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Calcium phosphorus bio-coating on carbon/carbon composites: Preparation, shear strength and bioactivity

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A B S T R A C T

Microwave hydrothermal (MH) combining supersonic atmospheric plasma sprayed (SAPS) calcium phosphorus (Ca-P) bio-coatings on carbon/carbon (C/C) composite has been widely used due to their osteoconductivity and osteoproducitivity. However, the erratic shear strength between coatings prepared only by SAPS (outer coating) and C/C substrates has attached more attention over the implant failure. Adding a coating prepared by MH (inner coating) before SAPS can possess superior shear strength to conventional outer coating. The inner coating with fine Ca-P particles was prepared through a unique MH method under different concentrations (10, 500 and 1000 mmol/L). The influence of concentration on microstructure, phase composition, roughness and shear strength are investigated in this paper. In particularly, the roughness of inner coatings on C/C substrates was found to related to the morphologies and particle size. Results showed that inner coatings have higher roughness which was beneficial for the promotion of shear strength between the obtained Ca-P bio-coating and the C/C substrates. Subsequently, the specimens were immersed in a simulated body fluid (SBF) to investigate the bioactivity.

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1. Introduction

Carbon/carbon (C/C) composites which are promising bone replacement material process excellent mechanical properties, stability and biocompatibility [1–4]. They would not only exhibit good cell responses, but also show compatibility in vivo [5,6]. In addition, their properties, such as the low density, porosity and mechanical strength are similar to that of the human bone. However, the biological inertness of C/C composites limits their wide medical application [7]. Thus, Ca-P bio-coatings on bioinert C/C substrates have brought much more attention in orthopedics. In recent years, hydroxyapatite (HA) coatings on C/C substrates have been widely reported. Cao et al. studied the methods of sand-blasting pretreatment combining plasma spraying to fabricate HA coatings on C/C substrates [8]. Zhang et al. used electrochemical deposition (ECD) method to prepare HA coatings on C/C substrates [9]. Fu et al. reported that the SiC nanowires reinforced the cohesion strength between the HA coating and C/C substrate [10].

Except for HA coatings, Ca-P based bio-coatings have gotten extensively attention and applied in manufactured biomaterials [11,12]. Synthesized Ca-P coatings are distinguished by its good bioactivity, biocompatibility, bone attachment ability and osteoconductivity. However, there are some issues that Ca-P substances are served as the bioactive coating. For example, Sun et al. illustrated the performance of HA-coated implants prepared by plasma sprayed method on metal, which exist drawbacks except faster and stronger fixation and more growth on bone [13]. Ariffin et al. showed the poor properties about the substrate and the coating, such as bio-inertness and low bonding strength, and review the interaction of the HA and substrate under different conditions [14]. In this sense, numerous studies about the utilization of Ca-P bio-coatings would may come from the instability between substrates and coatings. Therefore, many techniques about enhancing the shear strength between substrates and Ca-P bio-coatings are reported [4,15]. Among them, SAPS as one of the members for plasma spray (PS) is widely becoming more and more popular for preparing coating on substrates [16,17]. At present, Sui et al. have developed a coating with the shear strength of ~7.4 MPa using single plasma spray [18]. Fielding et al. have doped the silver and strontium into the plasma sprayed HA-coatings and gotten bonding strength of about 18.21 MPa [19]. However, few reports contributed to the bio-coating fabricated using SAPS. Meanwhile,
there are some potential issues about this technology, such as residual stresses in coatings, and the micro-crack propagation which influence the bonding strength between the coatings and substrates. Specifically, the mechanical properties of bio-coating on substrates, which describe their ability to suffer the loads and the duration in implant body, are always ‘hot topics’ [20–22]. In this sense, MH method is employed to facilitate the bonding strength [23,24]. It is well known that some methods, such as conventional hydrothermal, prepared Ca-P coatings on substrates are tedious and time consuming [25]. Recently, MH with strong penetration ability has more widely application in the preparation of coatings since it could provide fast, controlling, homogenous heating, which decreases reaction time and cost [26]. In our previous work, we used the MH combined SAPS method to increase the bonding strength and had the remarkable results [27]. In this study, the MH used before SAPS also aims to reinforce the shear strength between the coating and C/C substrate. The reason may be that dense crystal grains are fabricated during MH process. They could supply different surface roughness, large specific area and form multiple interface effect to contact with the coating prepared by SAPS on substrates. The results display that MH method contributes to the improvement of the shear strength.

2. Experimental procedure

2.1. Substrate material and feedstock powder

C/C substrate (8 mm × 8 mm × 2 mm) was cut from the bulk C/C composite (with a density of 1.40 g/cm³) identified by chemical vapor infiltration (CVI) [28,29]. Then, the specimens were polished with 80-grit and 320-grit SiC paper, ultrasonically cleaned by acetone, ethanol and distilled water, and dried in stove for 12 h at 60 °C. The commercial HA powder with the average size of 90 ± 15 μm, was used for SAPS process.

2.2. Preparation of inner coatings

The MH method was employed for the synthesis of inner coatings. Briefly, the coatings were produced by using Ca(NO₃)₂·4H₂O (with the concentrations of 10, 500 and 1000 mmol/L) as a calcium source and NH₄H₂PO₄ as a phosphorus source. Then, 20 mL NH₄H₂PO₄ solution was dropped into a beaker with 20 mL Ca(NO₃)₂·4H₂O solution. It is worth noting that the molar ratio of Ca/P is 1.67 in the mixing solution. After that, C/C substrates were put in it, and then transferred into a sealed Teflon microwave reac-
2.3. Preparation of outer coating

The HA powder after pelleting with an average size of 50–90 µm was used to spray. SAPS was performed under the condition of a voltage of 117 V, current of 430 A. It is worth noting that all the outer coatings were sprayed under the power 50 kW which aimed to produce a similar structure in the outer coating. Otherwise, it is beneficial to study the shear strength and the accuracy of the data at the same condition in the future. Argon and hydrogen were used as the plasma arc gases, whereas argon was used as the powder carrier gas. The spraying distance of 100 mm, the feeding rate of 4.4 g/min and the spraying number of 20 times were used. The spray plume was perpendicular to specimens, and the inner diameter of injector was 5.5 mm. The outer coating was donated as SAPS-C/C. Additionally, the inner coating with calcium ionic concentrations of 10, 500 and 1000 mmol/L, combined with outer coating (Ca-P bio-coating) was defined as SAPS-MH10-C/C, SAPS-MH500-C/C, SAPS-MH1000-C/C, respectively.

2.4. Test and characterization

Morphological features of the Ca-P bio-coating are measured by scanning electron microscopy (SEM, JSM-6460) coupled to energy dispersive spectroscopy (EDS) with an accelerating voltage of 20 kV. Crystalline phase of Ca-P bio-coating is examined with X-ray diffraction (XRD, X’Pert PRO MPD) with Cu Kα radiation at 40 kV and 35 mA. The scanning speed is 0.28°/s and the range of scanning angle is from 10 to 89°. Fourier transform infrared (FTIR) spectra of coatings are obtained on a Magna IR 560 spectrometer (Nicolet, USA). An Axis Ultra X-ray photoelectron spectroscopy (XPS, Kratos, Manchester) with an Al monochromatized source at 1486.6 eV is used to exploit the compositions of inner coatings. Before the XPS testing, the specimens are cleaned using Ar gas. Then the obtained...
binding energy about the specimens is compared with that of C1s at 284.5 eV. To investigate the mechanical properties, the specimens are cut to required square bulks keeping the joining area approximately 8 mm \times 8 mm and fixed in the clamp and sleeve as shown in Fig. 2b. The position of typical pressure is also marked in Fig. 2a, and c gives the detailed information about the specimens. The shear strength of the specimens is tested using a CMT5304 30 KN universal testing machine with a 0.5 mm/min constant loading rate. The shear strength ($\tau$) between the C/C substrate and the Ca-P bio-coating is calculated using the following equation:

$$\tau = F/S$$

In the formula, $\tau$ is the tested shear strength (MPa), $F$ is the maximum load (N) and $S$ is the joining area ($mm^2$). Surface roughness of inner coatings is detected by a 3D confocal laser microscope (Optelics C130, Lasertec, Japan).

The bioactivity of the specimens is evaluated by soaking them in an acellular simulated body fluid (SBF) which ion concentration is approach to those of human blood plasma. The order, reagents and amounts of SBF are given in Table 1 according to the process developed by Kokubo etc. [30]. The buttering is at pH = 7.40. After soaking at 36.5 °C for 1 day, 3 days, 5 days, 7 days and 14 days, the resulting specimens are taken out from SBF and gently cleaned them in distilled water, and dried at 60 °C for 24 h in a dry stove.

![Fig. 4. Scheme illustration of a possible formation mechanism of inner coatings. (a) Ca$^{2+}$ and PO$_4^{3-}$ transform to Ca-P nucleus on C/C substrate; (b) microwave heating; (c), (d), (e) microwave heating under different concentrations for 10, 500 and 1000 mmol/L, respectively.](image)

![Fig. 5. SEM image of SAPS-C/C for (a) 50 kW and (b) XRD pattern.](image)

3. Results and discussion

3.1. Morphological analysis of inner and outer coatings

In general, MH method has a good influence on the formation of inner coatings. To investigate the relationships between the different Ca$^{2+}$ concentrations and morphologies, many experiments are carried out. Fig. 3 shows the results of SEM images that inner coatings are covered on the C/C substrates entirely with certain morphologies. The homogeneous and dense particles fill these imperfections exist in C/C substrates. In Fig. 3a, the specimens consist of vast flower-like particles exhibiting irregular shapes. With the increase of concentration, the flower-like particles are replaced

| Table 1 |
|---|---|---|
| Order | Reagent | Amount (g/L) |
| 1 | NaCl | 7.996 |
| 2 | NaHCO$_3$ | 0.350 |
| 3 | KCl | 0.224 |
| 4 | K$_2$HPO$_4$·3H$_2$O | 0.228 |
| 5 | MgCl$_2$·6H$_2$O | 0.305 |
| 6 | 1 mol/L HCl | 40 mL |
| 7 | CaCl$_2$ | 0.278 |
| 8 | NaSO$_4$ | 0.071 |
| 9 | (CH$_2$OH)$_2$CNH$_2$ | 6.057 |
by sheet-like particles (Fig. 3b). It can be seen from Fig. 3c that the coating density increases and a large majority of block-shaped and interlocked particles are found. Additionally, the particles of MH1000-C/C are approximately 10–30 µm in length and 2–7 µm in thickness. From the above results, it can be indicated that the morphologies of inner coatings have a series of changes for different Ca\(^{2+}\) concentrations. The typical principle can be concluded as Fig. 4. Calcium ions combine with phosphate ions to form Ca-P nucleus. Then the nucleus begins to grow into various morphologies on C/C substrate under different Ca\(^{2+}\) concentrations. The reason may be that increasing the concentration of Ca\(^{2+}\) will increase the reaction potential and lead to the precipitate of Ca-P appeared on the surface of C/C substrate [31]. Due to the different Ca\(^{2+}\) concentrations, namely the different of supersaturation of the solution, the rate of calcium ions combined with phosphate ions is remarkably different. Thus, the nucleus of different Ca/P molar ratio appear and then grow into different morphologies.

Especially, the interface among the flower-like, sheet-like and block-shaped inner coatings has the excellent shear strength with little defect, indicating that MH combined with SAPS methods could obtain thickness of related coating and favorable coating. Above results indicate that Ca\(^{2+}\) concentrations under the action of MH process are served as the driving forces in the shape of inner coatings. The flower-like, sheet-like and block-shaped particles stack for each other. These special particles assembly different morphologies could provide various different surface roughness and large specific area, contributing to the higher shear strength. In this section, the inner coating architecture is fabricated through MH method. Ca-P nucleus are formed in solution and then deposited on the surface of C/C substrates. By EDS analysis, the C, O, Ca and P elements are detected according to the relative inner coatings. The results show that the Ca/P atomic weight ratio for MH-C/C is around 1.0 and 1.67, respectively.

Fig. 5a show typical SEM images of outer coating. It is obviously seen that the outer coating consisted of irregular splats, such as micro-cracks (yellow dotted lines), unmolten particles and spherical grains (yellow arrow), namely unmolten particles [32]. The unmolten particles are obtained under 50 kW indicate that the power could not provide enough energy to melt the HA powder. The spherical grains are formed because the HA powder has a sudden cold while the melted powder from the spray plume reach the cold substrate during spraying. Meanwhile, the sudden cold can easily
generate residual stress in the coating and then the micro-cracks appear.

Meanwhile, the corresponding polished cross-section morphologies of inner and outer coatings are shown in Fig. 6. The thickness of the MH10-C/C, MH500-C/C and MH1000-C/C are approximately 8.2, 21.31 and 32.29 μm, respectively (Fig. 6a, e and f). The Ca-P bio-coatings possess the thickness of 109.84, 122.98 and 136.9 μm are corresponding to that of SAPS-MH10-C/C, SAPS-MH500-C/C and SAPS-MH1000-C/C (Fig. 6b, d and e). It is known that the physical bonding mainly happens in the interfacial bonding. Furthermore, the rough and porous substrate or interface coating can increase the shear strength.

3.2. The characteristics of inner and outer coating analysis

Figs. 7–9 illustrate the XRD patterns, FTIR and XPS spectra of inner coatings. From Fig. 7, it can be seen that the diffraction peaks for MH10-C/C, MH500-C/C and MH1000-C/C are HA and DCPA. It is indicated that HA and DCPA are produced as the main new product on the inner coatings. The FTIR spectra of the inner coatings are shown in Fig. 8, the absorption peaks of water locate at around 3424 and 1636 cm\(^{-1}\), PO\(_4^{3-}\) peaks are typically located at around 1100, 1034 and 603 cm\(^{-1}\), respectively. Meanwhile, the absorption peaks observed around 872 and 633 cm\(^{-1}\) are the characteristic absorption peaks of HPO\(_4^{2-}\) and OH\(^-\), respectively. Fig. 9 shows XPS spectra and the images of measurement of Ca2p, P2p, O1s for the inner coatings. The Ca2p spectra is measured as two peaks and the P2p spectra only has a single peak. From the XPS spectra of Ca2p and P2p, it can come to a conclusion that the element P in a form of phosphate exists in the inner coatings. In addition, O1s is identified as a single peak. According to the binding energies, it is deduced that there is no remarkable difference about the Ca2p, P2p, and O1s spectra for the specimens produced under different reaction concentrations. Based on the above reactions, there is a high probability to get both DCPA and HA.

Moreover, XRD pattern of the outer coating is presented in Fig. 5b. As illustrated, there are two other foreign phases appeared in the diffraction peaks except for HA phase. They are CaO and TCP peaks which can be obtained at 2\(\theta\) = 30.792°, 37.393°, 53.30° for CaO and 2\(\theta\) = 24.127°, 31.782°, 34.225° for TCP phase, respectively. Besides, the CaO and TCP phases are formed due to the dehydra-

\begin{equation}
2\text{Ca}_3(\text{PO}_4)_2(\text{OH}) \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \uparrow
\end{equation}

3.3. Shear strength test

Typical load-displacement curves for shear test are shown in Fig. 10. Compared with the value of 7.85 ± 0.15 MPa for SAPS-C/C, SAPS-MH10-C/C on C/C substrate reaches its highest value of 20.47 ± 0.21 MPa, 160.76% more than that of SAPS-C/C. In addition, the curves show the analogous shape and the peak value of each curve decline from 20.47 ± 0.21 MPa, 13.40 ± 0.13 MPa to 10.80 ± 0.12 MPa with the increasing of Ca\(^{2+}\) concentration. In the case of shear strength, the roughness of the surface plays a significantly important role in our present work. Moreover, a rougher surface can enhance the shear strength. 3D morphologies of the coatings for C/C substrate, MH10-C/C, MH500-C/C and MH1000-C/C are tested to evaluate the surface roughness, and the values of roughness are listed in Table 2. The roughness of the surface coating after MH is affected by the reasons as follows; Ca\(^{2+}\) concentrations and size of crystalline grains, with highest roughness resulting at the lowest concentration and fine crystal size (10 mmol/L). The changes of morphology show that the inner coating fabricated under different Ca\(^{2+}\) concentrations owned different surface morphologies. Hence, the shear strength between the C/C substrate and Ca-P bio-coating is enhanced as the lowering concentration. Taken together, the rough surface of MH-C/C has more specific surface area than that of C/C substrate. The larger specific surface area of inner coating (MH10-C/C) can provide more contact area and mechanical interlock than C/C substrate, MH500-C/C and MH1000-C/C while are fabricated to enhance the shear strength. Thus, it can be concluded that the MH10-C/C has the largest roughness value which owns the highest shear strength adding before SAPS-C/C among the all specimens in this work. Furthermore, the shear failure happened in the interfacial between the Ca-P bio-coating and C/C substrate as well as the outer coating and inner coating. The typical fracture morphology of the shear strength has been shown in Fig. 10b and c. In Fig. 10b, it can be seen that some pulling-out fibers on the C/C substrate. It is demonstrated that the HA powder bond well with carbon fibers and inner coating during spraying. Additionally, the pull out of some particles (yellow arrows in Fig. 10c) appeared on the surface of C/C substrate and this means the shear strength happened between the Ca-P bio-coating and C/C substrate.

3.4. Characterization of specimens after immersion in SBF

Fig. 11 shows SEM image changes of the Ca-P bio-coating surface after immersion in SBF for a period of days, as well as the molar ratios of Ca/P for the specimens after SBF immersion. After being immersed in SBF for 14 days, the Ca-P bio-coating is covered by a
Fig. 9. XPS spectra as well as the images of measurement for Ca2p, P2p and O1s corresponding to (a) MH10-C/C; (b) MH500-C/C and (c) MH1000-C/C.

Fig. 10. Typical load-displacement curves by (a) shear strength test with different concentrations of Ca2+ : SAPS-C/C; SAPS-MH10-C/C; SAPS-MH500-C/C and SAPS-MH1000-C/C, and typical fracture morphology of the shear strength (b and c).

Table 2

<table>
<thead>
<tr>
<th>Specimens</th>
<th>C/C</th>
<th>MH10-C/C</th>
<th>MH500-C/C</th>
<th>MH1000-C/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa (μm)</td>
<td>9.575</td>
<td>14.219</td>
<td>13.067</td>
<td>12.851</td>
</tr>
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It can be inferred that there is a new coating on the surface of the Ca-P bio-coating, which exhibits fine morphology. In Fig. 11c, it shows that the Ca/P molar ratio of the new coating is in the range of 1.31–1.68, which also indicates that a new Ca-P coating can be found from SBF solution.
Additionally, growth mechanism of the new apatite on the surface after soaking in SBF solution can be described as shown in Fig. 12. The reaction on the surface of the outer coating includes the deposition and dissolution parts. The OH\(^{-}\) appear because of the transformation of the phase about the outer coating. Thus, Ca\(^{2+}\) ions in solution move towards to the surface of the outer coating and reform the Ca-rich positive layer. The apatite nuclei are formed on everywhere (especially for the micro-cracks) of the coating while Ca\(^{2+}\) ions are combined with HPO\(_4\)^{2-} or PO\(_4\)^{3-}. It is worth noting that the growth of the apatite nuclei slowly consume the calcium and phosphate ions of the supersaturated SBF. Meanwhile, the spherical grains and the micro-cracks begin to dissolve, which is exhibited in Fig. 2(a). As the increasing of soaking time, the micro-cracks have been deposited by the apatite and dissolved. The spherical grains have also dissolved into powder. Furthermore, the micro-cracks in the surface are healed. Finally, a new apatite layer can be obtained on the original surface as shown in Fig. 12(b).

4. Conclusions

A new method to promote the long-period durability of the implants in clinical applications is microwave hydrothermal combining supersonic atmospheric plasma spraying methods. To verify the influence of the Ca\(^{2+}\) concentration during MH process on shear strength, inner coating is designed by means of variations of Ca\(^{2+}\) concentrations for microwave heating 30 min at 180 °C. Micrograph analysis of the inner coatings infers that the different ion concentrations within MH process show different morphologies, which is related to the shear strength further. In addition, the behavior of the Ca-P bio-coating in SBF indicates that the Ca-P bio-coating is bioactive in SBF.

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