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The plasma electrolytic oxidation micro-discharge channel model and its microstructure characteristic based on Ti tracer

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ABSTRACT

This study focuses on the individual discharge channel of ceramic coating prepared by plasma electrolytic oxidation (PEO), and attempts to reveal the mechanism of breakdown discharge at low voltage. Titanium (Ti) was employed as a substrate with the layer of aluminum deposited on it (aluminized Ti). The shape and microstructure of the discharge channels in PEO coatings were investigated using transmission electron microscope (TEM) and scanning electron microscopy (SEM). A schematic model of the individual discharge channel was proposed based on Ti tracer method. The shape of the discharge channel was mainly cylinder-shaped in the compact coating, with a groove-like oxidation region existed at the coating/substrate interface. In the groove-like oxidation region, the phase composition mainly composed of amorphous and mixed polycrystalline (aluminum titanate and mullite). β-Al_2O_3 was found in the ceramic coating. TEM morphology showed that nanometer sized micro channels existed in the ceramic coatings.

1. Introduction

Plasma electrolytic oxidation (PEO) is an efficient and environment-friendly surface technology, which is mainly applied on valve metals and alloys that are difficult to anodize with conventional anodizing processes [1–3]. The ceramic coatings fabricated by the PEO process have many excellent properties such as thickness, hardness and adherent [4]. The PEO process contains a number of discharge processes involving contributions from chemical, electrochemical, thermodynamical, and plasma-chemical reactions [5]. Researchers have studied in many aspects such as discharge model, shape of discharge channels, and temperature field of the individual discharge.

The experimental and numerical simulation methods have been widely employed in the study of discharge model. For instance, three individual famous models of the PEO process were proposed by Yerokhin [6], improving the discharge formation models based on analogy with the contact of glow discharge electrolysis. Hussein [7] introduced three types of discharge for the PEO process representing collective behaviors not individual discharge. Wang [8] simulated the temperature field distribution of a single discharge channel and discharge recession, based on the cylindrical micro discharge channel model and the thermal transfer formula of the point heat source. However, the cylindrical model did not match with experimental results.

Recently, many scientists have focused in investigating the shape of discharge channel. Xue [9] and Sah [10] have showed schematic diagram of microarc discharge and breakdown sites, respectively. Liu [11] employed Ti element as the tracer to study the discharge channel, and directly observed the discharge channel. However, the microstructure and mechanism of the individual discharge channel is still unclear.

In this paper, the shape and microstructure of the discharge channel in PEO coatings were characterized by TEM based on Ti tracer. And the phase composition of the ceramic coatings existed at the coating/substrate interface was investigated. The experimental results provide a support for further analyzing the discharge model of PEO process.

2. Experimental

Rectangular coupon (50 × 25 × 5 mm) of titanium was employed as the substrate coated aluminum (aluminized Ti) with the thickness of 60 μm, which was prepared by vacuum cathode arc technology. The PEO process temperature was controlled below 35 °C by adjusting the cooling water flow rate. The aqueous electrolyte was mainly consisted of Na_2SiO_3. The PEO process was carried out for 120 min at the current density of 0.4 mA/mm^2. The longer processing time was required to deplete the Al layer so that

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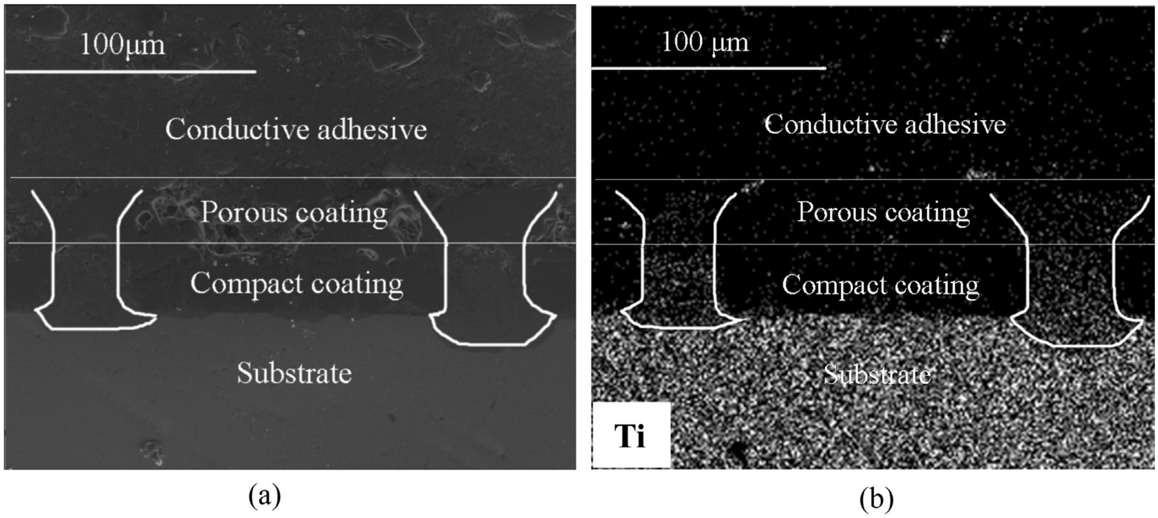

Fig. 1. Cross-section morphology of PEO coating formed on Ti-Al substrate at the initial stage of Ti spray (a) the SEM image; (b) Ti element distribution from whole region.

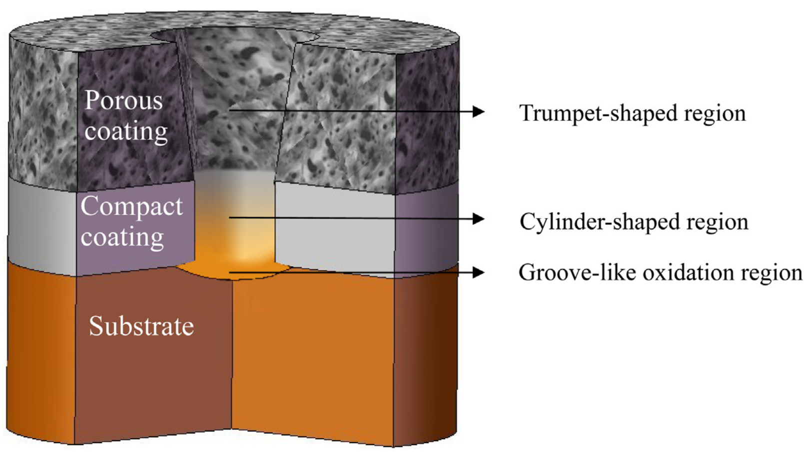

Fig. 2. Schematic model of the individual discharge channel in the PEO process for aluminized Ti sample.

the metal substrate was composed mainly of Ti, and the resulting Ti tracer discharge channel was clearer.

The cross-section morphology and element composition of PEO coatings were examined by a FEI Sirion400NC field-emission scanning electron microscopy (SEM) with energy dispersive X-ray system (EDX). A JEOL JEM-2100 transmission electron microscope (TEM) was applied to analyze the coating microstructure and the coating/substrate interface, operating at 200 kV. Cross-section TEM sample was prepared by using Gatan 691 with focused ion beam (FIB) operating at 5 kV.

3. Results and discussion

3.1. Model of discharge channel

In order to obtain the microstructure of the individual discharge channel, the initial stage that titanium began to participate in the PEO process was chosen, while aluminum layer was consumed completely. Fig. 1 shows the cross section element distribution of Ti in PEO coatings. Fig. 1(a) is the SEM image of a coated aluminized Ti sample surface. By tracing Ti element existed in the ceramic coatings, the shape of discharge channels was proposed as follows: the coatings were broken down partly in most of discharge locations (Fig. 1(b)), while there also existed some discharge places in which the coatings were broken down thoroughly [11]. After a transient discharge process, a groove-like oxidation region formed at the coating/substrate interface with the enrichment area of Ti elements. The discharge channel appeared the cylinder shape in the compact coating. On the other hand, the plasma state of matter ejected through the pores in the porous coating presented a trumpet-shaped channel.

Based on the distribution of Ti tracer elements in Fig. 1, the schematic model of the discharge channel for the PEO process is shown in Fig. 2. The discharge channel consists of three parts: groove-like oxidation region, cylinder region, and trumpet-shaped channel. A groove-like oxidation region of the discharge channel formed at the coating/substrate interface; a cylinder region generated in the compact coating; and a trumpet-shaped channel existed in the porous coating.

Plasma state of matter mainly including substrate, electrolyte and the ceramic coating, ejected from the coating/substrate interface under the high temperature and the strong electric field. In this condition, the compact coating discharged thoroughly, and the plasma state of matter spread through the pores in the porous coating cooled by electrolyte.

3.2. Microstructure of discharge channel

According to the enrichment distribution of Ti elements, the cross-section TEM morphology of the groove-like oxidation region

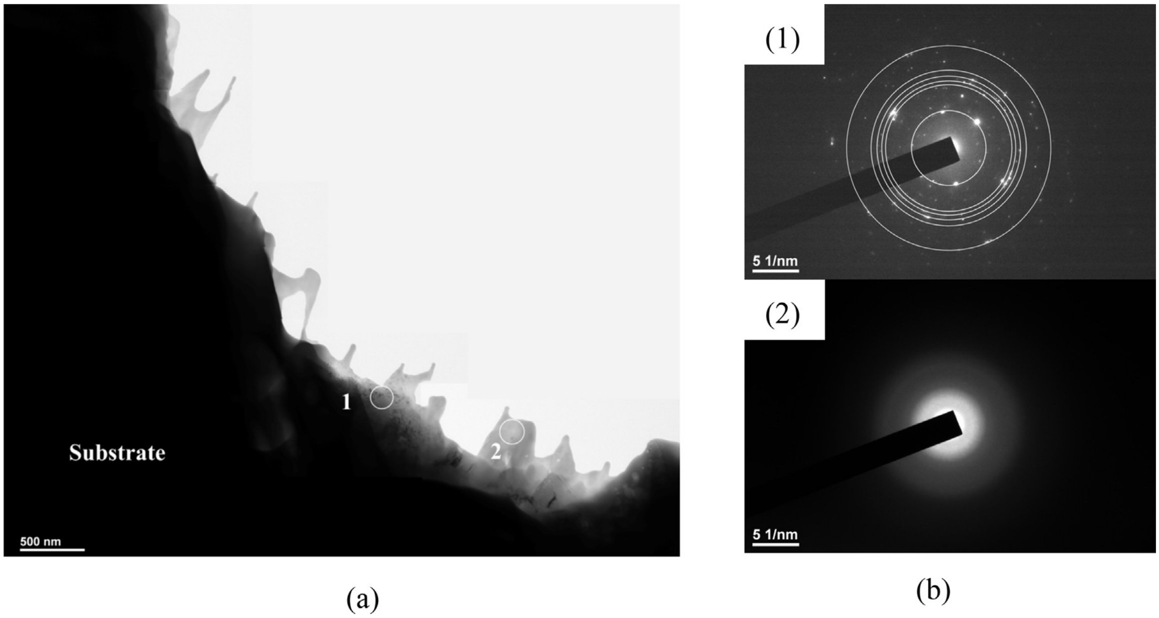

Fig. 3. (a) Cross-section TEM morphology of a discharge channel in the groove-like oxidation region using Ti tracer; (b) electron diffraction patterns of areas designated in (a).

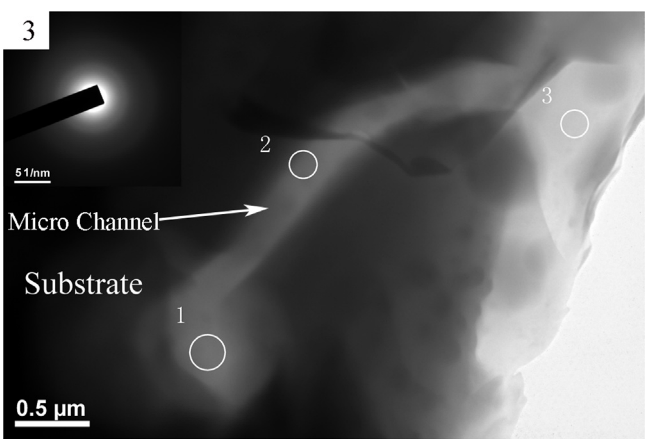

Fig. 4. Cross-section TEM image of a micro channel in the groove-like oxidation region.

is shown in Fig. 3 (a). Fig. 3 (b) shows the selected area electron diffraction (SAED) pattern at the positions 1 and 2. At the position 1, Al_2TiO_5 and Al_2SiO_5 existed according to diffraction rings from the SAED pattern and EDS. At position 2, electron diffraction patterns comprised diffuse rings indicating an amorphous structure. The phase compositions in the groove-like oxidation region were complicated, mainly composing of amorphous phase and mixed polycrystalline phase (aluminum titanate and mullite).

Mullite was found in the groove-like oxidation region. As we know, the conditions for synthesizing mullite are as follows: (1) the discharge channels surrounded by Al and alumina, (2) large volumes of SiO_2 existed in the ceramic coating, and (3) the temperature of the discharge micro areas reached as high as 2000 °C. Based on above conditions, SiO_2 would react with alumina to form mullite, and many large size grains formed polycrystalline phase at the high temperature.

Fig. 4 shows the TEM microstructure of a micro channel in the groove-like oxidation region. The amorphous phase was formed at position 3. The pores existed in the ceramic coating at the macro level, while the nanometer sized channels existed at a micro level. The micro channels were considered to be the microstructures located at the interface after the solidification of plasma matter.

Table 1
Various element distribution in the micro channel.

Substrate			Electrolyte		
Position	Ti (at%)	Al (at%)	Si (at%)	O (at%)	Na (at%)
1	5.87	4.18	11.38	58.93	9.96
2	3.72	6.36	10.63	61.12	12.88
3	3.34	24.76	6.65	56.16	6.75

Table 1 shows the substrate and electrolyte element distribution in the micro channel. There were titanium oxide in the groove-like oxidation region and the electrolyte (Na_2SiO_3) in channel, respectively.

The mechanism of PEO discharge is not ceramic coating breakdown but distinct barrier layer breakdown. During the discharge process, the electrolyte flowed into the channel even to the coating/substrate interface under the high temperature and the strong electric field, resulting in the conductivity of the barrier layer improving significantly. It could reduce the breakdown voltage to some extent. Therefore, the electrolyte flowing into the micro channels provides basic conditions for PEO discharge.

3.3. *Structure of ceramic coating*

TEM results for the compact layer of the ceramic coatings are shown in Fig. 5. Equiaxed nanocrystalline existed in the ceramic layer was β-Al_2O_3 and α-Al_2O_3 identified by electron diffraction.

Al_2O_3 has three main existence forms, namely, α-Al_2O_3, β-Al_2O_3 and γ-Al_2O_3. α-Al_2O_3 is the steady phase. The coatings on Al alloys after PEO process mainly consist of α-Al_2O_3 and γ-Al_2O_3, which are the dominant phases in the coatings [12,13]. However, a small amount of β-Al_2O_3 was found in the ceramic layer prepared by the sodium silicate system solution [14]. In this study, we also found β-Al_2O_3 as the transitional phase of Al_2O_3 existed in the ceramic coatings. This is mainly due to the presence of alkali metal sodium

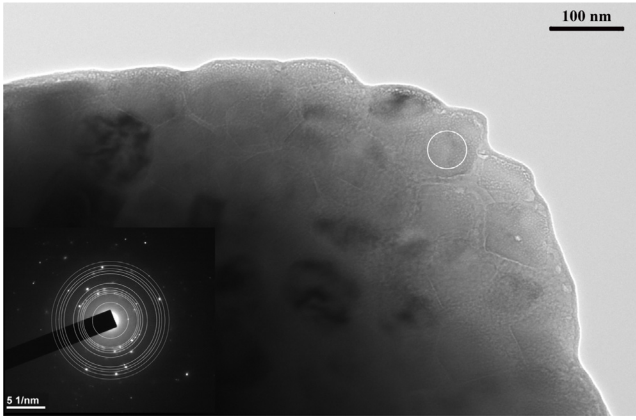

Fig. 5. Cross-section TEM image of compact layer in the ceramic coating.

ions in the electrolyte. In the high temperature environment, a large number of free sodium ions can promote the formation of layered structure β-Al_2O_3 with certain electrical conductivity. For the rapid cooling of the liquidoid, multiphase coexistence phenomenon existed in the ceramic layer which was not only α-Al_2O_3/γ-Al_2O_3 but β-Al_2O_3. It suggested that the PEO as a typical non-equilibrium reaction is a complex process.

4. Conclusions

(1) A schematic model of the individual discharge channel has been proposed: groove-like oxidation region at the coating/substrate interface, cylinder-shaped discharge channel in the compact coating, and trumpet-shaped in the porous coating.

(2) In the groove-like oxidation region, the phase composition mainly composed of amorphous phase and mixed polycrystalline phase simultaneously (aluminum titanate and mullite). And β-Al_2O_3 was found in the ceramic coating.

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