



Fabrication, characterization and in-vitro evaluation of nanostructured zirconia/hydroxyapatite composite film on zirconium



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ARTICLE INFO

Article history:

Received 15 July 2013

Accepted in revised form 19 October 2013

Available online 1 November 2013

Keywords:

Zirconia/hydroxyapatite film

Plasma electrolytic oxidation

Electrophoretic deposition

Corrosion resistance

Bioactivity

Cell adhesion

ABSTRACT

The present study aims to fabricate ZrO₂/hydroxyapatite [HA] composite film on Zr by plasma electrolytic oxidation coupled with electrophoretic deposition process in a single step. Further, ZrO₂/HA film formation mechanism was studied as a function of treatment time in the range of 2 to 6 min in an aqueous electrolyte system consisting of dissolved tri sodium orthophosphate and suspended HA nanoparticles. The phase composition, surface morphology and elemental composition of the formed films were examined by X-ray diffraction [XRD], Raman spectroscopy and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy. Surface roughness, wettability, corrosion resistance, bioactivity and osteoblast cell adhesion characteristics of the ZrO₂/HA film were also investigated. Uniform and dense ZrO₂/HA films with thickness varying from 42 to 75 μm were formed at 2 to 6 min of treatment time. XRD results revealed that the films were comprised of nanocrystalline cubic zirconia and monoclinic zirconia. During the film growth process, HA particles were dragged into the discharge channels and subsequently entrapped into the oxide film by electrophoretic deposition. Additionally, calcium that originated from partial melting of HA enters the sites of Zr thereby stabilizing cubic ZrO₂ phase. Raman spectrum confirmed the presence of HA phase along with ZrO₂ phases. ZrO₂/HA film exhibited better wettability and high surface energy compared to untreated Zr. Potentiodynamic polarization test revealed that the ZrO₂/HA film formed at 6 min treatment time showed superior pitting corrosion resistance compared to untreated Zr in simulated body fluid [SBF] environment. Bone-like apatite layer was formed on entire surface of ZrO₂/HA film after soaking in SBF for 8 days, indicating its significantly enhanced in-vitro bioactivity. Cell adhesion test results showed that the human osteosarcoma cells could attach, adhere and propagate well on the surface of ZrO₂/HA film, suggesting the potential application of ZrO₂/HA coated Zr as orthopedic implant material.

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1. Introduction

Zirconium [Zr] and its alloys have been the material of choice for orthopedic and dental implants, hard tissue replacements due to its excellent technological properties including chemical and dimensional stability, high flexural strength, fracture toughness, lower cytotoxicity, good corrosion resistance and biocompatibility [1–4]. Zr is expected to be a surgical implant material due to its low elastic modulus [92 GPa] which is viewed as a biomechanical advantage as it can result in minimal stress shielding of the host bone compared to titanium and its alloys [100–110 GPa], stainless steel [189–205 GPa] and CoCr alloys [230 GPa] [5]. The good corrosion resistance of Zr has been mainly attributed to its native oxide film. Nevertheless, this oxide film shows morphological fixation with the surrounding tissues without producing any chemical or biological bonding when implanted, because of its poor bioactivity and due to the encapsulation phenomena by the fibrous tissues [6]. Additionally, this native oxide film can be lost soon when Zr is used in long

term load bearing applications. The improvement of the bioactivity and corrosion resistance of Zr implants has been the key research focus in the recent years.

Plasma electrolytic oxidation [PEO], also called microarc oxidation [MAO] or spark plasma anodization, is gaining attention as a novel and unique technique for development of firmly adherent and relatively thick oxide films on light metals such as Zr, Al, Mg and Ti [6–10]. Further, uniform coatings can be obtained on the relatively complex geometries in the PEO technique, as it is not a line of sight process [11] and it has been proven as an effective, eco-friendly substitute to conventional techniques primarily in terms of oxide films being formed in environmental friendly electrolytes [12]. PEO fabricated zirconia [ZrO₂] films have demonstrated promising in-vitro corrosion resistance, acting as a chemical barrier against the release of metal ions from the implants [13,14]. However, being bioinert, the chemical bond with the living bone in the body is not very strong with ZrO₂. Some researchers have focused on improving bioactivity of PEO treated Zr by secondary treatments. For instance, Yan et al. [15] reported that chemical treatments in which immersion in acid or alkaline solutions after PEO treatment can enhance the apatite formation ability of Zr in SBF medium. Zhang

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et al. [16] investigated the PEO treated Zr when photo excited by UV light of energy greater than its band gap resulted in abundant basic Zr–OH groups on the surface and exhibited an enhanced apatite formation during immersion in SBF solution. Further, calcium ions are successfully incorporated into the ZrO₂ film during MAO process using an electrolyte solution containing calcium precursor, which resulted in a significant enhancement in the apatite forming ability of Zr in SBF medium [5].

Yet another approach to improve the bioactivity and corrosion resistance of Zr is by forming ZrO₂/HA composite film, as hydroxyapatite [HA, Ca₁₀(PO₄)₆(OH)₂] can spontaneously bond to and integrate with bone in living body. ZrO₂/HA composite coating has been proved to be an excellent coating option on nitinol and stainless steel substrates to simultaneously impart diverse properties such as corrosion resistance and bioactivity [17,18]. However, available literature on the fabrication of ZrO₂/HA coatings on Zr is limited. Plasma spraying is one of the most widely adopted processes. ZrO₂/HA composite coating on Zr by plasma spraying revealed that the addition of HA to ZrO₂ showed undoubtedly superior biological properties to that of ZrO₂ coating, while maintaining its biocompatibility [19]. However, plasma sprayed coatings lack reliability as a result of residual stress and further, it is not possible to prepare uniform coatings on Zr implants with complex geometries. In recent years, electrophoretic deposition [EPD] is gaining more interest to produce ZrO₂/HA composite coatings. EPD is a simple, inexpensive and highly versatile coating technique for the development of ceramic coatings, in which coatings are formed on the electrode by migration of charged ceramic particles under the influence of an electric field [20]. Additionally, in the context of orthopedic and dental implant coatings, EPD has been proposed especially for the fabrication of bioactive glass coatings or composite coatings combining bioactive glass with other ceramics from organic or aqueous suspensions [21]. However, EPD requires a post-heat-treatment process to improve the adhesion of the coatings to the substrate.

Thus, in order to combine the potential advantages of PEO and EPD processes, in this study, a novel and rather simple approach based on coupling the PEO and EPD processes [hereafter named as “PEOEPD”] has been employed to fabricate bioactive ZrO₂/HA composite film on Zr substrate in a single step. For this purpose, charged HA nanoparticles were added to base electrolyte to develop ZrO₂/HA film on Zr substrate. In order to study the ZrO₂/HA film formation during the process and also to simultaneously understand the nature of phases being formed and associated phase transformations, PEOEPD was performed on Zr substrate as a function of treatment time in the duration of 2, 4 and 6 min. Based on the analysis of experimentally obtained data pertaining to the surface morphology, phases evolution and surface roughness as a function of PEOEPD treatment time, the ZrO₂/HA composite film formation mechanism has been explained. Further, the efficacy of ZrO₂/HA composite film on in-vitro corrosion resistance, bioactivity and biocompatibility of PEOEPD treated Zr substrate has been investigated.

2. Materials and methods

2.1. Materials

Commercially available Zr [purity > 99.5 wt.%] coupons with the dimensions of 20 mm × 15 mm × 1.5 mm were used as substrate material in the present study. Prior to PEOEPD treatment, the specimens were ground with SiC abrasive paper [with five grades: 80, 240, 400, 800 and 1200 grit] and then cleaned ultrasonically with acetone and de-ionized water bath to avoid surface contamination. The development of ZrO₂/HA composite film involves three steps, namely synthesis of HA nanoparticles, preparation of electrolyte and finally PEOEPD treatment. In the present study, HA nanoparticles were prepared by microwave synthesis method. Analytical grade calcium hydroxide [Ca(OH)₂, E. Merck, Germany] and di-ammonium hydrogen phosphate [DAP, (NH₄)₂HPO₄, E. Merck, Germany] were used for the synthesis of HA nanoparticles.

The experimental procedure for microwave synthesis of nanosized HA [15–20 nm width and 60–80 nm length] particles was reported in one of the author's previous study [22].

2.2. Preparation of PEOEPD electrolyte

HA aqueous suspension was prepared by adding 5 g of HA powder, 10 ml of ethylene glycol [C₂H₆O₂, Merck, India] and 5 ml of triethanolamine [C₆H₁₅NO₃, Merck, India] simultaneously to 1 l of distilled water taken in a conical flask. Ethylene glycol was used to charge HA nanoparticles negatively, while triethanolamine was used to stabilize the suspension of nanoparticles. The aqueous HA suspension was then sonicated using an ultrasonic vibrator [Sonics, 750 W, 20 kHz, USA] for 45 min to obtain a stable dispersion. Later, 5 g of tri-sodium ortho phosphate [TSOP; Na₃PO₄·12H₂O, Merck India Pvt. Ltd.] was added and then dissolved in the prepared aqueous HA suspension under uniform magnetic stirring conditions. This TSOP dissolved aqueous solution with negatively charged HA particle suspension serves as electrolyte for PEOEPD process.

2.3. Development of ZrO₂/HA films by PEOEPD treatment

For PEOEPD treatment, the electrolyte prepared in the previous step was taken into a stainless steel bowl which serves as cathode and Zr coupons immersed in electrolyte serve as anode. The PEOEPD treatment was performed at constant current density of 150 mA/cm², frequency of 50 Hz and duty ratio of 95% for 6 min of treatment time using a pulsed DC power supply unit [Milman Thin Films Pvt. Ltd., Pune, India] of 900 V/15 A capacity. More technical details about the experimental set up employed in the present study were reported in our previous work [13]. During the PEOEPD process, at higher voltages, the negatively charged HA particles that are dispersed in the electrolyte are attracted and migrate toward the anode (Zr substrate) due to the electric field between anode and cathode, and eventually gets deposited into the oxide film grown via PEO process. Thus, formation of oxide layer via PEO and deposition of charged HA particles into oxide film via EPD will take place simultaneously, thereby forming ZrO₂/HA composite layer. In order to study the ZrO₂/HA composite film formation mechanism, PEOEPD process was interrupted at 2 and 4 min of treatment time. After the PEOEPD treatment, the samples were taken out from the electrolyte, washed with distilled water, air dried at room temperature and stored in vacuum desiccator for further characterization. The identification codes for the PEOEPD treated Zr samples at 2, 4 and 6 min treatment time were hereafter represented as HA2, HA4 and HA6, respectively, while the substrate was referred as “S”.

2.4. Surface characterization of ZrO₂/HA composite films

The phase composition of HA2, HA4 and HA6 films were studied by a Rigaku Ultima III X-ray diffractometer [40 kV, 30 mA] with a Cu K_α [λ = 1.5406 Å] radiation over a 2θ range from 20° to 70° with a scan speed of 1° min⁻¹ and a step size of 0.05°. The corresponding phases were identified by matching relevant data from the JCPDS [Joint Committee on Powder Diffraction Standards] cards. To provide further information on phase composition, Raman spectral analysis was performed on the surfaces of HA2, HA4 and HA6 films by WiTec Raman spectroscopy [Alpha300, Germany] using Nd:YAG laser light of 532 nm wavelength. The surface morphology, film thickness, elemental composition and mapping of HA2, HA4 and HA6 films were observed using scanning electron microscope [SEM, Hitachi, S3000 N] equipped with energy-dispersive X-ray spectroscopy [EDS]. Before SEM analysis, PEOEPD treated samples were sputtered with a thin gold layer to make the coating surfaces conductive. The average surface roughness [R_a] of untreated Zr and HA2, HA4 and HA6 samples was measured using surface profilometer [Surtronic 25, Taylor-Hobson, Precision, UK] with accuracy of 0.01 μm. Contact angle of untreated Zr and HA2,

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