Mutual Effect of Oxide Peg Growth and Reactive Element Distribution in Ti-doped CoNiCrAlY Alloys

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Abstract. CoNiCrAl alloys are widely employed as a high temperature resistant material in thermal barrier coating (TBC) systems. In such materials, the adherence between the thermally grown oxide (TGO) Al₂O₃ scale and the alloy is strengthened by oxide pegs formed by dispersed oxide addition or the oxidation of doped reactive elements. In this study, the addition of Ti as the reactive element to a CoNiCrAlY alloy has been addressed. We investigated the mutual effects between Ti and the oxide pegs in alloy samples that had been subjected to a cyclic oxidation process. The alloy with a higher Ti content exhibited a uniformly fine β-phase and fewer voids at the scale/alloy interface, the scale growth rate was lower for Ti-containing alloys. In addition, the formation and growth of oxide pegs led to an irregular distribution of Ti in the scale and at the scale/alloy interface, which resulted in local variations in the features of the scale, with fewer voids and a thinner scale at the sites that are far from the oxide pegs. Meanwhile, the incorporation of Ti to the Y-rich oxide led to an increase in the bonding strength between the peg core and the Al₂O₃ sheath.

Keywords: Alloys; Oxidation; Oxide peg; Reactive element; Mutual effect.

1. Introduction
Substantial effects in the bond coat oxidation resistance in thermal barrier coating systems at high temperatures derive from the reactive element effect (REE) [1]. When suitable amounts of elements that have a high affinity for oxygen or dispersed particles, such as Re [2, 3], Hf [4-6], Y [7-9], and HfO₂ [10], were added as dopants by alloying or ion implantation into heat-resisting alloys such as MCrAl (M: Co and/or Ni) and NiAl, a significant improvement in the resistance of the alloys to oxidation conditions was observed. Numerous hypotheses on the REE have been presented and are summarized in a detailed review by Whittle and Stringer [11]. These hypotheses include concepts such as the modification of the scale growth process, a vacancy sink model that primarily focuses on the interface between the scale and alloy, and the oxide peg of the scale into the alloy. Among these concepts, the oxide peg is a widely accepted mechanistic model. The pegs formed in the scale during the alloy oxidation at high temperatures increase the contact area between the alloy and scale, thus improving scale adherence. Based on the model for the oxide peg forming process proposed by Mennicke [12], we introduced a three-step model for the oxide peg formation and growth process in alloys doped with precipitated Y and solid solute Ti [13].

Herein, CoNiCrAlY alloys with different amounts of the reactive element Ti were subjected to cyclic oxidation conditions. The characteristics of the scale and the scale/alloy interface at sites that were situated near and far from the pegs were examined. The mutual effect between the oxide peg growth and the Ti distribution was subsequently elucidated on the basis of the experimental results.
This paper is the third part of our work for the systematic study of CoNiCrAlY with Ti doped: The first part is exploring different Ti contents on the oxidation behavior of alloy [14]; The second part is the detailed characterization of oxide peg (length, width, amount, et al.) and proposed a new model of peg formation [13]; The third part this paper is the effects of Ti additions on microstructure of coating materials and their resultant responses.

2. Experimental
In a vacuum electric arc furnace (SK-II non-consumable vacuum arc furnace), Co (≥ 99.9%), Ni (≥ 99.9%), Cr (≥ 99.2%), Al (≥ 99.9%), and Y (≥ 99.5%) commercial powders were molten with different amounts of Ti. Homogeneous ingots were obtained by melting the alloys at least twice. The chemical compositions of alloys A, B, C, and D with 0, 0.1, 0.3, and 0.5 wt.% Ti content, respectively, Co as the balance element, and constant contents of the other metals are listed in table 1.

| Sample | Co | Ni | Cr | Al | Y | Ti | S | O | N |
|--------|----|----|----|----|---|----|---|---|---|
| A      | Bal. | 32 | 20 | 8  | 0.40 | 0.0 | 0.001 | 0.019 | 0.002 |
| B      |     |    |    |    | 0.1| 0.3 |      |    |    |
| C      |     |    |    |    | 0.3|     |      |    |    |
| D      |     |    |    |    | 0.5|     |      |    |    |

A number of 10 × 10 × 3 mm³ samples with a V-shaped break (see figure 1 in Ref. [14] for details) were carved from the ingots and subjected to a heat treatment similar to that used in the final manufacturing step of turbine blades [15, 16]. The samples were placed in a vacuum environment at 1120 °C for 2 h, followed by 845 °C for 24 h, and each subsequent air cooling to room temperature 21-24 °C.

After grinding with SiC papers of grit size #60, 150, 400, 600, 800, 1000, 1200, 1500, and 2000, and polishing with a diamond paste, the samples were cleaned ultrasonically in ethanol for at least 5 min. Alumina crucibles (φ20 × 30 mm²) and boats (100 × 40 × 15 mm³) were preheated at 1150 °C to a constant weight [17]. Next, the samples were placed in the alumina crucibles, which were set in a large alumina boat and the latter was inserted into a box furnace (Nabertherm) for oxidation. The oxidation cycle consisted of heating the samples at 1150 °C for 4.5 h followed by air cooling for approximately 0.5 h. The samples were subjected to 20 successive cycles for a total of 100 h.

After the heat treatment, the microstructural surface morphology of the alloy samples, the fracture morphology of the scale, and the cross-section peg morphology were examined by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS: JSM-7001F, JEOL). The number of voids at the scale/alloy interface at sites near and far from the pegs (where near refers to the peg around and far refers to sites between neighboring oxide pegs) were determined. The percentage of the smooth areas at the interface corresponds to the number of voids [18]. Additionally, the scale thickness at the sites near and far from the pegs was measured. In order to decrease errors, the proportion of smooth areas and the scale thickness near and far from the pegs were obtained from at least 20 data points.

3. Results and Discussion

3.1. Ti Distribution
After the heat treatment, samples A–D were similar with regard to their microstructures, which consisted of a lighter γ-phase, a darker β-phase, and Y-rich intermetallic inclusions at the γ- and β-phase boundaries. In samples B–D, Ti functions as a solid solute in the β-phase [14]. The β-phase of sample D is finer and more uniform than that of sample A (figure 1) because of the boundary drag of the reactive element during the β-phase reprecipitation from the γ-phase at the temperature decrease stage of the heat treatment [19].
Figure 2 shows the morphology of the scale fracture. The scale consists of a top equiaxed and a bottom columnar grain layers. The chemical compositions of the sites 1, 2, and 3 were determined by EDS and are displayed in Table 2. Ti was detected at the interface between the scale and the alloy (site 1), at the columnar grain boundaries (sites 2) and the area close to free surface (site 3), demonstrating that Ti diffuses from the alloy to the scale/alloy interface and through the scale to the free surface, similar to other reactive elements [11].

![Figure 1. Backscattered electron images of samples A and D prior to oxidation.](image1)

![Figure 2. The fracture morphology of an Al$_2$O$_3$ scale consisting of equiaxed (top) and columnar grains (bottom).](image2)

| Sites | Co   | Ni  | Cr  | Al  | Y   | O   | Ti  |
|-------|------|-----|-----|-----|-----|-----|-----|
| 1     | 19.8 | 21.3| 8.4 | 21.0| 2.1 | 27.1| 0.5 |
| 2     | /    | /   | /   | 30.6| /   | 65.2| 4.2 |
| 3     | /    | /   | /   | 36.7| /   | 61.5| 1.8 |

Figure 3 shows the surface morphology of the alloy surrounding an oxide peg in the scale spalled zone. According to Ref. [18], the features of the smooth areas (dashed circle) suggest that they are voids formed during exposure, intimate scale/alloy contact is only maintained in areas where the oxide imprints the angular morphology on the alloy. Figure 4 shows the average percentages of smooth areas on the spalled surface at the sites near and far from the pegs (blue and yellow bars, respectively) for all samples, revealing that the average void amount decreases with the increase in the amount of Ti. These results demonstrate that the Ti at the scale/alloy interface behaves similarly to other reactive elements such as Sc [20], forming complexes with excess vacancies or providing internal oxide boundaries for the condensation of excess vacancies, which would have otherwise condensed at the oxide-substrate interface and formed the voids responsible for oxide spallation. Alternatively, capture of the impurity element S by Ti would lower the segregation of S at the interface, thus increasing the adherence of the
scale [21-23]. However, the low content of S in the studied alloys (10 ppm) suggests that Ti decreases voids mainly by the vacancy sink model [11, 20]. Additionally, figure 4 shows that the addition of Ti affects the number of voids at the sites near and far from the pegs differently. For samples B–D, the voids at the interface near the peg are greater in number than those far from the peg.

**Figure 3.** Backscattered electron image of the spalled surface morphology near an oxide peg highlighting important structural features.

**Figure 4.** The percentage of voids on the alloy surface at sites near and far from the oxide pegs for samples A–D.

The scale average thickness of all samples are shown in figure 5, where red circles and blue triangles indicate the thickness at the sites near and far from the pegs, respectively. The results reveal that the addition of Ti to the alloy led to the formation of scales of uniform thickness. For alloys B–D with increasing Ti content, the growth rate of the scale was decreased. According to Ref. [14] of the oxidation kinetics, the alloy mass gain decreases with an increase in the Ti content of up to 0.3 wt.%. However, in the range of 0.3–0.5 wt.% Ti content, the mass gain increase is due to the inner oxidation of Ti and not the formation of a thicker scale. According to the explanation in Ref. [11] that the reactive element additions in alloys will promote the contribution of oxygen transport to scale growth and may even make this contribution predominant and lower the growth rate of the scale. Additionally, the average thickness of the scale in Ti-containing alloys B–D is higher near the pegs than far from them (figure 5).
Figure 5. The scale thickness at sites near and far from the oxide pegs for samples A–D.

Figure 6. Schematic representation of the irregular Ti distribution in the scale and scale/alloy interface.

The addition of Ti led to a decrease in the amount of voids and lowered the scale growth rate more substantially at the sites far from the pegs (figures 4 and 5). These findings suggest that the uneven distribution of Ti at the scale/alloy interface and in the scale was induced by the oxide peg in the course of its formation and growth. A schematic depiction of this phenomenon is provided in figure 6. The driving force for the Ti diffusion toward the growing oxide peg is the oxygen potential gradient, as the pegs within the scale act as short circuit diffusion paths for the oxygen transport [24, 25]. Hence, the Ti content in the peg-neighboring area (figure 6, dashed purple line) is lower than in more remote ones (dashed red line). The uneven distribution of Ti at the interface caused a decrease in the voids, whereas that in the scale influenced the latter’s growth rate.

3.2. Bonding Strength between the Peg Core and the Al₂O₃ Sheath

Ref. [14] showed that, during the scale spalling, small oxide pegs are usually expelled and large ones are severed. However, an examination of sample A showed that only the core of some pegs was expelled, leaving the surrounding Al₂O₃ sheath behind (figure 7). Furthermore, this phenomenon was not observed in samples B–D.

During the steel solidification in metallurgic processes, precipitation of the second phase (such as MnS and TiN inclusions) on the initially generated phase (such as MgAl₂O₄ and Al₂O₃ inclusions) requires a lattice mismatch of less than 12% [26], and larger lattice mismatch values hinder the formation of the second phase on the first phase. Regarding the oxidation at high temperatures, a large lattice mismatch between Al₂O₃ and the oxide peg core lowers the bonding strength between them. The fact that some peg cores were expelled from their Al₂O₃ sheaths in sample A, but not in samples B–D.
B–D, demonstrates that the addition of Ti led to an increase in the bonding strength between the peg core and the Al$_2$O$_3$ sheath. The lattice mismatch between Al$_2$O$_3$ (0001) and Y$_2$O$_3$ (001) or Ti$_2$O$_3$ (0001) is 16.2 and 7.4%, respectively. The lattice mismatch between Al$_2$O$_3$ and a Y, Ti-rich oxide depends on the diffusion of Ti into the Y-rich oxide to form a solid solution or a new phase, and is estimated in the range of 16.2–7.4% for a solid solution, further investigations of the lattice mismatch between the Y, Ti-rich peg core and the Al$_2$O$_3$ sheath will ensue. If the bonding strength between the peg core and surrounding Al$_2$O$_3$ sheath is poor, a new mode of scale spalling in which the crack between the scale and alloy spreads along the outer edge of the oxide peg core occurs (figure 8), resulting in the presence of cavities in the alloy (hollow Al$_2$O$_3$ sheaths figure 7).

**Figure 7.** Alloy surface morphology at the spalled zone of sample A featuring a hollow Al$_2$O$_3$ sheath that resulted from expulsion of the oxide peg, and schematic depiction of the lattice mismatch.

**Figure 8.** Schematic representation of a new scale spalling process in the vicinity of an oxide peg as a consequence of the low bonding strength between the peg core and the surrounding Al$_2$O$_3$ sheath.

**4. Conclusions**

In this study, CoNiCrAlY alloys containing different amounts of the reactive element Ti were subjected to 100 h of cyclic oxidation at a temperature of 1150 °C and subsequently examined regarding the number of voids and the thickness of the scale at the sites near and far from the oxide pegs, which led to an elucidation of the mutual effect between the oxide peg growth and the distribution of Ti. In addition, higher Ti content in the alloy led to an increase in the bonding strength
between the peg core and the Al$_2$O$_3$ sheath. Further investigations of the lattice mismatch between the Y, Ti-rich peg core and the Al$_2$O$_3$ sheath will ensue. This study further contributes to our systematic research on the effects of Ti and Y co-doped CoNiCrAl alloys, which have potential applications in high-temperature bond coat materials for airspace engine.

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References
[1] Pfeil L B 1937 Improvement in Heat-resisting Alloys UK, 459848.
[2] Chen L C, Zhang C, Yang Z G 2011 Corro. Sci. 53: 374-380.
[3] Salam S, Hou P Y, Zhang Y D, Wang H F, Zhang C, Yang Z G 2015 Corro. Sci. 95: 143-151.
[4] Haynes J A, Pint B A, More K L, Zhang Y, Wright I G 2002 Oxid. Met. 58: 513-544.
[5] Pint B A 2004 Surf. Coat. Tech. 188-189: 71-78.
[6] Yan K, Guo H B, Peng H, Gong S K 2016 Rare Met. 35: 513-519.
[7] Schumann E 1995 Oxid. Met. 43: 157-172.
[8] Schumann E, Yang J C, Rühle M, Graham M J 1996 Oxid. Met. 46: 37-49.
[9] Jedliński J, Mrowec S 1987 Mater. Sci. Eng. 87: 281-287.
[10] Allam I M, Whittle D P, Stringer J 1979 Oxid. Met. 13: 381-401.
[11] Whittle D P, Stringer J 1980 Phil. Trans. R. Soc. Lond. A. 295: 309-329.
[12] Mennicke C, He M Y, Clarke D R, Smith J S 2000 Acta Mater. 48: 2941-2949.
[13] Yang L, Zheng Y, Wan C L, Gong Q M, Zhang C, Chen H, Yang Z G Rare Met. In press.
[14] Yang L, Choi R, Zheng Y, Bidabadi M H S, Rehman A, Zhang C, Chen H, Yang Z G Rare Met. In press.
[15] Salam S, Hou P Y, Zhang Y D, Lan H, Wang H F, Zhang C, Yang Z G 2014 Corro. Sci. 89: 318-325.
[16] Lan H, Zhang W G, Yang Z G 2012 J. Rare Earths. 30: 928-933.
[17] He J, Zhang Z, Peng H, Gong S K, Guo H B 2015 Corro. Sci. 98: 699-707.
[18] Allam I M, Whittle D P, Stringer J 1978 Oxid. Met. 12: 35-66.
[19] He J 2016 Study on the mechanisms of reactive elements in the two phase ($\gamma'$+\beta) Ni-Al alloys Beijing: Beihang University.
[20] Tien J K, Pettit F S 1972 Metall. Trans. 3: 1587-1599.
[21] Zhang T, Guo H B, Gong S K, Xu H B 2013 Corro. Sci. 66: 59-66.
[22] Funkenbusch A W, Smeggil J G, Bornstein N S 1985 Metall. Trans. A. 16: 1164-1166.
[23] Hou P Y, Stringer J 1995 Mater. Sci. Eng. A 202: 1-10.
[24] Pint B A 1996 Oxid. Met. 45: 1-37.
[25] Hindam H, Whittle D P, Electrochem J 1982 Soc. 129: 1147-1149.
[26] Bramfitt B L 1970 Metall. Trans. 1: 1987-1995.