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Surface Rumpling Behavior of Hf/Zr Single-Doped and Co-Doped β-NiAl Coatings during High-Temperature Cyclic Oxidation

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Abstract: Reactive elements like Hf- and Zr-doped β-NiAl are considered to be promising candidate materials for protective coatings used at ultra-high temperatures. However, the role of reactive element co-doping on cyclic oxidation behavior and the surface rumpling of β-NiAl coatings remains unclear. Thus, in this paper, Hf and Zr single-doped and co-doped β-NiAl coatings were deposited on a single crystal superalloy by electron beam physical vapor deposition and the cyclic oxidation at 1150 °C was investigated. The coatings yielded a similar oxidation rate during cyclic oxidation. Obvious surface rumpling appeared in the single-doped coatings, whereas it was effectively alleviated in the co-doped coating. Related mechanisms were discussed, including thermal expansion mismatch, martensitic transformation and phase transformation from β-NiAl to γ′-Ni3Al. The non-uniform phase transformation from β to γ′ was finally believed to be responsible for the discrepancy in the rumpling extents between the single-doped and co-doped coatings.

Keywords: NiAl coating; reactive elements; co-doping; rumpling; cyclic oxidation

1. Introduction

Thermal barrier coatings (TBCs), as typical high-temperature protective coatings, are used to protect superalloy components from oxidation and hot-corrosion in advanced aero-engines [1–3]. MCrAlY (M: Ni, Co or both) with two-phase (B2 β-phase and γ-phase) structure is widely used as bond coat material in TBCs and exhibits satisfying performance at temperatures below 1100 °C. However, as the turbine-inlet-temperature in aero-engines increases continually, the traditional MCrAlY bond coat cannot fully meet the application demands, mainly because the accelerated thickening and accompanied cracking of thermally grown oxide that develops on the bond coat would result in TBC failure [4,5].

For decades, NiAl-based alloy with single β-phase has attracted attention due to its excellent properties, including high melting point, low density and ability to form a dense and slow-growing alumina scale at elevated temperatures. Hence, β-NiAl has been considered as a promising candidate material for the bond coat in TBCs [6–10]. Nevertheless, the alumina scale formed on NiAl tends to spall during high-temperature cyclic oxidation, mainly due to the growth of voids at the NiAl scale interface and rumpling of the scale during thermal cycling [11–13].
A lot of work has been focused on improving the cyclic oxidation behavior of β-NiAl at high temperatures. It has been shown that minor addition of reactive elements (REs), like Hf, Zr, Y and Dy, can both improve the oxide scale adhesion and reduce the scale growth rate [14–21]. The effects of various RE dopants in β-NiAl were investigated by Guo et al. [22], indicating that the addition of Hf and Zr exhibited a better RE effect than Dy, Y and La. Moreover, to further improve the cyclic oxidation resistance of β-NiAl, a co-doping strategy was proposed [22]. Hf and Zr, as well as Y and La co-doping revealed a synergistic effect that led to a lower oxidation rate than the corresponding single-RE doping [23]. This implies that a combination of different REs may produce an enhanced coupling effect.

During prolonged thermal exposure, Al depletion of the bond coat usually occurs due to the formation of alumina scale and interdiffusion between the coating and superalloy substrate, leading to the inevitable phase transformation from β-NiAl to γ′-Ni₃Al [6,24,25]. As a result, the effect mechanisms of REs in a β + γ′ alloy or coating would be more complicated than those in a single-phase system. In addition, the coating/substrate interdiffusion leads to the formation of harmful topologically close-packed phases in the interdiffusion zone, which deteriorates the mechanical properties of the superalloy substrate [26,27]. Hence, it is of significance to investigate the oxidation behavior of the NiAl bond coat when β/γ′ phase transformation occurs during thermal exposure.

The rumpling, also termed as ratcheting or undulation instability, that occurs during cyclic oxidation, can cause separation and cracking between the top coat and bond coat in a TBC system, and eventually results in failure of the TBCs due to large-scale buckling and spallation [28]. Previous studies have focused on the mechanisms of rumpling mainly in the (Ni, Pt) Al system, and several theoretical models and simulations were proposed to explain the phenomenon [12,13,29–34]. However, the relevant mechanism of rumpling in the β-NiAl system still needs further investigation.

In the present work, Hf and Zr single-doped and the corresponding co-doped β-NiAl coatings were deposited onto single crystal superalloy René N5 by electron beam physical vapor deposition (EB-PVD). A comparative investigation of the cyclic oxidation behavior was carried out on the single-doped and co-doped β-NiAl coatings at 1150 °C, and the mechanisms of rumpling were studied.

2. Materials and Methods

A Ni-based single crystal superalloy (René N5) was used as the substrate. The chemical composition of René N5 is listed in Table 1. René N5 substrates were cut into rectangular specimens (10 × 10 × 2 mm³) and then ground up to 800 grit with SiC abrasive paper. After which, the specimens were ultrasonically cleaned in alcohol and later in acetone for 30 min before coating deposition. The ingots of Ni–49Al–1Hf, Ni–49Al–1Zr and Ni–49Al–0.5Hf–0.5Zr (all in at.%) were prepared by arc-melting and annealed in vacuum furnace for 24 h at 1300 °C, aiming to guarantee good homogenization. And finally, they were cut into cylindrical targets with the diameter of 68.5 mm.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Al</th>
<th>Ta</th>
<th>Re</th>
<th>Hf</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>8.17</td>
<td>8.11</td>
<td>1.25</td>
<td>1.64</td>
<td>13.84</td>
<td>2.33</td>
<td>0.97</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

An EB-PVD apparatus (UE205, Paton Electric Institute of Welding, Kiev, Ukraine) was used to produce the β-NiAl coatings. During deposition, the vacuum of the evaporation chamber was maintained at ~10⁻³ Pa, and the substrate specimens were heated by one of the electron beam guns to ~850 °C. Another electron beam gun was used for evaporating the ingots and the EB current was set at ~1.3 A. After deposition, the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings were annealed in vacuum at 1050 °C for 2 h to improve the interfacial bonding strength between the coating and substrate. The chamber pressure was ~10⁻³ Pa during the annealing.
The three types of coatings underwent cyclic oxidation at 1150 °C in an air tube furnace. Before oxidation, the superficial area (denoted as \( A \)) of each specimen was calculated according to its real size measured with a vernier caliper. Then, all the specimens were placed separately in constant-weight alumina crucibles with covers to capture the spalled oxides. The original weight of the specimen with crucible and cover (denoted as \( m_{g0} \)) was recorded by an electronic balance (Sartorius CPA225D, Germany) with a precision of 0.01 mg. During every cycle of the oxidation, the specimens underwent 50 min heating in dry and static air at 1150 °C and 10 min cooling out of the furnace to ambient temperature by compressed air. After a number of certain cycles, the weight of the specimen with crucible and cover was measured again, which was recorded as \( m_{gt} \). Thus, the mass gain of each specimen after the certain cycle was obtained by the following equation:

\[
\text{Mass Gain} = \frac{(m_{gt} - m_{g0})}{A}
\]

It should be noted that the mass gain for each type of coating was calculated from the average mass gain of two samples.

The surface and cross-sectional microstructure of the samples before and after oxidation at high temperature were observed by a field emission-scanning electron microscope (FE-SEM, Quanta 200F, PSV Eindhoven, Netherlands) which was equipped with energy-dispersive X-ray spectroscopy (EDXS). The chemical compositions of as-deposited coatings were detected by X-ray fluorescence spectrometry (XRF, Thermo ADVANT'XP, Waltham, MA, USA). And the other chemical compositions were detected by electron probe micro-analyzer (EPMA, JXA8100, Tokyo, Japan). The phases of the NiAl coatings and oxide scales grown on the coatings were analyzed by X-ray diffraction (XRD, Rigaku D/max2200PC, The Woodlands, TX, USA) with Cu Kα radiation. The microstructures of the oxide scales and underlying coatings were characterized by transmission electron microscopy (TEM, FEI-F20, Raleigh, NC, USA) equipped with energy-dispersive X-ray analysis (EDAX). Focused ion beam (FIB, TESCAN-LYRA3, BrNo, Czech Republic) technology was used to prepare the cross-section specimens for TEM.

3. Results and Discussion

3.1. Microstructures of As-Deposited Coatings

The chemical compositions of the as-deposited NiAl coatings were determined by XRF, as shown in Table 2. Note that the compositions of the coatings are slightly different from those in ingots. The concentrations of Al in the coatings are basically the same, slightly lower than the nominal composition of the ingots. The chemical composition of the NiAl coating is related to the deposition and the secondary evaporation process of the Ni and Al elements. The substrate temperature was ~850 °C during the deposition NiAl coatings. During the coating deposition, the substrate temperature is ~850 °C, and there exists the secondary evaporation of Ni and Al. Since the equilibrium vapor pressure of Al is higher than that of Ni element, more Al is evaporated, causing less Al content in the coating. The content of Hf and Zr in the corresponding single-doped coatings are both in the level of ~1 at.%, while in the co-doped coating, the total content of the dopants is also in the same level, which is evenly split between Hf and Zr.

<table>
<thead>
<tr>
<th>Coating Sample</th>
<th>Ni</th>
<th>Al</th>
<th>Hf</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl–Hf</td>
<td>Bal</td>
<td>45.98</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>NiAl–Zr</td>
<td>Bal</td>
<td>45.34</td>
<td>-</td>
<td>1.03</td>
</tr>
<tr>
<td>NiAl–Hf–Zr</td>
<td>Bal</td>
<td>45.63</td>
<td>0.49</td>
<td>0.49</td>
</tr>
</tbody>
</table>
Figure 1a–c show the surface morphologies of the as-deposited NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings, respectively. As can be seen, the three types of coatings reveal a similar domain structure, however, the grain sizes of the coatings are slightly different. The average grain size of the NiAl–Hf coating is in the level of ~3.2 µm (Figure 1a), while that of the NiAl–Zr coating is in the level of ~1.9 µm (Figure 1b). This indicates that Zr doping is more effective in grain refinement than Hf. The Ni and Al are deposited on the substrate in the form of atoms during NiAl coatings prepared by the EB-PVD process. The atoms of Ni and Al have a stronger diffusion ability due to the substrate temperature being ~850 °C. The solid solubility of RE dopant in β-NiAl was investigated by using first-principles calculations based on impurity formation energies [22]. It transpired that the solubility of Hf in β-NiAl is relatively higher than that of Zr in β-NiAl. Hence, Zr reveals more segregation at the β-NiAl grain boundaries and effectively inhibits grain boundary migration, which is regarded as a “solute drag effect” [35], thus leading to finer grains of NiAl coating. However, the Hf and Zr co-doped coating, which contains less Zr compared to NiAl–Zr, atypically reveals a slightly finer grain size of ~1.3 µm (Figure 1c). A supposition is proposed that Hf and Zr ions can co-segregate at the β-NiAl grain boundaries as ionic clusters, and significantly suppress the grain boundaries’ migration by synergistic effect [23], although further study should be carried out to confirm this.

Figure 1. The surface morphologies of the as-deposited coatings: (a) NiAl–Hf, (b) NiAl–Zr, (c) NiAl–Hf–Zr.

According to the XRD patterns shown in Figure 2, the as-deposited coatings mainly comprised single β-NiAl phase. As the equilibrium solid solubility limit of the RE ions in the β-NiAl lattice is extremely low (less than 0.05 at.%), RE ions should precipitate in the form of RE-rich phases. However, because EB-PVD is a non-equilibrium solidification process, the solid solubility of REs can be significantly improved. Most of the RE ions exist in NiAl coatings in the form of a solid solution, rather than precipitated phases. Therefore, the content of RE-rich phases is too low to be detected by XRD.
The cross-sectional morphologies of the coatings after 2 h annealing in vacuum at 1050 °C are shown in Figure 3. The thickness of all the coatings is ~45 μm, and there is an interdiffusion zone of ~6 μm in thickness at the coating/superalloy interface. Very few RE-rich phases are present in the as-annealed coatings, which is in agreement with the XRD results shown in Figure 2. In addition, some bright white granular or rod-like precipitates are observed in the interdiffusion zone, which have been identified as topologically close-packed phases.
3.2. Cyclic Oxidation of the Coatings at 1150 °C

The resistance to oxidation of the coating samples is usually evaluated by the mass gain, which is obtained by weighing the sample together with the crucible and cover. Thus, the oxide spalls (if present) are included. Figure 4 shows the mass gain of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings during 100 h cyclic oxidation at 1150 °C. The mass gains after 100 h cyclic oxidation for the NiAl–Hf and NiAl–Zr coatings are ~0.55 and 0.69 mg/cm², respectively. The Hf and Zr co-doped coating yields a mass gain of ~0.61 mg/cm², which is lower than that of the NiAl–Zr coating, but slightly higher than that of the NiAl–Hf coating. The almost similar mass gains of the coatings indicate that Hf and Zr co-doping does not effectively decrease the oxidation rate of the NiAl coating as compared to Hf or Zr single-doping.

Figure 4. The mass gain of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings during 100 h cyclic oxidation at 1150 °C.

The growth of alumina scale formed on NiAl coatings is controlled by anions and cations diffusion through the scale, the oxidation kinetics can be described as a parabolic law:

\[(\Delta m/A)^2 = K_p t\]  \hspace{1cm} (2)

where \(\Delta m/A\) is the mass gain unit surface area in time \(t\), and \(K_p\) is the parabolic rate constant.

Figure 5 shows the square of the mass gain of the three types of coatings during 100 h cyclic oxidation at 1150 °C. The values of \(K_p\) are \(0.66 \times 10^{-12}\), \(1.04 \times 10^{-12}\) and \(0.84 \times 10^{-12}\) g²/cm⁴·S at steady-state oxidation for the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings, respectively. The three types of coatings have similar microstructures, where the coating is dense after heat treatment, without cracks or pores inside and around the surface. In this study, the grain sizes of NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings are 3.2, 1.9 and 1.3 µm, respectively. There is no significant difference in grain sizes and thus the grain sizes and columnar gaps are not the main factors affecting the mass gain.

In our previous work [23], the Hf and Zr ions in NiAl bulk alloys tended to co-segregate at the oxide grain boundaries and acted as ionic clusters to suppress the outward transport of Al ions. As a result, Hf/Zr co-doped NiAl bulk alloy exhibited a lower oxidation rate than Hf or Zr single-doped bulk alloy. However, the role of REs in a coating/superalloy system is more complicated than that in a single β-phase bulk alloy system. First, the EB-PVD coatings have a columnar grain structure, while in the cast β-NiAl alloys, the grains are equiaxed. Since the REs play their main role at the grain boundaries, the different grain structure will cause different influences on the RE effect. Second, it is widely accepted that interdiffusion between the NiAl coating and superalloy substrate usually occurs at high temperatures. Thus, besides oxidation, inward diffusion of Al from the NiAl coating to the
superalloy substrate leads to the further consumption of Al and phase transformation from β-NiAl to γ′-Ni₃Al in the coating. Apparently, the mechanism of REs in a single β-phase NiAl will be quite different from that in a β/γ′ dual-phase NiAl [36]. Moreover, the outward diffusion of elements from a superalloy, such as Mo, Ta and W, can also have effects on the oxidation behavior of the NiAl coating. Detailed discussion will be provided later in this section.

Figure 4. The mass gain of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings during 100 h cyclic oxidation at 1150 °C.

Figure 6 shows the XRD patterns of the oxide scales grown on the coatings after 100 h cyclic oxidation at 1150 °C. The oxide scales formed on RE single and co-doped coatings mainly consist of α-Al₂O₃ phase, but no Hf-rich or Zr-rich oxides are present. Moreover, an amount of γ′-Ni₃Al phase was detected. This indicates that phase transformation from β-NiAl to γ′-Ni₃Al did occur in all three types of coatings after 100 h cyclic oxidation.

Figure 7a–f show the surface morphologies of the oxide scales after 100 h cyclic oxidation at 1150 °C. Granular α-Al₂O₃ with no scale spallation is visible for all three types of coatings, implying that improved scale adhesion is enhanced by both single-doping and co-doping. As shown in Figure 7a,c,e, the oxide scales exhibit a domain structure similar to that seen in Figure 1, but the size of each single domain is dozens of times larger. It is believed that the single domain in Figure 1 is composed of one or two NiAl columnar grains, while after oxidation the single domain (Figure 7) is composed of

![Graph](image-url)

**Figure 5.** Square of the mass gain of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings during 100 h cyclic oxidation at 1150 °C.

![XRD Patterns](image-url)

**Figure 6.** The XRD patterns of the oxide scales grown on the coatings after 100 h cyclic oxidation at 1150 °C. (a) NiAl–Hf, (b) NiAl–Zr, (c) NiAl–Hf–Zr.

Figure 7a–f show the surface morphologies of the oxide scales after 100 h cyclic oxidation at 1150 °C. Granular α-Al₂O₃ with no scale spallation is visible for all three types of coatings, implying that improved scale adhesion is enhanced by both single-doping and co-doping. As shown in Figure 7a,c,e, the oxide scales exhibit a domain structure similar to that seen in Figure 1, but the size of each single domain is dozens of times larger. It is believed that the single domain in Figure 1 is composed of one or two NiAl columnar grains, while after oxidation the single domain (Figure 7) is composed of
dozens or hundreds of $\text{Al}_2\text{O}_3$ grains (Figure 7b,d,f) formed on the NiAl columnar grains. It seems that the oxide domain structure is generated by the oxidation of the clusters of NiAl columnar grains, in which some relatively wide columnar gaps develop to be the inter-domain boundaries. Moreover, the oxide domains show significant unevenness (also known as rumpling), especially on the Hf or Zr single-doped coatings. It may be perceived that the unevenness is most likely due to the original surface roughness of the coatings. However, the three types of coating surfaces before oxidation are rather smooth and the root-mean-square roughness ($R_q$) of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings are 0.52, 0.47 and 0.36 $\mu$m, respectively. The root-mean-square roughness ($R_q$) after 100 h cyclic oxidation at 1150 $^\circ$C are 3.4, 3.9 and 2.7 $\mu$m, respectively. Thus, coating roughness is not the main cause of oxide rumpling. The mechanism for oxide scale rumpling will be discussed in the subsequent section.
To further investigate the effect of RE doping on the Al$_2$O$_3$ scale structure, the cross-sectional microstructure of the oxide scale on Hf/Zr co-doped coating after 100 h cyclic oxidation at 1150 °C was examined by TEM. Figure 8a,b show the TEM bright field image and dark field image of Al$_2$O$_3$ scale grown on the coating, where the oxide scale reveals a columnar grain structure due to the scale growth being mainly governed by the inward diffusion of oxygen [15,37]. Furthermore, the scale shows a compact bonding with the coating and no voids can be observed near the scale/coating interface. By combining these results with the morphologies shown in Figure 7, it can be concluded that the outward diffusion of Al is significantly suppressed by RE doping, and the growth of the oxide scale is governed by an inward growth mechanism.

![Figure 8](image-url)  
Figure 8. Transmission electron microscopy (TEM) bright field image (a) and dark field image (b) of Al$_2$O$_3$ scale grown on the Hf/Zr co-doped coating after 100 h cyclic oxidation at 1150 °C.

The cross-sectional morphologies of the oxide scales formed on the NiAl coatings after 100 h cyclic oxidation at 1150 °C are shown in Figure 9. All of the oxide scales mostly comprised Al$_2$O$_3$. Very few RE-rich oxides are present at the scale/coating interface, which is quite unusual compared to the phenomenon in the oxidized RE-doped NiAl bulk alloys. As seen in Figure 9, the NiAl coatings basically consist of light gray phase (marked as regions A, C, and E) and dark gray phase (marked as regions B, D, and F). In terms of our previous work and the XRD results shown in Figure 6, the light gray phase is determined to be γ′-Ni$_3$Al, and the dark gray phase the β-NiAl matrix. The presence of γ′-Ni$_3$Al phase is attributed to Al depletion caused by the oxidation and interdiffusion between the coatings and superalloy substrates. As compared to the single-doped coatings, the co-doped coating contains a relatively smaller amount of γ′-Ni$_3$Al phase. Since the as-deposited coatings contain almost the same Al concentration and the oxidation tests were carried out under the same conditions, it can be inferred that Hf/Zr co-doped NiAl coating may have better phase stability than Hf or Zr single-doped NiAl coatings. However, further study is required. According to the EPMA analysis of regions A, C, and E shown in Table 3, Hf and Zr are mostly distributed in γ′-Ni$_3$Al phase after 100 h cyclic oxidation at 1150 °C, due to their high solid solubility in γ′-Ni$_3$Al phase (far greater than 1 at.%).

Note that the designed doping concentration of Hf and Zr in the NiAl coatings is in the level of 1 at.%, which is nearly 20 times that in the NiAl bulk alloys (usually in a level of 0.05 at.%). In previous work, the 0.05 at.% Hf or Zr doped NiAl bulk alloy exhibited a low growth rate of oxide scale and enhanced scale adhesion, although when the Hf or Zr doping level reached 0.5 at.% in the bulk alloy, accelerated oxidation occurred due to the over-doping effect [7,22]. Interestingly, as shown in Figure 4, all three types of coating exhibit a quite low mass gain, even though the RE doping concentration in the coatings reaches 1 at.%. It is believed that in order to sufficiently exert an RE effect, REs should segregate at the matrix grain boundaries and diffuse into the Al$_2$O$_3$ grain boundaries to block the outward short-circuit transport of Al. Considering the fact that both Hf and Zr have a rather high solid solubility in γ′-Ni$_3$Al, the desirable doping content of REs in NiAl coating should be much higher than
that in $\beta$-NiAl bulk alloys when $\beta \rightarrow \gamma'$ phase transformation takes place during prolonged thermal exposure. Therefore, to ensure an excellent oxidation resistance, a relatively higher RE concentration in the coating is essential. Detailed work is under way to further determine the desirable concentration of REs in NiAl coatings.

Figure 9. The cross-sectional morphologies of the oxide scales formed on the NiAl coatings after 100 h cyclic oxidation at 1150 °C: (a) NiAl–Hf, (b) NiAl–Zr, (c) NiAl–Hf–Zr.

Table 3. Chemical composition of the corresponding regions in Figure 8 (in at.%, electron probe micro-analyzer (EPMA) data).

<table>
<thead>
<tr>
<th>Regions</th>
<th>Ni</th>
<th>Al</th>
<th>Hf</th>
<th>Zr</th>
<th>Cr</th>
<th>Co</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65.54</td>
<td>23.83</td>
<td>2.74</td>
<td>-</td>
<td>3.24</td>
<td>4.65</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>56.40</td>
<td>34.85</td>
<td>0.19</td>
<td>-</td>
<td>3.88</td>
<td>4.68</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>63.71</td>
<td>23.26</td>
<td>-</td>
<td>2.93</td>
<td>3.54</td>
<td>5.10</td>
<td>1.47</td>
</tr>
<tr>
<td>D</td>
<td>55.23</td>
<td>35.15</td>
<td>-</td>
<td>0.28</td>
<td>4.00</td>
<td>4.83</td>
<td>0.51</td>
</tr>
<tr>
<td>E</td>
<td>62.09</td>
<td>21.40</td>
<td>3.57</td>
<td>3.32</td>
<td>3.31</td>
<td>5.23</td>
<td>1.09</td>
</tr>
<tr>
<td>F</td>
<td>55.77</td>
<td>34.98</td>
<td>0.21</td>
<td>0.25</td>
<td>3.96</td>
<td>4.20</td>
<td>0.63</td>
</tr>
</tbody>
</table>

3.3. Mechanism of Rumpling

The rumpling of a metallic coating is considered to have an important impact when the coating is used as a bond coat in a TBC system, because it can initiate separation and cracking between the ceramic top coat and bond coat, eventually leading to spallation failure of the TBC [33,38]. As can be seen from Figure 9a–c, all three types of coatings reveal rumpling after cyclic oxidation, but there is a significant difference in the extent of rumpling. A quantitative characterization of the rumpling degree was applied by determining the normal displacement along the scale/coating interface in the FE-SEM.
cross-sectional images over a distance of approximately 500 μm with a step size of 2 μm, as described in [29,30]. Hence, rumpling of the coating surface is characterized by the root mean square roughness, \( R_q \), defined as:

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

where \( n \) is the number of data points, \( Z_i \) the normal displacement of each point and \( \bar{Z} \) the average normal displacement for the entire measured array. Then, the average rumpling amplitude of NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings represented by \( R_q \) are 3.2, 3.5 and 2.4 μm, respectively. It can be inferred that Hf/Zr co-doping further alleviates the rumpling of NiAl coating compared to Hf or Zr single-doping.

There are a few theoretical models and numerical simulations that have been proposed in the literature to explain the rumpling of aluminate coatings during cycle oxidation [12,13,29–34]. Although the rumpling mechanisms still need to be established, initial surface roughness of coatings, oxide growth, thermal expansion mismatch between substrate and coating and phase transformation of coatings are assumed to be the major factors causing coatings rumpling.

As can be seen in Figure 1a–c, the surfaces of NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings produced by EB-PVD have similar low roughness, which can be considered smooth. Thus, the existence of slight undulations on the coating surfaces prior to oxidation should not be the reason for the difference in the extent of rumpling.

In order to characterize the impact of oxide scale growth and thermal expansion mismatch, NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings were deposited onto the β-NiAl substrates, which were identical in terms of the chemical composition with the corresponding coatings, respectively. Figure 10a–f show the surface and cross-sectional morphologies of the β-NiAl coatings on the corresponding β-NiAl substrates after 100 h cyclic oxidation at 1150 °C. As can be seen, the thickness of the oxide scale grown on the coating deposited on NiAl substrate is nearly 2–3 times that of the scale on the coating deposited on the superalloy N5 substrate. This unexpected result may be ascribed to the abundance of REs (or Hf, Zr) diffusing from the homologous substrate to the coating surface, which can accelerate the oxidation since they are easily oxidized. This inference is well supported by the large number of Hf-rich or Zr-rich oxide pegs present at the surface/coating interfaces. However, for all the coatings on β-NiAl substrates, no rumpling occurred after cyclic oxidation. It seems that the thicker oxide scale causing larger growth stress does not have an effect on the surface rumpling, while the mismatch of the coefficient of thermal expansion (CTE) between the coating and the substrate plays a key role. As is known, the CTE of the superalloy René N5 and β-NiAl is ~17.2 × 10⁻⁶ and ~16.0 × 10⁻⁶ K⁻¹, respectively [39]. This difference in the CTE will cause thermal stress during the thermal cycle, which will accumulate to approximately several GPa after dozens of cycles. Thus, the coatings on N5 substrates reveal significant surface rumpling (Figure 9). In contrast, the mismatch between the coating and the homologous NiAl substrate is negligible. Meanwhile, the fine dense oxide pegs at the interfaces pin the scale to the coating, which further suppresses the surface rumpling. However, since the additions of REs have little effect on the CTE of β-NiAl [40–43], the CTE of the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings is basically the same. The CTE of β-NiAl and β-NiAl–2 at.%Hf are 15.28 × 10⁻⁶ and 15.35 × 10⁻⁶ K⁻¹, respectively [42]. As a result, the difference in the extent of rumpling for the three coatings on N5 substrates has little relation with the CTE mismatch and, therefore, other factors should be taken into consideration.

As it is reported that there is a reversible diffusionless transformation from a B2 (β) cubic structure to an L1₀ (β′) tetragonal structure via distortion in Ni-rich β-NiAl when it is quenched rapidly enough from high temperature [44]. The chemical compositions of the coatings will determine the transformation temperatures, Ms on cooling, and As on heating [31]. Figure 11 shows the cross-sectional TEM images of the NiAl–Hf coating deposited on the superalloy N5 after 100 h cyclic oxidation. As can be seen in Figure 11a, the β′-martensite phase is formed at the Al₂O₃/NiAl–Hf coating interface during cooling from 1150 °C. Furthermore, in the coating near the interface (Figure 11b), β′-martensite strips
with a width of 100~200 nm are observed. The chemical composition of the $\beta'$-martensite phase is determined by EDAX and the result shows the content of Ni is approximately 63~67 at.%. Generally, according to the presence of period stacking faults in the structure of martensite, it can be divided into 3R or 7R structure [45]. Moreover, the 3R structure martensite with ABC stacking corresponds to Ni concentration higher than ~63 at.%. Hence, the martensite phase formed in the NiAl–Hf coating can be deduced to be an $L1_0$ 3R structure. In addition, numerous nanometer-sized (~10 nm) precipitates are observed in the phase (Figure 11c). Based on the published phase equilibria data, the precipitates are most likely to be the Heusler phase Ni$_2$AlHf [46,47]. The reversible martensitic transformation is commonly associated with a volume change ranging from ~2.32% to 1.94% according to the calculated volumes of the B2 and $L1_0$ unit cells [24]. Thus, it is believed that the cyclic volumetric change leading to stress accumulation has a significant impact on the surface rumpling. However, similar martensitic transformation also occurred in NiAl–Zr and NiAl–Hf–Zr coatings during cyclic oxidation. As is revealed in Figure 12, the $\beta'$-martensite phase exists in NiAl–Hf–Zr coating after 100 h cyclic oxidation. Therefore, the martensitic transformation should not be responsible for the different rumpling extents of the three coatings. Then, the microstructure evolution comes into sight.

![Figure 10. The surface and cross-sectional morphologies of the $\beta$-NiAl coatings on the corresponding $\beta$-NiAl substrates after 100 h cyclic oxidation at 1150 °C: (a,b) NiAl–Hf, (c,d) NiAl–Zr, (e,f) NiAl–Hf–Zr.](image-url)
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Figure 10. The surface and cross-sectional morphologies of the NiAl–Hf coating deposited on the N5 superalloy after 100 h cyclic oxidation at 1150 °C: (a) Al2O3/coating interface, (b) β′-martensite phase in the coating, (c) β′-martensite phase with higher magnification. 

Figure 11. Cross-sectional TEM images of NiAl–Hf coating deposited on the N5 superalloy after 100 h cyclic oxidation at 1150 °C: (a) Al2O3/coating interface, (b) β′-martensite phase in the coating, (c) β′-martensite phase with higher magnification.

Figure 12. The cross-sectional TEM morphology of NiAl–Hf–Zr coating on the N5 superalloy after 100 h cyclic oxidation at 1150 °C.
Comparing Figure 10 to Figure 9, it can be seen that significant microstructure evolution occurs in the coatings deposited on the superalloy N5 substrates. A great deal of $\gamma'$-Ni$_3$Al phase is observed in the coatings shown in Figure 9, indicating the phase transformation from $\beta$ to $\gamma'$. This is due to the depletion of Al caused by the oxidation and the interdiffusion between the coating and superalloy substrate. Meanwhile, in Figure 10, since the coating and the underlying NiAl substrate are homologous, the interdiffusion is restrained and the consumption of Al during oxidation can be supplemented by the substrate. Thus, no phase transformation occurs after oxidation.

It is widely accepted that the phase transformation from $\beta$-NiAl to $\gamma'$-Ni$_3$Al is commonly associated with a volume decrease ranging from 8% to 38%, which is up to the share of the two depletion processes, namely “oxidation” and “interdiffusion” [29]. However, the volume decrease of the coating due to Al depletion does not necessarily lead to surface rumpling, depending on whether the decomposition of the $\beta$-NiAl occurs uniformly over the whole coating. If the decomposition occurs uniformly under the oxide scale and the resulting $\gamma'$ phase appears as a uniform sub-scale layer, the surface will not distort to form rumpling [12]. However, as shown in Figure 9, the cross-sectional morphologies of the NiAl coatings after cyclic oxidation show that the $\gamma'$ phase with various shapes and sizes is dispersed in different locations in the coating, as opposed to a uniform layer. Therefore, the local phase transformation from $\beta$ to $\gamma'$ will cause local volume reduction and distortion, which will also contribute to surface rumpling. According to the quantitative statistics conducted on the cross-sectional images, the volume fraction of $\gamma'$ phase in the NiAl–Hf, NiAl–Zr and NiAl–Hf–Zr coatings after cyclic oxidation are 20.5%, 24.2% and 13.7%, respectively. Thus, the more the $\gamma'$ phase precipitates in the coating, the more serious the distortion is. On the other hand, the CTE of $\gamma'$-Ni$_3$Al is only $\sim15.6 \times 10^{-6} \text{ K}^{-1}$ [39], which is lower than that of $\beta$-NiAl, and thus the existence of $\gamma'$ phase may aggravate the thermal expansion mismatch between the coating and N5 substrate. Based on the above, the non-uniform phase transformation from $\beta$ to $\gamma'$ certainly contributes to the surface rumpling and is believed to be the main reason for the discrepancy in rumpling extent between the single-doped and co-doped coatings.

Moreover, researchers have found that REs can increase the tensile strength and creep resistance of NiAl at elevated temperatures [48,49]. Accordingly, a hypothesis is proposed that Hf/Zr co-doping is much more effective in improving the mechanical properties of NiAl, and thus further alleviates surface rumpling. However, the related mechanism is still under investigation.

4. Conclusions

Hf and Zr single-doped and co-doped $\beta$-NiAl coatings were deposited on René N5 substrate by the electron beam physical vapor deposition process. The cyclic oxidation and surface rumpling behavior of the three types coatings were systematically investigated at 1150 °C. Some conclusions can be drawn as follows:

- The coatings revealed similar oxidation rate and good oxide scale adhesion during the cyclic oxidation. Hf/Zr co-doping did not show any obvious synergetic effect in that the oxidation rate of the co-doped coating was not further decreased.
- The coatings exhibited different extents of surface rumpling after 100 h cyclic oxidation, while Hf/Zr co-doping effectively alleviated surface rumpling.
- The mismatch of CTE, the martensitic transformation and the phase transformation from $\beta$ to $\gamma'$ contributed to the surface rumpling during the cyclic oxidation, and among them, the third factor is likely to be responsible for the discrepancy in rumpling extents between the single-doped and co-doped coatings.

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