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Role of electrolyte composition on structural, morphological and *in-vitro* biological properties of plasma electrolytic oxidation films formed on zirconium

Sandhyarani M[a], Prasadrao T[b], Rameshbabu N[a,*]

[a] Department of Metallurgical and Materials Engineering, National Institute of Technology, Tiruchirappalli 620015, Tamilnadu, India
[b] Department of Physics, Koneru Lakshmaiah University, Vaddeswaram, Guntur 522502, Andhra Pradesh, India

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ABSTRACT

Development of oxide films on metallic implants with a good combination of corrosion resistance, bioactivity and cell adhesion can greatly improve its biocompatibility and functionality. Thus, the present work is aimed to fabricate oxide films on metallic Zr by plasma electrolytic oxidation (PEO) in methodically varied concentrations of phosphate, silicate and KOH based electrolyte systems using a pulsed DC power source. The oxide films fabricated on Zr are characterized for its phase composition, surface morphology, chemical composition, roughness, wettability, surface energy, corrosion resistance, apatite forming ability and osteoblast cell adhesion. Uniform films with thickness varying from 6 to 11 μm are formed. XRD patterns of all the PEO films showed the predominance of monoclinic zirconia phase. The film formed in phosphate + KOH electrolyte showed superior corrosion resistance, which can be ascribed to its pore free morphology. The films formed in silicate electrolyte showed higher apatite forming ability with good cell adhesion and spreading over its surface which is attributed to its superior surface roughness and wettability characteristics. Among the five different electrolyte systems employed in the present study, the PEO film formed in an electrolyte system with phosphate + silicate + KOH showed optimum corrosion resistance, apatite forming ability and biocompatibility.

1. Introduction

Excellent biocompatibility, high mechanical strength and fracture toughness, reasonably good corrosion resistance, low thermal conductivity, together with low elastic modulus (92 GPa) and low magnetic susceptibility (-13.8×10^{-6} cm^3/mol) make zirconium (Zr) one of the best implant material in orthopedic and dental restoration fields [1,2]. The biocompatibility and high corrosion resistance of Zr are ascribed due to the formation of a native oxide film on its surface. However, this native oxide (zirconia, ZrO_2) film is categorized as bio-inert [3] that restricts the formation of chemical bonds with bone tissue during implantation, which could be a drawback since, an early integration between biomaterial and bone is advantageous for most implant applications. In addition, this native oxide layer is very thin, at most 2–5 nm [4] and can be lost soon due to wear, when Zr is used in high load (body weight) bearing implant applications [5], e.g., total hip and knee arthroplasties. Further, pitting corrosion on Zr surface has been observed at lower potentials in simulated body fluid (SBF) conditions [6]. This consequence in an increase in corrosion rate and in turn may reduce the biological performance and service time of the Zr implant. As a result, appropriate surface treatment is required to improve the bioactivity and corrosion resistance of Zr, without sacrificing its biocompatibility.

In this theme, various surface modification techniques, e.g., physical or chemical vapor deposition, sol–gel process, plasma spray coating, thermal oxidation, anodization and plasma electrolytic oxidation (PEO) have been adopted in recent years to improve surface properties of Zr [4,7–11]. Of these, PEO also termed as micro arc oxidation (MAO) or spark plasma anodization (SPA) is an emerging technique to develop firmly adherent, crystalline, porous, relatively rough and thick oxide coatings on Zr and other valve metals in environmental friendly alkaline based electrolytes. The oxide layers developed by PEO offer a unique combination of wear and corrosion resistance of aluminum, titanium and magnesium alloys [12–14]. Further, the morphology and thickness of the oxide films formed during PEO can be controlled over a wide range by changing both intrinsic parameters (electrolyte concentration, composition and pH) and extrinsic parameters (electrical

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* Corresponding author. Tel.: +91 431 2503464; fax: +91 431 2500133.
E-mail addresses: rameshrohith@gmail.com, nrb@nitt.edu (R. N).

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parameters, electrolyte temperature and treatment time) [15]. Therein, electrolyte composition and concentration play a key role in obtaining the desired coatings of special phase composition and microstructure [14,16]. Each electrolyte introduces different cations and anions into the electrolyte solution which consequently gets incorporated during the oxide film growth, thereby strongly influencing the resultant coating characteristics such as, nature of the pore and its size distribution, the phases present in the coating and its corrosion, wear and biological properties [13,14,16].

Among the wide range of electrolytes, silicate and phosphate based electrolytes were commonly used to form oxide films on magnesium and titanium, especially, when these implants are specified for biomedical applications [17,18]. Cheng et al., done series of works for developing wear resistant oxide films on Zircaloy 2 and Zircaloy 4 in silicate and phosphate electrolytes [19–22]. PEO coatings formed in silicate based electrolytes are usually a combination of monoclinic zirconia (m-ZrO_2) and tetragonal zirconia (t-ZrO_2), and t-ZrO_2 increases with increase in concentration of the electrolyte, suggesting that silicon species stabilize t-ZrO_2 [21,22], and the coatings formed in phosphate based electrolyte comprised of m-ZrO_2 [19,20,22]. Zho et al., produced 11–15 μm thick PEO coatings on a Zr–1Nb alloy in phosphate electrolyte and the corrosion protection of these coatings in 0.5 M Li–OH was studied [23]. Wang et al. [5] and Chen et al. [24] produced thin oxide coatings of 6–15 μm thick on Zr–2.5Nb alloy in silicate electrolyte using high frequency DC power source. The coatings comprised of high amount of m-ZrO_2 and provide better wear and corrosion resistance than a commercial autoclaved black oxide coating. Matykina et al. reported a 100 μm thick oxide coating on Zr alloy (Zirlo) under AC conditions in an alkaline silicate electrolyte and its corrosion resistance in H_2SO_4 environment was studied [25]. Studies were also focused toward understanding the PEO process, luminescence characteristics and growth kinetics during the oxide film formation on Zr in AC [26] and DC current regime [6,27]. Although the surface modification of Zr by PEO in silicate and phosphate based electrolytes are widely investigated, the studies were mainly focused toward understanding the growth kinetics of oxide film formation and phase transformation. Further, the earlier works were concentrated on improving the wear and corrosion resistance properties for nuclear applications. However, no literature at present is available regarding the potential use of PEO coated oxide films in silicate and phosphate based electrolytes for biomedical applications. The surface properties such as, wettability, roughness, corrosion resistance in physiological environment, apatite forming ability and biocompatibility of the oxide films formed in silicate and phosphate based electrolytes remain unexplored.

The effect of PEO treatment time on the composition and corrosion resistance of the oxide films formed on Zr in phosphate based electrolyte has been reported by the authors' group [28]. The present work is aimed at evaluating the *in-vitro* biological (corrosion resistance, bioactivity, cell adhesion) characteristics of the oxide films formed on Zr by PEO treatment in methodically varied concentrations of phosphate, silicate and KOH based electrolyte systems and to recommend the suitable electrolyte system for PEO treatment on Zr to have optimum properties for orthopedic implant applications.

2. Experimental

2.1. Formation of oxide films on Zr

Commercial purity Zr (>99.5 wt%) with coupon dimensions of 20 mm × 15 mm × 1.5 mm were used for the present study. Prior, to PEO treatment, the coupons were polished with abrasive papers, and then cleaned with acetone and deionized water in an ultrasonic bath. A DC power supply unit (with a maximum output current of 15 A and a maximum peak voltage of 900 V) was employed to carry out the PEO process. The Zr coupons were then treated in five different electrolyte solutions containing methodologically varied concentrations of tri-sodium *ortho* phosphate ($Na_3PO_4{\cdot}12H_2O$, Merck India Pvt. Ltd.), sodium meta silicate ($Na_2SiO_3{\cdot}9H_2O$, Merck India Pvt. Ltd) and potassium hydroxide (KOH, Merck India Pvt. Ltd) for 6 min at a constant current of 1 A corresponding to 150 mA/cm^2 current density at the workpiece. The applied duty cycle and frequency was 95% and 50 Hz, respectively. The observed variation in voltage during the PEO process time of 6 min at a constant current of 1 A is reported in Fig. 1. To control the bath temperature close to the room temperature, the electrolyte bath was water cooled during the process thereby avoiding thermally driven growth process. To ensure uniform electrolyte concentration and dissipation of heat generated during the process, the electrolyte solution was kept under continuous stirring by a digital magnetic stirrer (Q 20A model, REMI make, India). The breakdown voltage was recorded in all electrolyte systems by a careful physical observation of the appearance of the micro sparks on the anodic surface. The breakdown voltage was recorded in triplicate and the average value was reported in the present study. The final voltages observed at the end of 6 min in all electrolyte systems were also recorded. After PEO process, the treated samples were cleaned with deionized water and air dried at room temperature. The composition and concentration of five different electrolytes used in the present study with their identification codes are presented in Table 1. The PEO treated Zr samples are further referred to with these identification codes and the untreated Zr is referred as "S".

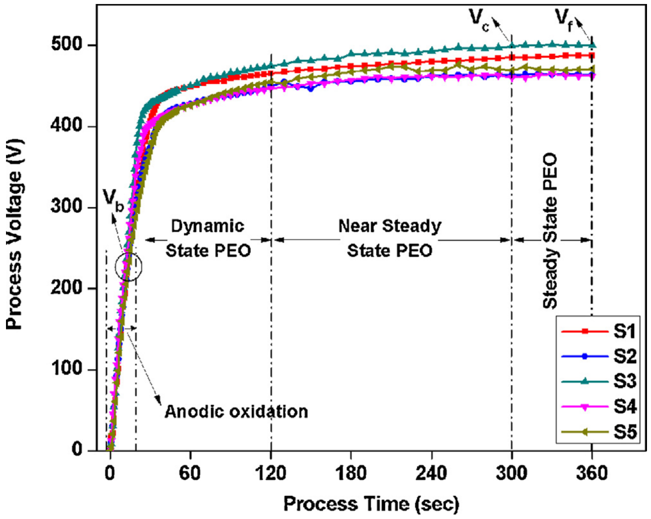

Fig. 1. Variations of cell voltage with PEO process time for a period of 360 s observed during the formation of S1–S5 films.

Table 1
Composition and concentration of electrolytes used in the PEO film formation and the identification codes for the films.

Sl. no.	Electrolyte composition	Electrolyte concentration	Sample code
1	$Na_3PO_4{\cdot}12H_2O$	13 g/L	S1
2	$Na_3PO_4{\cdot}12H_2O$ + KOH	10 g/L + 3 g/L	S2
3	$Na_2SiO_3{\cdot}9H_2O$	13 g/L	S3
4	$Na_2SiO_3{\cdot}9H_2O$ + KOH	10 g/L + 3 g/L	S4
5	$Na_3PO_4{\cdot}12H_2O$ + $Na_2SiO_3{\cdot}9H_2O$ + KOH	5 g/L + 5 g/L + 3 g/L	S5