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Ca-P bioactive coating prepared by combining microwave-hydrothermal and supersonic atmospheric plasma spraying methods

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ABSTRACT

Ca-P based coatings on carbon/carbon composite (C/C) were manufactured via a combined method comprising of microwave-hydrothermal (MH) and supersonic atmospheric plasma spraying (SAPS) techniques. However, a weak mutual interaction between the coating and C/C substrate has been a critical issue for a long time. Herein, we reported a new method for shear strength enhancement without compromising the osteoconductivity and osteoproductivity. Results showed that the inner layer has a strong mechanical interlocking with C/C substrate and the failure mode of outer layer changed from the coating cohesion (within the coating) to adhesive (at the coating/substrate interface) fracture. The shear strength between Ca-P bioactive coating-C/C substrate by MH/SAPS was significantly improved as compared to that prepared by SAPS. The Ca-P bioactive coating exhibited a good bioactivity as evidenced by the formation of a uniform carbonate-apatite layer formed on coating after immersing into stimulated body fluid for a specified period of time.

1. Introduction

Carbon/carbon composite (C/C) has potential application in bone tissue engineering owing to their lower density, good mechanical strength and excellent bio-stability, especially, in comparison with metallic materials [1]. However, the intrinsic inertness of C/C restricts their further application in orthopedics. Hydroxyapatite (HA), tricalcium phosphate (TCP) and calcium hydrogen phosphate (ADCP) have been widely used as bioactive coatings to repair the injured bone tissues, restoration of dental roots and alveolar ridge, hip and knee endoprostheses etc. In addition, they have been proved as the important material for the application in surface of coating on bone implants by virtue of its excellent bioactivity, osteoconductivity and biocompatibility. Moreover, these materials promote the attachment and growth of cells along surface of implant known as osteoconductivity [2].

Several methods have been appeared to prepare the calcium phosphate (Ca-P) contained bioactive coating such as injection and sinter [3], electrophoretic deposition (EPD) [4], ion beam-assisted deposition (IBAD) [5], supersonic atmospheric plasma spraying (SAPS) [6], microwave-hydrothermal (MH) [7] etc. Among them, SAPS is still the most popular technology commercially used for depositing Ca-P bioactive coatings onto C/C substrate. SAPS is faster and more efficient in fully melting the powders as compared to atmospheric plasma spraying (APS). Moreover, the density, porosity and the bonding strength of the coating by SAPS are also higher than the coating prepared by APS [8–10]. Additionally, SAPS can increase the shear strength of Ca-P bioactive coating [11]. Cao and Bai [12] found that HA coating produced by SAPS (outer layer) exhibited excellent biological responses both in vitro and in vivo tests. Sui and Li [13] prepared an HA coating by plasma spraying technique and found a strong adhesive interface between the HA coating and C/C substrate. Moreover, the MH technique has better control over particle size, shape and morphology [14–16]. Coatings by MH method (inner layer) are characterized by a high reaction rate, reduced energy consumption, short time and high efficiency compared with conventional heating techniques [17–19]. Han et al. [17] studied the HA with needle and spherulite shapes has been synthesized by using MH method. Wang and Fu [15] prepared HA nanoparticles of very high purity and crystallinity by MH method. All these single preparation methods have their merits and demerits. The new concept presented in this research is to prepare Ca-P bioactive coating using a combined method comprising of MH and SAPS method (denoted as MH/SAPS), with an aim of improving the shear strength between the MH/SAPS and C/C substrate.

In MH method, the consequences of selecting reaction temperature with constant time and concentration on the microstructure, phase composition and crystallinity are explored by studying the experimental results. HA powder with a controlled particle size was used for outer layer. Shear strength after SAPS were studied.

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2. Experimental

2.1. Preparation of C/C substrate

The C/C with a density of 1.40 g/cm^3 used in this work was prepared by a chemical vapor infiltration (CVI) technique as detailed in [20–24]. In a typical process, the carbon fiber preform was infiltrated by H_2 gas in a hermetically closed CVI reactor, and carbon matrix deposits on fiber surfaces filling the gaps/space between fibers. The C/C was machined into thin plates with a size of 8 × 8 × 2 mm^3. The plates were polished with 320 and 800-grit abrasive paper respectively, then cleaned with ethanol in an ultrasound bath for 30 min, and finally dried at 60 °C for 2 h.

2.2. Preparation of coatings by a combined method

Inner layer was prepared using $Ca(NO_3)_2 \cdot 4H_2O$ as the calcium source and $NH_4H_2PO_4$ as the phosphorus source. The specimens were immersed in the mixed solution containing 1670 mmol/L $Ca(NO_3)_2 \cdot 4H_2O$ and 1000 mmol/L $NH_4H_2PO_4$ under constant stirring condition at room temperature for 10 min. Afterwards, they were put into the microwave reactor (MDS-10) and heated to different reaction temperatures of 120, 150 and 180 °C for 30 min. The specimens prepared by MH method were washed with deionized water and dried at 60 °C for 12 h. The inner layer prepared by MH method at 120, 150 and 180 °C were donated as MH-120 °C, MH-150 °C and MH-180 °C, respectively.

MH-120 °C, MH-150 °C and MH-180 °C were used as substrates to prepare outer layer using HEPJ-100 sprayer. The detail information of the machine principle could be found elsewhere [25,26]. The samples were perpendicular to the plasma arc and injector. The detailed information of spraying parameters is summarized in Table 1. The coating slurry was composed of distilled water (49 wt%), polymeric binder (2 wt%) and HA particles (49 wt%). Fig. 1 is a typical SEM image of the agglomerated powders with a particle size ranging from 50 to 90 μm. In this work, the outer layer is donated as CP-SAPS.

2.3. Characterization

Scanning electron microscopy (SEM, JMS-6460 20 kV and tungsten filament) equipped with energy dispersive spectroscopy (EDS) was employed to examine the morphologies and chemical composition of the coatings. The samples were coated with a thin layer of gold prior to observation. The phase and crystallinity were measured by X-ray diffraction (XRD, X'pert Pro MPD) with a Cu Kα radiation of wavelength 0.154 nm operated at 40 kV, 35 mA. The testing parameters were as given; a step size of 0.03°, the scan speed of 0.28°/s, humidity of 50% and temperature of 22 °C. Fourier transform infrared spectra of coating were obtained on a FTIR spectrometer (Nicolet iS50 FT-IR) using transmission (KBr pellet) mode. The compositions of the inner layer were characterized by an Axis Ultra X-ray photoelectron spectroscopy (XPS, Kratos, Manchester) with an Al Kα X-ray source (1486.6 eV). After purging with Ar gas, the obtained binding energies were compared with that of C1s at 284.6 eV. The MH/SAPS were immersed in stimulated body fluid (SBF) for various periods of time (1, 3, 7, 14 days) to investigate apatite precipitation behavior in vitro at 36.5 °C. The SBF was prepared by dissolving reagent NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $NaSO_4$ and $(CH_2OH)_3CNH_2$ using deionized water and constant stirring. Hydrochloric acid was added into the solution to keep the pH at 7.40 [27].

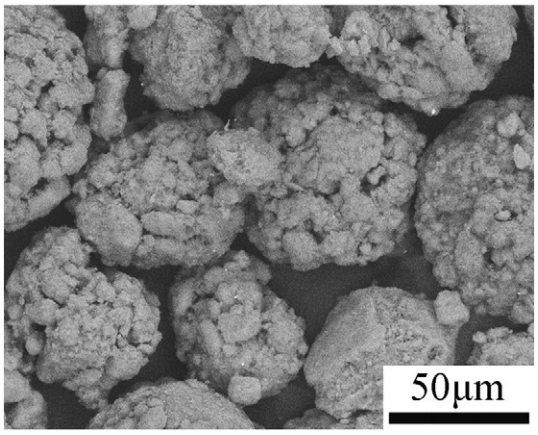

Fig. 1. SEM image of the agglomerated powder.

The shear strength of the coating on C/C substrate was measured on a CMT5340-30 KN universal testing machine and a schematic of shear testing is shown in Fig. 2a. The samples were cut from the coated samples with an approximate size of 8 mm in length, 8 mm in width and 4 mm in thickness (except the thickness of the MH/SAPS) being shown in Fig. 2b. The left loading surface contacts the left half of the top surface, which is perpendicular to the laminate planes and the right loading surface contacts to the right half of the bottom surface of the specimen. Two vertical guides support the left and the right sides of the specimen to prevent it from rotating or moving horizontally. The right and the left loading surface move down under the pushing, to generate the direct inter-laminar shear force along the central plane of the specimen until failure. In addition, one interface between C/C substrate and MH/SAPS was joined with binding agent (DG-3S with the standard shear strength of 19.61–25.49 MPa) and dried under 60 °C, ensuring that the fracture occurs at the interface between MH/SAPS and C/C substrate. Therefore, the measured values are the exact shear strength of MH/SAPS-C/C substrate.

Table 1
Details of the spraying parameters for as-sprayed coating.

Content	Parameters
Spraying current (A)	400
Spraying voltage (V)	113
Primary gas Ar (L/min)	80
Carrier gas Ar (L/min)	10
Second gas H_2 (L/min)	5
Powder feed rate (g/min)	20
Spraying distance (mm)	100
Injector internal diameter (mm)	5.5
Injector position	Perpendicular to the surface of the coating

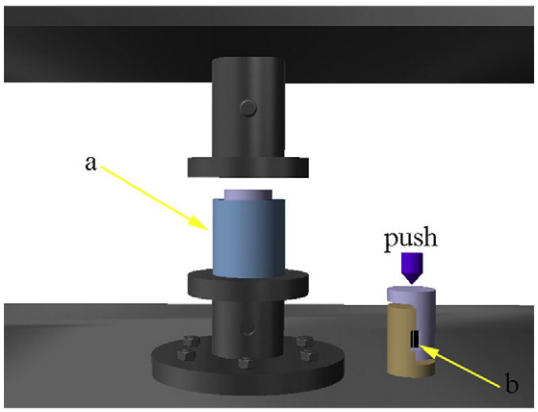

Fig. 2. Schematic of the shear testing between C/C substrate and MH/SAPS.