Materials Chemistry and Physics 114 (2009) 434–438

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Preparation of enhanced HA coating on H_2O_2-treated carbon/carbon composite by induction heating and hydrothermal treatment methods

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ARTICLE INFO

Article history:
Received 11 May 2008
Received in revised form
12 September 2008
Accepted 22 September 2008

Keywords:
Biomaterials
Coatings
Chemical techniques
Adhesion

ABSTRACT

An adherent hydroxyapatite (HA) coating was applied onto H_2O_2-treated carbon/carbon composite (HT–C/C) substrate by induction heating and hydrothermal treatment techniques. Specimens of C/C were initially modified by immersed in an autoclave with 2 M H_2O_2 solution at 433 K, and then coated with monetite crystals by induction heating method. Subsequently, monetite coating on HT–C/C was converted to HA coating by hydrothermal treatment in an autoclave with the ammonia solution at pH of 10 at 433 K. The compositions, structures and morphologies of the coatings on HT–C/C were analyzed by EDS, SEM and XRD, and the adhesive strength of HA coating on HT–C/C was evaluated by a scratch test. The results showed that the coatings of monetite and HA display no significant changes in their morphologies before and after hydrothermal treatment. They have rectangular crystals stacking one another, and a strong adhesive interface has formed between the HA coating and HT–C/C substrate. The HA coating on HT–C/C was not scraped off until the applied load reached 13.12 N (i.e., shear stress of 61.4 MPa).

1. Introduction

Carbon/carbon composites are studied as potential substitution and repair material for human bones owing to their excellent biocompatibility [1]. They have major mechanical properties closer to that of human bone than other common bone-repairing materials available, and especially, the match of elastic modulus between C/C implant and human bone helps to avoid "stress shielding" and sequential bone absorption caused by implant materials with high modulus [2]. However, they fail to form chemical bond with host bone and may release carbon particles due to the friction during surgical procedure [3]. Therefore, it is an effective strategy to coat C/C with hydroxyapatite as the mineral component of the bone. This has been done by plasma spray technique [4]. In this method, however, hydroxyapatite powder is momentarily heated over 10,000 °C, and partially molten particles are deposited on the carbon/carbons. Therefore, it is difficult to control the composition and crystallinity of the hydroxyapatite. The resultant hydroxyapatite layer weakly adheres to the carbon substrate dominantly by the mechanical bond. The average shear strength of the HA coating and C/C composite is only 7.15 MPa. Furthermore, the plasma spray technique is a line-to-sight process that produces a non-uniform coating when applied to porous surfaces. Many other techniques have been explored for the same purpose [3,5], such as dip-sintering coating, electrochemical preparation, sol–gel processing, biomimetic deposition, each of which has its own technical limitations, so far an optimal technique for producing interfacially adherent and physiologically stable Ca–P coatings on complexly shaped carbon has yet not been reported.

Induction heating deposition is a novel technique to form calcium phosphate coating on the surface of conductive biomaterials [6]. In this method, the power supply sends alternating current through the coil, generating an alternating electromagnetic field. When the conductive specimen is placed in the coil, this electromagnetic field induces eddy currents on the conductive surfaces of the specimen. The eddy current dissipates heat by the Joule effect. The resultant heat will induce the supersaturation of Ca and P ions in either a perpendicular or a parallel direction to the laminar flow on the specimen, resulting in the deposition of calcium phosphate to form coatings on the substrate of the specimen. This technique was found to have the following advantages: thinner films, better control over the deposited solid phase, the ability to deposit porous or complex shapes, and lower processing temperature. The aim of this study is to develop enhanced HA coating on C/C substrate by using the syntactic techniques of induction heating deposition and hydrothermal treatment.

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0254-0584/$ – see front matter.
doi:10.1016/j.matchemphys.2008.09.059

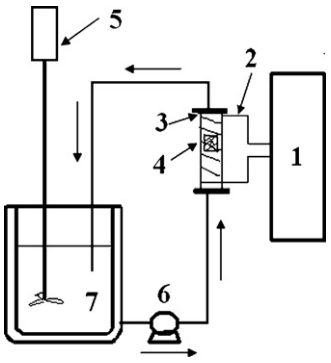

Fig. 1. Schematic graph of induction heating deposition (IHD) equipment: (1) induction powder, (2) copper coil, (3) glass tube, (4) C/C sample, (5) agitator, (6) peristaltic pump and (7) feeding.

2. Experimental procedures

2.1. Experimental setup and mother solution

The experimental setup for induction heat deposition process was shown in Fig. 1. This setup is composed of an induction current power consisting of a copper coil with appropriate water cooling, a glass tube of 20 mm diameter inside the coil, a peristaltic pump, a feeding tank and tubes connecting the feeding tank to the bottom of the glass tube and the top of the glass tube to the tank for the residual solution. Inside the glass tube there are two glass tubes of 16 mm diameter for supporting the C/C samples in a vertical position. The mother solution used in this study was prepared by dissolving given amounts of reagent-grade chemicals of 4.0 M $Ca(NO_3)_2$ and 2.4 M $NH_4H_2PO_4$ into distilled water. This solution was buffered to a pH of 4.5 with an adequate amount of ammonia. On the other hand, the feeding tank was heated to 323 K prior to deposit the monetite coating on C/C.

2.2. C/C substrates and pretreatments

C/C composites were prepared by chemical vapor infiltration (C/C) processing in Northwest Polytechnology University (NPU) in China. The density and Shore scleroscope hardness of them are average 1.72 g cm^{-3} and 36.1, respectively. C/C samples were cut from the block and had a diameter of 8 mm and a length of 10 mm. Prior to the coating runs, each sample was polished with No. 600 and No. 1000 abrasive paper, rinsed with distilled water, then cleaned ultrasonically in acetone, and dried in a desiccator. And H_2O_2 in analytical grade was dissolved in deionized water to prepare 2.0 M solution at ambient temperature. Then, samples were pretreated in high pressure steam in a 5-L autoclave with H_2O_2 solution at 433 K. After removal from H_2O_2 solution, these cylinders were rinsed ultrasonically with deionized water and dried in air.

2.3. Coating experiments and post-treatments

The deposition experiments were initially carried out at the applied current of 500 A at 323 K and finished at 353 K of the mother solution. At the end of each run, the coated cylinders was rinsed with distilled water and then hydrothermally treated in an autoclave with the ammonia solution at pH of 10 at 433 K for 2 h. After hydrothermal treatment, all the coated samples were annealed in vacuum to removal of water in the coatings at 473 K for 1 h.

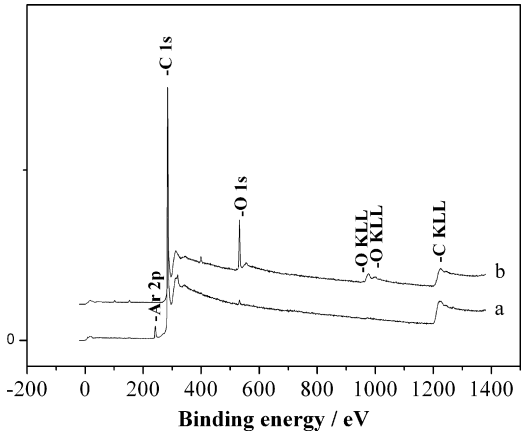

Fig. 2. XPS spectra of C/C full spectrum before (a) and after (b) H_2O_2 treatment.

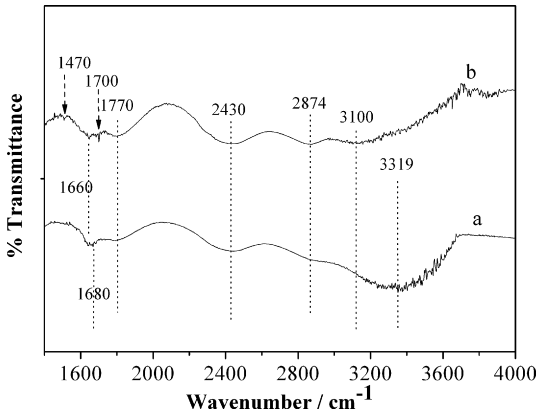

Fig. 3. FTIR spectra of original C/C before (a) and after (b) H_2O_2 treatment.

2.4. Characterization

Chemical compositions of elements in the pretreated C/C composites were investigated by X-ray photoelectron spectroscopy (XPS; ULVAC-PHI 1800, Japan) with Al Kα X-ray source (1486.6 eV). Prior to XPS measurement, each sample was etched using an argon gun. The energy of Ar^+ was 4 keV with a current equal to 1 μA and erosion time close to 1200 s. The functional groups on C/C were quantitatively identified by Fourier transform infrared (FTIR). The FTIR spectra were recorded in the 1400–4000 cm^{-1} range, resolution 4 cm^{-1}, using PerkinElmer instruments Spectrum One Spectrometer and KBr pellet technology. The crystalline structure, morphologies and compositions of the coated samples were characterized by X-ray diffraction (XRD) using a D8 advance X-ray diffractometer (Cu Kα radiation), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis with a s-3400N (Japan) microscope. Finally, the mechanical properties of the coatings deposited on C/C substrates were determined by the scratch test method using an s-3400N scratch tester fitted with a Rochwell C 0.2 mm-diamond stylus with a preload of 1 N, load speed 10 N min^{-1}, scratch speed 5 mm min^{-1} and the maximum load of 20 N. Scratch-induce damage of the coatings, specifically fracture or delamination were examined by a Stereo microscope (STM).

3. Results and discussion

It is demonstrated that CVI–C/C from NPU are known to hydrophobic and thus cannot induce deposition of calcium phosphate in the supersaturation solution containing Ca and P ions [3]. It is not easy for them to form the chemical bond with calcium phosphate through employing wet methods. So it could be expected

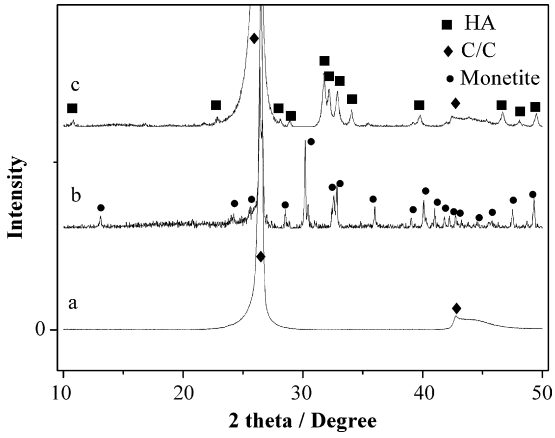

Fig. 4. XRD spectra of: (a) HT–C/C, (b) monetite coating on HT–C/C by induction heating deposition and (c) transformed hydroxyapatite coating from monetite by hydrothermal treatment on HT–C/C.