



Investigation of the discharge mechanism of plasma electrolytic oxidation using Ti tracer

Xiaojing Liu ^{a,b}, Guang Li ^{a,*}, Yuan Xia ^{a,**}

^a Institute of Mechanics, Chinese Academy of Sciences, Beijing, 100190, China

^b Graduate University of Chinese Academy of Sciences, Beijing, 100049, China

ARTICLE INFO

Article history:

Received 21 July 2011

Accepted in revised form 1 May 2012

Available online 9 May 2012

Keywords:

Plasma electrolytic oxidation

Ti tracer

Discharge mechanism

Coatings' growth

ABSTRACT

The study focused on the discharge mechanism of plasma electrolytic oxidation (PEO). Titanium with a layer of aluminum deposited on it (Ti-Al) was used as the substrate. When PEO process for Ti-Al substrate developed for a period of time, by analyzing the distribution of Ti element in oxide coatings, the existence of oxide film dielectric breakdown in discharge process was testified and the general shapes of discharge channels were also obtained. From the study on discharge channels' shapes we found that: in most of discharge locations, the coatings were broken down partly, while there also existed some discharge places in which the coatings were broken down thoroughly. Moreover, it was found that the oxide films grew toward the outer as well as the interior of PEO coatings, through analyzing the distributions of Si and Ti elements in discharge channels.

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1. Introduction

Plasma electrolytic oxidation (PEO) is a kind of new surfaces modification technology to grow ceramic oxide coatings on valve metals such as Al, Mg and Ti alloys [1]. PEO coatings have many excellent properties such as high hardness, anti-corrosion, wear resistance and good thermal stability [2–4], showing considerable potential for a number of industrial applications.

PEO coatings are formed by ways of thermal and plasma chemical reactions primarily at the discharge zone [5]. So besides the studies on process technology, coatings' microstructure and properties, discharge mechanism of PEO is gaining more and more attention [6–8].

The discharge process is a transient and complicated event. So it is difficult to gain experimental results about the discharge mechanism. In earlier works, there only existed some theories and assumptions to interpret it [7,9,10]. Thus the experimental research about the discharge mechanism is more essential. Considering the difficulties of monitoring the evolution process of a discharge, R.O. Hussein et al. [11] studied the discharge formation using optical emission spectroscopy (OES) and scanning electron microscopy (SEM). And we believe that using tracer will be helpful because it can give some messages about the instantaneous discharge through analyzing the tracers' distributions in PEO coatings.

Matykina et al. [5] used ¹⁸O to investigate the growth mechanism of PEO coatings of aluminum under AC conditions. However it did not

pay much attention on a specific discharge process. In this paper, Ti element was used as a tracer to study the discharge mechanism of PEO. Specifically, we deposited a layer of aluminum on titanium substrate (called as Ti-Al); during the PEO process, when the upper aluminum layers were consumed for a period of time, the titanium began to participate in the process; through analyzing the Ti element' distribution in PEO coatings, the shapes of discharge channels were depicted and the existence of oxide film dielectric breakdown in discharge process was identified. Besides that, combining with analyzing

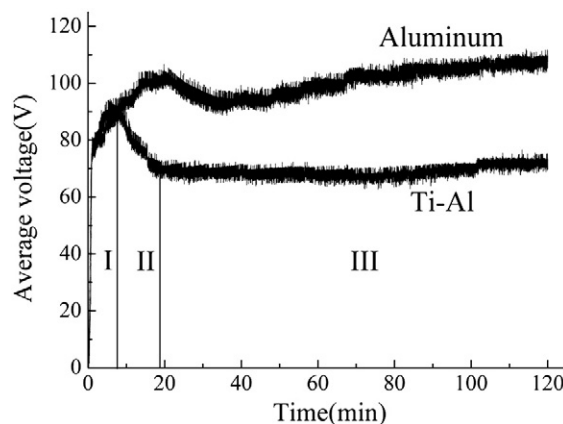


Fig. 1. The voltage variation with treated time during PEO process for aluminum and Ti-Al respectively.

* Corresponding author. Tel.: +86 10 82544266; fax: +86 10 62561284.

** Corresponding author. Tel.: +86 10 82543858; fax: +86 10 62561284.

E-mail addresses: lghit@imech.ac.cn (G. Li), xia@imech.ac.cn (Y. Xia).

the distribution of Si element in discharge channels, PEO coatings' growth mode was also studied in this paper.

2. Experimental details

PEO equipment included a pulsed AC source, an automatic data collection system and an electrolyte container. Titanium substrate (24 mm × 19 mm × 3 mm) covered by a layer of aluminum (Ti-Al), which was prepared by vacuum cathode arc technology and about 60 μm in thickness, was used as the anode. We also used commercially pure aluminum as the anode to compare the result with the Ti-Al circumstance. The samples were all polished and cleaned to obtain a uniform surface. The electrolyte was silicate system with a compound

of 20 g/L Na₂SiO₃ and 1 g/L KOH. A constant current density was set as 0.4 mA/mm² and the temperature of electrolyte was controlled below 35 °C. A FEI Sirion400NC field-emission scanning electron microscopy (SEM) with energy dispersive X-ray system (EDX) was used for analyzing the morphology and the element composition of cross section of PEO coatings.

3. Results and discussion

3.1. Voltage variation during the PEO process

Fig. 1 shows the voltage variation with treated time during PEO process for aluminum and Ti-Al substrate. The voltage variation process

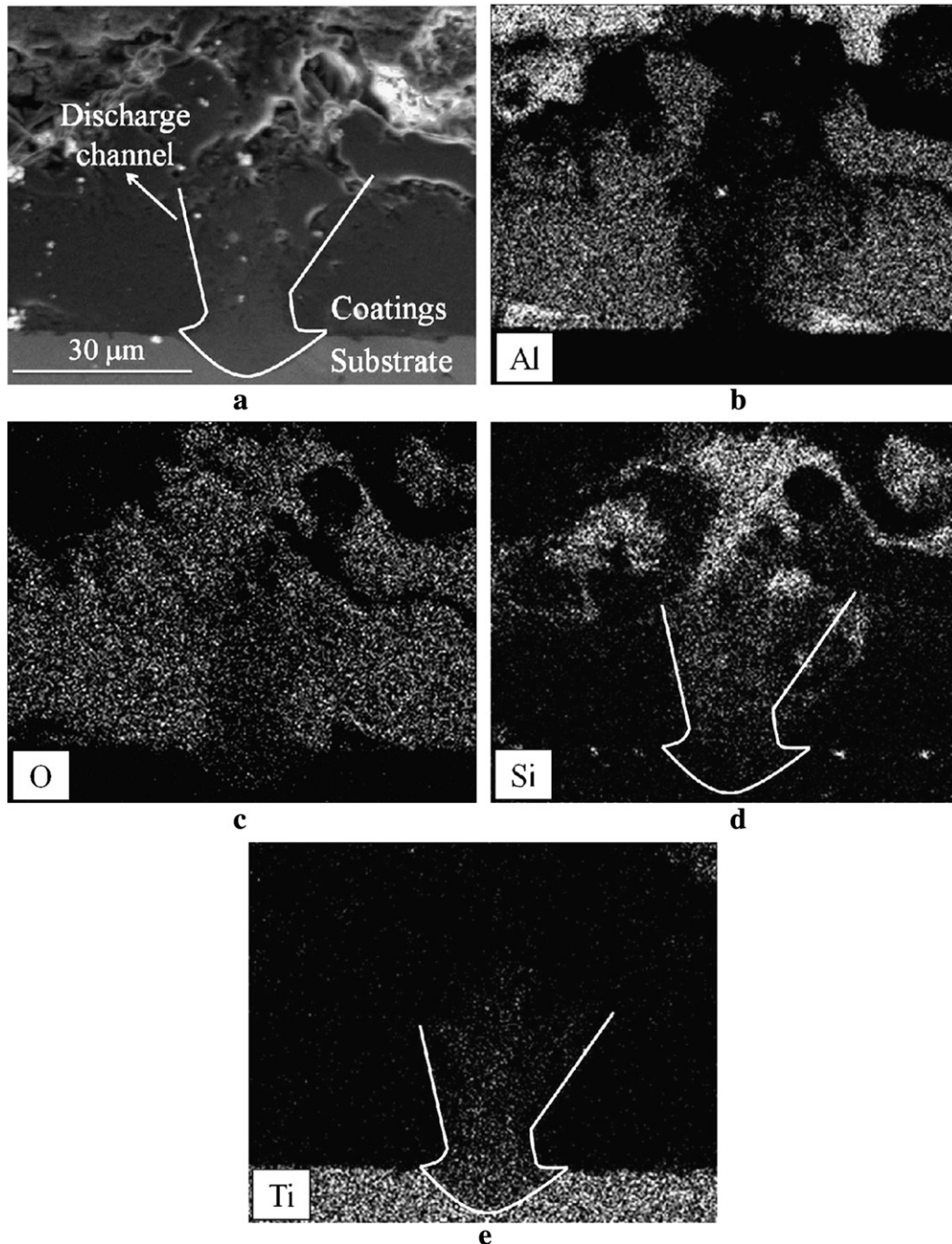


Fig. 2. Cross section EDX analysis of PEO coatings formed on Ti-Al substrate at 120 min in a special location: (a) the SEM micrograph; (b–e) elements distributions from whole region.

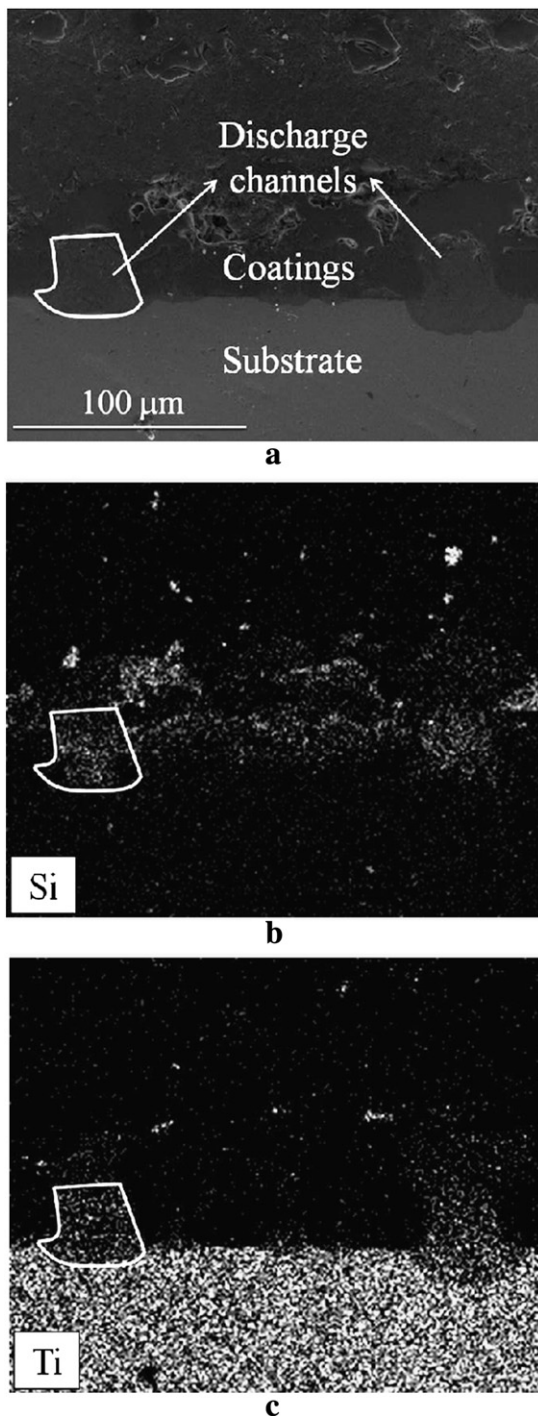


Fig. 3. Cross section EDX analysis of PEO coatings formed on Ti-Al substrate at 120 min in common location: (a) the SEM micrograph; (b–c) elements distributions from the whole region.

for Ti-Al substrate could be divided into three stages: in the first stage, the voltage increased just like what the voltage did for aluminum substrate, as shown in Fig. 1 (I); in the second stage, the voltage started to decline and deviate from the normal route that the aluminum substrate did, as shown in Fig. 1 (II); in the third stage, after the voltage declined to some extent from the second stage, the voltage kept stable for the later period, as shown in Fig. 1 (III).

During the first stage, for Ti-Al substrate, the surface aluminum layers played a leading role in the PEO process, so its voltage trend was almost the same as that of aluminum. As to the second and the

third stages, the voltage for Ti-Al substrate was always lower than that of aluminum, which indicated that titanium began to participate in the PEO process while aluminum layers were consumed for a period of time. So we chose 120 min treated coatings to study the discharge mechanism in PEO process.

3.2. Discharge mechanism

Fig. 2 shows the cross section morphology and elements distributions for PEO coatings formed on Ti-Al substrate at 120 min. It indicated that the substrate was mainly composed of titanium and original aluminum layers had nearly been run out with some scattered pieces left. The PEO coatings were mainly composed of Al, Si and O elements, which indicated that during the previous PEO process the aluminum layers played the leading role as anode metal and titanium only started to participate in it. Through studying the distributions of Ti and Si elements in oxide coatings, the discharge mechanism in PEO process with its effects on coatings' growth could be interpreted.

Considering the discharge's nature, two individual models of discharge were suggested in earlier work [7,9,10]. The first model considered the discharge's process as a result of oxide film dielectric breakdown under a strong electric field [9]; the second one regarded each discharge as a gas discharge occurring in a micro-pore of the oxide coatings and the gas were thought to be resulted by a initial dielectric breakdown of a barrier layer in their bottom [7,10]. R.O. Hussein, et al [11] also distinguished the two individual discharge models by analyzing the emission intensity data, the temperature variation and the SEM/EDX results during PEO process. Anyhow, they all admitted the existence of oxide film dielectric breakdown but less solid direct evidences. In Fig. 2e, Ti element could be seen pouring out across the coatings with a clear profile compared with the surrounding regions, which could be caused by the discharge. Therefore it gave a great evidence for the existence of oxide film dielectric breakdown in discharge process. In addition, discharge channel's shape could be depicted which was illustrated on Fig. 2a, which showed that the coatings were broken down completely.

In fact, there also existed another common trait of discharge channels according to analyze the distribution of Ti element (Fig. 3c) in the coatings. It could be seen that the contents of Ti element in coatings near the substrate were obviously more than that of other locations. So the oxide films were broken down partly and the discharge channel's shape might be illustrated on Fig. 3a. Due to the defects in the outer layers, little amount of Ti element also could be sent out into the electrolyte through them.

The coatings were also growing accompanied with being broken down by a number of discrete discharges. E. Matykina et al. [5] revealed that PEO coatings formed by transport of oxygen species to the inner part of the coatings, where fresh alumina was formed by reaction of the aluminium with oxygen that was originally present in the water of the electrolyte, using ^{18}O tracer. They gave the fact that the coatings mainly grew toward the interior of PEO coatings, but no showing whether the coatings grew toward the outer of PEO coatings. In this study, from the distributions of Si and Ti elements in Figs. 2 (d–e) and 3 (b–c), it could be seen that both elements existed in the discharge channels, which might come from the substrate and the anion in electrolyte separately. It indicated that both elements from the substrate and the electrolyte participated in the reactions of PEO process; from analyzing the Si element's distribution at the bottom of PEO coatings and the Ti element's distribution at the upper location of PEO coatings it could be concluded that the PEO coatings grew toward both the interior and the outer of PEO coatings.

4. Conclusions

The PEO process of titanium with a layer of aluminum deposited on it was investigated. It could be divided into three stages by the

aspect of voltage variation. With further research on the distribution of Ti element in PEO coatings, the existence of oxide film dielectric breakdown in discharge process was testified and the general shapes of discharge channels were also depicted. From the study on discharge channels' shapes we found that: in most of discharge locations, the coatings were broken down partly, while there also existed some discharge places in which the coatings were broken down thoroughly. Combining with analyzing the distribution of element Si in discharge channels, it could be given that the oxide films grew toward the outer as well as the interior of PEO coatings.

Acknowledgment

The author would like to thank the financial support of the Nature Science Foundation of China (No. 10832011).

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