloy or coating [14]. The benefits of REs on the oxidation of  $\beta$ -NiAl can also be easily compromised or even eliminated by inappropriate concentration control, owing to the extremely low solubility of REs in  $\beta$ -NiAl [4]. It may be possible that the use of finely dispersed REOs are potentially beneficial for the oxidation resistance of NiAl used as bond coats in TBC systems.

The dispersed REOs such as  $Y_2O_3$ ,  $La_2O_3$ ,  $HfO_2$ ,  $CeO_2$ , have been incorporated to  $\beta$ -NiAl alloys by mechanical mixing followed by hot extrusion [14-16]. However, it has not been clearly established whether the effect of a REO on oxidation behavior of  $\beta$ -NiAl alloy is identical to that of the counterpart RE element [16, 17]. Besides, little research on  $\beta$ -NiAl coatings doped with dispersed REOs has been reported, due to the difficulty of introducing uniformly dispersed REOs into  $\beta$ -NiAl coatings by conventional techniques such as plasma spraying, diffusion-aluminizing, or EB-PVD. In recent studies, spark plasma sintering (SPS) has been introduced to fabricate coatings with homogenous microstructures and controlled compositions, for the goal of fabricating laboratory samples without complex geometry [18-23]. It is a sintering technique to perform high speed consolidation of the powders, which enhances densification over grain growth promoting diffusion mechanisms and maintains the intrinsic properties of nano-powders with fully dense sintering [24]. Compared with techniques such as plasma spraying, diffusion-aluminizing, or EB-PVD, this process has several advantages including very fast processing, minimum waste of materials, dense and homogenous structures with good adherence onto substrates. Moreover, SPS combined with the process of nano-powder mixing could solve the difficulty of

introducing uniformly dispersed REOs into  $\beta$ -NiAl coatings.

The objective of this work is to study the effects of REO species and concentrations on the oxidation behavior of the  $\beta$ -NiAl coatings. We used a combined process of nano-powder mixing and SPS, to produce uniform and dense  $\beta$ -NiAl coatings doped with controlled REO species and concentrations. The oxidation behavior of these coatings were investigated, and the effects of the REO species and concentrations on the oxidation behavior were discussed in relation to the oxide growth rates, the stress of the oxides, and the spallation resistance.

## 2. Materials and methods

### 2.1 Sample preparation

The preparation procedures of REOs ( $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$  and  $\text{HfO}_2$ ) doped NiAl coatings are summarized as follows. Nickel powders (99.9%, Cwnano) and aluminum powders (99.95%, Aladdin) were thoroughly mixed with a small amount of  $\text{CeO}_2$  (99.9%, Aladdin),  $\text{Y}_2\text{O}_3$  (99.9%, Aladdin) or  $\text{HfO}_2$  (99.9%, Aladdin) for 50 minutes, using high-speed vibrating ball mill (QM-3B, NanDa). The average particle sizes of the original powders were less than 1  $\mu\text{m}$ . The mole fractions of Ni to Al were 48:52 in all powder mixtures with and without REOs. The compositions of each REO species have three levels: 0.05 at.%, 0.1 at.% and 0.5 at.% (RE elements exclude O) in powder mixtures with REOs. The mixed powders were then compacted into green pieces with a thickness of 1 mm and a diameter of 30 mm.

Following powder mixing and compaction, the green pieces were placed on the Hastelloy X superalloy substrate (30 mm $\times$ 30 mm $\times$ 2 mm) with a composition (wt.%)

of 46.8Ni-22.0Cr-18Fe-9.0Mo-1.5Co-0.6W-1Si-1Mn-0.1C. The fabrication of the overlay NiAl coatings was performed using SPS (FCT-HPD 25/4-SD, FCT system GmbH), held for 20 minutes at 1050 °C and 20 MPa in a vacuum (<0.1 Pa) furnace. After SPS, the coating surfaces were polished using 1000 grit Al<sub>2</sub>O<sub>3</sub> paper.

## 2.2 Thermal treatment

The as-deposited specimens were cut into slices of 5 mm×5 mm×2 mm, followed by isothermal heat treatment at 1150 °C in air furnace [25], with holding time (hours) of 12, 24, 48, 72, 96, and 120, then cooled naturally to ambient temperature.

## 2.3 Characterization methods

The microstructures of the powder mixtures and the coatings were investigated by a scanning electron microscope (SEM, Inspect F50, FEI) coupled with energy dispersive spectrometer (EDS, Rontec). The chemical compositions of the sintered coatings were determined using electron probe micro-analyzer (EPMA, JXA-8100, JEOL). The phases of the powder mixtures and the sintered specimens were detected using X-ray Diffraction (XRD, Ultima IV, Rigaku) with a Cu-K $\alpha$  radiation at recorded 2 $\theta$  range from 10° to 90° (40 kV and 30 mA). The phases of selected regions in the coatings were studied using the transmission electron microscope (TEM, Talos F200, FEI), and the TEM samples of the selected regions were prepared using the scanning electron microscopy coupled with dual beam systems (FIB-SEM, GAIA3 model 2016 GMH/GMU, TESCAN). The composition of oxide grain boundaries in the oxidized specimens was investigated using the scanning transmission electron microscopy coupled with energy dispersive spectrometer (STEM-EDS, Talos F200, FEI). Raman

spectroscopy (LabRAM HR Evolution, Horiba), with an excitation of 532 nm (Ar laser), was employed to distinguish phases and measure the stresses of the scales in the oxidized specimens with different oxidation durations. For all samples, at least 30 positions far from the spalled areas of scales were randomly selected and the peak positions of the spectrums identified by fitting with a mixed Lorentzian-Gaussian function using the Labspec 6 software.

### 3. Results

#### 3.1 The morphologies and phases of the powder mixtures

Fig. 1a shows the morphologies of the powder mixtures of NiAl. The powders of Ni and Al were thoroughly mixed after 50 minutes milling. The compositions of the powder mixtures would be close to the nominal compositions as only a small quantity of weight loss (less than 2%) was measured for Ni and Al powders after milling. This has been confirmed by the EPMA analysis of final coatings as below. The phases of the powder mixtures were still Ni and Al, without other mechanically alloyed phases, confirmed by the XRD analysis (Fig. 1b). The morphologies and phases of the powder mixtures doped with different REO species and concentrations were almost the same as the undoped specimens owing to the low concentrations of the REOs (less than 0.5 at.%).

#### 3.2 The microstructures of as-fabricated coatings

Fig. 2 shows the cross-sectional images of the as-prepared coatings. From the EPMA analysis, atomic ratios of Ni/Al=47.21 ( $\pm 0.11$ ):52.79 ( $\pm 0.16$ ) were detected with a small amount of oxygen in all coatings that have a nominal Ni/Al atomic ratio of

48:52. As expected, the experimental measured composition falls in the regions of single  $\beta$ -NiAl phase in the Ni-Al phase diagram. The actual concentrations of Ce, Y and Hf in the sintered coatings with nominal REO concentrations of 0.5 at.% are 0.47( $\pm$ 0.11) at.%, 0.43( $\pm$ 0.13) at.% and 0.44( $\pm$ 0.15) at.%, respectively. For the samples with lower REO concentrations (0.05 at.% and 0.1 at.%), it was very difficult to quantify with EPMA as these concentrations are already close to or smaller than measurement errors. The results suggested that all the coatings consist of predominantly  $\beta$ -NiAl with minor amounts of alumina phase, as confirmed by the XRD analysis (Fig. 3). The microstructures of the coatings doped with different REO species and concentrations were almost the same. The coatings had a thickness of about 220  $\mu$ m, and an interdiffusion zone (IDZ) with a thickness of  $\sim$ 3  $\mu$ m between the coating and the substrate. The IDZ contained refractory elements (Cr, Mo) diffused from the substrates.

### 3.3 The oxide scales of NiAl coatings after oxidation

Fig. 4 and 5 (a, c, d and e) show the surfaces and cross-sectional morphologies of the NiAl coatings (doped with 0.1 at.% CeO<sub>2</sub>, 0.1 at.% Y<sub>2</sub>O<sub>3</sub>, 0.5 at.% Y<sub>2</sub>O<sub>3</sub> and 0.5 at.% HfO<sub>2</sub>) oxidized for 120 hours at 1150°C, respectively. Oxide scales with minor RE-rich oxides (Ce, Y and Hf-rich oxides) were formed on the surfaces of  $\beta$ -NiAl coatings after oxidation as confirmed by the EDS analysis. The oxide scales exhibited columnar grains near the bottom and an upper-layer of equiaxed grains (Fig. 6). The amounts of RE-rich oxides on the scale surfaces (estimated by the area ratio of RE-rich oxides to alumina on the scale surfaces) in the Y<sub>2</sub>O<sub>3</sub>-doped coatings were

much higher than those in the  $\text{CeO}_2$ - and  $\text{HfO}_2$ -doped coatings, which are 8.41%, 18.01%, 2.58% and 1.67% for the 0.1 at.%  $\text{Y}_2\text{O}_3$ -, 0.5 at.%  $\text{Y}_2\text{O}_3$ -, 0.1 at.%  $\text{CeO}_2$ - and 0.5 at.%  $\text{HfO}_2$ -doped coatings, respectively.

### 3.4 The microstructures of the NiAl coatings after oxidation

The microstructures of REOs-doped coatings changed after oxidation at  $1150^\circ\text{C}$  for 120 hours. The  $\text{CeO}_2$  in the  $\text{CeO}_2$ -doped coatings was reduced into  $\text{CeAlO}_3$  with adjacent alumina particles or directly  $\text{Ce}_6\text{O}_{11}$  (Fig. 5b and Fig. 7a). The compound oxides of Y-Al-O were formed in the  $\text{Y}_2\text{O}_3$ -doped coatings, due to a reaction with adjacent alumina particles during oxidation. A Hf- and C-rich layer ( $\sim 3 \mu\text{m}$  thickness) above the IDZ was observed in the  $\text{HfO}_2$ -doped coatings (characterized by the EDS analysis in Fig. 5e and f), identified as  $\text{HfC}$  (Fig. 7b).

### 3.5 The effect of REOs on the spallation of scales

Fig. 8 plots the degree of spallation, which is defined as the ratio of the spalled area to the total area of the scales, as a function of oxidation time. It can be seen that the NiAl coatings without REOs doping exhibited the worst spallation resistance (55% spalled area after 12 hours oxidation). In addition, plenty of large voids with average size of  $\sim 5 \mu\text{m}$  were observed at the scale/coating interface (Fig. 9a). With the addition of REOs, the spallation degree of oxides decreased remarkably, suggesting the REOs can significantly improve the spallation resistance of scales (except the 0.5 at.%  $\text{CeO}_2$ -doped coatings). But the effects of REOs on the spallation of scales showed dependence on concentrations and species of REOs. For the  $\text{CeO}_2$ -doped coatings, the spallation degree of scales initially decreased and then increased as the  $\text{CeO}_2$

concentrations increased. For the  $Y_2O_3$ - and  $HfO_2$ -doped coatings, the spallation degree of scales decreased as the concentrations increased (Fig. 8a, b and c).

For the NiAl coatings doped with different REO species at a concentrations of 0.05 at.%, the spallation degree of scales decreased in the REOs-doped coatings as well as the number of voids at the spalled areas compared with undoped specimens (Fig. 9 b, d, e and f). The  $HfO_2$ -doped coatings had the highest spallation degree compared with the  $CeO_2$ - and  $Y_2O_3$ -doped coatings (Fig. 9d). For REO species at the concentrations of 0.1 at.%, the spallation degree of scales decreased significantly and no voids could be observed at spalled locations for  $CeO_2$ - and  $Y_2O_3$ -doped coatings, but for  $HfO_2$ -doped coatings voids were still observed at spalled areas (Fig. 9f) and the spallation degree of scales was the largest compared with the  $CeO_2$ - and  $Y_2O_3$ -doped coatings (Fig. 8e). For REO species at the concentrations of 0.5 at.%, almost no spallation of scales occurred in the  $Y_2O_3$ - and  $HfO_2$ -doped coatings after 120 hours oxidation (Fig. 8f), while large areas of outer-layer scales delaminated in the  $CeO_2$ -doped coatings at an early oxidation duration of 24 hours owing to severely internal oxidation (Fig. 5b and Fig. 9c).

### 3.6 The effect of REOs on the oxidation kinetics

Fig. 10 shows the average thickness of the oxide scale versus oxidation time in the  $\beta$ -NiAl coatings at 1150°C. The growth rate constant,  $k_p$ , was obtained through the parabolic equation [26]:

$$t = A + B\Delta h + C\Delta h^2 \quad (3)$$

$$k_p = C^{-1} \quad (4)$$

where  $\Delta h$  is the average thickness of the oxide scale at time  $t$ , A, B, and C are the coefficients obtained from curve fitting. The evaluated  $k_p$  values of the NiAl coatings were listed in Table 1. It can be seen that the  $k_p$  of NiAl coatings with the addition of REOs decreased remarkably compared with that of the undoped coatings except for the coatings doped with 0.5 at.% CeO<sub>2</sub>.

For the CeO<sub>2</sub>-doped coatings,  $k_p$  increased by 42% with 0.1 at.% dopant concentration, and further by three orders of magnitude at the doped concentrations of 0.5 at.%. For the Y<sub>2</sub>O<sub>3</sub>-doped coatings,  $k_p$  decreased slightly as the Y<sub>2</sub>O<sub>3</sub> concentrations increased in the coatings. For the HfO<sub>2</sub>-doped coatings,  $k_p$  decreased by 80% as the HfO<sub>2</sub> concentrations increased to 0.5 at.%.

The growth rate,  $k_p$ , of the HfO<sub>2</sub>-doped coatings was much higher than those of the CeO<sub>2</sub>- and Y<sub>2</sub>O<sub>3</sub>-doped coatings at 0.05 at.%, but was lower at 0.5 at.%. The growth rate of the CeO<sub>2</sub>-doped coatings was higher than the HfO<sub>2</sub>- and Y<sub>2</sub>O<sub>3</sub>-doped coatings at both 0.1 at.% and 0.5 at.%. At 0.5 at.%, the growth rate of the CeO<sub>2</sub>-doped coatings was three orders of magnitude higher than the other two.

### 3.7 The effect of REOs on the residual stress of scales

Fig. 11 demonstrates the residual stresses of the oxide scales as a function of oxidation time after heat treatment at 1150 °C. The residual stress  $\sigma$  could be evaluated using R2 peak shift of the luminescence spectra [3, 27-29]:

$$\Delta\nu = 5.07(\text{cm}^{-1}\text{GPa})\sigma \quad (5)$$

where  $\Delta\nu$  is the peak shift of the scale from a stress free sapphire, the stresses were compressive due to the alumina growth and thermal misfit.

For the CeO<sub>2</sub>-doped coatings, the residual stresses in the scales increased slightly at 0.1 at.% but decreased dramatically at 0.5 at.% with longer oxidation durations. For the Y<sub>2</sub>O<sub>3</sub>-doped coatings, the residual stresses of the scales seemed to decrease as the concentrations of REOs increased. It also can be seen that the residual stresses of the scales in the 0.1 at.% and 0.5 at.% Y<sub>2</sub>O<sub>3</sub>-doped coatings reduced slightly with longer oxidation durations. For the HfO<sub>2</sub>-doped coatings, the residual stresses of the scales increased slightly with an increase of HfO<sub>2</sub> concentration, and the residual stresses in the 0.5 at.% HfO<sub>2</sub>-doped coatings increased slightly with an increase of oxidation time. For all the doped coatings, the residual stresses of the scales did not vary significantly with oxidation time and the effect of dopant concentrations only induce residual stress fluctuations within a  $\pm 0.5$  GPa range with an exception of 0.5 at.% CeO<sub>2</sub>.

#### 4. Discussion

##### 4.1 The effect of REOs on the scale growth

The oxidation behavior of the NiAl coatings in this study clearly indicated that the REOs can significantly lower the growth rate of oxide scales, mirroring the effect of the REs on the oxidation behavior of  $\beta$ -NiAl coatings [30]. Fig. 12 shows the oxidation mechanisms for the REOs doped NiAl coating. The effect of the REOs on the growth of the scales is primarily attributed to the decomposition of REOs under the low oxygen pressure in the  $\beta$ -NiAl coatings, RE ions dynamically segregate into the grain boundaries and then to the scale surfaces, driven by their high oxygen affinity and the oxygen potential gradient across the metal-oxide-gas system [30, 31].

It is confirmed by STEM-EDS that the RE element Hf segregates on oxide grain boundary (Fig. 13). The presence of RE ions at oxide grain boundaries provides effective barrier for the diffusion of Al and O, lowering the growth rate of the oxide scales, whereas the scale grows by simultaneous Al outward transport and O inward transport in the undoped NiAl coatings [32, 33].

#### 4.1.1 The effect of REO concentrations

It can be argued that the growth rate constant,  $k_p$ , of scales could decrease significantly as an increase of the REO concentrations, owing to the “blocking effect” is more effective to reduce the scale growth when more available RE ions diffuse towards the grain boundaries of the oxide scales. In the case of CeO<sub>2</sub>, however, the  $k_p$  of the scales increases gradually with an increase of the dopant concentration and reaches three orders of magnitude at the doping level of 0.5 at.%. Such abnormal phenomenon could be attributed to the reduction of CeO<sub>2</sub> in the  $\beta$ -NiAl coatings under a reducing atmosphere (or low oxygen partial pressure,  $P_{O_2}$ ) at high temperatures (Fig. 5b, Fig. 7a and Fig. 12). It is suggested that the reduction of CeO<sub>2</sub> usually causes the formation of oxygen vacancies in the oxide lattices [34]. The reduced CeO<sub>2</sub> near the scales/coatings could act as oxygen conductor and compromise the RE effect. As a result the oxygen transportation can be enhanced with the increase of CeO<sub>2</sub> concentrations, leading to the serious internal oxidation observed at dopant level of 0.5 at.% (Fig. 5b and Fig. 12). The critical concentration of CeO<sub>2</sub> for no apparent internal oxidation is about 0.1 at.%. For Y<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> doped coatings,  $k_p$  decreases with increase of concentrations. But for Y<sub>2</sub>O<sub>3</sub> the effect of concentration is

not as significant as  $\text{HfO}_2$ . One possible reason is that  $\text{Y}_2\text{O}_3$  can react with Al to form large amounts of  $\text{YAlO}_3$  at both the gas-scale interfaces as well as inside the coatings (Fig. 5d and Fig. 12) [35]. This reaction leads to decreased Y ion concentrations at oxide grain boundaries and therefore reduces the blocking effect to the diffusion of Al and O ions.

#### 4.1.2 The effect of REO species

The growth of the scales also differs with different oxide species. It is suggested that when comparing with  $\text{Ce}^{4+}$  and  $\text{Y}^{3+}$ , the Hf ions make the strongest adhesion at the grain boundary in both the NiAl coatings and the oxide scales, resulting in a lower self-diffusion in the NiAl coatings and a more effective barrier to diffusion of Al and O along the scale grain-boundaries [36]. For the first 12 hours of oxidation, the  $\text{HfO}_2$ -doped coatings exhibit the highest of value  $k_p$ , owing to  $\text{Hf}^{4+}$  ions mostly stay in the NiAl coatings and insufficient  $\text{Hf}^{4+}$  ions diffuse into scale grain-boundaries. With higher doping concentrations and longer oxidation time (after 12 hours oxidation), a more effective ‘blocking effect’ resulted from sufficient  $\text{Hf}^{4+}$  ions diffuse outward and segregate at scale grain boundaries. Thus the  $k_p$  value of the 0.5 at.%  $\text{HfO}_2$ -doped coatings is the lowest compared with those in the 0.5 at.%  $\text{CeO}_2$ - and 0.5 at.%  $\text{Y}_2\text{O}_3$ -doped coatings.

#### 4.2 The residual stresses of the scales

The residual stresses of the scales in the  $\text{CeO}_2$ -doped coatings decrease dramatically with the dopant concentration at 0.5 at.%, owing to the spallation of scales resulted from seriously internal oxidation. The residual stresses of the scales in the 0.5 at.%

$Y_2O_3$ -doped coatings reduce mainly due to the formation of  $YAlO_3$  [35]. Since the formation of  $YAlO_3$  has a volume shrinkage, the local strain field tends to generate micro cracks (Fig. 4c) and the stresses resulted from oxide growth are therefore released [37]. This effect tends to take place in the samples with high  $Y_2O_3$  concentrations where more micro cracks are generated as a result of higher volume fraction of  $YAlO_3$  phase, whereas in the samples with lower  $Y_2O_3$  concentrations (0.05 at.% and 0.1 at.%) the stress relieving effect is not significant due to marginal micro crack generation and the residual stresses in the oxide scales continue increasing with heat treatment time (Fig. 11b). The residual stresses of the scales in the 0.05 at.%  $HfO_2$ -doped coatings decrease with oxidation time (Fig. 11c), which is consistent with the spallation behavior of the 0.05 at.% doped samples in Fig. 8c. As the coatings are doped by increased concentration of 0.5 at.%, the residual stresses increase with oxidation time but do not accumulate to a significant level [38, 39].

Overall, with the exception of  $CeO_2$ -doped coatings, the residual stresses in the coatings do not vary significantly with both oxidation time and REO concentrations.

#### 4.3 The spallation of scales

According to the established theory, the scale spallation is driven by the strain energy in the oxides, and resisted by the interfacial adhesion [40]. The strain energy:

$$G = h\sigma_0^2/E(1 - \nu^2)$$

where the  $\nu$ ,  $E$ ,  $h$  and  $\sigma_0$  represent Poisson's ratio, Young's modulus, the thickness of oxide scales and the residual stress of oxide scales, respectively. It is suggested that reducing growth rate (low  $h$ ) and the stress would be helpful in preventing the

spallation of oxide scales [30, 39]. Since the residual stresses in the scales for different NiAl coatings (except the 0.5 at.% CeO<sub>2</sub>-doped coatings), and the growth rates of the scales change little at early 24 hours of oxidation (based on the changes of scale thickness are less than 7% in Fig. 10a, b and c), the improved spallation resistance of scales in the coatings with REO additions (compared with undoped coatings), as well as increasing of REO concentrations, could be mainly attributed to the improved interfacial adhesion. It was found that most interfacial voids usually nucleated at the early stage of oxidation, due to Al outward transport [41]. The voids weaken interfacial adhesion by reducing the interfacial contact area. Thus, the improved interfacial adhesion could be achieved by suppressing the void formation at the scale/coating interface (Fig. 9), when the segregation of RE ions into scales inhibiting the Al outward diffusion [4, 42].

For the REO species at the concentrations of 0.05 at.% and 0.1 at.%, the HfO<sub>2</sub>-doped coatings have the smallest improvement of spallation resistance compared with the CeO<sub>2</sub>- and Y<sub>2</sub>O<sub>3</sub>-doped coatings, due to the higher scale growth rate (Table 1 and Fig. 10d) and the lower interfacial adhesion caused by large interfacial voids (Fig. 9e) [41]. Since Hf ions have a lower self-diffusion in the NiAl coatings and a more effective barrier to diffusion of Al and O along the scale grain-boundaries [36], the beneficial effects of Ce and Y ions could work at a lower concentration. It is consistent with the observations that Hf-rich oxides at the scale surface were seldom observed in the 0.05 at.% and 0.1 at.% HfO<sub>2</sub>-doped coatings (Fig. 9e and f), whereas plenty of Ce and Y-rich oxides were formed at oxide scale surface in the 0.1 at.% CeO<sub>2</sub> and 0.05 at.%

Y<sub>2</sub>O<sub>3</sub>-doped coatings (Fig. 9b and d). For the REO species at the doping level of 0.5 at.%, the enough Hf<sup>4+</sup> ions diffuse to the scales due to higher Hf<sup>4+</sup> concentrations near scale/coating surface with higher doping concentrations in the coatings. Hf<sup>4+</sup> ions are more effective in reducing scale growth rate and suppressing voids formation at the scale/coating interfaces than Ce<sup>4+</sup> and Y<sup>3+</sup> ions. Thus the spallation resistance of the scales in the HfO<sub>2</sub>-doped coatings is the highest at 0.5 at.%. Besides, the impurities, mainly C, from the substrate (with 0.1 wt.% C) could also play an important role on the spallation behavior. It could diffuse outward and react with HfO<sub>2</sub> near the IDZ to form HfC (Fig. 5e and Fig. 12b). Thermodynamically, this reaction could be favored by a high carbon activity (high carbon concentration) and a low oxygen activity (low oxygen partial pressure) at the coating/substrate interface. The formation of HfC layer could serve as an element diffusion barrier layer between coating and substrate, and help to improve the spallation resistance.

## 5. Conclusions

In this study, the combination of nano-powder mixing and SPS approach was employed to prepare dense overlay  $\beta$ -NiAl coatings with controlled microstructure and REO concentrations. Effects of the REO species and concentrations on the isothermal oxidation of the  $\beta$ -NiAl coatings were investigated. The conclusions are summarized in the following.

- (1) The undoped NiAl coatings showed the worst spallation resistance due to the formation of voids at scale/coating interfaces. REOs can effectively inhibit the formation of interfacial voids and improve the spallation resistance of the oxide

scales.

- (2) CeO<sub>2</sub> tended to increase the oxidation rate of the NiAl coatings probably due to the increased oxygen diffusion rate as a result of the reduction of CeO<sub>2</sub>. Y<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> decreased the oxidation rate of the NiAl coatings compared with undoped NiAl coatings.
- (3) The residual stresses of alumina scales in the REO doped coatings did not vary significantly with oxide species and concentrations, apart from the 0.5 at.% CeO<sub>2</sub>-doped coatings which demonstrates severe spallation.
- (4) With an increase of the REO concentrations in the NiAl coatings, the spallation resistance of scales in the Y<sub>2</sub>O<sub>3</sub>- and HfO<sub>2</sub>-doped coatings increased, the spallation resistance of scales in the CeO<sub>2</sub>-doped coatings was improved with 0.05 at.% and 0.1 at.% but deteriorated with 0.5 at.% CeO<sub>2</sub>, compared with undoped NiAl coatings. The HfO<sub>2</sub>-doped coatings had the smallest improvement of spallation resistance at the concentrations of 0.05 at.% and 0.1 at.%, but had the largest improvement at 0.5 at.% compared with the Y<sub>2</sub>O<sub>3</sub>- and CeO<sub>2</sub>-doped coatings.

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## Figure Captions

Fig. 1. (a) The morphology of the Ni-Al powder mixtures after ball milling. The higher magnification image was shown as inset. (b) The XRD patterns obtained from the mixed Ni-Al powder after ball milling.

Fig. 2. The cross-section images of as-fabricated coatings: (a) without REOs, (b) 0.05 at.% CeO<sub>2</sub>, (c) 0.1 at.% CeO<sub>2</sub>, (d) 0.5 at.% CeO<sub>2</sub>, (e) 0.05 at.% Y<sub>2</sub>O<sub>3</sub>, (f) 0.1 at.% Y<sub>2</sub>O<sub>3</sub>, (g) 0.5 at.% Y<sub>2</sub>O<sub>3</sub>, (h) 0.05 at.% HfO<sub>2</sub>, (i) 0.1 at.% HfO<sub>2</sub>, (j) 0.5 at.% HfO<sub>2</sub>.

Fig. 3. XRD patterns of NiAl coatings doped with various REOs measured from the surface.

Fig. 4. The surface morphologies of the REOs-doped NiAl coatings oxidized for 120 hours at 1150 °C: (a) 0.1 at.% CeO<sub>2</sub>, (b) 0.1 at.% Y<sub>2</sub>O<sub>3</sub>, (c) 0.5 at.% Y<sub>2</sub>O<sub>3</sub>, (d) 0.5 at.% HfO<sub>2</sub>.

Fig. 5. The cross-section images of the REOs-doped NiAl coatings oxidized at 1150 °C: (a) 0.1 at.% CeO<sub>2</sub> oxidized for 120 hours, (b) 0.5 at.% CeO<sub>2</sub> for 24 hours, (c) 0.1 at.% Y<sub>2</sub>O<sub>3</sub> for 120 hours, (d) 0.5 at.% Y<sub>2</sub>O<sub>3</sub> for 120 hours. (e) 0.5 at.% HfO<sub>2</sub> for 120 hours, (f) Profiles of EDS elemental line scan across the interdiffusion zone between the coating and the substrate (along the line shown in Fig. 5e).

Fig. 6. Cross sectional view of the fractured oxide scale formed on different REOs-doped NiAl coatings oxidized for 120 hours at 1150 °C: (a) 0.1 at.% CeO<sub>2</sub>, (b) 0.5 at.% Y<sub>2</sub>O<sub>3</sub>, (c) 0.5 at.% HfO<sub>2</sub>.

Fig. 7. The FIB-cutting positions and TEM images of the NiAl coatings oxidized at 1150 °C: (a) 0.5 at.% CeO<sub>2</sub> oxidized for 12 hours, (b) 0.5 at.% HfO<sub>2</sub> oxidized for 120 hours. (A, B and C are the selected area electron diffraction patterns of CeAlO<sub>3</sub>, Ce<sub>6</sub>O<sub>11</sub> and HfC, respectively)

Fig. 8. The spallation degree of the oxide formed on NiAl coatings with and without REOs doping as a function of the oxidation time.

Fig. 9. The spalled morphology of the different NiAl coatings oxidized at 1150 °C: (a) undoped NiAl coatings for 12 hours, (b) 0.1 at.% CeO<sub>2</sub> for 48 hours, (c) 0.5 at.% CeO<sub>2</sub> for 24 hours (d) 0.05 at.% Y<sub>2</sub>O<sub>3</sub> for 48 hours, (e) 0.05 at.% HfO<sub>2</sub> for 12 hours, (f) 0.1 at.% HfO<sub>2</sub> for 48 hours.

Fig. 10. The average thickness of the oxide scale as a function of the oxidation time for the NiAl coatings doped with various REOs.

Fig. 11. The residual stresses of the oxide scales as a function of the oxidation time for the NiAl coatings doped with different REOs.

Fig. 12. Schematic illustration of the oxidation mechanism for the REOs-doped NiAl coatings: (a) CeO<sub>2</sub>, (b) Y<sub>2</sub>O<sub>3</sub>, (c) HfO<sub>2</sub>.

Fig. 13. (a) STEM image showing the grain boundaries of oxide scale in the 0.5 at.% HfO<sub>2</sub> coating oxidized for 120 hours; (b) EDS map acquired from the area marked on the STEM image (Section A is far from grain boundary, Section B is on grain boundary).

## Table Caption

Table 1. The parabolic rate constants ( $k_p$ ) for the NiAl coatings doped with various REOs.

Table 1. The parabolic rate constants ( $k_p$ ) for the NiAl coatings with various REOs

Composition (at. %)	$K_p$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )	Time (h)		$K_p$ ( $\text{cm}^2 \cdot \text{s}^{-1}$ )	Time (h)
Ni-52Al	$2.55 \times 10^{-12}$	12	Ni-52Al(0.1Y <sub>2</sub> O <sub>3</sub> )	$3.49 \times 10^{-13}$	120
Ni-52Al(0.05CeO <sub>2</sub> )	$3.44 \times 10^{-13}$	48	Ni-52Al(0.5Y <sub>2</sub> O <sub>3</sub> )	$3.36 \times 10^{-13}$	120
Ni-52Al(0.1CeO <sub>2</sub> )	$4.91 \times 10^{-13}$	120	Ni-52Al(0.05HfO <sub>2</sub> )	$6.82 \times 10^{-13}$	24
Ni-52Al(0.5CeO <sub>2</sub> )	$3.89 \times 10^{-10}$	24	Ni-52Al(0.1HfO <sub>2</sub> )	$3.60 \times 10^{-13}$	48
Ni-52Al(0.05Y <sub>2</sub> O <sub>3</sub> )	$3.72 \times 10^{-13}$	48	Ni-52Al(0.5HfO <sub>2</sub> )	$1.14 \times 10^{-13}$	120

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### Highlights

1.  $\beta$ -NiAl coatings with controlled reactive element oxide additions were prepared using spark plasma sintering.
2. Effects of reactive element oxide additions on the oxidation resistance of  $\beta$ -NiAl coatings were investigated.
3. REO additions significantly improved the oxidation resistance of  $\beta$ -NiAl coating.
4. CeO<sub>2</sub> at high concentrations (>0.5 at.%) was less effective than Y<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>.
5. HfO<sub>2</sub> at low concentrations (<0.1at.%) was less effective than Y<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>.

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