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Al₂O₃ coating fabricated on titanium by cathodic microarc electrodeposition Qian Jin, Wenbin Xue*, Xijin Li, Qingzhen Zhu, Xiaoling Wu

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ABSTRACT

A Al₂O₃ coating was prepared on titanium substrate by cathodic microarc electrodeposition method in Al(NO₃)₃ ethanol solution. The coating thickness was about 80 µm when a 400 V cathodic potential was applied. The morphology and phase constituent of the Al₂O₃ coating were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). The isothermal oxidation at 700 °C and electrochemical corrosion behavior of the coated titanium were analyzed. The coating was composed of γ -Al₂O₃ and little α -Al₂O₃ phases. The oxidation resistance of the titanium subjected to cathodic microarc treatment was obviously improved. The polarization test indicated that the coated titanium has better corrosion resistance.

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1. Introduction

Ti and its alloys are widely applied in aeronautics, chemistry, shipbuilding, medical materials and other areas. However, the industrial applications of Ti are limited by its poor corrosion resistance in deoxidized acid, low wear resistance and poor oxidation resistance at elevated temperature [1,2]. In order to improve the properties of titanium, many surface treatment processes have been applied, such as anodizing [3,4], physical vapor deposition (PVD) [5,6], plasma and laser nitriding [7], thermal oxidation [8] and ion implantation [9,10].

Microarc oxidation (MAO) or plasma electrolytic oxidation (PEO) is a promoting method to prepare for ceramic coating on Ti and its alloys [1,11,12]. During MAO treatment, the Ti workpiece acts as anode. Many papers about microarc oxidation on Ti have been published [1,12–14]. The MAO coating can significantly improve the corrosion and wear resistance of Ti alloys [1,12], however, this coating is mainly composed of rutile and anatise TiO₂, or Al₂TiO₅ phase formed in NaAlO₂ solution [13]. The diffusion coefficient of oxygen in TiO₂ and Al₂TiO₅ phases are rather high and the MAO coating could not effectively impede the oxygen diffusion. Furthermore, a pure alumina coating without TiO₂ phase could not be fabricated by microarc oxidation. Therefore, microarc oxidation process is not an effective method to improve the oxidation resistance of Ti and its alloys.

Cathodic microarc electrodeposition is a new method to produce oxide coatings on metal substrates [15–17]. Up to now, the relevant

papers about this technique are less published. The two electrodes are placed in the electrolyte and the workpiece acts as cathode, which is different from anodic microarc oxidation. When the critical potential is reached, the vapor envelope over the cathode will be broken out and microarc discharge happens. Then the ions in the electrolyte will be deposited on the metal to form ceramic coatings.

In this study, we applied cathodic microarc electrodeposition to fabricate a pure Al_2O_3 coating on Ti substrate. The morphology, microstructure and phase constituent of the coating were analyzed. Thermal shock test was carried out to estimate the adhesion between the coating and Ti substrate. The oxidation resistance of the coating was evaluated. Furthermore, electrochemical corrosion behaviors of coating and Ti substrate were analyzed.

2. Experimental procedure

The substrate materials were TA2 pure titanium. All samples were cut into the size of 30 mm \times 15 mm \times 1 mm. The surfaces were ground to 800[#] emery paper, and then cleaned with distilled water.

A 30 kW pulse power supply with the frequency of 50 Hz was used. Ti samples and stainless steel bath acted as cathode and anode, respectively. The electrolyte was 0.4 mol/L Al(NO₃)₃·9H₂O ethanol solution. The temperature of the solution was controlled below 60 °C. After deposition, the coated sample was cleaned using distilled water, and then dried by hot air. The coating thickness was measured by an eddy-current thickness gauge. Table 1 displays the coating thickness can reach 80 μ m under 60 min electrodeposition.

A X' PERT PRO MPD X-ray diffractometer (XRD) was used to examine the phase components of the coating. The morphology and microstructure of the coating were observed using a Hitachi S4800 scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). Thermal shock test was performed for 100 cycles. In each cycle, the coated sample was heated to 700 °C and kept for 5 min, then quenched into water. The longest crack on the coating surface was measured using an optical microscope. Isothermal oxidation of the coated sample and Ti substrate was performed at 700 °C. The mass of the samples was measured by an analytical balance with an accuracy of 10^{-4} g. Thus their oxidation kinetic

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Table 1

Deposition parameters of the cathodic microarc coating

Applied potential (V)	400
Deposition time (min)	60
Concentration of Al(NO ₃) ₃ (mol/L)	0.4
Coating thickness (µm)	80

curves were obtained. Potentiodynamic polarizations in 3.5% NaCl solution were carried out using a CS300UA electrochemical workstation to evaluate corrosion behaviors before and after cathodic microarc electrodeposition on Ti substrate. A three-electrode cell, with the Ti sample as working electrode, saturated calomel electrode (SCE) as reference electrode and platinum coil as counter electrode, was employed in this test. The area of samples was 1 cm². After 5 min initial delay, scan was conducted at 1 mV s⁻¹ from -250 mV versus open circuit potential towards more noble direction.

3. Experimental results

3.1. Morphology and microstructure of the coating

The surface morphology of cathodic microarc coating on Ti is indicated in Fig. 1. The coarse and rough surface of coating is composed of granules. Melting particles and residual discharge pores appear on the coating surface. These pores correspond to the spark channels. This surface morphology in Fig. 1 is similar to that of microarc oxidation coating on Ti [1,12,14], however, the pore quantity of cathodic microarc coating seems to be less than that of microarc oxidation coating. Furthermore, comparing to the MAO coating [12,14], Fig. 1(b) displays that many deposition particles are observed on cathodic microarc coating surface. That implies



Fig. 1. Surface morphology of cathodic microarc coating on titanium, (b) is a magnified image (a).



Fig. 2. Cross-sectional microstructure of cathodic microarc coating on Ti.

that the cathodic microarc electrodeposition and microarc oxidation have different formation mechanism. The former depends on the electrolyte deposition, but the latter mainly comes from the Ti substrate oxidation.

The cross-sectional microstructure of coated sample is displayed in Fig. 2. The thickness of coating is about 80 µm. The coating consists of a porous outer layer and an inner layer. The inner layer about 15 µm close to the coating/Ti interface adheres well with Ti substrate. Table 2 provides EDS composition analysis results at different points of A. B. C as shown in Fig. 2. The A. B. C refer to the Ti substrate, inner layer coating and outer layer coating, respectively. A little amount of Al and O elements are detected in the Ti substrate close to the coating/Ti interface (see point A in Table 2). That means some elements from electrolyte under cathodic microarc discharge also diffuse into the Ti substrate near the interface. In fact, when the EDS testing point is only several microns away from the interface, Al and O will not be detected in the Ti substrate. On the other hand, the coating is mainly composed of Al and O elements, which corresponds to Al₂O₃ (see point B and C in Table 2). However, a little amount of Ti element was also detected in the coating of both inner layer and outer layer. It confirms that a little amount of Ti near the interface involves in the sintering process in cathodic microarc discharge zone and some titanium atoms diffuse into the whole coating. However, the Ti content in the cathodic microarc coating is much lower than that in anodic microarc oxidation coating.

3.2. XRD analysis

Fig. 3 depicts XRD pattern of cathodic microarc coating on titanium. The coating formed in Al(NO₃)₃ ethanol solution consists of α -Al₂O₃ and γ -Al₂O₃ phases. The Ti peaks in Fig. 3 is contributed from the Ti substrate. Comparing the relative intensity of feature peaks of α -Al₂O₃ (2θ = 43.3°) and γ -Al₂O₃ (2θ = 45.9°), it is found that the γ -Al₂O₃ content in the coating is much higher than α -Al₂O₃ content. EDS analyses in Table 2 have identified the existence of a little Ti element in the coating, but XRD pattern of coating in Fig. 3 has not detected titanium oxide. That results from the low Ti content in the coating.

Table 2		
		C . 1

EDS composition analyses of the coating at different positions in Fig. 2

Element (wt.%)	А	В	С
Al	1.26	48.71	42.00
0	0.96	43.97	53.41
Ті	97.78	7.32	4.59



Fig. 3. XRD pattern of cathodic microarc coating deposited on Ti in Al(NO $_3$) $_3$ ethanol solution.

3.3. Thermal shock test

In order to evaluate the thermal shock resistance of cathodic microarc coating, the coated Ti sample of 80 μ m thick was subjected to 100 times thermal cycles by quenching into water from 700 °C. After 100 times thermal cycles, no cracks on the coating surface were observed, meanwhile the coating was not delaminated from the Ti substrates. That proves that the coated titanium by cathodic microarc electrodeposition has better thermal shock resistance. Fig. 3 shows that the cathodic microarc coating deposited in Al(NO₃)₃·9H₂O ethanol solution mainly consists of γ -Al₂O₃, and the content of α -Al₂O₃ phase is less. The γ -Al₂O₃ phase has better ductile property than α -Al₂O₃ phase, which is favor of improving the adhesive strength of coating/Ti interface. On the other hand, the porous layer in the coating benefits to decrease thermal stress and depress the generation and propagation of the thermal cracks.

3.4. Isothermal oxidation test

Fig. 4 depicts the mass variation of the Ti substrate and coating sample with thermal oxidation time at 700 °C in air. It is indicated that the oxidation resistance of the coated sample is much better than that of the Ti substrate. Each curve in Fig. 4 consists of two stages. In the initial 10 h, the mass of Ti substrate increases quickly. After 10 h oxidation, the rate of its weight gain reduces, and the weight gain almost increases linearly. However, for the coated sample, its weight gain is obviously lower than the Ti substrate. After 5 h oxidation, the weight gain of coated sample is rather low. It



Fig. 4. Isothermal oxidation dynamics of Ti substrate and cathodic microarc coating sample at 700 °C in air.



Fig. 5. Polarization curves of the coating and Ti substrate.

is observed that at 100 h isothermal oxidation, the weight gain of Ti substrate is about five times higher than that of coated sample. Hence, cathodic microarc electrodeposition is a potential method to improve the high-temperature oxidation resistance of Ti and its alloys.

3.5. Corrosion resistant test

Potentiodynamic polarization curves of 80 μ m coating and Ti substrate are given in Fig. 5. The corrosion current density of coating with 6.83 \times 10⁻⁷ A cm⁻² is nearly one order of magnitude lower than that of Ti substrate with 4.7875 \times 10⁻⁶ A cm⁻². In addition, the corrosion potential of coated sample is about 300 mV higher than that of substrate. Hence, the cathodic microarc electrodeposition also improves the corrosion resistance of titanium.

Figs. 1 and 2 show that the cathodic microarc coating is porous. However, the coating close to coating/substrate interface has a thin compact layer, which hinders the Cl⁻ ions in the solution penetrate into the Ti substrate. So this thin compact layer plays an important role in improving the corrosion resistance of titanium.

4. Discussion

When the Ti sample as a cathode is immersed in electrolyte and a negative potential is applied, many bubbles appear on Ti cathode and gradually cover the whole sample. The main reaction at cathode is the hydrogen gas evolution, following with electrolysis of $Al(NO_3)_3$.9H₂O. In this stage, no sparks appear, and the covering hydrogen film provides a barrier layer for microarc discharge.

When the potential exceeds a threshold value, the hydrogen film around Ti cathode is broken down. Small and weak sparks appear on the local Ti surface. After several minutes, the whole surface is covered with wandering sparks. The temperature in microarc or spark discharge zone is high enough to cause some physical and chemical reactions. Hence $Al(OH)_3$ is deposited on the Ti substrate and then sintered into Al_2O_3 phase:

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_{3}\downarrow \tag{1}$$

$$2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \tag{2}$$

The OH^- ions may come from reduction reactions of O_2 , NO_3^- and H_2O [11,18]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
 (3)

$$2NO_2^- + 3H_2O + 4e^- \rightarrow N_2O + 6OH^-$$
(4)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (5)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

(6)

When a thin Al_2O_3 coating deposits on Ti substrate, it becomes the barrier layer. The cathode microarc discharge always happens at the relatively weak areas of Al_2O_3 film, thus sparks could move on the coating and form a uniform coating.

Different from anodic microarc oxidation, the coating fabricated by cathodic microarc electrodeposition is mainly composed of γ -Al₂O₃ (see Fig. 3). In our previous papers about formation mechanism of ceramic phases in anodic microarc oxidation coatings on 2024 Al alloys [19,20], we have proposed that both α -Al₂O₃ and γ -Al₂O₃ phases come from the rapid solidification of alumina melt in microarc discharge zone, and high cooling rate is favor of the formation of γ -Al₂O₃ phase. In fact, this explanation may also apply to the formation of cathodic microarc coating. As shown in Fig. 2, the cathodic microarc coating is porous, especially in the outer layer, thus the cooling rate of melt in cathodic microarc discharge zone is very high, even if in the interior of coating. Therefore, the cathodic microarc coating in this work mainly consists of γ -Al₂O₃ phase, which is consistent with the XRD result in Fig. 3.

Although Ti substrate involves in the formation process of cathodic microarc coatings, Ti content in the coating is rather low (see Table 2). Thus a relative pure and continuous alumina coating may be formed on the Ti substrate. That results in a good high temperature oxidation resistance for cathodic microarc coatings as shown in Fig. 4. The cathodic microarc electrodeposition process is a promising effective method to improve the oxidation resistance of Ti and its alloys.

5. Conclusions

- Continuous Al₂O₃ coating was prepared by cathodic microarc electrodeposition on Ti substrate in Al(NO₃)₃ ethanol solution.
- (2) The coating is about 80 μm and mainly composed of γ-Al₂O₃ and α-Al₂O₃. The α-Al₂O₃ content is less than 15%.
- (3) Thermal shock test implied that the coating adheres well to the substrate.

- (4) The oxidation rate of the coated Ti reduces about five times under 700 °C isothermal oxidation test.
- (5) By cathodic microarc treatment, the corrosion current density of Ti substrate reduces about one order of magnitude.

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