Effect of Multi-arc Ion Plating Chromium Coating on Oxidation Resistance of TiAl Intermetallics

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Abstract. The chromium coating was deposited on the γ-TiAl alloy by multi-arc ion plating (MAIP). The morphology, microstructure and phase composition of coating were investigated by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Oxidation tests indicated that the chromium coating at high temperature can form a protective film on γ-TiAl alloys at 650-950 ℃. Oxide film is mainly divided into two layers. The outer layer of oxide film at 650 ℃ is mainly Cr2O3, at 750 ℃ is mainly TiO2 and at 950 ℃ is mainly Al2O3. The inner oxide film is Ti-Al-Cr mixed oxide film. The Ti-Al-Cr diffusion layer can effectively prevent the diffusion of oxygen into the substrate, significantly improve the γ-TiAl high temperature oxidation resistance ability.

Keywords: γ -TiAl alloys, MAIP, The chromium coating, High temperature oxidation.

1. Introduction

γ-TiAl alloys are regarded as a potential candidate for lightweight structural materials due to the good combination of their properties including high melting point, low density, high elastic modulus, low diffusion coefficient and good structural stability [1-3]. These alloys are of great significance for the development of aerospace, automotive and industrial steam turbine. However, the poor oxidation resistance restricts their application regions [4, 5]. Some researches show that fabricating oxidation resistance coatings could solve this problem [6-8]. Even though γ-TiAl alloys own high amount of aluminium element, the dense and continuous Al_2O_3 film is not observed in their surface, which can be explained that the Gibbs free energy values of TiO_2 and Al_2O_3 were very close. Aluminium priority selective oxidation phenomenon was not occurred in γ-TiAl alloys [9]. The rutile TiO_2 is loose structure, and play protective effect between 750 ℃ and 800 ℃ [10]. In addition, the loose TiO_2 is easily become an oxygen/nitrogen channel at high temperature, which could cause the deterioration of mechanical properties, particularly in fatigue property. According to some researches, it is considered two ways to enhance their oxidation resistance, one is the integral alloying method by adding a few alloying elements like niobium and tungsten, the other is surface treatments including ion implanting Si, Nb [11, 12], Low oxygen pressure processing processing [13], alloying coatins, laser surface alloying [14].

Some researches show that Cr mainly plays two effects on oxidation resistance property of γ-TiAl alloys. On the one hand, Cr promotes the formation of the protective Al_2O_3 film because Cr reduced the critical aluminium amount needed to form Al_2O_3 film. On the other hand, Cr accelerates oxidation speed due to the doping effect. Cr increases the concentration of oxygen vacancy, thus accelerating the growth of TiO_2 [15]. Cr alloying layer formed in the surface of γ-TiAl alloys could avoid the doping effect caused by integral alloying method, and enhance their oxidation resistance. However, the traditional surface treatments have some shortcomings including the limited improvement of anti-oxidation temperature and peeling off coatings [16]. In this paper, multi-arc ion plating technology was applied to improve γ-TiAl alloys oxidation resistance by forming Cr alloying layer. We mainly research the oxidation resistance property of the Cr alloying layer under different temperature, and exploit the effect of element Cr on the oxidation mechanism. Meanwhile the mutual diffusion mechanism of Ti-Al-Cr under high temperature is also investigated.

2. Experimental procedures

2.1 Materials and methods

The high purity chromium was used as the target material for supplying the alloying elements. Each substrate sample was prepared by cutting cast γ-TiAl (Ti-46.5Al-2.5-V-1V) into coupons of 14mm×14mm×4mm, which provided by Beijing Institute of Iron and Steel. The test was carried out in MIP-8-800 coating machine. Polished the substrates' surfaces to mirror finish with a series of SiC polishing paper. Each of them was grinded out four chamfers. Washed them with ultrasonic cleaner in an acetone bath for 10 min, and then they were placed in chamber.

Imported Ar_2 to the chamber when the air pressure in the furnace reached 1.0×10^{-2}Pa. The surface of the substrates was bombarded by ion with pulse negative bias voltage, to eliminate the impurities on the surface and improve the bonding strength between coating and matrix. The process parameters of coating as followed: Ar_2 air pressure was 0.2-0.4Pa, arc current was 70A, negative bias voltage was -100V, distance between the electrodes was 30cm, heating temperature of multi-arc ion coating was about 200 ℃, deposition time was 100min. The samples rotated with the rotating stand in the process of deposition, to equalize the thickness of the coating.

2.2 Oxidation Test

After the calculating the surface area and the weight of the sample, it should be placed in an alumina crucible which was heated till constant weight in advance. The oxidation test was operated at a test temperature of 650-950 ℃ with static air. The oxidation time of the sample is 100h, every once in a while removed it from the muffle furnace, cooled to room temperature and then weighted the sample and crucible with a sense of the amount of 0.lmg of FAloo4 type electronic balance, next the sample should be reinserted into the resistance furnace to oxidation. So again, get the oxidation kinetics of the sample. X-ray diffraction (XRD), scanning electron microscopy (SEM/EDX) and other analytical tools on the microstructure and composition of the samples were observed and analyzed.

3. Results and discussion

3.1 Microstructure Morphology and Characterization

The surface and cross-section morphologies of the multi-arcion plating Cr samples were visibly observed by SEM micrograph, typical results are shown in Fig. 1. It is shows that no microcracks or pores detected on the surface of the coating, which implies a dense surface structure obtained after arc plasma deposition. Fig.1 (b) shows that the cross-section of the sample is consisted of the γ-TiAl substrate and the Cr deposition layer (the white area) with about 2μm in thickness.

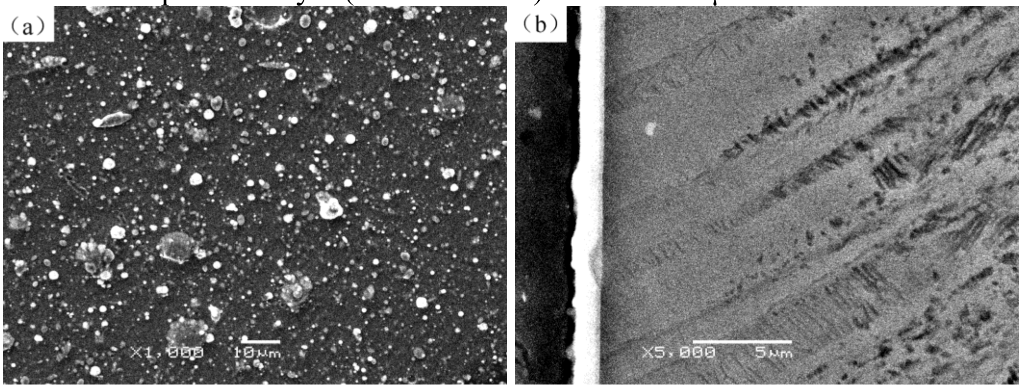

Fig.1 SEM micrographs showing morphology of multi-arc ion plating (MAIP) chromium layer(a)surface, (b)cross section

The alloying elements concentration of the coating is shown in Table 1. It can be seen that the content of Cr in the coating is in agreement with the target (94.82wt% of the coating), which implies that the coating formation is in process of deposition of the evaporation Cr atoms. The Ti element is detected (about 5.18 wt %) in the coating due to the weak binding between Cr deposition layer and the matrix. Thus, before the coating preparation, the γ-TiAl substrate was firstly treated by plasma plating Ti with pure Ti target. And then, the Cr coating can combine with the substrate strongly because of the existence of the Ti transition layer.

Table 1 EDS analysis of Chromium layer

Element	Wt%	At%
Ti	05.18	05.60
Cr	94.82	94.40

3.2 The analysis of oxidation kinetics

Fig.2 (a)-(c) shows the dynamics curves of constant temperature at 650 ℃, 850 ℃, 950 ℃, respectively. The dynamics curves of the treated samples are all presented aparabolic oxidation at different temperature and the oxide layers does not peel off from the samples. However, the substrate displays an opposite results at 850℃. The oxidation of the substrate peel off the layer and the dynamic curve shows a liner type which implies the γ-TiAl oxidation is not stable when tested at 850 ℃.

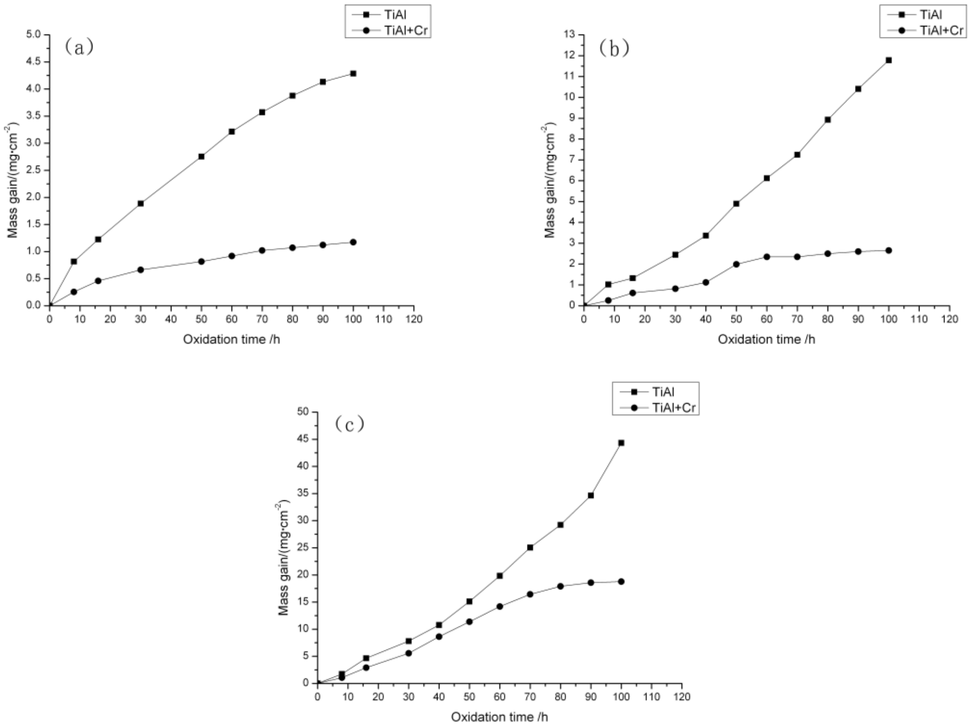

Fig2 Oxidation kinetics of specimens at different temperatures(a) 650 ℃, (b)850 ℃, (c)950 ℃

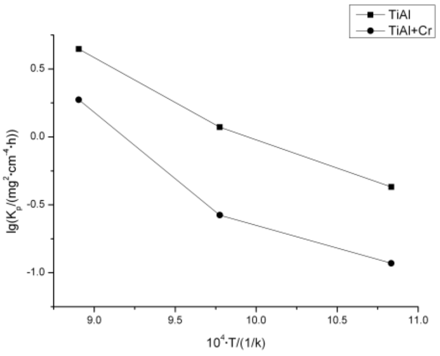

Fig.3 Temperature dependence of the parabolic rate constants for different specimens

Fig. 3 shows temperature dependence of the parabolic rate constants for different specimens. Parabolic oxidation rate of the oxidation can be described by the equation $\Delta W = Kpt^{1/2}$ (where w is the weight gain by oxidation per unit area, t is the oxidation time, kp is the oxidation rate constant)

[17]. From the Fig.3, it can be inferred that oxidation rate of the sample planted Cr was lower than that of γ-TiAl matrix. And during the oxidation, oxidation rate constant of the plating Cr has exponent relation to the temperature, indicating consistency of the oxidation mechanisms.

3.3 Morphology of oxide scale

X-ray diffraction pattern indicates the presence of TiO_2, Al_2O_3 and Cr_2O_3 on the surface of sample oxidized at different temperature for 100h. Fig.4 shows the chemical composition of chrome plated sample after isothermal oxidation at 850 ℃ for 100h measured by XRD.

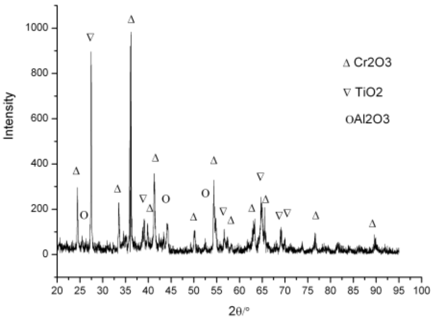

Fig.4 XRD pattern of multi-arc ion plating (MAIP) chromium layer oxidized at 650 ℃ for 100h

Fig.5 shows the microstructure and morphology of chroming oxidation film oxidation at 650 ℃ for 100h. There was little variation in surface morphology of the clad layer. And it consisted of agglomerative granule, which was compactly heaped up. The oxidation film kept perfectly and faultless, exfoliation of oxidation film didn’t happen. The cross-sectional microstructure indicates outer layer of oxidation film was Cr_2O_3, and the inner layer was a mixed film of TiO_2,Al_2O_3 and Cr_2O_3 [18]. EDS analysis shows that the internal diffusion of Cr was significantly less than the external diffusion of Ti and Al. Researches show that nucleation of TiO_2, Al_2O_3 was prior to that of Cr_2O_3 in the same case, which restrained the diffusion of Cr. After oxidation for 100h at 650 ℃, diffusion between Ti-Al-Cr lead to the very inefficient oxidation increase of chrome plated samples, and effectively resisted the invasive diffusion of the oxygen.

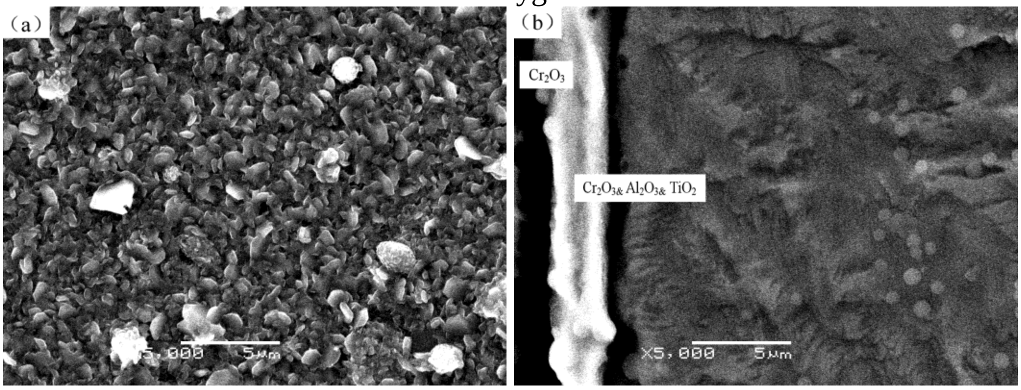

Fig.5 Surface and cross section morphology of multi-arc ion plating (MAIP) chromium layer oxidized at 650 ℃ for 100h (a) surface, (b) cross section

Fig. 6 shows the characteristic morphologies of plating Cr samples after 850 ℃ oxide for 100h. It can be seen that a dense oxide film covered the substrate which has a columnar structure. The outer layer is TiO_2 film due to the Cr_2O_3 decomposition into CrO_3 under the high temperature which is volatile easily [19]. Moreover, Ti atoms were diffusion outward to form a coarse columnar structure layer of TiO_2 on the surface of treated sample, such a carry diffusion was observed in Ag-Cu alloy oxidation test firstly [20]. The middle layer is consisted of TiO_2, Al_2O_3 and Cr_2O_3 which implies the Ti, Al and Cr elements taken a mutual diffusion induce the formation of mixed oxide film. Ti-Al-Cr mutual diffusion zone thickening and the organization more even after 850 ℃ oxidation for 100h.

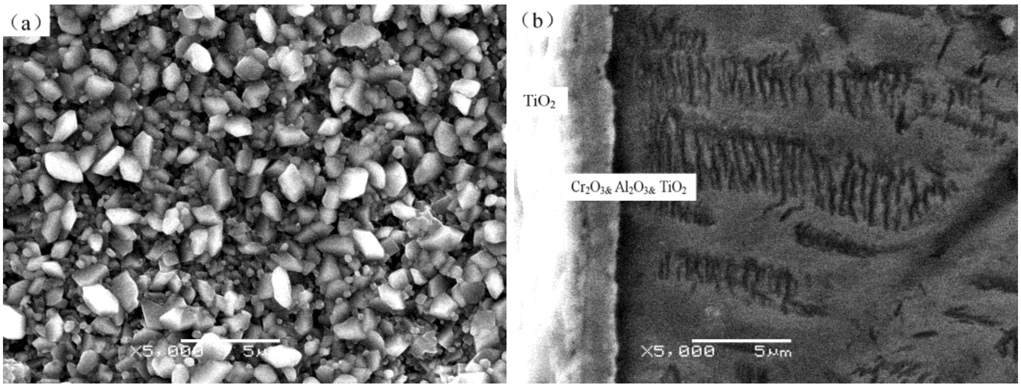

Fig.6 Surface and cross section morphology of multi-arc ion plating (MAIP) chromium layer oxidized at 850 ℃ for 100h (a) surface, (b) cross section

Fig.7 depicts the surface and cross section morphology of multi-arc ion plating (MAIP) chromium layer oxidized at 950 ℃ for 100h. The oxide film exhibits a flocculent structure, whose form was more complicated.

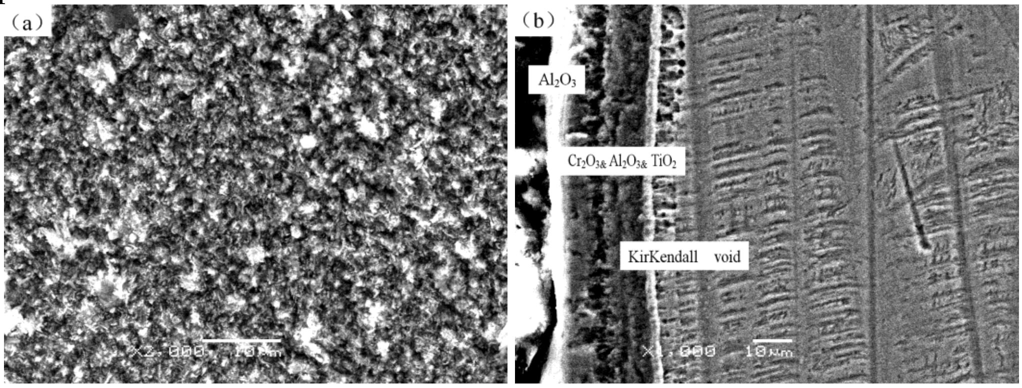

Fig.7 Surface and cross section morphology of multi-arc ion plating (MAIP) chromium layer oxidized at 950 ℃ for 100h (a) surface; (b) cross section

According to the result of the EDS, the outer oxide layer is composed of much of Al oxides and little of Cr, Ti oxide. This is mainly because the activity of Al was further increased at high temperature, and the activity of Ti didn't change much. Perkins hold the view that the formation Al_2O_3 protective membrane in Ti-Al-Cr alloys is due to the Cr, BCC beta Ti stable elements, which is help to maintain beta phase. In beta phase, the diffusion coefficient of Al was much larger [21]. What's more, the addition of Cr to reduce the solubility of interstitial such as O, N. And according to the formula of Wagner from dynamics Angle, the addition of Cr is be beneficial to the formation of promote Al_2O_3 protective film.

The inner oxide layers consist of TiO_2, Al_2O_3 and Cr_2O_3 hybrid membrane. When the Ti, Al spread out of the base, there appeared about 5 microns thick poor Ti, Al area and a large number of kirkendall void gap, as result of Ti, Al element spreading outward. With the influence of thermal stress, a gap between the oxide film and the substrate generated. After 100h, 950 ℃ oxidation is still limited to the oxide film, and prevents the further oxidation of substrates in 950 ℃.

4. Conclusions

1) After modified by multi arc ion plating Cr, the surface morphology of alloy layer on the γ-TiAl alloy was smooth, dense and crack-free. The alloy layer was closely connected with the matrix, and there were no defects such as voids and cracks between the layer and matrix.

2) With the formation of the protective oxide film on the Cr modified sample under high temperature, the mass gain of the γ-TiAl oxidation was effectively reduced, improving the antioxidant capacity of γ-TiAl.

3) During the process of oxidation, in addition of Cr internal diffusion, the Ti and Al elements spread outward the significantly in the matrix.

Acknowledgements

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