Journal of Alloys and Compounds 741 (2018) 211–222

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of morphology on the electrophoretic deposition of hydroxyapatite nanoparticles

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ARTICLE INFO

Article history:
Received 20 October 2017
Received in revised form
29 December 2017
Accepted 8 January 2018
Available online 11 January 2018

Keywords:
Spherical hydroxyapatite nanoparticles (SHA)
Fiber hydroxyapatite particles (FHA)
Electrophoretic deposition (EPD)
Alcoholic suspensions
Corrosion

ABSTRACT

Electrophoretic deposition (EPD) was performed from alcoholic suspensions of spherical (SHA) and fiber (FHA) hydroxyapatite nanoparticles. FHA particles were horizontally aligned in deposits prepared at lower voltages since they can find enough space and time to rotate upon reaching the deposit and sit horizontally on it. While, they are more randomly oriented at higher voltages since more FHA particles aligned parallel to electric field reach to the substrate and also particles cannot find enough time and space for rotation. FHA particles are highly interlocked together in FHA deposits reinforcing them and also the drying shrinkages are lower for them resulting in their less cracking. The cracks are parallel to each other in FHA coating deposited from methanolic suspension at 5 V due to the more horizontal and parallel alignment of FHA particles in it. The crack-free SHA coating decreased the corrosion rate of substrate more efficiently due to its less porosity.

1. Introduction

Hydroxyapatite (HA) is the calcium phosphate ceramic very similar to the inorganic part of the human bone and teeth both in morphology and composition [1,2]. HA has been widely used in biomedical applications because of its good bioactivity, biocompatibility, osteoconductivity and biodegradability [3–6]. However, compared to natural bone, HA has poor mechanical properties like low fracture toughness and hardness [7–12]. To overcome this problem, usually HA is applied as the coating on the metallic implants like titanium and 316L stainless steel. By this method the bioactivity of the implant is also promoted since HA surface has higher bioactivity than metallic surfaces. Also the corrosion rate of implant decreases considerably in body fluid when it is coated by HA or other corrosion resistant coatings [13,14]. The corrosion of implant releases the metallic ions into the surrounding tissues and can results in the implant failure [15]. Various techniques have been used to deposit HA coatings on the metallic substrate such as sol-gel, electrodeposition, thermal and plasma spray and so on [16–21]. Electrophoretic deposition (EPD) is another method which has been widely used to deposit HA coatings on the metallic substrates [22–33]. EPD is based on the movement of charged particles dispersed in a suitable solvent towards the oppositely charged electrode under the influence of an applied electric field and then their deposition on it [34]. EPD is a simple, low-cost and fast technique capable to control the microstructure and thickness of coatings by simple adjustment of process parameters like voltage and time [34]. The porous coatings can accelerate implant fixation by bone ingrowths into the pores [35–37]. One of the inherent characteristics of EPD is the porous nature of the coatings obtained by it [38]. So EPD is attractive method to deposit bioactive coatings on the metallic implants. In this work the effects of HA particles morphology (spherical and fiber) on the EPD process and the characteristics of obtained coatings have been investigated.

2. Experimental

Hydroxyapatite nanoparticles with spherical (SHA) and fiber (FHA) morphologies were synthesized by wet chemical methods described in Refs. [39] and [40], respectively. The synthesized powders were characterized by XRD, FTIR and SEM analysis. Different alcoholic (methanol (Merck, 99.99%), ethanol (Merck, 99.8%), isopropanol (Merck, 99.8%) and butanol (Merck, 99%)) suspensions of SHA and FHA particles (10 g/L) were prepared using triethanolamine (TEA, Merck, reagent grade) as the dispersing agent. Firstly, different concentrations of TEA (0, 0.67, 1.33 and 2.67 mL/L) were dissolved in alcohols by stirring magnetically for

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https://doi.org/10.1016/j.jallcom.2018.01.101
0925-8388/

15min. Then, 10 g/L of SHA and FHA particles were added into them followed by magnetic stirring for 24 h and finally ultrasonic dispersing for 10min. The zeta potential of particles was determined in different suspensions using Malvern instrument. The samples were diluted by the procedure described in Ref. [41]. Electrophoretic deposition (EPD) was performed at 60 V using a D.C power supply. *In-situ* kinetics of deposition and the current density during EPD were recorded according to the method reported in Ref. [41]. Voltage was applied for 6min and then switched off for 2min during *in-situ* recording of the EPD kinetics. Sticking parameter (*f* factor) was also calculated at initial times of EPD using the following equation [41]:

$$f = \frac{J_i}{J_i + J_d} \qquad (1)$$

where J_i and J_d are the mass flow of particles incorporated in and detached from the deposit, respectively. J_i and J_d are equal to the slope of kinetics curve at initial times of EPD and after switching off the voltage, respectively.

The wet density and wet thickness of deposits prepared at 60 V from different alcoholic suspensions of SHA and FHA particles with optimum concentration of TEA (TEA*) was determined against EPD times according to the method described in Ref. [42]. The dry thickness of coatings was also measured using a coating thickness gauges (Qnix 8500, Germany).

The microstructure of the SHA and FHA coatings deposited at 60 V for 1min from the suspensions with optimum concentration of TEA (TEA*) was observed by optical (OM) and electron (SEM) microscopes.

The corrosion rate of bare and coated substrates in simulated body fluid (SBF) at 37.5 °C was measured by electrochemical polarization method. SBF was synthesized according to the method described in Ref. [43]. The coatings for corrosion studies were deposited at 60 V for 1min from different alcoholic suspensions of SHA and FHA particles with TEA*. The coatings were dried overnight at room temperature and then sintered at 800 °C for 1 h (heating rate: 4 °C/min) under the flowing argon gas atmosphere.

3. Results and discussion

Fig. 1 shows the XRD pattern of the synthesized SHA and FHA powders. As can be seen the spectra of both powders only show the characteristic peaks of hydroxyapatite proving their high purity. Also the spectra of FHA particles have more intensive and narrower peaks implying their more crystallinity and/or coarser primary particles size. The SEM image from the synthesized SHA and FHA particles is shown in Fig. 2. The SEM images verify the spherical and fiber morphologies of synthesized SHA and FHA particles, respectively. Also FHA particles are relatively coarser than SHA particles in agreement with the XRD pattern. The FTIR spectra of the SHA and FHA particles are shown in Fig. 3. The related bonds are also specified for each peak. The peaks at 565, 600, 1038 and 1088 cm^{-1} are attributed to phosphate groups ((PO4)$^{3-}$) [44]. The symmetric stretching vibration of P-O bond results in the peak at 961 cm^{-1} [45]. The peaks at 1628 and 3420 cm^{-1} are due to the water adsorbed on the particles [46,47]. The peaks around 632 and 3573 cm^{-1} are related to OH$^-$ groups of HA [48]. The peaks around 1420, 1450 and 873 cm^{-1} are due to the carbonate groups (CO_3^{2-}) in HA [45,47]. In contrast to SHA particles, there are no peaks at 1420 and 1450 cm^{-1} in the spectra of FHA particles. Also the intensity of peaks attributed to OH$^-$ groups is weaker in case of SHA particles. These results imply that OH$^-$ groups of SHA particles are partially substituted by carbonate ions; so SHA particles are partially carbonated.

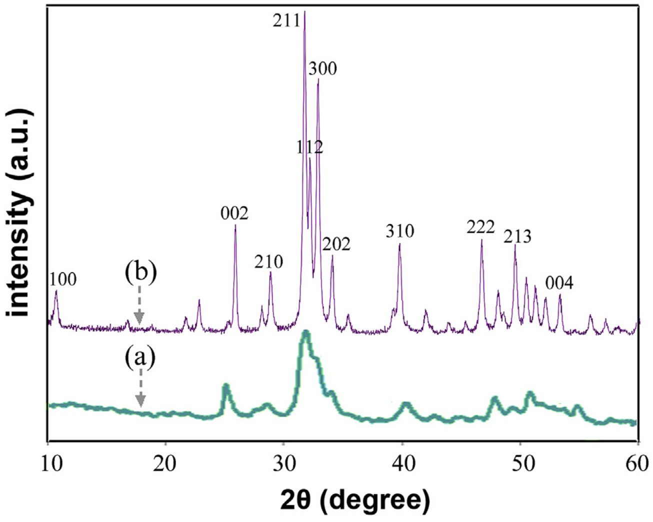

Fig. 1. XRD pattern for synthesized (a) SHA and (b) FHA powders.

The zeta potential of SHA and FHA particles in different alcoholic suspensions against TEA concentration is shown in Fig. 4. As can be seen, firstly the zeta potential of both SHA and FHA particles increases with TEA addition until reaching the maximum value (at TEA*) and then decreases with its further addition. It was found in author previous work [28] that H$^+$TEA ions are generated through the protonation of TEA in alcoholic suspensions; these H$^+$TEA ions are then chemically adsorbed on the surface of HA particles via hydrogen bonding with their surface P-OH groups leading to the increase in their surface charge and so zeta potential. The surface of particles is saturated by H$^+$TEA ions at TEA* so that it's further addition only results in the reduction in double layer thickness and so zeta potential. The optimum concentrations of TEA are 0.67, 0.67, 1.33 and 2 mL/L in methanolic, ethanolic, isopropanolic and butanolic suspensions of SHA particles, respectively. In case of FHA particles, the optimum concentrations are 0.67, 2, 0.67 and 1.33 mL/L in methanolic, ethanolic, isopropanolic and butanolic suspensions, respectively.

The variations of current density during EPD at 60 V from different alcoholic suspensions of SHA and FHA particles are shown in Fig. 5. As can be seen the current density decreases during EPD for all suspensions except the TEA containing methanolic suspensions of SHA particles. Also current density decreases more rapidly in case of FHA suspensions. The reduction in current density during EPD is due to the formation of layer with higher resistivity than the corresponding suspension. The wet EPD deposits are composed of ceramic particles with extremely large resistivity dispersed in the continuous liquid phase with less resistivity; so the resistivity of deposits is nearly equal to that of their continuous interparticles liquid phase. The higher the volume fraction of liquid phase in the deposit the lower is its resistance. Compared to SHA deposits, the volume fraction of interparticles liquid phase is less in FHA deposits due to the coarser size of FHA particles leading to their higher resistance and so faster current density reduction for them.

Fig. 6 shows the *in-situ* kinetics of EPD at 60 V from different alcoholic suspensions of SHA and FHA particles. The weight of deposits continuously increases in the period of time when the voltage is connected (0–6min). The deposition weight remains constant in case of all FHA and SHA suspensions without TEA after switching off the voltage. However, it decreases with time for TEA containing SHA suspensions after switching off the voltage. Reduction in deposition weight after switching off the voltage is because of the particles detachment from deposit into the