ULTRASOUND ASSISTED ANODIC OXIDATION TREATMENT OF CARBON/CARBON COMPOSITES AND DEPOSITION OF STRONG BONDING CALCIUM PHOSPHATE COATINGS ON THE TREATED SUBSTRATE

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Abstract

This work described the ultrasound assisted anodic oxidation treatment of carbon/carbon (C/C) composites with H₃PO₄ which aims to create a chemical bonding between the surface-treated C/C composites and subsequently deposited calcium phosphate (CaP) coatings. The results revealed that the surface energy of C/C which had experienced the ultrasound assisted anodic oxidation treatment with 0.5 M H₃PO₄ at the current density of 50 mA/cm² (USAT-C/C-50) (93.31 mJ/m²) was much higher than that of untreated C/C (10.43 mJ/m²). And the high content of O-containing groups and some amounts of P-containing groups were obtained on the USAT-C/C-50. When the USAT-C/C-50 was used as the substrate of CaP coatings deposited by ultrasound assisted electrochemical deposition (USECD), the surface of USAT-C/C-50 turned to have a strong CaP induction ability and large amounts of CaP were deposited on it in the initial deposition process. After USECD, very strong CaP coatings were formed on USAT-C/C-50. The average of shear bond strength of the coatings obtained on the USAT-C/C-50 (12.14 ± 1.30 MPa) was about two times of the coatings obtained on the untreated C/C (6.78 ± 1.06 MPa).

Keywords: Ultrasound assisted anodic oxidation treatment; Carbon/carbon composites; Ultrasound assisted electrochemical deposition; Calcium phosphate; Bond strength

1 Introduction

Carbon fiber reinforced carbon composites (C/C composites) possess not only the intrinsic biocompatibility of carbon material but also excellent mechanical properties of fiber reinforced composites. In particularly, their major mechanical properties are close to that of loaded human bones and the low rigidity (5-80 GPa) of C/C composites is similar to that of human cortical bone. Hence C/C composites are one kind of potential substitution and repair material for human bones [1, 2]. However, this kind of material cannot form chemical bonds with the host tissue and may release carbon debris to the surrounding tissues due to the friction during surgical procedure [2, 3]. To eliminate this problem, some bioactive calcium phosphate (CaP) coatings have been applied to C/C composites [1-3].

Several coatings methods such as plasma spray, sol-gel, electrophoretic deposition, RF sputtering and electrochemical deposition (ECD) are being used to coat implant surfaces [4]. Among these methods, ECD has received considerable attention because of its unmatched advantages. However, the poor bonding between the coatings and substrate is one of the main concerns that need to be solved. In order to obtain improved bonding strength between coatings and C/C substrate, ultrasound assisted electrochemical deposition (USECD) was put forward through introducing ultrasound irradiation to the ECD in our previous work. In this work, another simple and effective technique is applied to further improve bonding strength between CaP coatings and C/C composites. The technique is to graft some chemical groups onto the surface of C/C composites by ultrasound assisted anodic oxidation treatment (USAT). Then the surface-treated C/C composites were used as the substrate of CaP coatings deposited by USECD subsequently. Thus a chemical bonding was formed between the C/C composites and CaP coatings and very strong coatings were obtained on the C/C substrate.
2 Materials and methods

C/C composites were prepared by chemical vapor infiltration processing in Northwestern Polytechnical University (NWPU) in China. C/C samples were cut from the block and were polished with Nos. 400, 800, 1200 and 1500 abrasive paper. The final dimensions of C/C samples were 10 mm×10 mm×2 mm. Then the samples were cleaned ultrasonically in turn by acetone, alcohol, and deionized water.

In the process of anodic oxidation treatment, the C/C samples and graphite electrode acted as the anode and the parallel cathode respectively. Anodization of C/C composites was carried out for 20 min at 30~35 °C. Ultrasound was introduced by an emitting device with the frequency of 45 kHz and the power of 100 W. The C/C samples were anodized in 0.5 M H₃PO₄ aqueous solution. The current density at 25 or 50 mA/cm² were conducted in the process of anodic oxidation treatment. In order to ascertain the effect of ultrasound on anodic oxidation treatment, the C/C samples were anodized either in the presence of ultrasound or in the absence of ultrasound.

Before C/C composites being introduced into the electrolyte for deposition of CaP coatings, they were initially treated at 50 mA/cm² by USAT. In the process of USECD, the C/C samples and graphite electrode acted as the cathode and the parallel anode respectively. The electrolyte solution consisted of 2.00×10⁻² mol/L NH₄H₂PO₄ and 3.34×10⁻² mol/L Ca(NO₃)₂ solution. The initial pH value was adjusted to 4.8. Ultrasound was introduced by an emitting device with the frequency of 45 kHz and the power of 100 W. Constant current of 1.6 mA/cm² were applied for 120 min and the temperature was controlled at 50±3 °C.

Static contact angles of test liquids on the untreated and treated C/C composites were measured in air using a software-controlled video contact angle system OCA 20 (Dataphysics Corp., Germany). The two test liquids are deionized water and glycerol. The surface energy values of the samples were obtained from the Owens-Wendt-Kaeble’s equation [5]. The chemical states of atoms in the untreated and treated C/C composites were investigated by a kratos axilx ultra spectrometer with an Al Kα X-ray source (1486.6 eV). In order to complete the study of the chemical modification of the C/C composites after USAT, Raman spectroscopy was performed with a Renishaw InVia system utilizing a 514 nm Ar laser. The roughness of C/C composites before deposition was measured with a confocal laser scanning microscope (CLSM) (Optelics C130, Lasertec Corp., Yokohama, Japan). A JEOL JSM - 6700 scanning electron microscope (SEM) was employed to observe the surface morphology of the deposited coatings. Quantitative element analysis of C, O, P and Ca was carried out by energy-dispersive X-ray analysis (EDXA) (INCA, Oxford, England). A Shimadzu XRD-7000 X-ray diffraction (XRD) instrument was used to analyze the crystal structure of the coatings. The shear bond strength of the CaP coatings on the untreated and treated C/C were evaluated on a universal testing machine (MTS Systems (Shanghai) Co., Ltd) in accordance with ASTM F1044-87.

3 Results and discussion

Nomenclature of the untreated and treated C/C composites is given in Table 1.

3.1 Contact angle and surface energy

Fig. 1 shows the photos and values of contact angles toward deionized water for UT-C/C, AT-C/C, USAT-C/C-25 and USAT-C/C-50. The UT-C/C are known to have hydrophobic properties with a contact angle of 110.0 ± 1.9°. However, the contact angle value decreased significantly after anodic oxidation treatment. AT-C/C, USAT-C/C-25 and USAT-C/C-50 had a contact angle of 29.6 ± 1.1°, 18.1 ± 4.7° and 13.8 ± 1.4°, respectively. This suggested that C/C surface subjected to AT or USAT had some hydrophilic functional groups on their surfaces which increased the wettability. Among the three kinds of treated C/C samples, USAT-C/C-50 had the lowest contact angle. This was due to the largest amount of hydrophilic groups grafted onto the C/C composites when they were anodized in the presence of ultrasound.

UT-C/C and USAT-C/C-50 had a contact angle toward glycerol of 102.1 ± 2.1° and 47.0 ± 2.7°, respectively. Their surface energy were 10.43 and 93.31 mJ/m², respectively. The increased surface energy of USAT-C/C-50 surface was possibly attributed to the variation of the surface composition and the increase of the specific surface [5]. The specific surface was caused by increasing surface roughness (see section 3.4).
3.2 XPS spectra of C/C composites

The XPS spectra of untreated and treated C/C composites are displayed in Fig. 2 (a). The UT-C/C showed peaks only for O and C elements. While the treated C/C showed peaks for O, C and P elements. Fig. 2 (b) shows the O/C and P/C atomic ratios obtained from high resolution XPS. The UT-C/C displayed a lower O/C ratio (0.1120) than the ones (0.3177-0.3867) of the treated samples. Especially USAT-C/C-50 showed the highest O/C ratio among the treated samples. This meant that O-containing groups had been introduced onto the C/C substrate with anodic oxidation [6]. The content of O-containing groups introduced onto USAT-C/C-50 was greater than that introduced onto AT-C/C-50 or USAT-C/C-25. It was the high content of O-containing groups (hydrophilic functional groups) that increased the wettability of the treated C/C. And the results of water contact angle and XPS both implied that high current density and the introduction of ultrasound helped to obtain high content of O-containing groups. The P/C atomic ratios shown in Fig. 2 (b) remained in the range of 0.05-0.07 at all levels of oxidation. The result indicated the presence of some amount of P-containing groups obtained from H$_3$PO$_4$ solution.

Fig. 3 shows high resolution XPS spectra of the selected C 1s, O 1s and P 2p for the corresponding C/C. Deconvolution of the C 1s spectra gives four peaks. Peak III (286.2-286.9 eV) was assigned to the carbon atom in hydroxide (C-OH) or ether (C-O-C) groups. The C ls signal from C-P type group also falls into this range [7]. Peak IV (288.8-289.1 eV) corresponded to the carbon atom in carboxyl (COOH) or ester (COOR) type groups [8]. As seen in the high resolution XPS spectra of C 1s, USAT-C/C-50 contained the highest amounts of carboxyl group among the untreated and treated C/C. This indicated that high current density and the introduction of ultrasound helped to graft high amounts of carboxyl (-COOH) group onto C/C composites in the anodic oxidation process. During subsequent deposition of CaP coatings on USAT-C/C-50, the carboxyl group on the surface would become negative charged in the electrolyte. The negative charged carboxyl group bonded with the calcium ion (Ca$^{2+}$) in the electrolyte. This kind of binding has a great effect on interface behavior and mechanical properties [9].

As shown in Fig. 3, the oxygen O 1s spectra have the best fit with three peaks. Peak I at 531.6-531.8 eV was attributed to the C=O or P=O group. Peak II at 532.5-532.8 eV correlated with P-OH, C-O-P or C-O-C, C-OH group. Peak III at 533.5-533.6 eV was due to carboxyl oxygen atoms in carboxyl group [8]. The phosphate P 2p spectra were fitted with three peaks. The peak at 132.9-133.5 eV was attributed to pentavalent tetra coordinated phosphorus (PO$_4$ tetrahedra) surrounded by different chemical environment. And phosphonates (compounds with C-P bonding) also fell in this region [10]. A larger contribution of the peak I for USAT-C/C-25 (46.63 %) and USAT-C/C-50 (35.49 %) than the one for AT-C/C was observed. This trend could be explained by the following reasons. Ultrasound in the electrolyte caused ‘acoustic streaming’ and/or the formation of cavitation bubbles. The formation and decay of cavitation bubbles involved transient extremes of temperature and pressure, and the bubbles could form microjets that impinged towards a surface [11]. On the one hand, transient extremes of temperature and pressure would increase ‘activated points’ in aromatic carbon ring system. Interaction of phosphorus with carbon may be strengthened. On the other hand, phosphoric acid near the anode gradually dehydrated and condensed into polyphosphates at transient extremes of temperature [10].

3.3 Raman spectra of treated C/C composites

The Raman spectra of carbon fiber and pyrolytic carbon in the treated C/C composites are represented in Fig. 4. For the UT-C/C, the Raman spectra of carbon fiber contained two prominent peaks, locating at about 1356 (D band) and 1585 (G band) cm$^{-1}$. The two prominent peaks of pyrolytic carbon located at about 1356 (D band) and 1591 (G band) cm$^{-1}$. The two prominent peaks of pyrolytic carbon located at about 1356 (D band) and 1591 (G band) cm$^{-1}$. For carbon fiber and pyrolytic carbon, the peaks at 643-647 cm$^{-1}$ were attributed to C-P bonds [12]. This implied that phosphate-like structure may be bonded with C/C by C-P bonding. Raman spectra show the Raman shift variations of the G bands with different treatment. For carbon fiber, 1585 (G band) cm$^{-1}$ for UT-C/C shifted to 1598, 1586, 1604 cm$^{-1}$ for AT-C/C, USAT-C/C-25 and USAT-C/C-50, respectively. The Raman shift for carbon fiber of USAT-C/C-50 showed a major shift. For pyrolytic carbon, 1591 (G band) cm$^{-1}$ for
UT-C/C shifted to 1606-1607 cm\(^{-1}\) for treated C/C. Especially for USAT-C/C-50, the frequency upshift of G band for carbon fiber and pyrolytic carbon were 9 cm\(^{-1}\) and 7 cm\(^{-1}\) respectively. The frequency upshift of G bands indicated electrochemical oxidation of carbon fiber and pyrolytic carbon in the C/C composites. The O-containing functional group could be grafted onto both carbon fiber and pyrolytic carbon by polarized covalent bond [13].

Combined with the XPS results, we inferred that the high content of O-containing groups and some amounts of P-containing groups were obtained on USAT-C/C-50. This suggested the O-containing group formation may be promoted by the energy input of the ultrasound and electrical field. P-containing groups by the linkage of C-P bonds with C/C were not seriously affected by electrical field while P-containing group formation may be promoted by ultrasound when C/C composites were treated with \(\text{H}_2\text{PO}_4\) (See section 3.2).

3.4 CaP coatings on the treated C/C composites by USECD

A layer of biomimetic CaP coatings were prepared on the surface of UT-C/C and USAT-C/C-50 by USECD. XRD results (data not shown) showed that the coatings on the UT-C/C and USAT-C/C-50 consisted of brushite (DCPD: dicalcium phosphate dihydrate, \(\text{CaHPO}_4\cdot2\text{H}_2\text{O}\)). And by EDAX quantitative analysis, the value of mole ratios of \(\text{Ca/P (n(Ca)/n(P)) of the coatings on UT-C/C and USAT-C/C-50 were } 0.98 \text{ and } 1.10 \text{ respectively, which are approximately the } \text{n(Ca)/n(P) value of DCPD. Nevertheless, n(Ca)/n(P) value of the coatings on USAT-C/C-50 was slightly higher than that of the coatings on AT-C/C. Fig. 5(a, b) shows SEM images of the coatings on UT-C/C and USAT-C/C-50 for 120 min. The DCPD coatings exhibited plate-like morphology. These results indicated the C/C subjected to treatment in \(\text{H}_2\text{PO}_4\) had a little effect on the structure, composition and morphology of the coatings deposited for 120 min.

Fig. 5(c-f) shows SEM images of the coatings on UT-C/C and USAT-C/C-50 for 30 s. Larger amount of CaP were deposited on the surface of USAT-C/C-50 compared with that being deposited on UT-C/C. By EDAX quantitative analysis, the \(\text{n(Ca)/n(P) of the coatings on the USAT-C/C-50 was obviously higher than that of the coatings on the UT-C/C.}

Especially for the flat CaP layer on the USAT-C/C-50, \(\text{n(Ca)/n(P attained 1.21. This indicated the C/C subjected to treatment in } \text{H}_2\text{PO}_4\text{ had a great effect on the composition and morphology of the coatings deposited in initial period. We assumed two factors that would be responsible for this:}

On the one hand, the USAT-C/C-50 had more active groups, such as \(-\text{PO}_4^{3-}\), \(-\text{COO}\), as demonstrated by XPS and Raman spectra. When the USAT-C/C-50 were immersed in the solution containing Ca and P ions in the process of USECD, these groups would attract Ca\(^{2+}\) via the following reactions [9]:

\[
\text{Ca}^{2+}+2\text{COO}^{-}\cdot\text{C} \rightarrow \text{Ca(COO-C\_)}_2 \quad (1)
\]

\[
3\text{Ca}^{2+}+2\text{PO}_4^{3-}\cdot\text{C} \rightarrow \text{Ca}_3(\text{PO}_4\cdot\text{C\_})_2 \quad (2)
\]

The large amounts of Ca\(^{2+}\) on USAT-C/C-50 would lead to the high \(\text{n(Ca)/n(P) of coatings.}

On the other hand, the solution supersaturation was constant for all types of specimens in this study. The critical free energy for the heterogeneous nucleation \(\Delta G_{\text{heter}}\) on the USAT-C/C-50 surface was reduced because of the increased surface energy of USAT-C/C-50 [14]. Thus, the surface of USAT-C/C-50 had a strong CaP induction ability and the large amounts of CaP were deposited on the surface.

The shear bond strength between the coatings and the C/C substrates were determined by the test. The average of shear strength of the coatings on the UT-C/C was 6.78±1.06 MPa while the average of shear strength of the coatings obtained on the USAT-C/C-50 was 12.14±1.30 MPa. The shear strength value of the coatings obtained on the USAT-C/C-50 was about two times of that of the coatings obtained on the UT-C/C. The shear strength of CaP coatings on UT-C/C was greater than that of CaP coatings deposited on C/C composites by plasma-spraying (7.15 MPa). It was also higher than that of C/C composite-bone which was 2.44 MPa, 20 weeks after implantation in mouse [3]. The probable reasons were as follows:

(1) The groups on USAT-C/C-50 could bond chemically to DCPD at the interface. The DCPD was linked with USAT-C/C-50 by the formation of carboxyl-calcium linkage \(-\text{Ca(COO-C\_)}_2\) and/or phosphate-calcium linkage \(-\text{Ca}_3(\text{PO}_4\cdot\text{C\_})_2\). As demonstrated in Fig. 5, the CaP layer covered the surface of the treated C/C intimately due to the chemical bonding between them. So the adhesion between the USAT-C/C-50 substrate and the CaP layer was strong.

(2) Using CLSM, we obtained the
roughness (Ra) of UT-C/C and USAT-C/C-50 to be 0.534 and 0.768 μm, respectively. The roughness of USAT-C/C-50 were higher than that of UT-C/C. This would lead to good adherence between coatings and substrates [15].

4 Conclusions

This work for described ultrasound assisted anodic oxidation treatment of carbon/carbon composites with \( \text{H}_3\text{PO}_4 \). The results revealed that the high content of O-containing groups and some amounts of P-containing groups were obtained on USAT-C/C-50. The surface of USAT-C/C-50 had a strong CaP induction ability and the large amounts of CaP were deposited on the surface of USAT-C/C-50 in the initial deposition process. The average of shear strength of the coatings obtained on the USAT-C/C-50 was 12.14±1.30 MPa and was about two times of that of the coatings obtained on the UT-C/C (6.78±1.06 MPa). By combining USAT with USECD techniques, relatively strong and compact coatings were obtained on the treated C/C substrate.

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References


Table 1
Nomenclature of the untreated and treated C/C composites

<table>
<thead>
<tr>
<th>Untreated or treated with or without ultrasound</th>
<th>Untreated</th>
<th>without ultrasound</th>
<th>with ultrasound</th>
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<tbody>
<tr>
<td>Current density (mA/cm²)</td>
<td>0</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>Nomenclature</td>
<td>UT-C/C</td>
<td>AT-C/C</td>
<td>USAT-C/C-25</td>
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Fig. 1. Photos and values of contact angle toward deionised water for (a) UT-C/C, (b) AT-C/C, (c) USAT-C/C-25 and (d) USAT-C/C-50.

Fig. 2 Survey scan XPS spectra and (b) XPS O/C and P/C atomic ratios of untreated and treated C/C.

Fig. 3. High resolution XPS spectra of the selected C 1s, O 1s and P 2p for (a) UT-C/C, (b) AT-C/C, (c) USAT-C/C-25 and (d) USAT-C/C-50.

Fig. 4. The Raman spectra of (a) UT-C/C, (b) AT-C/C, (c) USAT-C/C-25 and (d) USAT-C/C-50.

Fig. 5. SEM images of the coatings on (a) UT-C/C, (b) USAT-C/C-50 for 120 min, (c, d) UT-C/C and (e, f) USAT-C/C-50 for 30 s.