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Microstructural, corrosion and mechanical behavior of two-step plasma electrolyte oxidation ceramic coatings

H. KHANMOHAMMADI, S. R. ALLAHKARAM, N. TOWHIDI

Mechanically Assisted Corrosion Laboratory, School of Metallurgy and Materials Engineering, College of Engineering, University of Tehran, P. O. Box 11155-4563 Tehran, Iran

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Abstract: Plasma electrolytic oxidation (PEO) is considered as a cost effective and environmentally friendly surface treatment process for improving surface properties of light alloys. The formation of ceramic coatings on Ti6Al4V alloy was reported by two-step PEO process and its structural, electrochemical and mechanical properties with the coated samples were compared by one-step PEO process in an alkaline electrolyte. The structural properties were studied using field-emission scanning microscope (FESEM) and X-ray diffraction (XRD). Electrochemical studies were carried out using linear polarization method and in addition mechanical behaviors were investigated by means of Knoop microhardness and nanoindentation method. Results showed that the second step process resulted in an increase of both porosity percentage and average pore diameter on the surface. The two-step process resulted in a small increase of thickness from about 12.5 to 13.0 μm. Electrochemical test results showed that applying the second step resulted in the decrease of both polarization resistance from 1800.2 to 412.5 kΩ/cm^2 and protection efficiency from 97.8% to 90.5%. Finally, the nanoindentation results indicated that the PEO coatings became softer but more ductile after applying the second processing step in acidic electrolyte.

Key words: plasma electrolytic oxidation; microstructure; corrosion; nanoindentation

1 Introduction

Titanium and its alloys are widely used in different industries such as aerospace, marine and biomedicine. This broad range of application of these alloys is due to their high specific strength, good corrosion behavior and biocompatibility [1−5]. On the other hand, low surface hardness and weak wear behavior limit their usage in tribological applications [6,7]. Therefore, different surface treatment processes have been developed for improving the tribological behavior of this group of alloys (i.e. anodizing, chemical vapor deposition (CVD), physical vapor deposition (PVD), ion implantation and laser nitriding [8,9]).

Plasma electrolytic oxidation (PEO) which is also called micro-arc oxidation [1,10,11] is a relatively new surface engineering process to apply ceramic-like coatings on light alloys such as titanium, magnesium, aluminium and zirconium [12−16]. Applying the oxide coatings by this method can enhance the corrosion behavior [17−20], but there are limited studies on the mechanical properties of these coatings [21]. The general mechanism of PEO process (regardless of type of substrate, chemical composition of electrolyte and electrical parameters of process) can be summarized as follows:

1) Formation of a thin natural passive film on the surface;

2) Production of gas bubbles on the surface which results in the growth of a porous film with a columnar structure perpendicular to the surface;

3) Start of micro-discharging when the voltage exceeds the intrinsic breakdown voltage of the oxide film on the surface [10];

4) Formation of plasma atmosphere in electrolyte near to the interface of electrolyte−anode which results in ionization of some elements of electrolyte and entrance of these ions into the coating.

Two-step plasma electrolyte oxidation, which consists of a primary PEO process in alkaline electrolytes and a final short-time PEO process in acidic electrolytes, was proposed by some researchers to achieve better adhesion of coating to substrate [22] and

Corresponding author: S. R. ALLAHKARAM; Tel: +98-21-61114108; E-mail: akaram@ut.ac.ir
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higher corrosion resistance of the coatings [23].

Nanoindentation is a mechanical characterization method for thin film systems and small volumes of materials [24]. Usually, the principal goal of such testing is to obtain elastic modulus and hardness of the specimen. The forces involved in this method are usually in the millinewton range and were measured with a resolution of a few nanonewtons. The depth of penetration is in the order of nanometers [24,25].

In the present study, one-step and two-step PEO coatings on the surface of Ti−6Al−4V alloy were prepared and the effect of the second step on the microstructure, corrosion resistance and mechanical behavior of the coatings was discussed.

2 Experimental

2.1 Substrate preparation

In this study, Ti6Al4V titanium alloy was used as substrate. The samples were cut in the shape of disks with 30 mm in diameter and 4 mm in thickness. The disks were ground with SiC abrasive paper (60−1500#), then polished by alumina nanoparticle suspension and at the end washed with distilled water and acetone.

2.2 PEO process

A bipolar pulse galvanostatic power supply was employed for plasma electrolyte oxidation. Two different electrolytes were used in this study: an alkaline electrolyte (based on our previous study on the effect of electrolyte chemical composition [26]) containing sodium aluminate (15 g/L $Na_2Al_2O_4$), sodium phosphate (2 g/L Na_3PO_4) and sodium fluoride (1.5 g/L NaF) and an acidic electrolyte used in two-step PEO process (containing 0.1 mol/L H_2SO_4 and 0.1 mol/L H_3PO_4) [22]. The applied current density, positive duty cycle, negative duty cycle and frequency were designated to be 0.12 A/cm^2, 50%, 25% and 1000 Hz, respectively. Temperature of the electrolyte was kept below 25 °C using a cooling system as shown in Fig. 1. Table 1 summarizes the processing steps to achieve the coatings.

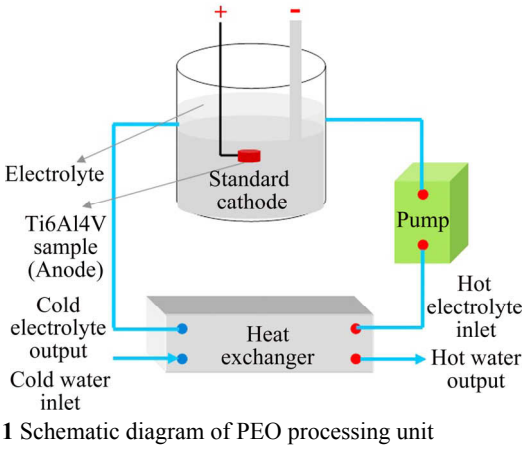

Fig. 1 Schematic diagram of PEO processing unit

Table 1 Processing electrolytes and duration time of different steps

Sample	Step 1		Step 2	
	Electrolyte	Time/s	Electrolyte	Time/s
1S	Alkaline	360	−	−
2S	Alkaline	360	Acidic	30

* In all tests, current density, positive and negative duty cycles and frequency of the PEO process were 0.12 A/cm^2, 50%, 25% and 1000 Hz, respectively.

2.3 Microstructure

The cross-section samples were mounted and ground with SiC emery papers up to 4000# and then were polished using alumina nanoparticle suspension. Surface morphology and cross-section images of the coatings were examined using a scanning electron microscope (SEM, JEOL6300). All the samples were coated with about 50 nm gold layer to avoid surface charging. The thickness of the coatings was measured using cross-section SEM images. The obtained surface morphology images were processed by means of Image Processing Lab software to estimate the surface porosity and the average porosity diameter on the surface of each coating. Chemical composition on the surface and on different parts of the cross-sectional samples was investigated via energy dispersive spectrometer (EDS). Phase composition of the coatings was also analyzed by means of X-ray diffractometer (XRD, Philips X'Pert, with Cu K_α radiation by scanning in the range of 2θ=10°−90°).

2.4 Mechanical properties

Hardness and elastic modulus of the coatings and the substrate have been obtained by nanoindentation test from the cross-sectional samples. All nanoindentation tests were carried out using a Nanoindentor G200 Agilent Technologies. A Berkovich diamond tip was used, whose area function was calibrated in a pattern of fuse silica. The nanoindenting process was carried out on 25 different points on the samples and the average value was reported. Each nanoindentation test was performed with maximum penetration depth of 400 nm. The nanohardness and elastic modulus of each coating were plotted versus penetration depth. The effect of substrate on nanoindentation data of coatings could be considered negligibly if each edge of the indentation track was smaller than 10% of the thickness of the coatings [24]. Equation (1) shows the relationship between the projected area of nanoindentation (A) and penetration depth (h) [24].

$$A = 3\sqrt{3}h^2 \tan^2\theta \quad (1)$$

The value of θ is 65.27° based on the geometry of