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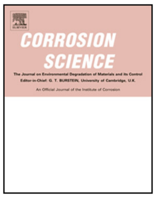

Preparation and hot corrosion behaviour of Pt modified AlSiY coating on a Ni-based superalloy

R.D. Liu, S.M. Jiang, H.J. Yu, J. Gong, C. Sun*

Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

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ABSTRACT

A Pt modified AlSiY coating was prepared on a Ni-based superalloy DD5 by electroplating and arc ion plating (AIP). The outer layer of the coating was mainly composed of β-(Ni,Pt)Al with dispersed CoWSi. The hot corrosion behaviour of Pt modified AlSiY coating at 900 °C was investigated. Compared to AlSiY coating, the Pt modified AlSiY coating provided improved hot corrosion resistance. The addition of Pt in AlSiY coating accelerated the phase transformation from θ-Al_2O_3 to α-Al_2O_3 in the initial stage, improved the scale adhesion and effectively suppressed the formation of internal oxides and internal sulphides.

1. Introduction

Ni-based superalloys have been extensively used in turbine engines. However, because of the low Al and Cr contents, Ni-based superalloys exhibit poor oxidation and hot corrosion resistance at service temperature, which shortens the lifetime of turbine engines [1]. Therefore, protective coatings have been utilized in turbine engines to enhance their resistance to high temperature oxidation and hot corrosion. The simple aluminide coating, which mainly consists of β-NiAl phase, is one of the most widely used coatings due to its low cost and good oxidation resistance [2,3]. However, the hot corrosion resistance of the simple aluminide coating is poor [2]. To solve the problem, several elements such as Si [4,5], Pt [6–8] and reactive elements (REs) [9,10], have been added into the simple aluminide coating to improve its oxidation and hot corrosion resistance.

It has been reported that the addition of Pt in the simple aluminide coating enhances the scale adhesion [11], promotes selective oxidation of aluminium [12,13], and increases the outward diffusive flux of Al [14]. As a result, Pt modified aluminide coatings have the much enhanced performance at high temperature as compared to the simple aluminide coating [15]. Nowadays, Pt modified aluminide coatings are extensively used in turbine engines. Most commercial Pt modified aluminide coatings are commonly manufactured by first electroplating a thin Pt layer on the surface of blades, and then heat-treating the blades to dilute the Pt concentration at surface, finally aluminizing by pack cementation, above the pack cementation process or chemical vapour deposition (CVD) [16].

In view of the beneficial effects of Pt on aluminide coating, Pt has also been added to other protective coatings to improve their performance. For example, Pt modified MCrAlY coatings prepared by vacuum plasma spray(VPS) [17,18], the Tribomet process [19,20] or magnetron sputtering [21], and Pt modified β-NiAl coatings fabricated by electron beam physical vapour deposition (EB-PVD) [22] have been investigated. All the researches demonstrate that the addition of Pt significantly improves oxidation or hot corrosion resistance of protective coatings. Besides, these new techniques used to fabricate Pt modified coatings can simplify the procedure for preparing a Pt/another element co-modified coating. Consequently, the new method to prepare Pt modified coatings has been a hot research area in protective coatings.

The AlSiY diffusion coating prepared by arc ion plating (AIP) has been proved to offer protection to the substrate during high temperature oxidation and type-I hot corrosion [23]. And the AlSiY coating is a Si/Y co-modified aluminide coating due to the existence of minor Si and Y. The trace of Si element can enhance type I hot corrosion resistance of aluminide coating by forming SiO_2 scale [24,25]. Besides, AIP method is easy to control the thickness and composition of the coatings.

Considering the Pt, Si and Y positive effects on hot corrosion resistance of aluminide coating, Pt modified AlSiY coating was fab-

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* Corresponding author. Fax: +86 24 83978232.
E-mail address: csun@imr.ac.cn (C. Sun).

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ricated by AIP. Then the effect of Pt addition on the microstructure and hot corrosion behaviour of AlSiY coating were discussed.

2. Experimental procedures

The substrate used in the study was a commercial Ni-based single crystal superalloy DD5. The chemical composition of the DD5 was 7 wt.% Cr, 7.5 wt.% Co, 1.5 wt.% Mo, 5.0 wt.% W, 6.5 wt.% Ta, 6.2 wt.% Al, 3.0 wt.% Re, 0.15 wt.% Hf, traces amount of C and B, balanced Ni. Rectangular samples with dimensions of 14 × 13 × 2 mm^3 were ground to 800-mesh *SiC* paper, blasted with 200-mesh glass ball, and then were ultrasonically cleaned in acetone. First, a Pt layer with $2 \pm 0.2\ \mu m$ was electroplated on the substrate. Then a diffusion heat treatment at 1080 °C for 2 h in Ar atmosphere was conducted to dilute the Pt concentration near surface. Subsequently, an AlSiY layer with 20 μm was deposited on the surface by arc ion plating method (AIP). The chemical composition of AlSiY target was 93.7 wt.% Al, 4.8 wt.% Si and 1.5 wt.%Y. Coatings with and without Pt layer were vacuum annealed at 1030 °C for 3 h with a heating rate of 5 °C/min. All the samples, including the substrate were firstly shot peened and then ultrasonically cleaned in acetone before testing.

The hot corrosion tests were carried out in a muffle furnace in static air. Samples were coated by a mixed salt of 75 wt.% Na_2SO_4 + 25 wt.% K_2SO_4 or 75 wt.% Na_2SO_4 + 25 wt.% NaCl with 1 mg/cm^2. Next salt coated samples were espoused at 900 °C. After exposing these specimens for a certain period, they were taken out to be weighed by an electronic balance with a sensitivity of 10^{-5} g. Before being weighed, the samples were washed in boiling distilled water for three times to eliminate the salt and then were dried. Subsequently, a uniform salt coating was brushed again to continue the experiments.

The phases of the coatings were identified by X-ray diffraction (XRD). The surface and cross-sectional morphologies were characterized by electron probe microanalysis (EPMA) and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The quantitative concentrations of elements at the surface were analysed by EPMA. Raman spectroscopy (JY HR800, 1 μm spot size) at a laser wavelength of 632.8 nm was used to distinguish α-Al_2O_3 from θ-Al_2O_3. TEM (JEOL JEM 2010F) equipped with EDS was used to analyse the precipitates in coating. A thin Ni layer was plated on the surface of corroded specimens to avoid the spallation of scale.

3. Results

3.1. Microstructures of as-annealed coating

The cross-sectional images of as-deposited AlSiY coating and Pt modified AlSiY coating are shown in Fig. 1a and b, respectively. The inner bright layer in Pt modified AlSiY coating was Pt diffusion layer and the outer dark layer was AlSiY layer. According to the EDS analysis, the Pt diffusion layer contained 50–60 wt.% Pt, and the average composition of AlSiY layer was 93.0Al–5.2Si–1.8Y (wt.%). The typical cross-sectional images of AlSiY coating and Pt modified AlSiY coating after the vacuum annealing treatment at 1030 °C for 3 h are presented in Fig. 1c and d, respectively. Fig. 2 shows the XRD patterns of as-annealed two coatings. Both of the coatings consisted of an outer layer (including the Zone 1 and Zone 2 in Fig. 1c and d) with fine dispersed precipitates and an interdiffusion zone (IDZ). The outer layer of AlSiY coating was mainly composed of β-NiAl phase and the outer layer of Pt modified AlSiY coating primarily consisted of β-(Ni,Pt)Al phase, indicating that the Pt addition did not change the main phase of coatings. However, compared to AlSiY coating, all the diffraction peaks of β-NiAl in Pt modified AlSiY coating shifted towards the lower angle. This was because that Pt atom replaced the Ni site in the unit cell and the atom radius of Pt was larger than that of Ni, which enlarged the lattice parameter of NiAl. The intensity of (1 1 1) plane for Pt modified AlSiY coating increased slightly. Besides, there were two additional peaks near 40° in the XRD patterns of two coatings, which belonged to the dispersed white precipitates in the outer layers. As shown in Fig. 2, the sites of the two additional peaks for the two coatings were the same, revealing that the precipitates in the two coatings were identical.

Table 1 lists the average compositions of each zone in the two coatings. Both of the outer layers for the two coatings contained about 40 at.% Al. For Pt modified AlSiY coating, Pt was mainly enriched near the surface (as marked Zone 1 in Fig. 1d) with 5.9 at.%, while near the bottom of outer layer (Zone 2 in Fig. 1d), the Pt concentration was approximately 2.8 at.% and that was only 0.6 at.% in IDZ.

TEM was used to investigate the dispersed precipitates in the outer layer of Pt modified AlSiY coating, as shown in Fig. 3. The average grain size of the outer layer was ∼500 nm. Most precipitates distributed at grain boundaries and the others formed within the grains. The HAADF image indicated that all the precipitates had a high concentration of refractory elements. The STEM-BF image of precipitates and their corresponding element mappings are shown in Fig. 3b. The distributions of Al and Ni were similar. Meanwhile, the distributions of Si, Co and W were virtually identical. Thus the mappings of Al, Co, W are not shown in Fig. 3. The element mappings suggested that both the two kinds of precipitates were rich in Co, W, Si, Cr, and poor in Ni and Al. The Pt rich/poor areas were not observed. Since the intragranular precipitates were too small, only SAED patterns of the precipitates at grain boundaries were obtained.

Fig. 4 presents SAED patterns of the precipitate at grain boundaries. Based on the SAED patterns, it was calculated and concluded that the space group of the precipitates was Pm63/mmc with cell parameters of $a = b = 0.485$ nm, $c = 0.775$ nm, which was in accordance with the space group and cell parameters of CoWSi (PDF-15-0594. The standard cell parameters of CoWSi are $a = b = 0.473$ nm, $c = 0.772$ nm.). Interestingly, it should be noted that the nearest spots along *c*-axis in Fig. 4a were (±0001). However, in standard indexed patterns, when the electron beam is parallel to $[2\bar{1}\bar{1}0]$, the diffraction spots (±0001) are forbidden. Furthermore, there is no (0 0 0 1) peak in the standard XRD pattern of CoWSi. The diffraction spots (±0003) and (±0005) also appeared (as marked ⊠ in Fig. 4a). The additional spots (±000l): $l = 2n + 1$ were attributed to the double diffraction. As shown in Fig. 4, the spots of $(\bar{1}011)$ and $(10\bar{1}0)$were strong.

$$(\bar{1}011)+(10\bar{1}0) = (0001) \tag{1}$$

By adding these two vectors, the vector of (0 0 0 1) emerged. Since the (0 0 0 l): $l = 2n + 1$ spots were formed by the double diffraction, their intensity was weaker than that of the normal diffraction spots. The double diffraction was also found in other hcp structure materials, such as α-Ti [26].

During annealing, the system was a diffusion couple of AlSiY/Pt diffusion layer/substrate. For simplicity, minor elements (e.g. Si, Y) were omitted. In the Al/Ni-Pt/substrate system, Al diffused inwards and Ni diffused outwards. Both inward and outward diffusion of Pt occurred. First, phase transformation occurred along with the interdiffusion, followed by the formation of Ni-rich β-(Ni,Pt)Al at the Al/Ni–Pt interface.

$$\text{Ni–Pt} + \text{Al} \rightarrow \gamma'\text{-(Ni, Pt)}_3\text{Al} \rightarrow \beta\text{-(Ni, Pt)Al} \tag{2}$$

According to Ni–Pt–Al phase diagram [27], no $PtAl_2$ phase formed during annealing due to the relatively low Pt concentration in Pt diffusion layer. Previous research [28] showed that the intrinsic diffusion coefficient of Al in Ni-rich β-(Ni,Pt)Al phase