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Study plasma electrolytic oxidation process and characterization of coatings formed in an alumina nanoparticle suspension

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ABSTRACT

Alumina-silicate composite coatings were formed on titanium substrate by plasma electrolytic oxidation (PEO) process using a silicate-based electrolyte containing alumina nanoparticles. Microstructure, chemical and phase compositions, and thickness of the coatings were investigated to determine, coating mechanism and probable reactions during the process. The effect of processing time on corrosion resistance of the coatings was investigated using the potentiodynamic polarization test. Barrier layer (TiO_2) formation, micro arcs occurrence, and electrolyte ionization were the main stages of PEO coating growth process. Alumina nanoparticles were incorporated into the coating by cataphoretic and spark ignition mechanisms. During the PEO process, anionic components and nanoparticles were drawn into discharge channels and nanoparticles were sintered through the spark ignition which caused to fill the pores. PEO process resulted in improved corrosion resistance of titanium from 2.33×10^4 Ω to 1.67×10^5 Ω. Cavities that formed by discharge channels and amount of alumina particles that deposited to the surface were two main opponent factors that controlling the coating porosity. It was found that an optimum of 20 min processing time leads to minimum amount of porosity (15.2%) and maximum corrosion resistance.

1. Introduction

Titanium and its alloys because of their unique features such as biological behavior, corrosion resistance and high strength to weight ratio, have wide applications in industry [1,2]. However, the thin oxide layer (1.5–10 nm thick) that is formed naturally on the surface of titanium metal can be damaged by loads, resulting in galvanic and crevice corrosion of titanium metal through reaction with environment [1,3].

Plasma electrolytic oxidation (PEO), also called micro arc oxidation (MAO), is a novel method to make ceramic coatings on valve metals such as Ti, Al, Mg, Zr and their alloys to improve their wear, corrosion and thermal properties [4–14]. The PEO process is based on anodizing process with a high applied voltage and plasma discharge channels [15]. Some of the advantages of this method over the other surface treatments are single-step processing, excellent adhesion of coating to the substrate, environmentally friendly processing, and ease of controlling [15,16].

The composition, structure, and properties of coating produced by PEO process, depend on various parameters such as chemical composition and concentration of the electrolyte as the important ones.

Several investigations have been done to modify PEO treated coatings by adding various compounds and particles to electrolyte [17,18]. Fanya Jin et al. added Fe micro grains to electrolyte and achieved dense coatings with low porosity [19]. Aliofkhazraei et al. improved wear behavior of titanium substrate by coating sialon nanocomposite using Si_3N_4 nanoparticle suspension [20]. E. Matykina et al. added monoclinic zirconia particles to electrolyte and coated a layer composed of zirconia particles [21]. Aliofkhazraei et al. fabricated TiO_2/Al_2O_3 nanocomposite coating by adding Al_2O_3 nanoparticles to silicate-based electrolyte [22]. Although recent studies have been focused on coating by the PEO process in presence of nanoparticles in electrolyte, growth mechanism of coating and probable reactions that occur during the PEO process have not been studied well. Even if Xijin Li and Ben Li Luan investigated the mechanism of Al_2O_3 particle incorporation during the PEO process on Mg substrate, no investigation has been done yet for titanium substrate [23].

In this work, alumina nanoparticles were added to silicate-based electrolyte to form alumina-silicate composite coating on

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titanium by the PEO process in order to modify the coating and to fill the porosities, resulting in enhanced corrosion resistance. The main objective of the present work is to discuss growth mechanism of the coating and probable reactions occurring during the process in a suspension containing alumina nanoparticles. In the meantime, investigation of phase and chemical compositions, thickness, structure, and corrosion resistance of the coatings are the other attempts of this study.

2. Experimental procedure

2.1. Substrate preparation

Pure Titanium discs with 28 mm diameter and 5 mm thickness were used as substrate. The discs were polished with SiC abrasive paper (60-1500#) and then washed with distilled water and acetone.

2.2. PEO process

For the PEO process, a Galvanostatic bipolar mode system; comprising power supply, magnetic stirrer, cooling copper pipe, stainless steel cathode and titanium substrate as anode, was employed as shown in Fig. 1. The used electrolyte contained sodium silicate, alpha alumina nanopowder (produced by US Research Nanomaterials with 80 nm average particle size), potassium hydroxide to adjust electrolyte conductivity [24], sodium hexametaphosphate to densify the coating [25] and triethanolamine as surfactant [22]. Table 1 shows electrolyte components and their concentrations. Three samples with different processing time of 10, 20 and 30 min at constant current density, frequency and duty cycle were prepared, as shown in Table 2.

2.3. Characterization methods

Phase composition of the coatings was analyzed by X-ray diffractometer (XRD, Philips PW1800), using a Cu Kα radiation with 0.04° scanning step and 1 sec detecting time. Surface and cross section of the samples were observed by scanning electron microscope (SEM,VEGA\TESCAN-XMU). Chemical composition of the coatings was examined by energy dispersive spectrometer. Thickness of the coated samples was measured by eddy current technique (Fisher, Dual Scope M40). Surface porosity of the coating was calculated according to SEM micrographs and further image analysis by clemex ver3.5 software.

Table 1
Electrolyte components and their concentrations.

Component	Concentration (g/l)
Sodium silicate	15
Nano alpha alumina powder	6
Potassium hydroxide	3
Sodium phosphate	2
Triethanolamine (TEA)	0.048

Table 2
Instrumental parameters during PEO process.

Sample name	Time (min)	Current density (A/cm^2)	Duty cycle (%)	Frequency (Hz)
t_{10}	10	0.2	50	50
t_{20}	20	0.2	50	50
t_{30}	30	0.2	50	50

The corrosion resistance was carried out by potentiodynamic polarization tests which were examined by EG&G Model 273A system in a 3.5 wt% NaCl solution. Scan rate was 1 mV/s from −300 mV to +1200 mV with respect to the corrosion potential (E_{corr}).

3. Results and discussion

3.1. Voltage–time plot

As Fig. 2 shows, Voltage–Time plot during the PEO process consisted of three stages. Stage (1) showed linear increase of voltage with maximum gradient of 440.9 V/min, resulting from growth of the barrier layer on the substrate during anodizing process. In this stage gas bubbles are produced over the substrate surface. Slope of V–t plot decreased in stage (2) to about 13.3 V/min, when breakdown and spark ignition started. Main process of coating formation is attributed to stage (3), which is associated with almost constant voltage and monotonous micro arcs.

3.2. Study the mechanisms of nanoparticles absorption and coating growth

Coating mechanism in presence of nanoparticles in electrolyte was a combination of cataphoretic effect and spark ignition. Since isoelectric point of alumina lies between 8 and 9 and electrolyte

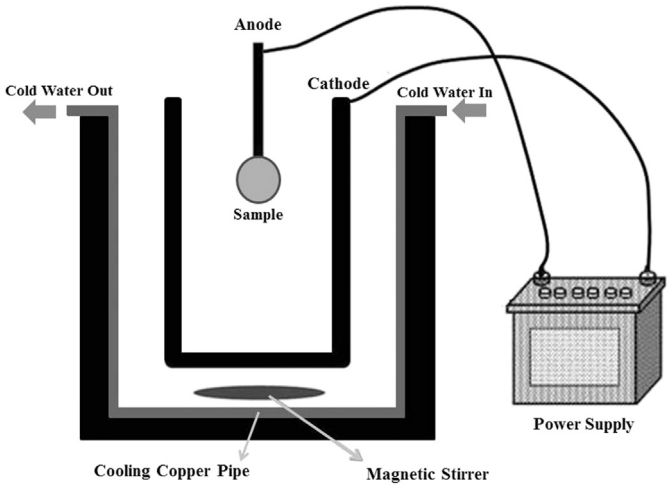

Fig. 1. (a) Schematic of PEO processing setup.

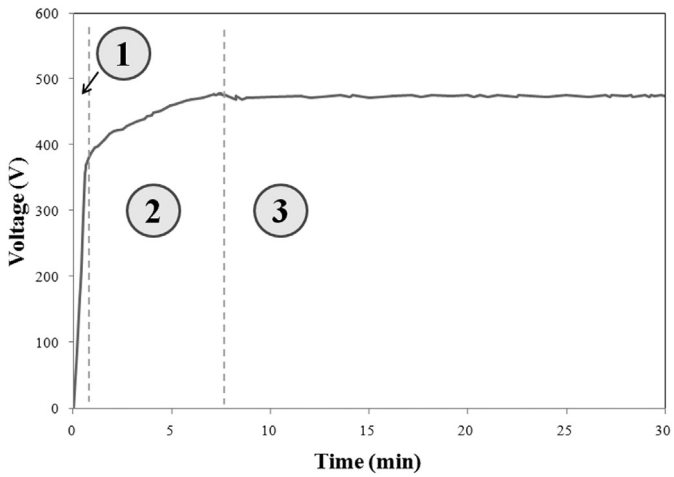

Fig. 2. Voltage–Time plot during PEO process.