



Direct fabrication of crystalline hydroxyapatite coating on zirconium by single-step plasma electrolytic oxidation process



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ABSTRACT

This is the first report on the growth of a crystalline hydroxyapatite (HA) coating on zirconium substrate using a facile plasma electrolytic oxidation (PEO) method. The crystalline HA layers were fabricated in a $\text{Ca}(\text{CH}_3\text{COO})_2 \times 5\text{H}_2\text{O}$, $\text{C}_3\text{H}_7\text{Na}_2\text{O}_6\text{P} \times 5\text{H}_2\text{O}$, and KOH containing electrolyte. The prepared coatings were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), contact angle goniometry (CAG) and energy dispersive spectroscopy (EDS). In addition, Fourier transform infrared spectroscopy (FTIR) was used to examine the molecular bond structure of the coating. The results revealed that the composition of the oxide layer formed on zirconium surface includes hydroxyapatite, calcium zirconium oxide, and monoclinic zirconia. The FTIR and XRD results confirmed the formation of crystalline HA layers on the surface of Zr substrate. It was concluded that PEO of Zr substrate is a valid method to prepare crystalline HA coatings with a low contact angle value for biomedical applications due to its easy and fast nature.

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1. Introduction

Zirconium (Zr) and zirconium-based materials have gained some interest for biomedical and dental applications due to their chemical and dimensional stability, high flexural strength, fracture toughness, corrosion resistance, and good biocompatibility [1–7]. In addition, the lower elastic modulus of Zr and Zr-based alloys makes them potential alternatives to titanium-based implant materials [8,9]. On the one hand, the lower elastic modulus of Zr (92 GPa), which is relatively close to the elastic modulus of bone (10–30 GPa), minimizes the stress shielding effect of the host bone compared to other commonly used implants including Ti and its alloys (100–110 GPa) and stainless steel (189–205 GPa) [8,9]. On the other hand, recent studies showed that in order to use Zr-based materials in biomedical applications, the cell growth capability of these materials needs to be improved [1,2,8–18].

A great deal of effort has been devoted to address the aforementioned challenges of Zr-based systems in biomedical and dental applications. For this purpose, various surface treatment techniques including physical or chemical vapor deposition, sol–gel process, thermal oxidation, anodization and plasma electrolytic oxidation (PEO) have been employed to enhance the corrosion resistance and the bioactivity [9, 10, 12, 15, 17–22]. Among these surface treatment methods, PEO offers more advantages because it produces well-adhered, crystalline, dense,

and thick coating layers with high tribological performance and high thermal–chemical stability [23–35]. Cheng et al. [36] studied the corrosion resistance of a ZrO_2 coating fabricated on Zircoloy 4 (Zr-1.2–1.7 wt.% Sn) using a PEO method. The authors showed that the corrosion resistance of the material increased after the PEO process, depending on the coating thickness. Wang et al. [37] modified the surface of a Zr-2.5 wt.% Nb alloy with ZrO_2 using a PEO process as a function of varying operation frequencies. The corrosion test results indicated that the coated material had a much higher corrosion resistance compared to its pristine counterpart.

Although the modification of Zr surface with a ZrO_2 layer enhances the corrosion resistance, the obtained oxide surface has been reported to have low bioactivity, which is required to be improved [38]. Yan et al. [12] aimed to enhance the bioactivity of ZrO_2 coating by conducting a PEO process in a Ca-containing solution to modify the ZrO_2 lattice with Ca^{2+} ions. The authors reported that the introduction of Ca^{2+} ions into the ZrO_2 lattice accelerated the formation of HA on the ZrO_2 surface. The same authors also tried to enhance the bioactivity of the coating surface by etching the surface with acidic and alkaline solutions. They observed that while the etched surface induced the formation of HA in simulated body fluid (SBF) in one day, the untreated surface did not show any activity even after 30 days [16]. In another approach, Han et al. [11] prepared ZrO_2 coatings on Zr surface and then irradiated the coated surface with ultraviolet light (UV). The results showed that the UV irradiation resulted in the formation of abundant Zr-OH groups on the surface, which in turn improved the bioactivity of the ZrO_2 -coated surface. Recently, a study in which HA

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nanorods were used to modify a ZrO_2 coating was published by Zhang et al. [15]. In the mentioned work, the authors prepared HA nanorods hydrothermally on ZrO_2 -coated Zr substrates. Sandhyarani et al. [8] described the use of a single step approach to prepare HA-decorated ZrO_2 surface. Specifically, the surface of Zr substrate was oxidized in a HA particle-suspended electrolyte solution. Based on the XRD and Raman results, a ZrO_2 /HA composite with non-crystalline HA phase was prepared.

Up to now, some work has been conducted to improve corrosion resistance and bioactivity of Zr and Zr-based materials for biomedical applications using various post-treatment methods [15,36]. Although the reported results are promising towards addressing the aforementioned problems, the proposed methods either contain multi-step processes, or do not produce a crystalline HA layer on the substrates. The main objective of the present work is to prepare crystalline a HA layer on Zr substrates with possibly enhanced bioactivity by a single-step PEO process. The prepared HA coatings were characterized using XRD, SEM, EDS, CAG, and FTIR.

2. Materials and methods

This contribution is a part of systematical study conducted in our laboratory to investigate the effect of process parameters such as electrical parameters and electrolyte on the properties of the resulting coating layers. In this paper, a portion of this systematic study is reported.

Zirconium substrates with the dimensions of $50 \text{ mm} \times 25 \text{ mm} \times 0.7 \text{ mm}$ were prepared from pure zirconium sheets (99.5%) (Alfa Aesar-Production no. 44253). The surface of the substrates was ground and polished using SiC papers (600–1200 grits) and diamond paste (3 and $1 \mu\text{m}$), respectively. Subsequently, the substrates were cleaned in an ultrasonic bath containing ethanol for 5 min.

The PEO process was carried out using a homemade PEO unit equipped (ELCON S.R.L Company) with a pulsed bipolar DC power supply for 5 min in a $30 \text{ g/l Ca}(\text{CH}_3\text{COO})_2 \times 5\text{H}_2\text{O}$, $8 \text{ g/l C}_3\text{H}_7\text{Na}_2\text{O}_6\text{P} \times 5\text{H}_2\text{O}$ powders and 2 g/l KOH granules containing electrolyte. The positive and negative current density values, and the pulsing frequency were set to 4 A/cm^2 and 400 Hz , respectively. The anodic (t_{on}^+) and cathodic (t_{on}^-) pulse values were both set to $500 \mu\text{s}$ and pulse break duration (t_{off}^+ and t_{off}^-) was $250 \mu\text{s}$ (Fig. S1). The coated Zr samples were washed with distilled water and ethanol successively and dried under air flow.

The thickness of the coating layer was measured using the eddy current method. Measurements were taken at ten different locations and the coating thickness values reported are their averages. X-ray diffraction data were recorded using a Rigaku D-MAX 2200 X-ray diffractometer (XRD) with a $\text{Cu K}\alpha$ radiation at the scan rate of 2° min^{-1} . The phase identification was applied through MDI-Jade phase analysis program. The microstructure, morphology, and chemical composition of the samples were examined using a SEM FEI/Philips XL30 FEG ESEM equipped with EDS. Bond structure and the surface functional groups of the coated samples were studied by Fourier transform infrared spectroscopy (FTIR; Perkin Elmer Spectrum 100) in the spectral range of $500\text{--}4000 \text{ cm}^{-1}$. The wettability of pristine substrate and the coating layer was measured using a Rame-Hart Contact Angle Goniometer (CAG). Deionized water droplet was applied to the surface of the samples at room temperature to calculate the static contact angle values. The measurements were conducted at three different sample locations.

3. Results and discussion

3.1. Phase analysis

The XRD pattern of the HA-coated Zr sample is shown in Fig. 1. The coating layer contained three different phases; hydroxyapatite-HA (JCPDS card no: 009-06423, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), calcium zirconium oxide-Ca-PSZ (JCPDS card no: 26-341, $\text{Ca}_{0.134}\text{Zr}_{0.86}\text{O}_{1.86}$), and monoclinic zirconia-baddeleyite (JCPDS card no: 072-1669, m- ZrO_2). The

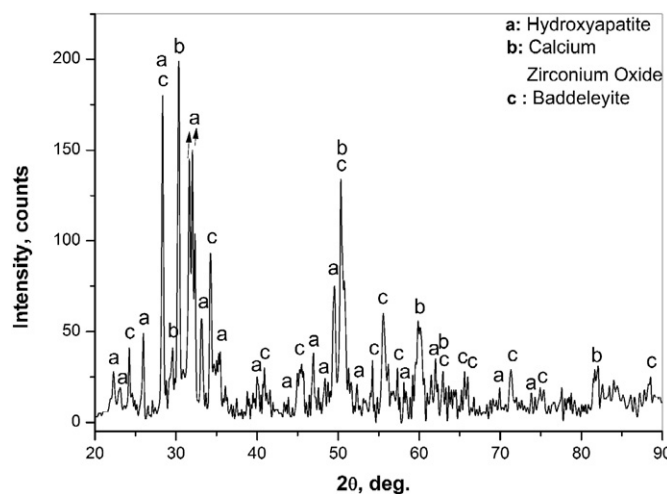


Fig. 1. The XRD patterns of coating layer on zirconium substrate.

presence of c- ZrO_2 phase which is stable above 2370°C is explained by the incorporation of Ca^{2+} ions into the ZrO_2 lattice. This phenomenon resulted in the formation of stabilized Ca-PSZ in the coating layer [9,12,39]. The growth of a crystalline HA layer during the PEO process is attributed to the formation of high energy pulses, which in turn induces complex reactions between Ca^{2+} and PO_4^{3-} ions on the substrate surface (Eq. (3)) [40,41]. It was reported that during the surface oxidation, high energy sparks are formed on the surface of the substrate, thus, the temperature and the pressure at these regions may be as high as 10^4 K and 10^3 MPa , respectively [42–45]. The high temperature and pressure values on the spark regions enable electro- and thermochemical oxidations of substrate surface in the electrolyte. The crystallinity of the HA was highlighted by the presence of characteristic HA peaks in the XRD pattern. It is known that the crystallinity and morphology of HA phases play a key role in cell growth, cell activity, and the stability of the implant materials [46–49]. In other words, non-crystalline calcium phosphate phases are not desired since their solubility is high in body fluid, which in turn results in instability problems when implanted [48,50,51]. These results confirmed the use of PEO as an effective method to prepare crystalline HA coatings on Zr substrates.

FTIR was used as a complementary method to X-ray diffraction to confirm the successful fabrication of HA layer on Zr surface. The recorded FTIR data shown in Fig. 2 exhibited several peaks located at 560, 863,

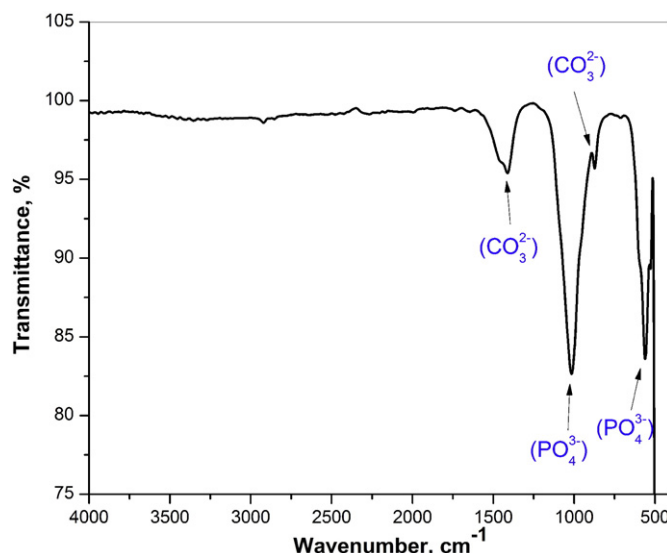


Fig. 2. FTIR results obtained from the coated materials.

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