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Cyclic oxidation behavior and oxide scale adhesion of Al/NiCrAlY coating on pure titanium alloy

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ABSTRACT

Al and Al/NiCrAlY coatings were deposited on pure titanium substrate by air plasma spraying method. Cyclic oxidation behavior and oxide scale adhesion at 800 °C for 100 cycles were investigated. For the single Al coating, a severe spalling of oxide scale and elemental interdiffusion occurred after 100 cycles. The mass loss of the single Al coating has reached to 1.39 mg/cm^2. The oxide scale on the duplex Al/NiCrAlY coating kept a good bonding with the underlay coating. The addition of NiCrAlY layer inhibited the outward diffusion of Ti atoms and inward diffusion of Al atoms. The propagation of cracks and the formation of pores were also suppressed by NiCrAlY layer. As a result, the duplex Al/NiCrAlY coating possessed a superior cyclic oxidation resistance.

1. Introduction

Titanium and its alloys have many excellent properties including low density, high specific strength and excellent corrosion resistance properties which have been widely used in aerospace and automobile manufacturing. However, their applications are restricted because of their poor oxidation resistance. Due to the formation of non-protective TiO_2 scale, the oxidation resistance of Ti alloys deteriorates, especially when the temperature is above 600 °C [1–3]. In order to safe applied at high temperature, the oxidation resistance of the Ti alloys must be improved. In recent years, many techniques have been used to improve the oxidation resistance of Ti alloys which can be divided to bulk alloying and surface modification [4–6]. Compared with bulk alloying, surface modification performs better in improving oxidation resistance. Adding alloying elements, such as Al, Nb or Mo, has a great influence on mechanical properties of the alloys. However, surface modification techniques, especially for adding coating, can keep good balance between specific mechanical properties and sufficient oxidation resistance of the components.

In recent years, several coatings have been applied for improving the oxidation resistance of Ti and its alloys, such as MCrAlYs [7], ceramics [8], aluminides [9], silicides [10] and so on. Among the numerous antioxidation materials, aluminized coating is widely used to provide high temperature protection due to its excellent capability of forming protective oxide films at the surface. In general, the aluminized coating on Ti alloys is $TiAl_3$ type. The research has reported the $TiAl_3$ type aluminized coating can provide good oxidation resistance when the temperature is below 800 °C [11]. The results show that a protective α-Al_2O_3 film is formed on the surface of the coating. According to the previous research, it can be concluded that the improvement of oxidation resistance can be attributed to the formation of complete oxide film on the surface of the coating. However, Al_2O_3 and $TiAl_3$ are easily to spall because of its inherent brittleness, especially for cyclic oxidation. In the process of cyclic oxidation, the spalling of oxide film results from large residue stress and weak adhesion to the underlay coating.

In order to improve the cyclic oxidation resistance of the aluminized coating, a lots of efforts have been done to enhance oxide film adhesion. Alloying elements, such as Si [12], Cr [13] and Pt [14], were doped in Al powder to product aluminide coatings. The effect of the alloying elements on the oxidation resistance are investigated. The results indicated the addition of alloying elements

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was beneficial to improve the oxide film adhesion. However, TiO_2 was also found in the oxide film except for Al_2O_3. This is because that an elemental interdiffusion has occurred between the coating and substrate. The formation of TiO_2 can destroy the continuity and integrity of the Al_2O_3 film, which is detrimental to the oxidation resistance of the coating. Therefore, it is necessary to prevent the outward diffusion of Ti atoms and restrain the formation of TiO_2. The ceramic layers act as the diffusion barrier can inhibit the elemental interdiffusion. However, the mismatch of thermal expansion coefficients is harmful to the bonding between coating and substrate. Our previous research [15] has found NiCrAlY coating also can play a role in diffusion barrier during isothermal oxidation. The results have shown the outward diffusion of Ti and inward diffusion of Al were suppressed by NiCrAlY coating effectively. This results indicated NiCrAlY coating not only can act as an oxidation resistance coating, but also can play a role in diffusion barrier. Although the effect of NiCrAlY on the isothermal oxidation and interdiffusion behavior of Al/Ti system has been investigated, the effect on the cyclic oxidation and oxide scale adhesion has not been investigated up to now. Therefore, an in-dept investigation on mechanisms of cyclic oxidation and oxide scale adhesion of the Al over-layer with a NiCrAlY diffusion barrier is desired.

In the present work, the single Al coating and duplex Al/NiCrAlY coating systems were prepared on the pure Ti alloy. A comparative research was carried out on them to investigate the roles of NiCrAlY in affecting the cyclic oxidation behavior, oxide scale growth rate and oxide scale adhesion. The microstructure evolution of the coatings were also systematically studied.

2. Experimental procedures

2.1. Substrate material and coating preparation

A commercial pure titanium ingot was used as substrate, whose nominal composition is shown in Table 1. Rectangular samples with the dimension of 30 mm × 15 mm × 2 mm were cut from the pure Ti alloy by wire-cutting. Before spraying, the specimen surfaces were ground with SiC papers to 800-grit, followed by sand blasting with 200 grid brown fused alumina. Then the specimens were ultrasonically washed with acetone. A commercial pure aluminum wire with a diameter of 2 mm was used to prepared Al coating. The Al coating were carried out on an arc spraying system. The NiCrAlY layer was prepared by plasma spraying with a commercially available NiCrAlY powder. The chemical composition of the powder is Ni–31.1Cr–9.84Al–0.67Y (wt.%). The spraying parameters of arc spraying and plasma spraying were listed in Tables 2 and 3, respectively. The thickness of Al coating is 250 μm while that of NiCrAlY coatings is 200 μm. Some of the specimens only coated with Al were used as counterparts.

2.2. Oxidation test

Cyclic oxidation tests of the Al coating with and without NiCrAlY diffusion barrier were conduct to evaluate cyclic oxidation resistance and oxide scale adhesion. The tests were performed in a muffle furnace with an accuracy of ±1 °C in static air. The specimens were put into corundum crucibles in the furnace at 800 °C for 50min and followed by 20min cooling to room temperature. The specimens were weighed by an electronic balance with a precision of 0.1 mg after regular intervals. The mass gain only includes the crucible and specimen, not including the spalled oxide. The mass change per unit area of the specimen was calculated by the equation as follow:

$$\Delta w = (m_i - m_0)/S$$

Where Δw is the mass change per unit area, m_0 is the original weight of specimen and alumina boat, m_i is the weight of the specimen and alumina boat after oxidation for regular intervals. A specimen was removed for subsequent analysis after exposure 10 h and 100 h.

The microstructures and chemical compositions of the coatings were observed using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). The phases of the coatings and oxide scales were identified by X-ray diffraction (XRD) analysis with Cu K_α radiation.

Table 1
Compositions of pure Ti substrate (wt.%).

Ti	O	C	N
Balance	0.35	0.10	0.05

3. Results and discussion

3.1. Oxidation kinetics

The kinetics curves of single Al and duplex Al/NiCrAlY coatings during cyclic oxidation at 800 °C for 100 h are shown in Fig. 1. The mass gain included only the scales which remained adherent to the coating. It can be seen that there is an obvious difference in cyclic oxidation behavior between single Al coating and duplex Al/NiCrAlY coating. The single Al coating exhibits a poor oxidation resistance because of a serious mass loss after 100 cycles. During the first 20 cycles, both coatings have a high oxidation rate. This is because that the oxide scales are not completed at this time. As the oxidation proceeded, the single Al coating has a severe mass loss after only 30 cycles. The mass loss of the single Al coating after 100 cycles is 1.39 mg/cm^2. This indicates an alternate spalling and formation of the oxide scale occurred during the thermal cyclic tests. On the contrary, the duplex Al/NiCrAlY coating displays continuous mass gain until 100 cycles. And its mass change keeps stable from 40 to 100 cycles. After 100 cycles, the mass gain of the duplex Al/NiCrAlY coating is 1.51 mg/cm^2 which suggests the oxide scale on the surface is still in good bonding with the coating. It is certain that NiCrAlY diffusion barrier is helpful to improve the cyclic oxidation resistance.

3.2. Oxidation behavior of the coatings

3.2.1. Initial oxidation stage of the coatings

Fig. 2 shows XRD patterns of the oxide scales on the surface of the single Al and duplex Al/NiCrAlY coatings after 10 cycles. After 10 cycles, the specimens were initially oxidized. Al_2O_3 peaks were detected on both coatings, but intensity of the peaks in duplex Al/NiCrAlY coating is higher than that in single Al coating. This indicates the growth rate of Al_2O_3 in duplex Al/NiCrAlY coating system is faster than that in single Al coating. The rapid growth of Al_2O_3 in initial stage is conducive to form a complete protective oxide film. Different from the isothermal oxidation behavior, TiO_2 was detected on the surfaces of both single Al and duplex Al/NiCrAlY coatings. However, our previous research has found TiO_2 was not detected on duplex Al/NiCrAlY coating until oxidation for 100 h. It is known that cyclic oxidation will result in large internal stress in the coating due to its alternating hot and cold. When the internal stress is larger than the critical fracture stress of the oxide scale, the oxide scale will spall locally. Once the oxide scale spalls, Al atoms will diffuse outward to generate a new protective film. At the meanwhile, Ti atoms also diffuse outward due to the concentration