

Fabrication and in vitro characterization of magnetic hydroxycarbonate apatite coatings with hierarchically porous structures

Yaping Guo, Yu Zhou*, Dechang Jia, Qingchang Meng

Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 433, Harbin 150001, China

Received 28 August 2007; received in revised form 15 February 2008; accepted 19 February 2008

Available online 4 March 2008

Abstract

Hydroxycarbonate apatite/ Fe_3O_4 composite coatings (MHACs) with hierarchically porous structures were fabricated by electrophoretic deposition of $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ particles on Ti6Al4V substrates followed by treatment with phosphate buffer solution (PBS) at 37 °C. The effects of Fe_3O_4 on the conversion rate of calcium carbonate to hydroxycarbonate apatite and the porous structures and in vitro bioactivity of MHACs were investigated. After soaking $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ coatings in PBS, hydroxycarbonate apatite nucleates heterogeneously on the surfaces of $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ particles and forms a plate-like structure. Fe_3O_4 increases the velocity of nucleus formation of hydroxycarbonate apatite. After soaking for 1 day, the percentage of unreacted calcium carbonate for MHACs is ~9.1%, lower than the ~41.0% for hydroxycarbonate apatite coatings (HCACs). As the $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ coatings are converted to MHACs, macropores with a pore size of ~4 μm on the coatings and mesopores with a pore size of ~3.9 nm within the hydroxycarbonate apatite plates are formed. The mesopores remain in the MHACs after treatment with PBS for 9 days, while they disappear in the HCACs. Simulated body fluid immersion tests reveal that Fe_3O_4 improves the in vitro bioactivity of biocoatings. The amount of bone-like apatite precipitated on the surfaces of MHACs is greater than that on the surfaces of HCACs.

© 2008 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Coating; Hydroxycarbonate apatite; Porous structure; Calcium carbonate; Magnetism

1. Introduction

Highly crystalline and stoichiometric hydroxyapatite (HA) crystals with a Ca/P molar ratio of 1.67 have been commonly applied to artificial bone graft substitutes as bulk and film forms in recent years. HA with a hexagonal structure in the space group $P6_3/m$ has anisotropic magnetic properties [1], so the crystal growth may be influenced under external high magnetic fields [2–5]. The *a*-axis of HA ceramic bulk and thick film produced by a process combining magnetic alignment and polymerization techniques is aligned in parallel to the direction of the magnetic field [4]. Magnetic fields have been used not only to control the grain orientation of HA, but also to improve the bio-

logical activity of biomaterials. After soaking in simulated body fluid (SBF) at 37 °C for 4 days, many large bone-like apatite crystals precipitate thickly on the surfaces of carbonate hydroxyapatite sintered samples with NaCaPO_4 as a second phase under a 14 T magnetic field, unlike those with no applied magnetic field [2]. It is reasonable to speculate that the local magnetic field produced by magnetite ferrite-based Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$ can influence the growth of apatite crystals and the bioactivity of materials. Moreover, magnetic particles with good biocompatibility have been developed as thermoseeds for hyperthermia treatment of bone tumors under an oscillating magnetic field [6]. The temperature of the thermoseeds rises in proportion to the weight ratio of magnetite powders, the volume of the thermoseeds and the intensity of the magnetic field.

Stoichiometric HA is known to be the most stable and least degradable form of calcium phosphate phases in aqueous solution [7], which limits its wide application in

* Corresponding author. Tel./fax: +86 451 86414291.

E-mail address: guohaodong1999@sina.com (Y. Zhou).

bioimplants. Fortunately, the trivalent anionic phosphate ions in the HA lattice can be substituted by both bivalent hydrogen phosphate ions and carbonate ions, and the hydroxyl ions can be replaced by carbonate ions [8]. The obtained hydroxycarbonate apatite similar to natural bone in terms of both chemical components and crystallinity degree has recently attracted much interest [9,10]. The bone-forming bioactivity of biomaterials is associated not only with the chemical composition and crystallinity, but also with the textural properties such as pore size, pore volume and pore structure [11–13]. The ideal porous structure of biomaterials comprises both mesopores (or micropores) and macropores. The mesopores (or micropores) can promote cell adhesion, adsorption of biologic metabolites and resorbability at a controlled rate to match that of tissue repair, while the macropores enable tissue ingrowth and nutrient delivery to the center of the regenerated tissue [14–16].

Recently, we reported a two-stage application route to fabricate hydroxycarbonate apatite coatings with hierarchically porous structures which consists of the deposition of CaCO_3 powders on Ti6Al4V substrates by the electrophoretic technique and the conversion of CaCO_3 coatings to apatite coatings by treatment with PBS [17]. The main aims of the present work were to fabricate magnetic hydroxycarbonate apatite coatings (MHACs) with hierarchically porous structures by the two-stage route, and to investigate the influences of Fe_3O_4 nanoparticles on the conversion rate of calcium carbonate to hydroxycarbonate apatite, and the porous structure and in vitro bone-forming bioactivity of MHACs.

2. Materials and methods

All chemicals were of analytical grade and used as received without further purification. All of the aqueous solutions were prepared with deionized water.

A 3.73 g quantity of ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and 8.15 g of ferric trichloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 100 ml of deionized water at room temperature. With magnetic stirring, a 0.50 mol l^{-1} ammonial solution was added dropwise to the mixed solution until the pH value was approximately 9.0, yielding a black suspension. The suspension was then stirred at 60 °C for 45 min. The products (Fe_3O_4) were washed with deionized water, collected by magnetic separation and dried in an oven at 60 °C.

A 2.54 g quantity of sodium carbonate (Na_2CO_3), 0.37 g of ethylenediaminetetraacetic acid (EDTA) and 0.22 g of Fe_3O_4 nanoparticles were dissolved in 200 ml of deionized water at room temperature, followed by ultrasonic treatment for 10 min. A 2.22 g amount of calcium chloride (CaCl_2) was dissolved in 200 ml of deionized water. With magnetic stirring, the CaCl_2 solution was added dropwise to the mixed solution containing Na_2CO_3 , EDTA and Fe_3O_4 , yielding a milky suspension. The suspension was stirred continuously for 20 min at room temperature. The

$\text{CaCO}_3/\text{Fe}_3\text{O}_4$ particles were washed with deionized water, collected by magnetic separation and dried in an oven at 60 °C. Calcium carbonate particles without Fe_3O_4 were produced in the same conditions.

The $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ particles were deposited on Ti6Al4V substrates by electrophoretic technique as described elsewhere [17]. After electrophoretic deposition, the obtained $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ coatings (MCCCs) were immersed in a beaker with PBS ($\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$), pH 7.4, and kept at 37 °C for 1 and 9 days, respectively. To maintain the pH value at 7.4, the PBS was replaced every day. At the end of the experiment the MHACs obtained were washed with deionized water and dried in a convection oven. MHACs converted from MCCCs by treatment with PBS for 1 and 9 days, are termed MHAC01 and MHAC09, respectively. For comparison, the referenced samples were prepared in the same conditions but without Fe_3O_4 in coatings. The hydroxycarbonate apatite coatings (HCACs) converted from calcium carbonate coatings (CCCs) by treatment with PBS for 1 and 9 days are termed HCAC01 and HCAC09, respectively. In order to obtain large enough amounts of magnetic hydroxycarbonate apatite to measure its porous structure and magnetic properties, the $\text{CaCO}_3/\text{Fe}_3\text{O}_4$ particles were treated with PBS without depositing on the substrates.

SBF with ion concentrations nearly equal to those of human blood plasma has been used widely for in vitro assessment of the bioactivity of bioceramics and biocoatings [18]. Each coating was soaked in 25 ml of SBF and kept at 37 °C. After given periods of time, the specimens were removed from the SBF, washed with deionized water and dried at room temperature.

Morphological observations of specimens were performed by transmission electron microscopy (TEM; CM200/FEG, Philips) with electron diffraction (ED) and scanning electron microscopy (SEM; S-4800, Hitachi) with energy-dispersive spectrometry (EDS). The crystalline phases of the coatings were examined with X-ray diffraction (XRD; D/max-II B, Japan) using Cu K_α radiation. Fourier transformed infrared spectra (FTIR; VECTOR22, BRUKER) were collected at room temperature using the KBr pellet technique. The magnetic properties were measured by using the physical properties measurement system of Quantum Design. N_2 adsorption–desorption isotherms were measured with an automatic surface area and porosity analyzer (AUTOSORB-1-C, Quantachrome) at 77 K. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The larger pore size distribution was measured by mercury porosimetry (Autopore IV 9500, Micromeritics). Thermal behavior was examined by thermogravimetric analysis (TGA; STA449C, NETSCH) with a heating rate of 10 °C min^{-1} . The percentages of unreacted calcium carbonate were calculated by the following formula:

$$X_{\text{Ca}} = \frac{(M_{\text{Ca}} \cdot X_{\text{C}})/M_{\text{C}}}{1 - X_{\text{F}}} \quad (1)$$

ID	Title	Pages
2104	Fabrication and in vitro characterization of magnetic hydroxycarbonate apatite coatings with hierarchically porous structures	9

Download Full-Text Now



<http://fulltext.study/article/2104>



Categorized Journals

Thousands of scientific journals broken down into different categories to simplify your search



Full-Text Access

The full-text version of all the articles are available for you to purchase at the lowest price



Free Downloadable Articles

In each journal some of the articles are available to download for free



Free PDF Preview

A preview of the first 2 pages of each article is available for you to download for free

<http://FullText.Study>