Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 4885–4893

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Modification of electrophoretically deposited nano-hydroxyapatite coatings by wire brushing on Ti–6Al–4V substrates

Hamidreza Farnoush [a], Jamshid Aghazadeh Mohandesi [a,*], Davoud Haghshenas Fatmehsari [a], Fathollah Moztarzadeh [b]

[a] *Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*
[b] *Biomedical Engineering Department, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*

Received 15 February 2012; received in revised form 24 February 2012; accepted 24 February 2012
Available online 5 March 2012

Abstract

In the present study, after successful synthesis of nano-HA powders by chemical precipitation method, wire-brushing (WB) treatment was effectively employed on Ti–6Al–4V substrates for the modification of electrophoretically deposited nano-hydroxyapatite coatings. The precipitated nano-HA particles were characterized by XRD, FT-IR, and DLS analyses. The morphology and particle size of synthesized nano-HA particles was observed by FE-SEM. The Ti–6Al–4V plates were initially wire brushed at different times and rotational speeds. Microhardness profile and AFM analysis of substrates were then studied. It was found that WB treatment at 16,000 rpm for 60 s leads to a maximum enhancement in the hardness and roughness of surface. Then, the electrophoretic deposition of nano-HA particles was carried out at constant voltage of 30 V and after 60 s. The results of adhesion test and potentiodynamic polarization measurements showed that WB treatment on Ti–6Al–4V substrates could efficiently increase the bonding strength between coating and substrate as well as corrosion resistance.

Keywords: A. Powders: chemical preparation; B. Surfaces; C. Strength; D. Apatite; E. Biomedical applications; Electrophoretic deposition

1. Introduction

Titanium and its alloy have been widely utilized in biomaterial applications due to their relatively excellent corrosion resistance, favorable biocompatibility, and high specific strength (strength per density) [1]. Regarding the poor osteoinductive properties of Ti, the use of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) coatings has received considerable attention [2]. On the other hand, HA is a very brittle bioactive ceramic material and the fabrication of HA coatings on tough metallic substrates take the advantages of both mechanical properties of metal substrates and biological performances of HA ceramics [2]. Among different techniques employed for preparing HA coatings on a metallic substrate, such as plasma spray [3,4], sol–gel [5,6], biomimetic [7,8] and ion implantation [9], electrophoretic deposition (EPD) [10,11] is an effective technique for the fabrication of dense and uniform HA coatings even on the substrates with complex geometries. This technique has the advantages of high production rate and low investment cost [12]. However, the poor adhesion strength between HA coating and Ti substrate limits its clinical application [12].

In fabrication process of Ti/HA coatings, due to degradation of metallic substrate and decomposition of HA, sintering temperatures should be below 1000 °C under which HA is difficult to be fully densified [13–15]. Furthermore, the thermal expansion coefficient of titanium substrate is much lower than that of HA [16–18], and the thermal contraction mismatch results in the formation of cracks when cooled from the elevated temperatures; Also, a significant firing shrinkage during sintering results in the formation of cracks in coatings as well [19].

Mechanical surface modification methods, such as machining [20,21], polishing [22,23], and blasting [24–27], is typically implemented for achieving specific surface topographies and roughness, removing surface contamination, and/or improving adhesion in subsequent bonding steps. Wire brushing (WB), another mechanical surface modification technique, removes surface contaminated layers and oxide layers. More importantly,

---

* Corresponding author. Tel.: +98 21 64542949; fax: +98 21 64542941.
E-mail addresses: farnoush@aut.ac.ir (H. Farnoush), jamshidaghazadeh@gmail.com (J. Aghazadeh Mohandesi).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2012.02.079

it forms a hardened cover layer on the surface [28,29] and increases the surface roughness. Since the bonding strength of HA coating is substantially affected by the surface roughness of the substrate [30,31], this method can be potentially applied for the modification of electrophoretically deposited nano-hydroxyapatite coatings. To the authors' best knowledge, there is no through work reporting the influence of WB treatment on the bonding strength of HA coatings.

The present work addresses a fairly complete investigation of the effect of WB treatment on the bonding strength of nano-HA coatings. The optimum WB parameters (i.e. rotational speed and time) were chosen by microhardness and roughness analyses on the WB-treated Ti–6Al–4V substrates. Then, the electrophoretic deposition of synthesized nano-HA particles was studied in the ethanol-based suspension. Finally, the electrochemical corrosion behavior in SBF (simulated body fluid) solution and bonding strength of WB-treated and as-received samples were discussed.

2. Experimental procedures

2.1. Synthesis of nano-HA powders

Nanocrystalline hydroxyapatite powders were synthesized by precipitation method using $Ca(NO_3)_2 \cdot 4H_2O$ (CNT, Merck No. 141231) and $(NH_4)_2HPO_4$ (PHA, Merck No. 21,599-6) as starting precursors and ammonia solution for pH adjustment. Firstly, 0.29 M CNT and 0.24 M PHA solutions were separately prepared in double distilled water. Then, PHA solution was slowly added dropwise to the CNT solution. In all experiments the pH of CNT solution was 11. The suspension was heated to 80 °C, rigorously stirred for 1 h, and finally kept for 24 h of ageing at room temperature. The HA precipitate was then washed by thrice repeating the following three steps: centrifugation at the rotation speed of 3000 rpm, supernatant decantation, and re-suspension in de-ionized water. The gel obtained was dried at 65 °C for 24 h in a dry oven and calcined at 900 °C for 1 h. The structure of the resulting powder after drying was evaluated by Fourier transform infrared (FTIR, Nicolet Nexus 670) spectroscopy in the wave number range of 4000–400 cm^{-1}. The phase transformation during heat treatment and crystallite size evolutions were carried out by X-ray diffraction analysis (XRD, Philips PW 1480) with Cu K_α radiation ($\lambda = 1.5405$ Å). The Scherrer method was used to estimate the crystallite size. The size and morphology of the precipitated HA nano-particles were assessed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4160).

2.2. Wire brushing of Ti–6Al–4V substrates

The as-received material (AR) was 3-mm-thick mill-annealed Ti–6Al–4V plates with the chemical composition of Al 6.28, V 4.90, Fe 0.29, Nb 0.05, Mn 0.03. Cr 0.02, Si 0.05, Sn <0.05, Mo <0.03, Cu <0.02, Zr 0.01, and Ti balance (all in wt.%). Wire brushing (WB) was carried out using a 64-mm-diameter circumferential brush with 0.3-mm-diameter stainless steel wires. The whole surface of a 10 cm × 2 cm work piece was subjected to wire brushing. The sheet was fixed along the rolling direction and wire brushed for 45, 60, and 75 s. The wire brush was rotated at 12,000, 16,000, 21,000, and 27,000 revolutions per min (rpm), while a force of 2 kg was applied vertically to the surface of the sheets. Cross and lateral sections of the wire brushed samples were mounted, and then mechanically polished, followed by etching in an etchant composed of 2.5% HNO_3, 1.5% HF, and 96% distilled water. The phase composition of brushed surface was analyzed by XRD (Philips PW 1480) in $2\theta = 20–100°$ range. The hardness profile was obtained using a scanning microhardness tester with a load of 10 N. Surface roughness and topography of AR and WB samples were characterized by scanning probe microscope (SPM, DME DS-95-50E)

2.3. Electrophoretic deposition of nano-HA particles on Ti–6Al–4V substrates

The suspension was prepared by adding 1 g of HA powders into 50 mL of absolute ethanol (Merck, USA). The addition of 1 g/L iodine (dispersant) to ethanol was resulted in positively charged particles. The prepared suspension was dispersed in a 50 kHz ultrasonic bath for 60 min, and then was immediately used for electrophoretic deposition (EPD) without further aging. The particle size distribution of powders in the suspension was analyzed by dynamic light scattering (Malvern ZEN 3600). All measurements of dynamic light scattering (DLS) were carried out with slurries containing a 0.4 g/L solid loading. Ti–6Al–4V substrate as the working electrode and 316 L stainless steel as the counter electrode were immersed in the suspension with a fixed distance of 10 mm. Prior to deposition, Ti–6Al–4V substrates were polished from 400 to 1200 grid SiC papers, then washed out with detergent and degreased with acetone, and finally passivated in a HF (100 mL/L)–HNO_3 (300 mL/L) solution. One side of the cathode was masked with a nonconducting tape. The surface area of the cathode was 1 cm^2. The EPD process was conducted for 60 s under a constant voltage of 30 V. After deposition, the green coatings were dried in air for 24 h at room temperature. Sintering of the coatings was carried out in an argon-purged atmosphere at 900 °C. The heating rate and cooling rate were the same (100 °C/h) and the dwell time was 1.5 h. The phase composition of coated surface was analyzed by XRD (Philips PW 1480), by scanning in $2\theta = 20–100°$ range at a step size of 0.02° and a count time of 0.6 s. The micro-structural characterization and surface topography of the as-deposited sample was carried out by using SEM (Philips XL 30) and SPM (DME DS-95-50E), respectively. To investigate electrochemical corrosion behavior of coatings on Ti–6Al–4V with and without wire-brushing treatment, samples were embedded in cold-curing epoxy resin, exposing a surface area of 1 cm^2. Potentiodynamic polarization test in a corrected-SBF solution [32], open to air at 37.4 °C and at the physiological pH 7.40, was performed using AutoLab PGstat 30. The chemical composition of the employed SBF is given in Table 1. All potentials were measured with respect to a saturated calomel electrode. Two parallel graphite rods served as the counter