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Role of electrolyte additives on in-vitro corrosion behavior of DC plasma electrolytic oxidization coatings formed on Cp-Ti

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ABSTRACT

The present investigation reports the effect of different electrolyte additives on in-vitro corrosion behavior of the plasma electrolytic oxidation (PEO) coatings formed on commercially pure titanium (Cp-Ti). PEO coatings were produced using a pulsed DC power source at a constant current density of 70 mA/cm^2 and a treatment time of 8 min. Different coatings were developed with different additives (sodium sulfate, Tris, di-ammonium hydrogen phosphate and ammonium acetate) added to a base electrolyte consisting of TSOP and KOH. PEO coatings were characterized for phase composition, elemental composition, surface and cross-sectional microstructure, corrosion behavior, apatite forming ability and osteoblast cell adhesion. The corrosion resistance of the developed oxide coatings was evaluated in a Kokubo simulated body fluid (SBF) by potentiodynamic polarization test and EIS study. The in-vitro bioactivity of all the PEO coatings and the untreated substrate was studied by soaking the samples in an SBF environment for 21 days. The TiO_2 layer formed in phosphate, sulfate and nitrite containing electrolyte highly enhances the apatite formation in SBF. An in-vitro cell adhesion test was performed on all coatings using human osteosarcoma cells for 48 h. SEM images of cell adhesion test showed that human osteosarcoma cells were well adhered and spread on all PEO treated samples. Among all the additives, Tris has provided higher corrosion resistance in the SBF environment with good apatite forming ability and osteoblast cell adhesion.

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1. Introduction

Titanium and its alloys play a major role in hard tissue replacements such as load bearing orthopedic implants and dental applications due to their low density, non-toxicity, corrosion resistance and biocompatibility [1,2]. It also possesses high mechanical strength, high thermal stability, and formability. Titanium metal oxidizes immediately when it exposes to the air or moisture at room temperature and forms a thin passive layer, which protects the Ti from further oxidation and corrosion. However, this native oxide layer can be lost quickly due to wear and corrosion occurs under harsh environments. Hence, the appropriate surface modification is required for titanium based alloys to improve the surface properties as well as bioactivity. There is a wide range of surface modification techniques available, such as physical vapor deposition, chemical vapor deposition, anodization, plasma spraying and plasma electrolytic oxidation (PEO), each has its own merits and limitations [3–5]. Among these techniques, plasma electrolytic oxidation (PEO) is a novel method for developing ceramic coatings on the surface of metals to improve corrosion properties and bioactivity [6,7].

Plasma electrolytic oxidation (PEO), also termed as spark plasma anodization (or) micro plasma oxidation (or) micro arc oxidation is an electrochemical oxidation technique to fabricate oxide coatings on metallic substrates such as aluminum, magnesium, titanium, zirconium and its alloys to improve bioactivity, wear and corrosion properties for biomedical and industrial applications [8,9]. The PEO coating properties depend on the process parameters such as the electrolyte chemistry, nature of the power supply mode, applied voltage, current density, duty cycle, frequency and processing time [3,4,10–12]. The oxide coating fabricated on Cp-Ti by PEO has a double layer structure composed of the outer porous layer and an inner barrier layer. The porous outer layer is more useful for the biological performance of the implant materials, and the inner barrier layer enhances its corrosion resistance [13].

The PEO coating phase composition, morphology, coating thickness and its properties can be significantly varied by varying the composition of the electrolyte. The addition of additives to the base electrolyte significantly varies the PEO process characteristics, such as, breakdown voltage and final voltage, which in turn had a marked influence on the properties of the fabricated coatings. Earlier research reported the role of anhydrous salts [3], hydrated salts [14] and fluoride containing salts [15] as electrolyte additives on the structural, morphological, compositional and electrochemical characteristics of the TiO_2 films formed on Cp-Ti by plasma electrolytic oxidation. It is found that the additives,

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which increased the electrolyte conductivity allowed easier and rapid formation of an oxide barrier layer on Cp-Ti during the initial stage of the PEO process and subsequently the coating exhibited higher corrosion resistance. Therefore, the selection of electrolyte additive is an important aspect to develop a good coating by PEO. In the present work, the role of various additives (such as sodium sulfate, Tris, di-ammonium hydrogen phosphate (DAP) and ammonium acetate) on the formation of PEO coatings on Cp-Ti was studied. To the best of authors' knowledge, the electrolyte additives chosen in the present investigation are yet to be explored for PEO coating on Cp-Ti and its corrosion resistance and osteoblast cell adhesion characteristics. As the PEO coating consists the elements from both the substrate and the electrolyte, it is envisaged that the phase composition (anatase: rutile ratio), morphology and corrosion resistance of the PEO coating can be significantly influenced by the chosen electrolyte additive born elements (C, N, P and S). Comparative study of these different additives on coating thickness, phase structure, surface morphology and the correlation to its corrosion properties was investigated. The corrosion properties are analyzed by potentiodynamic polarization study and electrochemical impedance spectroscopy (EIS). The apatite forming ability and cell adhesion characteristics of the PEO coatings were evaluated by in-vitro bioactivity test and cell adhesion test.

2. Materials and methods

2.1. Specimen preparation

The Cp-Ti samples with dimensions 20 mm × 15 mm × 1.5 mm were used as substrate materials in the present work. The substrates were mechanically abraded progressively from 400 grit to 1000 grit SiC abrasive paper to remove macro level surface defects. The samples were cleaned with a diluted mixture of hydrofluoric and nitric acids (5 ml HF in 100 ml deionized water and 5 ml HNO_3 in 100 ml de-ionized water) with volume fractions of 10% and 40% respectively, for 30 s to remove the natural surface oxide layer and surface contaminants. Finally, the samples were ultrasonically cleaned with acetone and deionized water for 10 min and dried in air before use.

2.2. Preparation of electrolyte and fabrication of TiO_2 coatings by PEO

10 g/l tri-sodium orthophosphate (TSOP, $Na_3PO_4 \cdot 12H_2O$) and 2 g/l potassium hydroxide (KOH) in 1 L of deionized water has been taken as a base electrolyte. Four different additives, such as sodium sulfate (Na_2SO_4), tris ($(HOCH_2)_3CNH_2$), di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and ammonium acetate ($C_2H_7NO_2$) of each 3 g/l were added to the base electrolyte to prepare 4 different electrolyte solutions. The electrolyte solutions along with their identification codes employed in the present study are reported in Table 1. Hereafter, both the samples and their corresponding coatings will be referred to these identification codes. The pH and conductivity of these electrolyte solutions were measured by Multi-parameter PCTestr 35(Oakton Instruments, Singapore) and ECTestr11+ (Oakton Instruments, Singapore) multirange conductivity meter at room temperature, respectively, and reported in Table 1. Coatings were formed using a pulsed DC PEO unit (Milman Pvt. Ltd., Pune, India) equipped with a stainless steel container, a stirrer, and a cooling system. The DC power supply unit used for this investigation has a maximum peak current of 15 A and a maximum peak voltage of 900 V. The sample and stainless steel container were used as anode and cathode, respectively. Simultaneously, a cooling water system was used to maintain the temperature of electrolyte solutions around 30–40 °C to avoid any thermally driven growth processes. A magnetic stirrer is used to maintain the uniformity of the electrolyte.

The PEO coatings were fabricated under a constant current density of 70 mA/cm^2, pulse duty cycle of 95%, pulse frequency of 50 Hz and treatment time of 8 min. The duty cycle percentage is expressed as $(t_{on}/(t_{on} + t_{off})) \times 100$, where t_{on} is on-duration of the pulse and t_{off} is the off-duration of the pulse during a single cycle. The schematic diagram depicting the pulse parameters employed during the PEO process is given in Fig. 1. All the PEO treated samples were rinsed thoroughly with deionized water and dried in ambient air at 40 °C after the PEO treatment.

2.3. Phase analysis and morphology of the PEO coatings

The phase composition of the PEO coating was identified by the X-ray diffraction technique (Ultima IV X-ray diffractometer, Rigaku, Japan) using CuKα radiation operated at 40 kV and 30 mA over a 2θ range of 20–60° with a step size of 0.05°. The Hitachi-S3000N scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) detector was used for studying the surface morphology, coating thickness and elemental composition of the PEO coatings on Cp-Ti.

2.4. Electrochemical corrosion study of the PEO coatings

Electrochemical corrosion experiments such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests were conducted using a computer controlled corrosion testing unit (ACM Instruments, Cumbria, UK). The electrochemical corrosion testing unit cell consisted of three electrodes, which are saturated calomel electrode (SCE) as a reference electrode, a platinum foil as a counter electrode and sample to be tested as a working electrode. The in-vitro electrochemical corrosion tests were conducted at 7.4 pH simulated body fluid (SBF) condition. The SBF solution was prepared according to the protocol suggested by Kokubo and Takadama [16]. Untreated and PEO treated samples were kept in contact with the SBF solution with an exposed area of 0.5 cm^2 during electrochemical measurements. All the test samples were exposed to the SBF solution for 4 h to allow stabilization. The potentiodynamic polarization tests were conducted in the potential range of −500 mV to 3000 mV with reference to the OCP at a scan rate of 10 mV/min. The scan rate of 10 mV/min was used for potentiodynamic polarization test as per the ASTM standard G59–97. The corrosion parameter values, namely, anodic (βa) and cathodic (βc) Tafel constants and corrosion current density (i_{corr}) of the untreated and PEO treated samples were obtained from the Tafel extrapolation method over a potential range of ±250 mV. The polarization resistance [R_p] was calculated using Stern-Geary equation:

$$R_p = \frac{\beta_a \times \beta_c}{2.303 i_{corr}(\beta_a + \beta_c)} \qquad (1)$$

where, β_c and β_a are slopes of cathodic and anodic Tafel plots, respectively, and i_{corr} is the corrosion current density. The EIS tests were

Table 1
The identification codes for the PEO coatings with their respective electrolyte composition, pH and conductivity.

Sl. No	Sample code	Electrolyte composition	pH	K (mS/cm)
1	SP1	10 g/l $Na_3PO_4 \cdot 12H_2O$ + 2 g/l KOH	11.1	19.1
2	SP2	10 g/l $Na_3PO_4 \cdot 12H_2O$ + 2 g/l KOH + 3 g/l Na_2SO_4	11.3	18.5
3	SP3	10 g/l $Na_3PO_4 \cdot 12H_2O$ + 2 g/l KOH + 3 g/l $(HOCH_2)_3CNH_2$	11.0	19.8
4	SP4	10 g/l $Na_3PO_4 \cdot 12H_2O$ + 2 g/l KOH + 3 g/l $(NH_4)_2HPO_4$	10.0	13.9
5	SP5	10 g/l $Na_3PO_4 \cdot 12H_2O$ + 2 g/l KOH + 3 g/l $C_2H_7NO_2$	10.5	15.4

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