



Effect of electrical parameters on morphology and in-vitro corrosion resistance of plasma electrolytic oxidized films formed on zirconium



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ARTICLE INFO

Available online 7 March 2015

Keywords:

Zirconium
Plasma electrolytic oxidation
Pulse duty
Frequency
Corrosion resistance

ABSTRACT

The objective of the present work is to study the effect of electrical process parameters (duty cycle and frequency) on morphological, structural, and in-vitro corrosion characteristics of oxide films formed on zirconium by plasma electrolytic oxidation in an electrolyte system consisting of 5 g/L of trisodium orthophosphate. The oxide films fabricated on zirconium by systematically varying the duty cycle and frequency are characterized for its phase composition, surface morphology, chemical composition, roughness, wettability, surface energy, scratch resistance, corrosion resistance, apatite forming ability and osteoblast cell adhesion. X-ray diffraction pattern of all the oxide films showed the predominance of m-ZrO₂ phase. Dense and uniform films with thickness varying from 9 to 15 μm and roughness in the range of 0.62 to 1.03 μm are formed. Porosity of oxide films is found to be increased with an increase in frequency. The water contact angle results demonstrated that the oxide films exhibited similar hydrophilicity to zirconium substrate. All oxide films showed improved corrosion resistance, as indicated by far lower corrosion current density and passive corrosion potential compared to the zirconium substrate in simulated body fluid environment, and among the four different combinations of duty cycle and frequency employed in the present study, the oxide film formed at 95% duty cycle and 50 Hz frequency (HDLF film) showed superior pitting corrosion resistance, which can be attributed to its pore free morphology. Scratch test results showed that the HDLF oxide film adhered firmly to the substrate by developing a notable scratch resistance at 19.5 ± 1.2 N. Besides the best corrosion resistance and scratch resistance, the HDLF film also showed good apatite forming ability and osteo sarcoma cell adhesion on its surface. The HDLF oxide film on zirconium with superior surface characteristics is believed to be useful for various types of implants in the dental and orthopedic fields.

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1. Introduction

Zirconium (Zr) has suitable characteristics for the fabrication of orthopedic and dental implants, such as good mechanical strength, high fracture toughness, low thermal conductivity, excellent biocompatibility, low elastic modulus, low magnetic susceptibility and esthetic quality [1–4]. These features make Zr a good alternative material to titanium alloys, which are currently the most widely used implant materials, but have drawbacks connected with their toxicity (due to alloying elements), tissue discoloration, high magnetic susceptibility and the allergic reactions of patients [5,6]. Further, Zr and its alloys are used as structural materials in water-cooled nuclear power reactors, fuel cladding tubes and pressure tubes [7]. These properties of Zr attribute to the formation of a native oxide film on its surface, and provide an excellent protection against corrosion. However, this native passive layer is very thin and can be lost quickly due to wear, when Zr is used in load

bearing implant applications over a long period of time. It was reported that the usage of Zr and its alloys at aggressive environments in nuclear reactor results in short service life [8]. Hence, the appropriate surface modification technique to improve the surface properties of Zr has important practical significance.

Plasma electrolytic oxidation (PEO), also termed as micro-arc oxidation or spark plasma anodization is one of the most promising surface treatment method for Zr and its alloys to improve their wear and corrosion properties [9–12]. PEO is an electro-chemical conversion coating technique, which enables to produce a uniform, thick, dense, hard, well-adhered and corrosion resistant oxide coating on the surface of light metals [13]. Researchers have indicated that the properties of PEO coatings can be controlled over a wide range by changing treatment time, electrolyte composition and concentration, PEO electrical parameters (namely, pulse duty, frequency, voltage, and current density) [14–17], etc. A lot of work about PEO of titanium, magnesium and aluminum has been reported. However, the effect of PEO process parameters on the properties of the oxide films formed on Zr is still in the early exploration [8,18–22]. Previous studies were mainly

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concentrated towards understanding the oxide film growth and its phase transformation. Moreover, the existing literature was focused on enhancing the corrosion and wear resistance of Zr alloys for nuclear reactor applications. Wang et al. [23] studied the wear and corrosion properties of oxide films formed on Zr-2.5Nb alloy by PEO at various frequencies ranging from 1000 to 4000 Hz. The coating produced at lower terminating voltage and high frequency (4000 Hz) showed higher corrosion and wear resistance. The effect of pulse duty and frequency in the oxide film formation on Zr and its in-vitro corrosion resistance for biomedical applications remain unexplored.

In our previous works, we studied the role of treatment time and electrolyte composition on corrosion resistance characteristics of oxide films formed on Zr [12,24]. This paper reports a study on the PEO electrical parameters, namely, pulse duty and frequency on the structural and morphological features of the plasma electrolytic oxide films formed on Zr and its in-vitro corrosion resistance and biocompatibility in a physiological environment in order to understand their potential for biomedical implant applications.

2. Experimental

2.1. Preparation of substrate and formation of oxide films by PEO

Commercial purity Zr (>99.5 wt.%, 20 mm × 15 mm × 1.5 mm dimensions) was used as the substrate material in this present study. The PEO experimental set up was reported in the authors' previous work [24]. Prior to PEO treatment, the coupons were polished with SiC abrasive papers up to 1000 grit and then cleaned by ultrasonically in acetone and deionized water. A DC power supply unit (with a maximum output current of 15 A and a maximum peak voltage of 900 V) was used to carry out the PEO experiments. The Zr samples were then treated for 6 min at different combinations of duty cycle and frequency in an electrolyte containing 5 g/L tri-sodium orthophosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, Merck India Pvt. Ltd.) at a constant current of 1 A corresponding to a current density of 150 mA/cm² at the work piece. The combinations of duty cycle and frequency employed in the present study with their identification codes are reported in Table 1. The variation in voltage during the PEO process time of 6 min at a constant current of 1 A was observed and reported. The PEO experimental set up was reported in the authors' previous work [24]. The visible spark voltage was recorded in triplicate for all combinations of duty cycle and frequency by a careful physical observation of the appearance of the micro sparks on the anodic surface, and the average value was reported in the present work. The voltage at the first inflection of the voltage-time curve was considered as the breakdown voltage. The final voltages observed at the end of 6 min in all combinations were also recorded. All voltages referred in this work are peak voltages. After PEO process, the treated samples were cleaned with deionized water and dried in hot air. The PEO treated Zr samples are further referred to with these identification codes based on their duty cycle and frequency (LDLF, LDHF, HDLF and HDHF) and the untreated Zr is referred as "S".

Table 1
Combination of electrical parameters used in the PEO film formation, identification codes for the films and voltage responses at a treatment time of 6 min.

Sl. No.	Duty cycle	Frequency (Hz)	Sample code	Visible spark voltage (± 3 V)	Breakdown voltage ($V_b \pm 3$ V)	Final voltage ($V_f \pm 1$ V)
1	20%	50	LDLF	288	380	583
2	20%	1000	LDHF	292	387	595
3	95%	50	HDLF	226	322	577
4	95%	1000	HDHF	265	359	518

2.2. Physico-chemical characterization of PEO treated Zr samples

The phases present in PEO formed oxide films were characterized by a Rigaku Ultima III X-ray diffractometer (30 mA, 40 kV) with a $\text{Cu K}\alpha$ radiation over a 2θ range of 20° to 70° with a scan speed of 1°/min and a step size of 0.05°. The phases formed in oxide films were identified by matching it with data from the Joint Committee on Powder Diffraction Standards (JCPDS) cards. The crystallite size 'd' (nm) of the formed phase can be determined by using Scherrer's formula [25]:

$$d(\text{nm}) = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where, θ is the diffraction angle in degrees, λ is the wavelength X-rays in nm and β is the full width of the peak at half maximum intensity (FWHM) in radians. The surface morphology, film thickness and elemental composition of all the formed films were examined using scanning electron microscope (SEM, S3000N, Hitachi, Japan) equipped with the energy-dispersive X-ray spectroscopy (EDS, Thermo Scientific UltraDry, USA). Prior to SEM analysis, all samples were sputtered with a thin layer of gold to make the surfaces conductive. The average surface roughness (R_a) of PEO treated Zr samples and untreated Zr was measured using a surface profilometer (Surtronic 25, Taylor-Hobson, Precision, UK) with an accuracy of 0.01 μm in ten different randomly selected locations, and the average values are reported. The thickness of the oxide films was measured using an eddy current coating thickness gauge (Premium 8500, QNIX, Germany) at ten different locations on their surfaces and the average values are reported with standard deviation. The wettability of Zr substrate and PEO treated Zr samples was determined by the sessile drop contact angle method with the Easy DROP equipment (DSA100, KRUSS, Germany) using distilled water as the contacting solvent. For each test, a drop of 3 μl liquid was carefully dropped on the surface of the tested sample, then the image of the drop was captured by a video camera. An image analysis software was used to measure the contact angle based on the average of left and right angles of each drop on the sample surface. Measurements were obtained at ten different locations on 2 sample surfaces of each coating group and the average contact angle was reported. The surface energy (E_s) of all films has been derived from the obtained contact angles using the equation [26]:

$$E_s = E_{vl} \cos \theta \quad (2)$$

where, E_{vl} is the surface energy between liquid and air under ambient conditions (which is 72.8 mJ/m² at 20 °C for pure water) and θ is the static contact angle.

2.3. Scratch testing of PEO treated Zr

The scratch test was accomplished using an automatic scratch tester (Revetest, CSM Instruments, Switzerland) and a spherical Rockwell C diamond stylus of 200 μm radius was used as the scratching body. For testing the oxide film adhesion to Zr substrate, a progressive load from 1 N to 40 N was applied with a loading rate of 20 N/min and the length of the scratch was 5 mm. Six scratches were made on two samples for each film group and subsequently analyzed with an optical microscope equipped with the scratch test unit. The critical load (L_c) was determined from the point of the adhesion failure of the oxide film from the Zr substrate in the scratch groove.

2.4. Electrochemical corrosion study

The corrosion behavior of Zr substrate and the PEO treated Zr samples were examined by Tafel analysis and potentiodynamic polarization (PDP) scan tests in 7.4 pH simulated body fluid (SBF) environment. The SBF test solution was prepared following the protocol suggested by

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