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Preparation of ceramic coating on Ti substrate by plasma electrolytic oxidation in different electrolytes and evaluation of its corrosion resistance: Part II

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ABSTRACT

The aim of this work is to discuss the growth characteristics and corrosion behavior of the prepared ceramic coatings on titanium by plasma electrolytic oxidation (PEO) technique in different electrolytes. PEO process was carried out on titanium under constant voltage regime using a pulse power supply. Three kinds of electrolytes, phosphate, silicate and borate based solutions, were used to evaluate the influence of electrolyte composition on the structure, surface morphology, phase composition and corrosion behavior of prepared ceramic oxide films (titania). The phase composition of the coatings was investigated by X-ray diffraction. Scanning electron microscopy was employed to evaluate the growth and surface morphology of coatings. Elements of coatings were investigated with energy dispersive spectrometer. Corrosion behavior of the coatings was also examined by potentiodynamic polarization and electrochemical impedance spectroscopy. The spark voltage of oxide films had a significant effect on the surface morphology, size and homogeneity of micro-pores, thickness and corrosion properties of coatings.

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1. Introduction

By virtue of an excellent combination of high strength-to-weight ratio, good corrosion resistance, good mechanical behavior and good biocompatibility, titanium and its alloys are used in many industries such as aerospace, marine, biomedicine, etc. [1–4]. A thin oxide surface layer (1.5–10 nm thick) is formed naturally on the surface of titanium metal in exposure to air at room temperature [1–5]. Titania (TiO_2) exists in three polymorphic forms: rutile, anatase and brookite. Rutile, stable form of titania at ambient condition, possesses unique properties [6,7]. However, contact loads damage this thin native oxide film and cause galvanic and crevice corrosion as well as corrosion embrittlement [1]. Moreover, the low wear resistance and high friction coefficient without applied protective coatings on the surface gravely limit its extensive applications [1–3]. The most accepted technique for the surface modification of Ti alloys is oxidation. Anodizing produces anatase phase of titania that shows poor corrosion resistance in comparison with rutile phase. Recent developments in high voltage anodizing cause a crystalline rutile/anatase film [1].

Attempts to improve surface properties of valve metals such as aluminum, titanium, magnesium and zirconium over the last few decades have led to development of plasma electrolytic oxidation (PEO) technique which is a process to synthesize the ceramic-like oxide films at high voltages [2,6–11]. This method is characterized by the possibility to reach a fast and simple conversion of the metal surface, at near-to-ambient bulk temperature, into the high temperature titanium oxide (rutile) modified by other oxide constituents [11]. Economic efficiency, ecological friendliness, corrosion resistance, high hardness, good wear resistance, and excellent bonding strength with the substrate are the other characterization of these coatings [2,12–14]. PEO process is based on the conventional anodic oxidation of metals or alloys in aqueous solutions under the additional condition of plasma discharge at the potentials above the spark voltage of the coating [3,11–15]. The discharge leads locally to high temperature and high pressure and plasma-chemical reactions, by which the coating can be formed [1,12–15].

The electrolytes that can be utilized in the production of oxide coatings on metal surface in PEO process may be divided into four common categories:

1. Electrolytes that provide fast dissolution of metal.
2. Electrolytes that provide slow metal dissolution.
3. Electrolytes that promote slight passivation of the metal.
4. Electrolytes that promote strong metal passivation.

Electrolytes from the groups (3) and (4) allow the sparking voltage to be easily reached and are the most beneficial for coating

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Table 1
The electrolyte concentrations and the PEO parameters during processing in different electrolytes.

Electrolyte code	Electrolyte components concentration (gr/L)	Applied voltage (V)	Spark voltage (V)	Oxidizing time (min)	Electrolyte temperature (°C)
NS	Na_3SiO_4: 10 KOH: 4	350	290	3	<35
NP	Na_3PO_4: 10 KOH: 4	350	310	3	<35
NB	$Na_2B_4O_7$: 8 KOH: 4	350	–	3	<35

production by the PEO technique [16]. These electrolytes can be classified within two main categories:

a. Electrolytes that only incorporate oxygen into the coating.
b. Electrolytes containing anionic or cationic components that incorporate elements other than oxygen into the coating.

In electrolytes of the group (b) the coating is formed by both; substrate oxidation and other electrolyte substances, which deposit on the substrate surface allowing a wide range of modifications for coating composition and properties [16].

Most of the research works has been focused on the evaluation of the effect of coating time and electric parameters like applied voltage, frequency and duty cycles [2,4,15,17,18] on the growth characteristics of the PEO films. However, the influence of electrolyte composition on the properties of the coatings is not concerned enough by investigators. Therefore, these parameters need further investigation. In the authors' previous work [19], the effect of aluminate and carbonate based electrolytes on the properties of titania PEO coatings were investigated. The coating produced on the sample in sodium aluminate electrolyte (group (b)) contained $TiAl_2O_5$ phase in addition to titania phases (rutile and anatase) in comparison to that produced on the samples in sodium and calcium carbonate electrolytes (group (a)). In addition, the coating prepared in aluminate based electrolyte showed better corrosion behavior than the others.

In the present research, in continuation to the previous work, the effect of phosphate, silicate and borate electrolytes on the composition, the growth characteristics and the corrosion resistance of the PEO coated titanium were investigated.

2. Experimental details

2.1. Materials and plasma electrolytic oxidation procedure

Disc samples of pure Ti with 20 mm diameter and 3 mm thickness were first polished with SiC abrasive paper (60-2000#) and then washed with acetone and distilled water. A pulsed DC power supply was employed. Based on the previous works [19,20], the optimum applied voltage, duty cycle, frequency and oxidizing time were selected to be 350 V, 40%, 1000 Hz and 3 min, respectively. These parameters control the sparking energy, the size of micropores, the coating thickness and the grain size to obtain coatings with adequate corrosion behavior in anodizing processes in each electrolyte. Samples were used as anodes and stainless steel plates were used as cathodes in different electrolytic bathes, which are shown in Table 1. Besides the oxide salts, the solutions may contain substances which increase the electrolyte conductivity. Based on the earlier work [19], potassium hydroxide (KOH) was added to all electrolytes In order to increase the electrolyte conductivity.

The temperature of the electrolyte was kept below 35 °C by adjusting a cooling water flow. Finally, the coated samples were flushed with water after the treatment and dried in warm air.

2.2. Coating structure and phase composition analysis

Surface morphology and cross-section of the anodic films were analyzed using a scanning electron microscope (SEM, CamScan MV 2300). The elemental composition of the coatings was also investigated with energy dispersive spectrometer (EDS).

Phase composition of the coatings were also examined using X-ray diffractometer (XRD; Philips, X'Pert, The Netherlands), by scanning in the range of $2\theta = 20–100°$.

2.3. Corrosion evaluation

Potentiodynamic polarization tests were carried out from −300 mV to +1000 mV with respect to the corrosion potential (E_{corr}) at a scan rate of 1 mV/s, using an EG&G Model 273A. Electrochemical impedance spectroscopy (EIS; Solarton 1260) in the frequency range between 10^5 and 10^{-3} Hz with ±10 mV amplitude was also employed. Both electrochemical tests were carried out in Ringer's solution (8.6 g/l NaCl, 0.3 g/l KCl and 0.33 g/l $CaCl_2·2H_2O$), at room temperature. Saturated calomel electrode was selected as reference electrode (SCE) and Pt mesh as a counter electrode. The working surface area for each specimen was chosen to be 0.5 cm^2. All EIS data were analyzed using Zview software.

3. Results and discussion

3.1. Growth of coatings

The practical realization of PEO processing requires careful matching of the metal–electrolyte combination. The electrolytes that can be utilized in the production of oxide coatings in the PEO process should promote passivation of the metal [16]. Therefore, silicate, phosphate and borate based electrolytes were selected to evaluate the effects of these electrolytes on the PEO process and obtained coatings properties.

During the PEO process, the voltage was slowly increased to the required level (350 V) over a period of 15 s, maintained at the same level throughout the experimentation. Within initial moment of the coating process in all electrolytes, an increase in voltage led to a quick increase in current and reflective Ti metal surface lost its glossy surface within a few seconds due to the oxidation and intense gas evolution (Eq. (2) in Section 3.4). The current of the working electrode decreased as anodic oxidation was occurred, the spark voltage of the oxide films in the silicate (NS) and phosphate (NP) electrolytes was reached and the spark discharging started on the surface of Ti metal. However, no sparking happened for the sample in borate (NB) electrolyte. The samples in the NS and NP electrolytes had different spark voltages (Table 1), which were determined by the nature of the electrolytes for the same substrate. Uniform, fine and dispersing micro-sparks were observed for the samples in NS and NP electrolytes at the beginning of the sparking process. A notable decrease in the number of micro-sparks occurred by increasing treatment time. However, the intensity and size of the sparks were increased.

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