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Effect of Pt content on initial TGO formation and available Al reserve of Pt-Al coatings during thermal cycling

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ABSTRACT

Platinum aluminide coatings with different Pt content were fabricated. Their oxidation kinetics and the growth behavior of TGO were investigated. By analyzing the effect of Pt content on the oxidation rate constant and the surface roughness, we found that 13.92–18.52 at.% Pt addition promoted the formation of TGO, and the coatings with ≤ 13.92 at.% Pt addition showed relatively low surface roughness. However, the mechanically induced chemical failure occurred on the coating with high Pt content (≥ 26.96 at.%) due to the decreased Al reserve. Our results indicated that the optimum Pt content was 13.92 at.% and excessive Pt addition decreased Al supplement of coatings for TGO sustainable growth.

1. Introduction

Thermal barrier coatings (TBCs) are used in the hottest part of gas-turbine engines. It consists of a ceramic coat and a metallic bond coat [1,2]. The bond coat works as an aluminum reservoir to form thermal growth oxide (TGO) in service. It also provides good adhesion between the ceramic coat and the superalloy substrate [3]. One typical bond coat alloy in use is platinum aluminide. Platinum aluminide (Pt-Al) coatings are fabricated by electroplating a layer of platinum and a following aluminization process [3]. With the increase of Pt layer thickness, the phase of the coating changes from β-(Ni,Pt)Al to $PtAl_2$ [4,5].

TGO layer mainly forms at initial stage of oxidation. Once a TGO layer with good adhesion forms, the lifetime of TBCs reaches up to thousands of hours [6]. While, the spallation of TGO directly leads to the delamination of ceramic coat [7]. The quality of TGO and Al supplement for TGO growth has an important effect on the adhesion of TGO, and therefore the formation and growth of TGO attracts more attention. Dryepondt et al. investigated the initial stage of TGO growth and proposed that the vertical displacement of the smaller grains initiated TGO rumpling [8]. Tolpygo et al. investigated the effect of temperature regime and Hf addition on the growth of TGO. The results exhibited that the rumpling operated principally at temperatures above 1000 °C and Hf decreased the rumpling extent of TGO [9,10]. It is known that Pt promotes the formation of TGO and increases the adhesion of TGO. Y. Chen's work suggested that addition of Pt to γ/γ′ bulk nickel aluminide increased the adhesion by suppressing the formation of a ridged oxide/alloy interface [11]. However, the optimum value has not been reported. Effect of Pt content on TGO growth is also unclear.

Pt content was generally controlled by the thickness of electroplated Pt layer. By this method, Krishna et al. investigated the role of Pt in microstructural development of Pt-Al coatings [5]. In present work, Pt content was controlled by the thickness of Pt layer and aluminizing condition to investigate the effect of Pt content on initial TGO growth of Pt-Al coatings.

2. Experimental details

50 mm × 50 mm DD5 Ni-based superalloy substrates were polished with 800-girt SiC paper before deposition. Platinum layer with different thickness was electroplated on the substrates by using a Pt contained electrolyte (Platinum-DNS-bath, Metakem GmbH, Germany, deposition rate: 2 μm/h). After electroplating, the samples were aluminized. The pack powder used here for aluminizing consists of 5 wt% Al, 0.2 wt% NH_4Cl and 94.8 wt% Al_2O_3. The preparation parameters are listed in Table 1. The as-prepared samples were polished and annealed to homogenize the composition of the coatings. Then, the coatings were thermally cycled between 1000 °C and room temperature with a frequency of 24 h per cycle. The average Pt content in coatings was measured by Energy Dispersive Spectrometer (EDS) map scanning. The phases of TGO after thermal cycles were determined by X-ray diffraction (XRD, 18 kW D/MAX2500V + /PC, Rigaku Corporation, Japan). The surface and cross-sectional morphologies of the specimens were examined by scanning electron microscopy (SEM) equipped with an EDS. The surface roughness was measured by a noncontact optical

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Table 1
The electroplating and aluminizing parameters.

Parameters/sample	#1	#2	#3	#4	#5	#6	#7	#8
Electroplating time (h)	1	1	2	2	2	3	3	3
Pretreatment time (h, @ 800 °C)	72	48	72	48	24	48	48	24
Aluminizing temperature (°C)	1050	980	980	1050	1050	1050	980	980

profiler. The profilometer provides digital images in the form of height, as a function of lateral position. Each sample was measured in three different areas. In this work, the size of the scanned area was 0.1 × 0.1 cm^2. The roughness value, *Rq* (RMS), is defined by the following equation [8]:

$$R_q = \sqrt{\frac{1}{MN}\sum_{i=1}^{M}\sum_{j=1}^{N} Z^2(x_i, y_j)} \quad (1)$$

3. Results

3.1. Characterization of the as-deposited platinum aluminide coatings

Table 2 shows the average chemical composition (at.%) and phase composition of as-prepared platinum aluminide coatings. The average chemical composition of the coatings was measured by EDS map scanning and the scanning area was shown in the square area in Fig. 1a. It is seen that the Al content keeps at a high level for all samples. But, it has little influence on the microstructure of the coatings [4]. While, the Pt content increases and the Ni content decreases from sample #1 to sample #8. Except for the three main elements, there is a small amount of other elements (such as Cr, Co). Such elements diffused into the coatings from the substrates during aluminizing [12,13]. With the increase of Pt content, the phase composition of the coatings developed from β-(Ni,Pt)Al to $PtAl_2$ through a mixed phase of $PtAl_2$ + β-(Ni,Pt)Al. $PtAl_2$ was detected firstly in sample #2 (8.19 at.%) as shown in Fig. 1b. The phase composition of the sample #2–7 are $PtAl_2$ + β-(Ni,Pt)Al. It is consistent with a previous research that the increase of Pt content favored the formation of $PtAl_2$ phase [14].

The phase composition was influenced by the thickness of Pt layer (electroplating time), pretreatment temperature/time and aluminizing temperature. Because a relatively low pretreatment temperature (800 °C) was chose, $PtAl_2$ was easily found. Additionally, Pt—Al bond is stronger than Ni—Al bond [15]. PtAl has the most negative formation enthalpy among PtAl, NiAl and NiPt stoichiometric B2 compounds calculated by statistical-mechanical Wagner-Schottky model [16]. Both the reasons are favorable to form more Pt—Al bonds. Therefore, with the increase of Pt content, it tends to form $PtAl_2$ phase by maximizing the number of Pt—Al bonds.

The cross-sectional morphologies of the as-prepared coatings are illustrated in Fig. 1. Fig. 1a shows that the thickness of the β-(Ni,Pt)Al coating is ~40 μm. Comparing with β-NiAl phase (cubic; B2-type superlattice), the XRD pattern of β-(Ni,Pt)Al shifted slightly due to Pt addition [17]. Within the interdiffusion zone (IDZ), there are many dots of precipitates [12,18]. Fig. 1b–g show the microstructural features of two-phase $PtAl_2$ + β-(Ni,Pt)Al coatings. Their thickness is 20–30 μm. Fig. 1h shows the cross-sectional morphology of $PtAl_2$ coating.

Table 2
The averaged chemical composition (at.%) and phase composition of as-prepared platinum aluminide coatings.

Sample	#1	#2	#3	#4	#5	#6	#7	#8
Pt	2.23	8.19	13.92	18.52	20.80	22.97	26.96	31.10
Al	49.04	50.67	49.47	57.31	52.71	60.53	61.12	68.90
Ni	45.12	41.15	24.50	13.14	15.69	8.66	6.43	–
Other	3.56	–	12.12	11.03	10.79	7.84	5.49	–
Phase	β-(Ni,Pt)Al	$PtAl_2$ + β-(Ni,Pt)Al						$PtAl_2$

3.2. Thermal cycling

The oxidation weight gain per unit area (Δ*W*/*A*) of the Pt-Al coatings during thermal cycles is shown in Fig. 2. According to the weight gain curves in Fig. 2a, the sample #1–6 had no TGO spallation and exhibited good TGO adhesion at the TGO/bond coat interface. The Δ*W*/*A* values of sample #1–6 increased rapidly, and then was slowed down by oxide grain growth [19]. However, sample #7 showed significant weight loss (Fig. 2b). The Δ*W*/*A* value of sample #7 with 26.96 at.% Pt increased at first 96 h and then decreased rapidly. At the range of 145–210 h, the Δ*W*/*A* value increased slowly again. It indicated that the coating tended to heal the exfoliated TGO by forming new oxide. However, it eventually failed and the TGO continued to spall off. Sample #8 also showed significant weight loss.

According to Wagner's theory about selective oxidation of alloys, only when the content of Al (*f*) in the alloys is higher than its critical value (C_{Al}), can the selective oxidation of alloys and sustainable growing of Al_2O_3 scale happen [20]. With the continuous consumption of Al, the coatings suffer from breakaway oxidation in two failure modes: mechanically induced chemical failure (MICF) and intrinsic chemical failure (InCF) [21–23]. When $f > C_{NOSH}$, Al is oxidized selectively to Al_2O_3 scale. Even if part of scale cracks or even spalls, the scale is able to self-heal. When $C_B < f < C_{NOSH}$, although the scale grows sustainably, when it cracks or spalls, the Al content is not adequate for self-healing. This failure of oxidation resistance is called mechanically induced chemical failure (MICF). When $f < C_B$, the Al content is not adequate for sustainable Al_2O_3 growing and other elements in the alloy begin to oxidize. Such failure is called intrinsic chemical failure (InCF) [24–26]. Thus, the failure of sample #7 is mechanically induced chemical failure (MICF) according to the definition above.

3.3. Effect of Pt content on initial TGO growth

3.3.1. The phase composition and morphologies of the initial TGO

After thermal cycling, all the TGO of the sample #1–6 consist of Al_2O_3 (Fig. 3). Chen et al. suggested that Pt addition can inhibit the formation of transient NiO at the very initial stage of oxidation [11]. The TGO acts as an effective oxygen diffusion barrier to prevent further oxidation [13,27]. The main phases of the coatings were also detected. It confirmed that the phase composition of the coatings developed from β-(Ni,Pt)Al to $PtAl_2$ with the increase of Pt content. It also indicated that the phases of the coatings kept their intrinsic crystal structure after oxidation. However, Ni_3Al, which is generated by Al depletion, was not observed after oxidation. It indicated that Al contents in sample #1–6 were not low, and the coatings had adequate Al reserve.

The surface morphologies of sample #1–6 after thermal cycling are shown in Fig. 4. The TGO surface morphologies developed to be denser from Fig. 4a to c, and from Fig. 4d to f, the TGO surface morphologies developed to be looser. It is seen that the surface of TGO is covered by countless sheet shaped particles. These particles introduced more surface area than planar surface. At the initial stage of oxidation, increased surface area added more contact area between oxygen and Al^{3+} and it subsequently promoted TGO formation. With the increase of TGO thickness, concentration gradient of Al^{3+} through the TGO layer decreased so that oxidation rate decreased rapidly.

As shown in Fig. 2a, sample #4–6 (18.52 at.%, 20.80 at.% and 22.97 at.%) had similar weight gain per unit area curves (Δ*W*/*A*), which resulted in a similar TGO thickening process. Thus, TGO growth behavior of sample #6 is chosen as representative. TGO growth behavior of sample # 1, 2, 3 and 6 are summarized in Fig. 5. It is seen that all the TGO have good adhesion to the coatings (#1–6). As shown in Fig. 5b, there were "oxide pegs" between TGO and coating, which increased the