The effect of yttrium addition on oxidation of a sputtered nanocrystalline coating with moderate amount of tantalum in composition

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The effect of yttrium addition on isothermal oxidation at 1050 °C of a sputtered nanocrystalline coating with moderate amount of tantalum in composition was investigated. Results indicate that yttrium addition delays transformation of metastable β-Al2O3 to equilibrium α-Al2O3 grown on the nanocrystalline coatings. It prevents scale rumpling and promotes the formation of oxide pegs at interface between the oxide scale and the underlying coating. Besides, yttrium prefers to segregate at grain boundaries of the nanocrystalline coating and retards the outward transportation of tantalum from coating to oxide scale, thus reducing the excessive oxidation of tantalum.

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1. Introduction

The continuing demand for increased efficiency in gas turbine engines has, in turn, driven the development of more reliable thermal barrier coating (TBC) systems that enable the turbine components to operate at increasingly high temperatures. A TBC usually consists of a thermal-insulating ceramic top coating and an oxidation-resistant metallic bond coating [1–3]. In the past few decades, aluminides, overlaying MCrAlY (M= Ni and/or Co), and B2 intermetallic β-(Ni, Pt)Al have been consecutively developed as the metallic bond coatings [4–6]. Their oxidation protection relies on the formation and maintenance of a slow-growing and adherent Al2O3 scale between the metallic bond coating and the ceramic top coating. However, they all face a serious problem with regard to elements interdiffusion with the underlying superalloy substrates. One of the interdiffusion results is the formation of secondary reaction zone (SRZ) and refractory element-rich topologically closed-packed (TCP) phases, which have deleterious effects on their mechanical properties. This problem becomes more serious for single-crystal superalloy substrates, where over 20 wt% refractory elements (such as Ta, Re, Mo, W) are deliberately added [7,8]. Sato et al. [9] reported that after interdiffusion with aluminide coating, the 2nd, 3rd and 4th generation single-crystal superalloys has experienced a severe drop in creep rupture life for over 60%, 75% and 85%, respectively.

Sputtering nanocrystalline coating with the same chemical composition to the alloy substrate has attracted more and more attention since its advent thirty years ago, by virtues of the fact that it avoids the elements interdiffusion with the underlying superalloy substrates. Moreover, it has been reported that the sputtering nanocrystalline coating provided higher resistance both to oxidation and to scale spallation than the traditional MCrAlY coatings on many polycrystalline superalloy substrates [10–14]. Its nano-grain microstructure favored Al transportation and the release of thermal stresses. Recently, the nanocrystalline coating was sputtered on a single-crystal superalloy for oxidation protection. It behaves a little different to the case sputtered on the polycrystalline one at high temperatures. Results indicated that the formed alumina scale rumpled heavily and a large amount of refractory element Ta segregated at the alumina grain boundaries. Upon the rumpled scale surface, cracks formed at the top of oxide ridges though the oxide scale was still intact and adhered well with the nanocrystalline coating. In terms of Ta segregation, it was found that it transferred the growth mode of alumina scale, i.e. from equiaxed to columnar

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Table 1
Composition of the single-crystal superalloy N5 (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Al</th>
<th>Re</th>
<th>C</th>
<th>B</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>7.5</td>
<td>7.0</td>
<td>1.5</td>
<td>5.0</td>
<td>6.5</td>
<td>6.2</td>
<td>3.0</td>
<td>0.05</td>
<td>0.004</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

grains. However, its excessive segregation leads to the formation of a large amount of less protective tantalum oxides (TaO2 or Ta2O5) [15,16].

Scale/coating rumpling has been previously observed during cyclic oxidation of almost all aluminide, MCrAlY and β-(Ni, Pt)Al coatings on nickel-based superalloys [17–22]. It appears that the failure of TBC can initiate from rumpling of the interface between the thermally grown oxide and the bond coating with thermal cycling. Tolpygo and Clarke [19–22] has conducted serials of detail investigations on scale/coating rumpling, where the effects of various factors, specifically initial surface roughness, oxidation conditions, cycle length, thermal expansion mismatch, and phase transformation in the bond coating are explored. In order to suppress or reduce the extent of surface rumpling, adding proper reactive element has been demonstrated a feasible way. Guo et al. [23,24] reported that Yb, Sc, Dy or Hf addition significantly suppressed scale rumpling on β-NiAl alloy/coating, while Sm, Gd, Nd, Nb and Ta had little effect (Nb and Ta are exactly not reactive elements). Yttrium is the most frequently researched reactive element in improving the high-temperature performance of protective coatings or superalloys. Huntz et al. [25] reported that the...
presence of yttrium promoted the oxygen diffusion along grain boundaries, while retarded Al short-circuit diffusion, thus reduced the growth rate of alumina scale on FeCr23Al5 alloy. Cueff et al. [26] and Choi et al. [27] further pointed out that yttrium addition delayed phase transformation form metastable $\alpha$-Al2O3 to the equilibrium $\alpha$-Al2O3. In our previous paper [28], yttrium was added in the sputtered K38 nanocrystalline coating, which reduced scale growth rate and retarded phase transformation as it did in the alloy or other traditional metallic coatings. However, none has concerned the effect of yttrium addition on the rumpling of sputtered nanocrystalline coating, especially on a single-crystal superalloy. In this paper, 0.5 wt% yttrium was added in the sputtering nanocrystalline coating on a single-crystal superalloy N5 for the primary purpose of suppressing scale rumpling. However, an unexpected effect of yttrium on segregation and oxidation behavior of Ta is observed. As a result, the effects of yttrium addition on scale rumpling and Ta oxidation are both discussed.

2. Experimental procedure

Cylindrical specimens of $\Phi$ 15 x 2.0 mm were machined from the single-crystal Ni-based superalloy N5 bars, whose nominal composition was shown in Table 1. The bare samples were ground with a final 1000# SiC paper, sand-blasted and then degreased by an ultrasonic cleaner in acetone and ethanol before sputtering. The target used for sputtering was a 382 x 128 mm sheet with the same composition of N5 superalloy (because the yttrium amount was very small, its addition did almost not alter the percentage of other components of the N5 alloy). The coating thickness was in the range of 20–30 $\mu$m. Sputtering parameters were depicted as follows: argon pressure: 0.24 Pa; sputtering current: 4.95 A; substrate temperature: 200 °C. Fig. 1 shows the fractural cross-section morphologies of the two as-sputtered nanocrystalline coatings. There were almost no differences between the two coatings. They both presented a columnar structure, with an average grain size of less than 200 nm. For convenience, the sputtered nanocrystalline coatings were denoted as SN for the ordinary case, and as SNY for the case of 0.5 wt% yttrium addition.

 Isothermal oxidation was carried out in static air at 1050 °C for 100 h with weight measurement performed at appointed intervals. Four parallel specimens placed in alumina crucibles were used. The alumina crucibles were all heat-treated in furnace at 1200 °C for enough time to ensure that their weight would not be changed in the following oxidation test. The weight change of the specimen together with the alumina crucible was recorded using an electronic balance (0.01 mg precision, Sartorius BP211D).

Phase constituent was characterized by using grazing incidence X-ray diffraction (GI-XRD, X: Pert PRO, PANalytical Co., Almelo, Holland, CuKa radiation at 40 kV). Morphologies and microstructures were examined by scanning electron microscopy (SEM, Inspect F 50, FEI Co., Hillsboro, Oregon) coupled with an energy dispersive spectrometer (EDS, X-Max, Oxford instruments Co., Oxford, UK), and by transmission electron microscopy (TEM, JEM-2100F, JEOL, Tokyo, Japan) in conjunction with energy-dispersive X-ray spectroscopy.

3. Results

3.1. Kinetics

Fig. 2 shows oxidation kinetics of the ordinary (SN) and the yttrium-added (SNY) nanocrystalline coatings on single-crystal superalloy N5 at 1050 °C. Both the SN and SNY coatings show a fast initial oxidation stage followed by a slower steady one and the rates of the steady stage obey parabolic kinetics. It seems that Y addition impedes the transformation of oxidation from the initial stage to the final steady one. As shown in Fig. 2B, the initial oxidation stage of the SN coating is very short and even lower than 5 h. While it
lasts for 40 h of the SNY coating. The parabolic rate constant, \( k_p \), is calculated following:

\[
y^2 = k_p t
\]

where \( y \) is weight gain and \( t \) denotes oxidation time. Though the total mass gain of the SNY coating (0.333 mg/cm²) is a little higher than that of the SN one (0.325 mg/cm²) after 100 h oxidation at 1050 °C, its parabolic rate constant at steady oxidation stage (from 40 to 100 h) is one third lower.

### 3.2. Phase constituents

The phase constituents of oxide scales formed on the nanocrystalline coatings after oxidation at 1050 °C in air are detected by GI-XRD and shown in Fig. 3. For the ordinary nanocrystalline coating after 50 or 100 h oxidation, the oxide scale is both composed of \( \alpha \)-Al₂O₃, NiAl₂O₄ and moderate amount of Ta₂O₅, among which \( \alpha \)-Al₂O₃ is the main oxide phase. This is in agreement with our previous study on oxidation of the nanocrystalline coatings at 1000 and 1100 °C [15,16]. Because the oxide film is very thin, strong signal of the underlying coating phase (\( \gamma \)-Ni) is detected even in the grazing incidence XRD patterns.

As shown in Fig. 3, \( \alpha \)-Al₂O₃ and NiAl₂O₄ are also the main oxide products formed on the SNY coating after 50 h oxidation. Besides, weak signal of \( \theta \)-Al₂O₃ is detected. Tantalum oxide phase (Ta₂O₅), which grows on SN coating after oxidation, disappears and is substituted by an oxide solid solution of Al and Ta (AlTaO₄) at this case. With oxidation of the SN coating prolonging to 100 h, the strength of NiAl₂O₄ peaks become weaker and weaker; while the diffraction peaks of \( \theta \)-Al₂O₃ keep their strength like the case of 50 h oxidation. However, if we compare the strength ratio of \( \theta \)-Al₂O₃ to \( \alpha \)-Al₂O₃, the percentage of \( \theta \) phase in oxide scale after 100 h oxidation is lower than the case of 50 h oxidation. An interesting phenomenon is that tantalum oxide Ta₂O₅ precipitates out from the oxide solid solution AlTaO₄ when the oxidation time of the SN coating prolongs from 50 h to 100 h. To be noticed, the strength of peaks of Ta₂O₅ grown on the SN coating is much weaker than those developed on the SN coating.

### 3.3. Surface and cross-section microstructure

#### 3.3.1. SN coating

Fig. 4 shows surface morphologies of the SN coating before and after oxidation at 1050 °C in air. Immediately after deposition, the nanocrystalline columns seem to connect with each other forming micro-sized clusters, as denoted by arrows in Fig. 4A and B. After oxidation, its surface is blurred by oxides. However, the oxide scale is very thin and uniform that the surface keeps generally the original columnar morphology of the as-sputtered nanocrystalline
coating. In an amplified view (Fig. 4D) it is observed that the oxides are granular with size of less than 1.5 μm.

The surface and cross-sectional microstructures of the SN coating after oxidation at 1050 °C in air for 100 h are shown in Fig. 5. The general surface morphology is similar to those after 40 h oxidation (Fig. 4C), except that it becomes much coarser. From the cross-sectional view, the scale thickness is 1.5 μm. No spallation of scale or interfacial detachment is observed after oxidation. Instead, the oxide scale along with the underlying SN coating rumples heavily. Rumpling of oxide scale is a typical way of stress relaxation of the nanocrystalline coating like scales formed on many other traditional coatings, such as AlP (Arc Ion Plating) NiCrAlY or Ni(Pt)-Al coatings [15–22]. To be noticed, the oxide scale is divided into two sublayers by a bright ribbon. EDS analysis indicates that Ta is enriched there.

In order to investigate the microstructure of the oxide scale in detail, its TEM bright field image is shown in Fig. 6. The oxide scale is divided into two sublayers by the discrete black particles, the largest of which is approximately 140 nm in diameter. The inner sublayer is 600–800 nm thick. This is in agreement with the SEM observation (Fig. 5C). Due to the fracture of the outer sublayer in metallographic process, its thickness obtained from Fig. 6 is lower than the real one. Comparing Fig. 6 with Fig. 5C, the Ta-rich bright ribbon in Fig. 5 should be composed of the discrete dark particles in Fig. 6. The composition of the oxide scale is analyzed carefully by TEM/EDS at three sites “a”, “b” and “c”, which represent the outer sublayer, the discrete particle at interface and the inner sublayer, respectively. EDS results are gathered in Table 2. The discrete particle is especially enriched with Ta and O. Combining with the XRD results (Fig. 3), it is identified as Ta2O5. Undoubtedly, Al and O are enriched in both the outer and inner sublayers of the oxide scale. α-Al2O3 is the main oxide product. Besides, there is still trace amount of Ta dissolved in α-Al2O3.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Al</th>
<th>Ta</th>
<th>Y</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN</td>
<td>a</td>
<td>49.69</td>
<td>45.15</td>
<td>1.04</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>31.52</td>
<td>6.64</td>
<td>37.21</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>47.24</td>
<td>48.90</td>
<td>0.73</td>
<td>–</td>
</tr>
<tr>
<td>Sny</td>
<td>d</td>
<td>42.20</td>
<td>52.07</td>
<td>0.41</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>e</td>
<td>43.54</td>
<td>37.84</td>
<td>–</td>
<td>10.74</td>
</tr>
</tbody>
</table>

#### 3.3.2. SNY coating

Fig. 7 shows the surface morphologies of the SNY coating before and after oxidation at 1050 °C in air. The original morphology of the SNY coating is similar to that of the SN one. However, it differs a lot to the SN coating after oxidation (Fig. 4). Its surface becomes much coarser, and the oxide products are not uniform. To be exactly, needle-like or leaf-like oxides develop on almost the whole scale surface, except that at some pits laminated oxides grow. According to the XRD analysis and many previous papers investigating on phase transformation of alumina, these oxides should all be Al2O3, among which the needle-like and leaf-like oxides are α phase while the laminated ones are α phase [25–28]. In addition, α-Al2O3 is found nucleated as well beneath the needle-like or leaf-like α-Al2O3.

Microstructures of the SNY coating after oxidation at 1050 °C in air for 100 h are revealed in Fig. 8. Some needle-like oxides of α-Al2O3 still exist at the scale surface with oxidation continuing from 40 h to 100 h. However, its content has decreased dramatically. This is consistent with the XRD analysis. After 100 h oxidation, its surface morphology exhibits large similarity with the SN coating (Fig. 5A). From the cross-sectional view, the oxide scale grown on the SNY coating is a little thicker than it on the SN one, which reaches 1.7 μm. No obvious tantalum oxides are observed at the central of oxide scale. It seems that the yttrium addition affects
oxidation of Ta. This is one of the main differences between the two nanocrystalline coatings with or without yttrium addition during oxidation. Besides, the yttrium addition retards rumpling of oxide scale and the underlying coating. As shown in Fig. 8B and C, the outer surface of scale is smooth and parallel to the interface of coating/substrate. However, the scale/coating interface that originally should be smooth like the case of SN coating (Fig. 5B and C) has become serrated. Many oxide pegs develop there. Even though many studies [23–28] has reported that the incorporated reactive elements are responsible for the formation of these oxide pegs and further pointed out that the reactive elements should be enriched at the central of oxide pegs, SEM/EDS is not as precise as possible to detect the concentration of any reactive elements there at this case. In order to make clear the oxidation mechanism of SNY coating precisely, microstructures of the SNY coating and the oxide scale are further investigated by TEM/EDS and shown in Figs. 9 and 10.

Fig. 9 shows TEM microstructures of the SNY coating after oxidation at 1050 °C in air for 100 h. The columnar nanocrystallines immediately under the oxide scale have grown to a grain size of larger than 700 nm. At grain boundaries, it is very easy to distinguish many elliptic dark regions from surroundings. These discontinuously dispersed dark ellipses are denoted by arrows in Fig. 9A and then analyzed by EDS. Fig. 9B shows the EDS elemental map, which reveals that Ta and Y are especially enriched there. Weight percentages of Ta, Y and Ni at points 1 to 5 in Fig. 9B are plotted in Fig. 9C. The maximum Y percentage at the dark ellipse ascends up to 48.5 wt%, which is even higher than the content of Ni. Considering the high activity of reactive elements, the concentration and diffusion of Y along grain boundaries is reasonable. The interesting thing is that Ta concentrates as well along grain boundaries. To be exactly, Ta follows Y. At other places apart from the dark ellipses along grain boundaries, no concentration of Ta or Y is observed. Though the concentrated elements at these dark regions can be easily identified by EDS analysis, its chemical formula is not settled from the SAED pattern (Fig. 9D) since no existed compounds composed of Ta, Y or Ni consists very well with the SAED pattern.

Fig. 10 shows TEM microstructure of oxide scale after oxidation at 1050 °C for 100 h of the SNY coating. No discrete dark Ta2O5 particles are found in Fig. 10, and the oxide scale is not divided into two sublayers as the one formed on the SN coating (Figs. 5 and 6). No grain boundaries are observed. As a result, it is difficult to illustrate the yttrium effect on microstructures of aluminum oxide, though EDS analysis (Table 2) reveals a moderate amount of yttrium (2.4 wt%) and a trace amount of Ta (0.5 wt%) in the alumina scale at point of “d”. Obviously, the percentage of Ta in oxide scale on the SNY coating is much lower than on the SN coating (Fig. 6). At the scale/coating interface, oxide pegs form. By virtue of higher resolution of TEM than SEM, yttrium is exactly detected concentrated at the central of oxide peg, as denoted by arrow and letter “e” in Fig. 10. Its EDS results are gathered in Table 2. The yttrium content at point “e” approaches to as high as 10.7 wt%, which should contribute to the formation of such oxide pegs and the final improvement of scale adherence as Refs. [23–28] reported.

4. Discussion

4.1. Effect on oxidation rate

The effects of reactive element Y on oxidation of metallic coatings have been comprehensively studied. It is now commonly accepted that Y delays transformation of aluminum oxide from metastable A or θ phase to the stable α phase [25–28]. This is the right reason why oxides of θ-Al2O3 grow on the SNY coating with increasing oxidation time till to 40 h at 1050 °C, and some of them even stay to 100 h. However, no signals of θ-Al2O3 are detected from scale formed on the SN coating by XRD and SEM. Of course, this does not indicate that θ-Al2O3 has not formed during oxidation of the SN coating. In fact, it has been reported that metastable alumina nucleates initially on many alumina forming coatings, followed by the formation of the stable α-Al2O3 or transformation of the original metastable alumina to the stable one [27]. This transformation develops very quickly when oxidation temperature has surpassed 1000 °C. As a result, θ-Al2O3 should exist only at the very early stage of oxidation of the SN coating at 1050 °C. Because atoms arrange more compact in α-Al2O3, diffusion rate of Al or O in α-Al2O3 is much lower than in θ-Al2O3 and thus the growth rate of α-Al2O3 is lower.

As observed by SEM in Fig. 7, θ-Al2O3 grows on SNY coating before 40 h oxidation. Thereafter, α-Al2O3 starts to nucleate below
\(\theta\)-\(\text{Al}_2\text{O}_3\) and phase transformation from \(\theta\)- to \(\alpha\)-\(\text{Al}_2\text{O}_3\) takes place. So the SNY coating should possess a higher oxidation rate at the initial 40 h oxidation. This is in agreement with its oxidation kinetics (Fig. 2A). While for the SN coating, no \(\alpha\)-\(\text{Al}_2\text{O}_3\) has been detected from the oxide scale by XRD and TEM at least in this investigation, and its oxidation enters quickly into a steady stage after only a very short initial oxidation stage (shorter than 5 h). Though the main oxide product is \(\alpha\)-\(\text{Al}_2\text{O}_3\) for both the SN coating and SNY coating after 40 h oxidation, the oxidation rate of the SNY coating is one third lower than that of the SN one. TEM/EDS (Figs. 6 and 10 and Table 2) reveal the difference in composition of their oxide scales, which might be responsible for their difference in oxidation rate. High percentage of Ta dwells in oxide scale formed on the SN coating, and some of them even segregated at the scale central to form a Ta2O5 ribbon that divides the oxide scale into two sublayers. However, only trace amount of Ta can be detected in oxide scale on the SNY one. Instead, moderate amount of Y is detected.

As we have previously studied, Ta segregation at grain boundaries promotes formation of columnar alumina grains and decreases the growth rate of scale. This effect is similar to reactive element effect (REE). However, much lower amount of Ta ruins its REE and too higher Ta segregation leads to the formation of less protective oxide Ta2O5. Obviously, there is much higher content of Ta segregated in the alumina scale on the SN coating that a continuous Ta2O5 ribbon even formed at the scale central. For the case of SNY coating, the content of Ta is much lower but moderate amount of reactive element Y is detected in the oxide scale. Though from the TEM images it is difficult to judge whether the alumina scale is of equiaxed or columnar structure, it can be inferred that the alumina scale with moderate amount of Y grows at a relatively low rate than the one with no Y incorporation from many Refs. [25–28].

4.2. Effect on scale rumpling

Rumpling is now a common problem that the sputtering nanocrystalline coatings and many Pt-modified \(\beta\)-NiAl coatings have suffered a lot [15–22]. Spallation nucleates easily at the convex surface of a rumpled scale after it has reached a critci thickness. In this investigation, rumpling is visible for the ordinary nanocrystalline coating (SN) after oxidation at 1050 \textdegree C for 100 h, as shown in Fig. 5. The oxide scale is only 1.5 \(\mu\)m thick thus no spallation sites are observed. However, for instance of 1100 \textdegree C oxidation of the same sputtering nanocrystalline coating for 100 h, the oxide scale grows to 5 \(\mu\)m thick that cracking and spalling occur at the top of ridges of the heavily rumpled scale [15]. As a result, it can be expected that scale rumpling will become heavier and heavier as the oxide scale grows thicker and thicker. Until to a critic value, cracking and spalling occur.

For the yttrium modified nanocrystalline coating (SNY), scale rumpling is prevented. Instead, many oxide pegs form at the interface between the oxide scale and the underlying SNY coating. It has been reported that many reactive elements can promote the formation of oxide pegs beneath alumina or chromia scales, improving largely scale adhesion. The mechanisms are illustrated in refs.
alloy [23,24], and the yttrium concentrated pegs are really observed in Fig. 10. With regard to yttrium preventing scale rumpling, the following two aspects are concerned. Firstly, scale rumpling might be a response of relaxation of thermal stress. Due to the different density of $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$, to be exactly the former is lower than the latter, phase transformation of alumina from the $\theta$ phase to the $\alpha$ one generates high stresses in the oxide scale. For the yttrium modified nanocrystalline coating (SNY), the phase transformation of oxide scale develops at a much slower rate than it on the ordinary SN one, as shown in Figs. 3 and 7. There has enough time to release such thermal stresses by way of creeping at high temperatures rather than by way of scale deformation. At such a case, the amplitude of scale rumpling on the SNY coating is largely reduced. Secondly, scale rumpling might be a result from creep of the underlying nanocrystalline coating. Abundant grain boundaries and defects, such as dislocations, twins and micropores, exist in the nanocrystalline coating. Besides, the nanocrystalline coating differs from the alloy substrate in its phase constituents. The alloy substrate was mainly composed of the two phases: $\gamma$-Ni and $\gamma$'-Ni$_2$Al. Though with the same composition, its sputtering nanocrystalline coating belongs to a single supersaturated $\gamma$-Ni phase structure, which is not of a thermally stable state. During the oxidation test, alloy elements, as well as dislocations, move quickly for the purpose of searching equilibrium. This movement of alloy elements and dislocations depends strongly on the density of grain boundaries, and finally results in the microstructure change and macroscopic deformation of the underlying nanocrystalline coating. In the yttrium modified nanocrystalline coating (SNY), the reactive element Y prefers to segregate at the grain boundaries. Due to its big atom radius and its strong chemical affinity with many alloy elements, Y segregation at grain boundaries will undoubtedly retard the movement of other alloy elements. As shown in Fig. 9, yttrium segregates at grain boundaries and catches alloy elements Ta and Ni to form atom cluster (elliptic area in Fig. 9) there. The atom clusters are even bigger than the single yttrium atom and reach 150 nm in width at some sites. They are more effective to retard movement of atom and dislocations. So, the high-temperature creeping and rumpling of the SNY coating is prevented.

4.3. Effect on Ta oxidation

Tantalum is one of the refractory elements added in almost all single-crystal superalloys, acting as substitute to Al in the lattice of $\gamma$'-Ni$_2$Al. Its strengthening effect has been widely accepted [29]. However, only few studies have been conducted on its effect on oxidation [23,30–33]. Conflicting results were obtained. However, they all stated that the effect of Ta on oxidation of superalloys or coatings was closely related to its content. Yang [30] reported that 1 at% addition of Ta improved significantly oxidation resistance of Ni-base superalloys by promoting early establishment of a protective $\alpha$-Al$_2$O$_3$ layer. However, it was also found that further increasing the content of Ta to 3 at% led to the formation of many less protective oxides, such as NiMoO$_4$, NiTa$_2$O$_6$ and TaO$_2$. Klein et al. [31] presented that 2 at% of Ta incorporation decreased oxidation resistance of Co-based superalloys. Park et al. [32] pointed out that less than 5 wt% of Ta was detrimental to oxidation resistance at 850 °C of Ni-base superalloys by preventing the formation of a continuous protective $\alpha$-Al$_2$O$_3$ layer. With increasing its content to 5 wt% and even to 6 wt%, however, Ta reduced the oxidation rate. Pint et al. [33] and Guo et al. [23] researched the REEs on growth of $\alpha$-Al$_2$O$_3$. They both found that trace amount of Ta (less than 0.17 at%) addition did not transform the growth mode of $\alpha$-Al$_2$O$_3$ though segregation of Ta at alumina grain boundaries really took place. In our previous study [15], it was proved that in the NS superalloy and its nanocrystalline coating Ta not only segregated at the boundaries of $\alpha$-Al$_2$O$_3$ grains, it also altered the growth mode of alumina scale by retarding the outward diffusion of Al along grain boundaries. The oxidation rate was therefore slowed down. However, the 6.5 wt% content of Ta is so high that the less protective oxide Ta$_2$O$_5$ formed, which offset to some extent its positive effect in oxidation resisting at 1100 °C.

In this study, the oxidation temperature of the SN coating decreases to 1050 °C, where the excess Ta is as well oxidized and concentrated at the central of oxide scale (Figs. 5 and 6) as the case of 1100 °C oxidation [15]. Obviously, this oxidation process includes the continuous supplying of Ta from the underlying nanocrystalline coating to the oxide scale. At the presence of yttrium, however the diffusion of Ta in the nanocrystalline coating is retarded. Since the supply of Ta is interrupted or weakened, no obvious (or much fewer) tantalum oxide will develop in the oxide scale upon the SNY coating (Figs. 8 and 10). TEM investigation (Fig. 9) further presents that Ta followed Y to concentrate at grain boundaries of the underlying SNY coating rather than in the oxide scale. It seems that Ta has strong chemical affinity to Y and even certain compound should be form. On the contrary, the solubility of Ta in Y or Ta in Y is less than 0.1 at% according to the binary phase diagram of Ta-Y [34]. There are no compounds in this Ta-Y system, and Ta and Y are even immiscible in the liquid state. However, many studies have shown that Ta and Y can form compound at the presence of certain third elements, such as TaYO$_4$ at the presence of O [35,36]. From the EDS analysis, there is 32.7 wt% Ni at point “3” in Fig. 9B in addition to 48.5 wt% Y and 14.7 wt% Ta. Whether Ni, Y and Ta form a ternary compound cannot be identified by the present EDS analysis and the selected area electron diffraction (SAED) pattern. Nevertheless, the yttrium addition retards the transportation of tantalum from the underlying nanocrystalline coating to the oxide scale, thus reduces its negative effect on oxidation resistance.

5. Conclusions

Nanocrystalline coatings with or without yttrium modification are prepared by magnetron sputtering on a nickel-based single-crystal superalloy N5. Their oxidation performance is investigated comparatively and the effect of yttrium addition on scale rumpling and tantalum oxidation is discussed. The following conclusions are drawn:

1. Yttrium addition delays transformation of aluminum oxide from metastable $\theta$ phase to the stable $\alpha$ one formed on the nanocrystalline coating. The yttrium modified nanocrystalline coating (SNY) possesses a higher rate at the initial oxidation stage than the ordinary one (SN). However, at the stable
oxidation stage the rate constant of the SNY coating is one third lower.

(2) Yttrium addition prevents rumpling of oxide scale but promotes the formation of oxide pegs at interface between the oxide scale and the underlying nanocrystalline coating.

(3) Yttrium segregates at grain boundaries of the underlying nanocrystalline coating. It retards the transportation of tantalum from the nanocrystalline coating to the oxide scale, greatly reducing the amount of tantalum oxides developed in the oxide scale on the nanocrystalline coating.

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References

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