



Electrophoretic enhanced micro arc oxidation of ZrO₂-HAp-TiO₂ nanostructured porous layers

F. Samanipour^a, M.R. Bayati^{a,b,*}, H.R. Zargar^c, F. Golestani-Fard^{a,d}, T. Troczynski^c, M. Taheri^a

^a School of Metallurgy and Materials Engineering, Iran University of Science and Technology, P.O. Box 16845-161, Tehran, Iran

^b Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, USA

^c Department of Metals and Materials Engineering, University of British Columbia, Vancouver, BC V6T 1Z4, Canada

^d Center of Excellence for Advanced Materials, Iran University of Science and Technology, P.O. Box 16845-195, Tehran, Iran

ARTICLE INFO

Article history:

Received 9 May 2011

Received in revised form 11 July 2011

Accepted 13 July 2011

Available online 23 July 2011

Keywords:

Micro arc oxidation

Electrophoretic deposition

Composite

Coating

Porous

ABSTRACT

Micro arc oxidation (MAO) and electrophoretic deposition (EPD) processes were simultaneously employed to grow ZrO₂-HAp-TiO₂ porous layers on titanium substrates under different conditions. Influence of the electrolyte composition and the growth time on surface morphology, topography, phase structure, and stoichiometry of the layers was investigated. The utilized electrolytes consisted of β-glycerophosphate, calcium acetate, sodium phosphate, and micron sized yttria-stabilized zirconia with different concentrations. AFM and SEM evaluations revealed a rough surface with a porous structure with a pores size of 50–750 nm. The pores size increased with the time and the electrolyte concentration. Based on the XRD and XPS results, the layers consisted of anatase, hydroxyapatite, monoclinic ZrO₂, tetragonal ZrO₂, ZrO, CaTiO₃, and α-TCP phases whose fractions were observed to change depending on the synthesis conditions. The average crystalline size of the HAp phase was determined as ~54 nm. The nano-sized zirconia particles (*d* = 20–60 nm) were dispersed not only on surface, but also in depth of the layers. Utilizing thicker electrolytes and prolonging the growth time resulted in decomposition of hydroxyapatite as well as tetragonal ZrO₂ to monoclinic ZrO₂. EDX results also showed that the zirconium wt% in the layers increased with the time. EPD-enhanced MAO (EEMAO) technique was expressed as an efficient route to fabricate ZrO₂-HAp-TiO₂ multiphase systems within short times and only in one step.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, much attentions have been directed to hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) as a substitute material for damaged teeth or bones due to its similarities with mineral component of hard tissues of vertebrates [1–3]. Its bioactivity results in proliferation of osteoblasts to HAp [4,5]. Unfortunately, this biomaterial has poor mechanical properties and, hence, is not suitable for load-bearing conditions [6,7]. HAp is brittle and weak and the clinical orthopedic and dental applications are limited due to its unfavorable mechanical properties [8,9]. Therefore, it is essential to mechanically support it for the long-term performance. To do that, titanium and its alloys have been used widely as load-bearing implants due to their excellent mechanical toughness, strength, biocompatibility, and corrosion resistance [10–12].

Another approach to enhance mechanical properties of HAp is reinforcing it with other ceramics [13]. To be effective as a reinforcing agent for a ceramic–matrix composite material, the strength of the second phase must be higher than that of the matrix [14]. An appropriate implant material would be a bioceramic composite, formed by a bioactive ceramic such as HAp and a bioinert phase namely zirconia and alumina [15–17]. Zirconia has excellent technological properties and characteristics namely chemical and thermal stability, wear resistance, high strength and fracture toughness, and bioinertness [18–21]. Combining hydroxyapatite and zirconia, favorable mechanical properties and bioactivity is achieved [22,23]. Thus, HAp–zirconia composites have shown promising improvements in strength, hardness, and toughness as compared to the pure HAp [24,25].

The HAp-based composite coatings have been already synthesized via various methods such as sintering [26], micro arc oxidation [27], sol–gel [28,29], mechanosynthesis [30], and simulated body fluid method [31]. In this study, electrophoretic deposition (EPD) and micro arc oxidation (MAO) processes were used to fabricate the HAp–ZrO₂ layers. The phenomenon of electrophoresis has been known since the beginning of the 19th century and it has found applications during the past 40 years mainly

* Corresponding author at: Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, USA. Tel.: +1 919 917 6962; fax: +1 919 515 7724.

E-mail address: mbayati@ncsu.edu (M.R. Bayati).

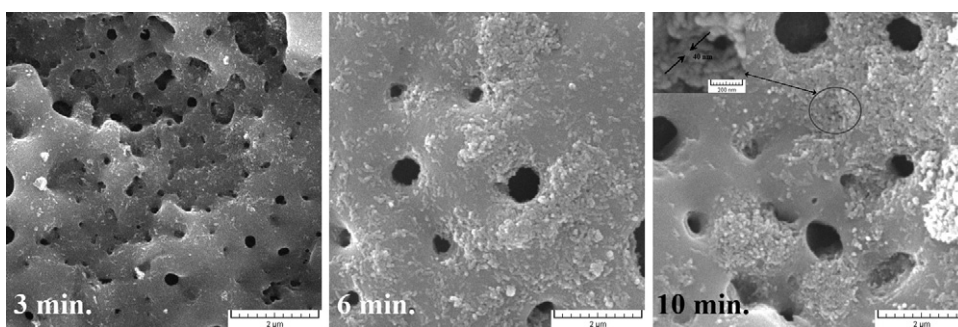


Fig. 1. SEM surface morphology of the composite layers fabricated in the electrolyte A for different times.

in traditional ceramic technology [32,33]. EPD is a simple and inexpensive technique making it possible to synthesize a wide range of coatings with varying morphologies and chemical compositions. This method has been developed to fabricate a variety of dense, nanostructured functional films. Electrophoretic deposition has attracted increasing attention that it can fabricate ceramic films with desirable thickness and parts with complicated shapes. Because of this capability, we employed EPD process to introduce oxide powder to a porous film grown via MAO method. Here, the powder particles dispersed in the liquid medium are attracted and migrate toward the electrode of opposite polarity on which they eventually get deposited [34–37]. MAO is a relatively convenient and effective technique for depositing various functional coatings with porous structures on the surfaces of Ti, Al, Mg and their alloys. In other words, it is a simple and promising approach for fabrication of different categories of oxide layers. It is an electrochemical technique for formation of anodic films by spark/arc microdischarges which move rapidly on the vicinity of the anode surface [38–41]. It is characterized by high productivity, economic efficiency, ecological friendliness, high hardness, good wear resistance, and excellent bonding strength with the substrate [42–44]. Moreover, it is very suitable for modifying various substrates with complex geometries [45]. In biomedical field, MAO has been used to improve the bioactivity of titanium implants [46–49]. More details about MAO [50–54] and EPD [55] methods can be found elsewhere. Employing MAO process, a wide range of ceramic coatings with different chemical compositions can be fabricated [56–62].

In our previous work, ZrO_2 -HAP- TiO_2 system was grown onto titanium substrate through EPD-enhanced MAO (EEMAO) process and effect of the applied voltage and the electrolyte concentration on their properties was investigated [63]. In this study, such layers are derived by EEMAO method and the influence of the electrolyte composition and the growth time on physical and chemical features of the layers is investigated. To the best of our knowledge, this is the first time that such layers are fabricated employing EEMAO technique, even though such layers have been already synthesized via other methods with varying morphologies. Beauty of this work

is that we could get nano-sized ZrO_2 particles in the layers, while added micron-sized powder to the electrolyte.

2. Experimental

Commercially pure grade II titanium foils with dimensions of $30\text{ mm} \times 15\text{ mm} \times 0.5\text{ mm}$ were used as substrate. Before coatings synthesis, the substrates were mechanically polished by abrasive paper No. 600 and, then, chemically etched in diluted HF solution (HF:H₂O = 1:20 vol.%) at room temperature for 30 s. Afterward, the substrates were ultrasonically cleaned in acetone for 15 min. The substrates were washed by distilled water after each step. The electrolytes were prepared by dissolution of the β -glycerophosphate disodium (C₃H₇Na₂O₆P, Merck) and calcium acetate (Ca(CH₃COO)₂, Panareac) salts with concentrations of 1 and 5 g l^{-1} in 75 vol.% DI-water and 25 vol.% ethanol. Then, micron-sized yttria-stabilized zirconia (8% mol, Tosoh) powder, with concentrations of 1 g l^{-1} (electrolyte A) and 5 g l^{-1} (electrolyte B), was mixed with the suspension by jar-milling for 48 h at room temperature. The pH of the suspensions was adjusted around 11.5 through the addition of sodium phosphate (Na₃PO₄·12H₂O, Panareac). Reason for choosing such a high pH is inducing negative charge on zirconia particles in the solution. Moreover, HAP and titania can grow easier in the basic electrolytes. Electrolyte temperature was fixed at $70 \pm 3^\circ\text{C}$ employing a water circulating system. The MAO/EPD treatment was carried out in the prepared solutions under the voltage of 350 V (direct current) for various times.

Surface morphology of the layers was examined by scanning electron microscope (TESCAN, Vega II). AFM (Veeco, Auto probe) method was also employed to evaluate surface topography of the fabricated samples. Surface roughness was determined by the AFM original software (Proscan ver. 1.7). X-ray diffraction (Rigaku, Multiflex), energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy (VG Microtech, Twin anode, XR3E2 X-ray source, using Al K α = 1486.6 eV) techniques were used to study phase structure and chemical composition of the synthesized layers. The peak fitting procedure and interpretation of the XPS results were fulfilled by SDP software ver. 4.1.

3. Results and discussion

SEM surface morphology of the layers grown at different times is depicted in Figs. 1 and 2 where formation of a porous structure is evident. The structural pores from by the electron avalanches taking place on the substrate [59,64]. As is seen, the pores size increases with the treatment time, from about 0.1–0.5 μm for 3 min to about 0.5–1.5 μm for 10 min treatment. It has been shown before that when a structural pore forms by an electrical spark during MAO,

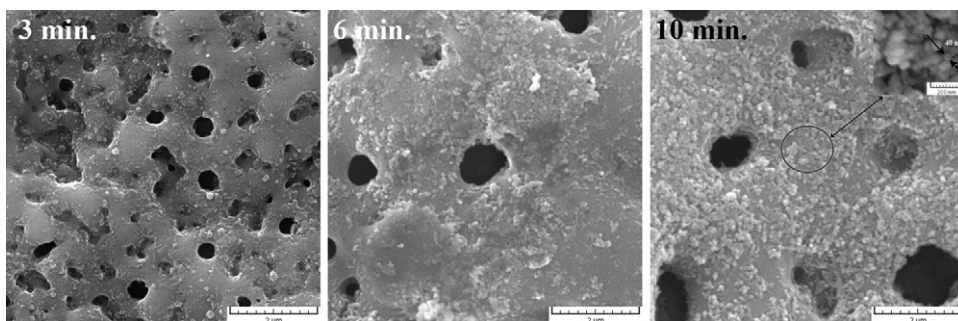


Fig. 2. SEM surface morphology of the composite layers fabricated in the electrolyte B for different times.

Download English Version:

<https://daneshyari.com/en/article/1616755>

Download Persian Version:

<https://daneshyari.com/article/1616755>

[Daneshyari.com](https://daneshyari.com)