

Microarc Oxidation Coatings Fabricated on Ti₃Al-Based Alloy in Silicate Electrolyte

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Abstract: The ceramic coatings with thickness up to 120 μm were prepared on Ti₃Al-based alloy in silicate electrolyte by microarc oxidation method. The morphology, microstructure, composition and phase constituent of the coatings were investigated. Microhardness profiles along the cross-section of the coating were determined. The maximum microhardness in the coating was about 3 times higher than that of the substrate. The thickness of the coating increased with the increasing of MAO time. There were two layers in the ceramic coatings: a dense layer and a loose layer. The coating was mainly composed of (Ti_{0.6}Al_{0.2}Nb_{0.2})O₂ phase. Scratching test revealed a good adhesion between the Ti₃Al substrate and the coating.

Instruction

With the development of space technology, Ti₃Al alloy was gaining increased attention as a new material nowadays. In order to improve its properties, some surface modification techniques have been developed [1-3].

Microarc oxidation (MAO) was a novel technology to fabricate a ceramic coating on valve metals. The MAO coating exhibits good adhesion to the metal substrate due to the in-situ growth of coating. The coatings were easily controlled by technique parameters such as the composition of substrate, the electrolyte and the electrical parameters, etc. [4]. Moreover, the thickness of the coatings fabricated can reach up to the order of 100 μm [5], which can be widely used to improve the properties of the metal substrate. Many researches have been done on the aluminum and magnesium by MAO method [4-6]. However, no papers have been published on the MAO treatment of the Ti₃Al. In this work, microarc oxidation was tentatively applied to Ti₃Al alloy and the coating properties were analyzed.

Experimental details

A Ti₃Al-based alloy having the nominal composition (at%) of 23% Al, 17% Nb, 60% Ti was used as the raw material in the present study. The samples of 3 mm×12 mm×30 mm were used. Prior to coating deposition, the samples were ultrasonically cleaned in the acetone and thoroughly dried. The 30kW AC pulse power was used in the MAO process. The electrolyte consists of 6g/L sodium silicate. The positive voltage was kept at 520 V.

The MAO treatment time was 30, 60 and 120 min, respectively. A eddy-current thickness gauge was employed to obtain the thickness of ceramic coatings. The morphology, cross-section microstructure and composition profiles across the coatings were analyzed using a Hitachi S4800 scanning electron microscope (SEM) with energy dispersive X-ray spectrum (EDX). X-Ray diffraction (XRD) was performed using an X' PERT PRO MPD X-ray diffractometer to identify the phase constituent in the coatings. A Vickers microhardness tester (HV-1000) was employed to obtain

the microhardness profiles of the coatings under 0.245 N load. The interfacial adhesion was measured by WS-97 coating scratcher, with a maximum load of 100 N and a loading rate of 100 N/min.

Results and discussion

Microstructure of the MAO coatings on Ti₃Al alloy

Cross-sectional microstructure of the MAO coatings and the composition profiles of Al, Ti, Si were shown in Fig. 1. The thicknesses of the coatings oxidized for 30 min and 60 min were about 50 μm and 120 μm, respectively, which was consistent with the results of eddy current measurement. It was obviously shown that the coatings comprise two layers: a dense inner layer and a loose outer layer. Comparing Fig 1(a) and 1(b), it was found that the thickness of the loose layer was almost same, while the thickness of the inner layer increased with oxidation time. There were some pores in the coatings close to the interface in the 30 min sample. However, for the 60 min coating, only a few pores could be observed in the near interface. The inner layer of the 60 min coating was more compact than that of the 30 min coating.

The distributions of Al, Ti and Si in the coatings oxidized for 30 min and 60 min were shown in Fig 1. In the different oxidation time, the composition profiles indicated a distinct multilayer structure in the coating. The element distribution curves were consistent with the microstructure of the coating. The element both Al and Ti decreased from the Ti₃Al substrate to the coating surface, while Si element distribution was reverse to Al element. In the outer layer, the content of Ti element was more than that of Al element, and Al element could hardly be detected on the coating surface. This might attribute to the different activity of Ti and Al elements in the coating and their different bonding energy with the oxygen. Si element distribution also shows the layered structure. There was higher Si content in the outer layer than that in the inner layer. With increasing oxidation time, Si content in the dense layer was reduced as shown in Fig 1(a) and 1(b). It was obviously shown that near the interface, the relative Si content in Fig 1(b) was higher than that in 1(a). The porosity of Fig.1 (b) was higher than that of Fig.1(a) on the scanning line. Therefore, Si entered the coatings mainly through the discharge channel, which was consistent with the deposition mechanism of the MAO.

Phase composition of the ceramic coatings

XRD results of samples for different oxidation time were shown in Fig. 2. When the MAO time was 30 min, the diffraction peaks of Ti₃Al substrate were still strongly (Fig.2(b)). For the 60 min MAO sample, the Ti₃Al peak was hardly detected both in the outer layer (Fig 2(c)) and the inner layer (Fig 2(d)).

The coatings under different oxidation time mainly consisted of a large amount of

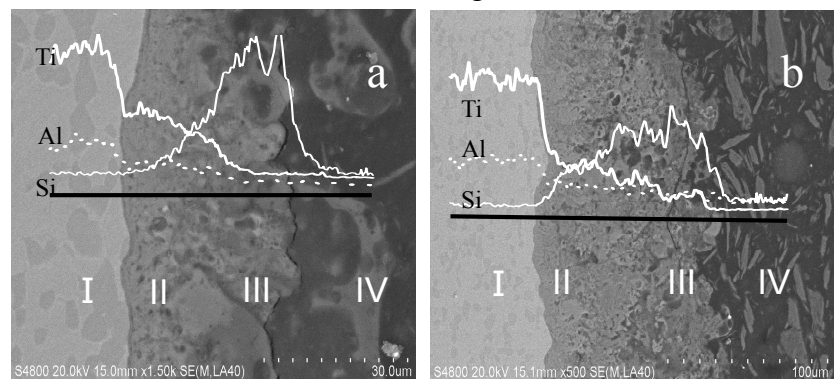


Fig. 1 Microstructure and composition distribution of microarc oxidation coatings on Ti₃Al alloy. I substrate, II inner layer, III outer layer, IV resin (a) 30min, (b) 60 min.

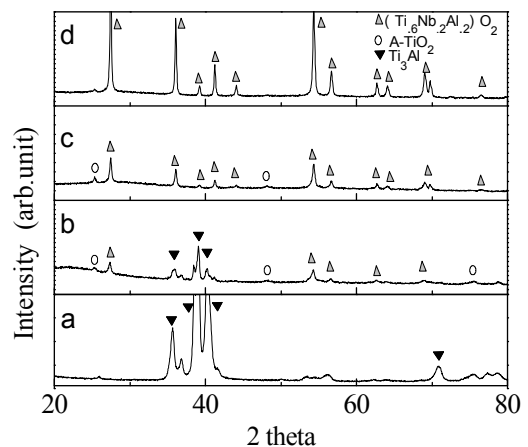


Fig. 2 XRD patterns of MAO coatings on Ti₃Al alloys at different time: (a) substrate, (b) 30min, (c) 60min, (d) dense layer of (c)

($\text{Ti}_6\text{Nb}_2\text{Al}_2\text{O}_2$) and a little anatase TiO_2 phases. EDX analysis in Fig. 1 identified Si content was high in the outer layer coating. However, the crystalline silica could not be observed in Fig. 2. It was estimated that there were lots of amorphous SiO_2 in the coating. In Fig. 2(b) and 2(c), a wide amorphous peak could be observed. But it could not be observed in the inner layer (Fig. 2(d)). Si element in the coating coming from the solution was combined with O element, and diffused into the coating through both the plasma discharge channel and thermal diffusion under high temperature. When melting oxide contacted with electrolyte, the temperature of melt was sharply reduced, then anatase TiO_2 was formed. From Fig. 2(c) and 2(d), it was shown that the anatase TiO_2 was detected only in the outer layer of the coating.

Microhardness profiles of the ceramic coatings

Microhardness test was carried out on cross-section specimens. The hardness of the outer layer in the near surface could not be accurately measured due to its porous structure. Fig. 3 showed that the maximum hardness increases with the increasing of coating thickness. On the sample treated for 60 min, the maximum hardness was 750 HV, while that on the sample treated for 120 min was 950 HV. The maximum hardness was about 5 μm away from the coating/alloy interface, and the peak distance slightly increased with the increasing of treating time.

According to the microhardness profile, there were two layers in the coating, which was in good accordance with the two-layer structure as observed in Fig.1. The microhardness curve could be divided into three areas of I, II, III, which corresponded to the substrate, dense layer and loose layer, respectively.

The phase composition and porosity determine the hardness of the coating. Fig. 1 has displayed that the inner layer was denser than the outer layer. Furthermore, the dense layer consisted of $\text{Ti}_6\text{Nb}_2\text{Al}_2\text{O}_2$ with high hardness, and there was lots of amorphous SiO_2 in the loose layer. Those induce higher hardness in the inner layer.

The interfacial adhesion of the coatings

The ultrasonic signals in Fig.4 during the scratch test display the interfacial adhesive strength between the coating and substrate. From Fig.4 it could be seen that the minimum adhesive force in this test was over 40 N. This indicated a perfect adhesion between the coating and the substrate. It was shown that the bonding strength was decreased with the increase of MAO treating time (Fig. 4 (a) and (b)). The adhesive force was 84 N for the coating treated for 30 min and only 51 N for that treated for 60 min. When the outer layer of the coating was polished off, only the inner layer was left (Fig. 4(c), (d)). The adhesive force was reduced to a lower value, for example, 42 N for 30 min treatment coating and 44 N for 60 min treatment coating.

The surface of the scratch sample was observed by SEM. From Fig. 5 (a), it was shown that there was some powder on the scratch surface in the outer layer of the coating. Thickness of the coatings were 40 μm and 20 μm for the sample a and b, respectively. It was assumed that the loose layer of the coating acted as lubricant. When the diamond head was loading, the scratching force was released by the loose layer. Therefore, the crack formation and propagation in the coating was prevented. In the dense layer, there was no obvious cracks near scratch trace and the coating was not been peeled off from the substrate (see Fig. 5(b) and (c)). That indicated the excellent adhesion between the substrate and the coating.

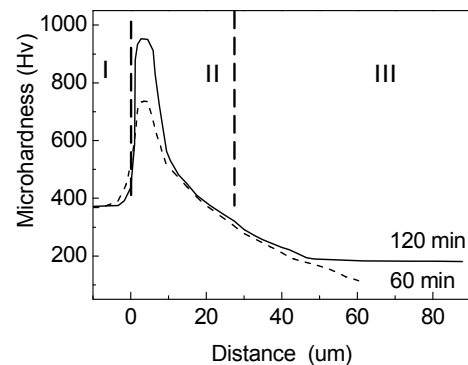


Fig. 3 Microhardness profiles of the MAO coatings formed in different oxidation time. I substrate; II dense layer; III looser layer

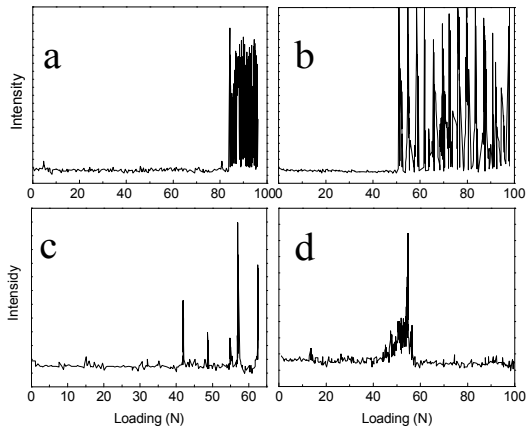


Fig.4 The curve of ultrasonic scratch signal for MAO coatings. (a) 30min; (b) 60 min; (c) dense layer of (a); (d) dense layer of (b)

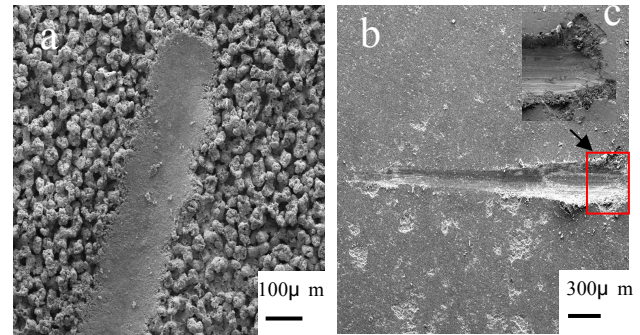


Fig.5 The morphology of the scratch. (a) unpolished surface (40µm); (b) polished surface (20µm); (c) selected section magnification area of (b)

Summary

The ceramic coating fabricated by MAO technique on Ti_3Al alloy was mainly composed of $(Ti_6Nb_2Al_2)O_2$. There were two different layers in the coatings, such as dense layer and loose layer.

The maximum microhardness of the coating was 3 times higher than the Ti_3Al substrate, which was up to 950 HV.

The adhesive force between coating and substrate reached up to 84 N and the minimum value was over 40 N in the coating. There was a good adhesion between the substrate and the coating.

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