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The effects of anodic and cathodic processes on the characteristics of ceramic coatings formed on titanium alloy through the MAO coating technology

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Abstract

This paper reports on the investigation into the effects of the different anodic j_a and cathodic j_c current densities on the variations of the anodic and cathodic processes and the associated changes in the characteristics of the coatings synthesized on Ti–6Al–4V alloy substrate by microarc oxidation technique. The coated samples were subjected to coating thickness and cross-section fracture observation. Phase and elemental composition at different depth of the coatings were evaluated through X-ray diffraction and energy dispersive spectrum analyses. The experimental results indicate that the increase of j_a leads to the increasing slope of anodic voltage U_+ versus oxidation time plots, the larger coating thickness and the more coarse surface morphology of MAO coatings; while the aggrandizement of the cathodic process results in the lower growth rate and more uniform structure of coatings. The changes of the elements distribution from the interface towards the coating surface with variation of j_a and j_c are affected by the Ti anodic dissolution and the electromigration of electriferous particles, such as $Al(OH)_4^-$, in electrolytes.

Keywords: Microarc oxidation; Anodic to cathodic current ratio; Electromigration; Titanium alloy

1. Introduction

The microarc oxidation (MAO), also called plasma electrolytic oxidation, anodic spark deposition or microarc discharge oxidation, is playing an increasing important role in the field of metal surface modification due to the excellent wear, corrosion, electrical and thermal properties of the MAO coatings. Many studies have been devoted to the synthesis and a series of performance evaluation of ceramic oxide coatings on a large number of Al and Ti alloys through the MAO process [1–5].

Various types of power source can be used to bring about plasma electrolysis. In recent studies, to produce the serviceable MAO coatings, the amplitude modulated ac and pulsed bi-polar electrical

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sources are widely used [5–10]. In these circuits, the positive and negative biasing alternately act on the samples and this alternation directly determines the discharge formation and discharge interruption in the MAO treatment. During the whole MAO process, the coating growth comprises different partial processes combing the oxide coatings formation, the anodic dissolution and the gas evolution [11]. And thus under these circumstances the issue of the influence of the cyclic change in the mode polarity (maybe with a currentless pause) on these partial processes becomes very important. Existing data in the literature on the explanation of anodic and cathodic processes have been incomplete with regard to the growth of MAO coatings.

In present work different anodic and cathodic current densities were employed to study the effect of weakening or strengthening the anodic or cathodic MAO process on the characteristics of MAO coatings, making the first step in this direction, since MAO is an energy-intensive process typically depending on the current density.

2. Experimental

2.1. Coating deposition

Round disc samples of Ti–6Al–4V with the diameter of 16 mm and the height of 5 mm were used in the experimental work. Prior to coating deposition, the samples were polished with the abrasive papers to obtain the uniform surface and degreased in HF–HNO_3 (1:1). The power supply is a 5 kW homemade pulsed bi-polar electrical source capable of voltage outputs to 700 V for positive biasing and 300 V negative. An aqueous electrolyte was prepared from a solution of sodium aluminate and hypophosphate. The temperature of the electrolyte was maintained at less than 35 °C for processing times of up to 70 min by a water-cooled system.

Samples were formed with same concentration of the electrolyte and oxidation time ($t = 70$ min) but j_a/j_c of 120/60, 90/60, 60/60, 60/90 and 60/120 mA cm^{-2} respectively, namely, j_a/j_c ratio of 2, 3/2, 1, 2/3 and 2.

2.2. Coating characterization

The MAO treated samples were subjected to the thickness measurement using an eddy current coating thickness indicator. The coating was measured over 20 positions to provide an average thickness value. X-ray diffraction (XRD) analysis was performed with an D/max-rB automatic X-ray diffractometer to identify the phase composition present in the samples. The cross-section fracture morphology of the coatings was observed by scanning electron microscopy (SEM) at different magnifications. An energy dispersive spectrum (EDS) attachment was employed for Ti, Al and O elemental analysis at different depth parallel to the substrate surface in the cross-section of the same sample; the more exact point analysis was adopted and the layers with same thickness was examined for three regions to achieve the mean value.

3. Results

3.1. Voltage–time response

The dependency of voltage (U_+, U_-) on the MAO treatment time (τ) obtained at different anodic and cathodic current densities is shown in Fig. 1(a) and (b), where the curves under the conditions of $j_a/j_c \leq 1$ and ≥ 1 are described separately. In the case of $j_a/j_c \geq 1$, the curves of U_+–τ follow the typical tendency [11], since the typical regions are identifiable in the plots, as illustrated in Fig. 1(a). In the first region, to ~440 V, the anodic voltage increased linearly with time, with the maximum slope in the whole curve, and there is no distinct difference before and after the visible sparking voltage (~280 V). Region (II) exhibits an approximately ‘flat’ phase lasting 10–15 min, with a sharply reduced slope ~2 V min^{-1}, indicating the oxide process entered a slow and steady growth stage. And with increasing j_a/j_c ratio, the temporal duration of region (II) slightly shorten. In region (III), the rate of voltage increase rises again; the bigger the j_a/j_c ratio is, the more quickly the voltage increases. With regard to U_-–τ curve, the cathodic voltage rapidly reaches the certain value (30–50 V) for a very short time (usually less than 30 s) and then changes little. Naturally, the higher cathodic current density leads to the higher cathodic voltage.