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Effects of cathode pulse at high frequency on structure and composition of Al_2TiO_5 ceramic coatings on Ti alloy by plasma electrolytic oxidation

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ABSTRACT

The aim of this work is to investigate the effects of cathode pulse under high working frequency on structure and composition of ceramic coatings on Ti–6Al–4V alloys by plasma electrolytic oxidation (PEO). Ceramic coatings were prepared on Ti alloy by pulsed bi-polar plasma electrolytic oxidation in $NaAlO_2$ solution. The phase composition, morphology and element distribution in the coating were investigated by X-ray diffractometry, scanning electron microscopy and energy distribution spectroscopy, respectively. The coating was mainly composed of a large amount of Al_2TiO_5. As the cathode pulse was increased, the amount and grain size of Al_2TiO_5 were first increased, and then decreased. γ-Al_2O_3 in the coating was gradually decreased to nothing with the increase in the cathode pulse whereas rutile TiO_2 began to form in the coating. As opposed to the single-polar anode pulse mode, the cathode pulse reduced the thickness of the coatings. However, as the cathode pulse intensity continued to increase, the coating then became thicker regardless of cathode current density or pulse width. In addition, the residual discharging channels were reduced and the density of the coating was increased with the appropriate increase of the cathode pulse.

1. Introduction

Plasma electrolytic oxidation (PEO) technique has been developed rapidly in recent years. The prepared coatings have fine properties such as corrosion resistance, anti-abrasion property or decorative property and the promising application prospect in many fields [1–4]. Recently, much research was focused on the composition, the structure and the mechanical properties of the prepared ceramic coatings to provide significant progress made to the preparation and application of PEO coatings [5–8]. However, relative little is understood about the coating-formation mechanisms in the PEO process.

During the PEO process, the three most important factors are the electrical source, electrolytes and type of metals. In all kinds of PEO power sources, electrical parameters (current density, duty ratio and pulse width and so on) play very important roles in the growth of the coating. In our previous study, we have investigated the effects of anode pulse electrical parameters on the growth characteristic of the ceramic coatings on Ti alloys in $NaAlO_2$ solution by pulsed single-polar PEO power source [9–11]. At present, the pulsed bi-polar PEO power source is being widely used due to its ability to achieve high quality coatings that have large thickness, high microhardness, and good adhesion to substrates [12–14]. Therefore, the objective of this work was to investigate the effects of cathode pulse under the high working frequency on the growth characteristics of the coatings on Ti–6Al–4V alloys in $NaAlO_2$ solution.

2. Experimental details

2.1. Preparation of plasma electrolytic oxidation ceramic coatings

Plate samples of Ti–6Al–4V alloy (wt.%: 89.3Ti, 6.26Al, 4.01V, 0.30Fe, 0.10C, and 0.03N) (supplied by Baoji Nonferrous metals manufactory, China) with a reaction dimension of 25 mm × 15 mm × 6 mm were used as working electrode and the electrolyser made of stainless steel served as the counter electrode. The electrolytes used in the experiments are Na_2AlO_2 solution with the concentration of 8 g L^{-1} and Na_3PO_4 with the concentration of 1 g L^{-1}. A home-made pulsed bi-polar PEO electrical source with power of 5 kW was used to prepare ceramic coatings. The electric parameters of the power source and PEO reaction time are shown in Table 1. The reaction temperature was controlled to be below 30 °C by adjusting the cooling water flow. After the PEO treatment, the coated samples were rinsed with water and dried in air.

2.2. Analysis of phase composition and structure of the coatings

Phase composition of the coatings was examined with a RICOH D/max-rB automatic X-ray diffractometer (XRD) using a Cu Kα source. The lattice parameters and cell volume of the crystal grain were calculated approximately by the jade 5.0 software. Surface and section morphology of the prepared coatings was studied by scanning electron microscopy (SEM; Hitachi S-570). The elemental composition and distribution were investigated by energy dispersive spectroscopy (EDS; US PN5502).

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Table 1
The electric parameters of the power source and PEO reaction time.

	Time (min)	Frequency (Hz)	Duty ratio (%)			Current density (A dm^{-2})	
			D_+	D_d	D_-	I_+	I_-
1	30	2000	20	–	–	20	–
2	30	2000	20	30	20	20	4
3	30	2000	20	30	20	20	10
4	30	2000	20	35	10	20	4
5	30	2000	20	20	40	20	4

D_+: the duty ratio of the anode pulse; D_d: the dead time between the anode and the cathode pulse; D_-: the duty ratio of the cathode pulse; I_+: the current density of the anode pulse; I_-: the current density of the cathode pulse.

The thickness of the coating was measured, using an eddy current-based thickness gauge (CTG-10, Time Company, China) with a minimum resolution of 1 μm. The average thickness of each coating was obtained from 10 measurements at different positions.

3. Results

3.1. Thickness of the coatings

Fig. 1 is the thickness of the coatings under different cathode pulses. It can be seen that the thickness of the coating was increased with the cathode pulse, whether considering cathode current density or cathode pulse width. When the cathode pulse was small, the thickness of the coatings under the bi-polar pulse mode was a little lower than that under the single-polar anode pulse mode.

3.2. Composition of the coatings

Figs. 2 and 3 are XRD patterns of coatings under different cathode current densities and cathode pulse widths, respectively. Obviously, the coating was composed of a large amount of Al_2TiO_5 (PDF Card #26-0040). Fig. 4 is the size of Al_2TiO_5 crystal grains of the ceramic coatings prepared under different cathode pulses. Increasing the cathode current density or the cathode pulse width, the amount and grain size of Al_2TiO_5 were first increased and then decreased. For the coating without the cathode pulse, there was also a little γ-Al_2O_3 in the coating; and γ-Al_2O_3 was decreased gradually and even disappeared with the increase of the cathode pulse. Quite oppositely, rutile TiO_2 began to emerge in the coating with the increase of the cathode pulse. Moreover, the diffraction peaks corresponding to Ti were also detected, whose intensities were reduced with the increase of the cathode pulse.

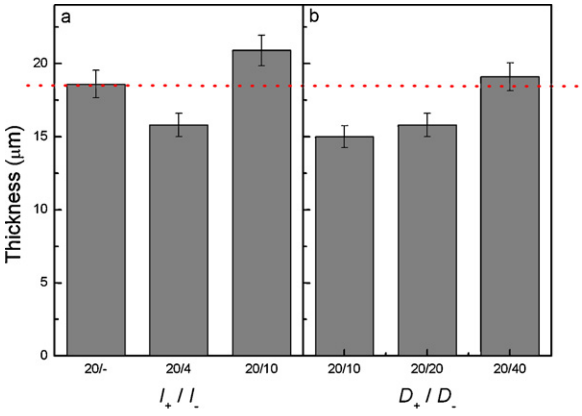

Fig. 1. The thickness of the coatings under different cathode pulse.

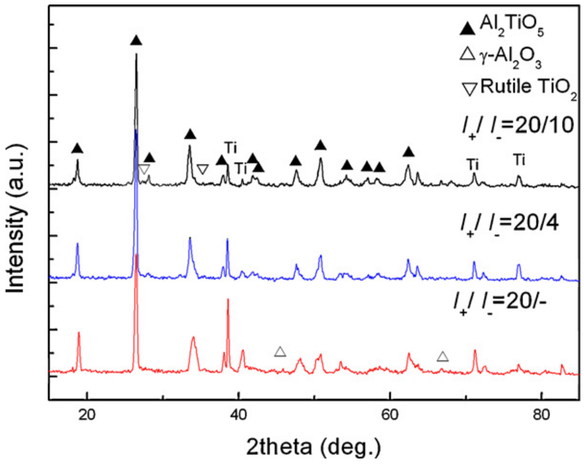

Fig. 2. XRD patterns of the coatings under different cathode current densities.

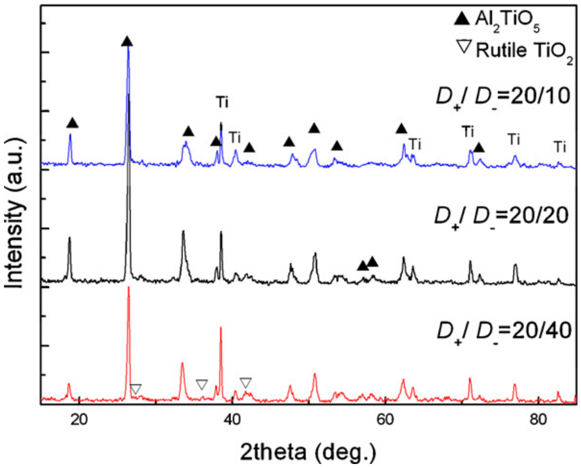

Fig. 3. XRD patterns of the coatings under different cathode pulse widths.

3.3. Surface SEM and the elemental analyses of the coatings

Fig. 5 is the surface SEM of the coatings under different cathode pulses. Panel (a) shows that there were many residual discharging

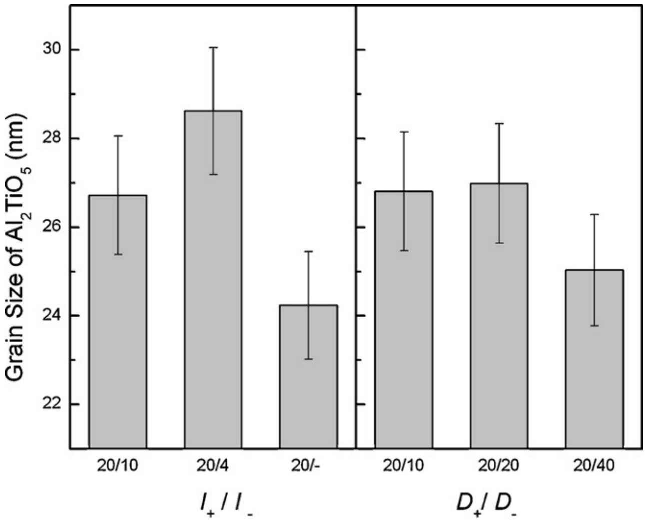

Fig. 4. The size of Al_2TiO_5 crystal grains of ceramic coatings prepared under different cathode pulses.