

PREPARATION OF FLUORINE-CONTAINING HYDROXYAPATITE COATING ON C/C COMPOSITES

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Abstract

To improve the osteo-integration ability of the surface of carbon/carbon (C/C) composites, Fluorine-containing hydroxyapatite coatings were prepared on C/C composites' surface using a two-step method of sono-electrodeposition and ion exchanges. The effects of ion exchanges on morphology, structure and composition of the as-received coating were investigated by SEM, EDAX, FTIR and XRD. The results show that, after the treatment of NaF, the diffraction peaks intensity of (112) and (300) of hydroxyapatite increased, while the diffraction peaks intensity of calcium phosphate decreased, implying that NaF can promote the change of tricalcium phosphate to fluoridated hydroxyapatite and increase the crystallization degree of the coating. The composition of coating are the mixture of HA and F-rich apatite (FA) at different ratio, and the diffraction angles of (112) and (300) peaks shift to a higher value than those of pure HA after the treatment by NaF. At the same time, the small plate-like crystals transformed to big ones. Fluorine content of the coating was 4.59wt.%. The bonding strength between the coating and C/C matrix increases slightly after immersion, which was up to 4.12MPa.

Keyword: Carbon composites; Coatings; Electrochemical treatment

1 Introduction

Carbon/carbon composites exhibit high toughness, high strength, resistance to fatigue and friction besides their biocompatibility. They are of pseudo- plastics. The small pores inside are beneficial to the growth of textures. Particularly, their modulus is equivalent to that of human bones. Compared with other biomaterials, Carbon/carbon composites were considered to be promising material for orthopedic and dental surgery. For their chemical bonding with bone tissue, speeding up the growth of new bone tissue and reducing occurrence of carbon debris, bioactive coating can be loaded on their surface [1-7].

Possessing both high conductivity and satisfactory bridging effect, the chemical performance of hydroxyapatite (HA) is similar with the calcium phosphate and inorganic salt in human bone tissue[8]. But the current problem is that the solubility of hydroxyapatite (HA) in the coating is quite high, thereby reduced the coating stability and prosthesis survivorship.

Fluorin is one of the microelements contained in human bone tissue and teeth [9,10]. Some recent researches indicate a small amount of F is helpful to enhance bone bonding capability. Because F ion is smaller than OH ion, F partly substituting OH in HA can improve the stability of HA as well as reduce its solubility. Hereby fluorapatite/hydroxyapatite possesses not only high stability but also good biocompatibility, which can guarantee good binding capability between prosthesis and bone tissue. Buy people find F ions(FA) substituting all the OH ions in HA not only lacks of bone conductivity but also can lead to decrease of bone activity owing to high content of F, which will even cause some kinds of adverse effects such as osteomalacia[11].

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Preparation of fluorapatite/hydroxyapatite coatings varies [12-15], such as plasma spraying, pyrolysis method, sol-gel method, electrophoresis technique etc.. By these methods, the coating was made under high temperature or possessed by high-temperature treatment. This will influence the stability of coating as well as decrease the bioactivity of the coating. Hence, exploring of a preparation which can both effectively control its microstructure, chemical composition and guarantee bioactivity of fluorapatite/hydroxyapatite coatings has a crucial practical significance.

This research takes a combined process of ultrasonic-electrodepositing method and ion exchange methods to prepare the fluorapatite/hydroxyapatite coating. First of all, prepare the hydroxyapatite on the matrix of carbon/carbon composites by ultrasonic-electrodepositing method, and then transform it into fluorapatite/hydroxyapatite coatings by ion exchange. On account of ultrasonic-electrodepositing method and ion exchange are both preceded smoothly under mild conditions; it can not only guarantee the bioactivity of coatings but also have more controllable test parameter so as to effectively control their microstructure chemical composition and the content of F in the coatings.

2 Experimental

2.1 Pretreatment of matrix

The matrix sample was a 2D-CVI carbon/carbon composites. The size was 10mm×10mm×2mm. The sample surface was grinded by 400[#] and 800[#] abrasive paper. Then it was ultrasonically cleaned by water, alcohol and acetone and dried in the air.

2.2 Experimental methods

2.2.1 Ultrasonic - electrodepositing method

Use platinum wires as anode and sample as cathode. Ultrasonic output frequency is 25kHz, and output power of ultrasonic equipment is 100W. Electrolyte is made up of 0.01mol·L⁻¹NH₄H₂PO₄ and 0.0167 mol·L⁻¹Ca(NO₃)₂ (Both are analytical reagent.) solutions. Use constant current ;current density is 5mA/cm²; the initial pH value of ammonia water or nitric acid solution is 5.0; apply circulating control system of constant temperature water bath 50℃; control range is ±1℃; dried in the air after depositing.

2.2.2 Ion exchange methods:

Soak the ultrasonic-electrodepositing sample in the mixed solution of $c(\text{NaF})=0.05 \text{ mol}\cdot\text{L}^{-1}$ and $c(\text{K}_2\text{HPO}_4+\text{KH}_2\text{PO}_4)=0.15 \text{ mol}\cdot\text{L}^{-1}$, pH=7.0 ; control system of constant temperature water bath 50℃; control range ±1℃; Soak time 24h.

2.3 Analysis measurement:

JSM-6460 (with energy spectrum EDAX) scanning electron microscope was applied in measurement of the surface topography and elements-scanning quantity analyzing; X'Pert PRO MPDX x ray diffractometer is used to investigate crystal structure of the coatings; EQUINOX55 Fourier

transform infrared spectrometry(FTIR) measures the vibration spectrum of phosphate and hydroxyapatite in the coatings. pHs-25 acidity meter is to measure the pH value of electrolyte.

2.4 Testing method for bond strength of coating

Bonding-tensile are used to analyze the bonding strength of the interface between the coating and substrate. Cement the samples by epoxy resin. Record the tensile stress when the coating is detached from the matrix carbon/carbon composites with the coating drawn by CMT7204 electronic universal testing machine at speed of 0.2mm/min. There are five parallel samples whose average value is used to show the bonding strength of the coating. The bonding strength of the interface between the coating and substrate should be calculated with the following formula $\sigma=F/S$ in which F refers to the maximum pulling force as the coatings fractures; S refers to the area of samples; σ refers to the bonding strength of interface.

3 Results and discussion

3.1 Composition and Structure of Coatings

Fig1 respectively shows XRD patterns of coatings on C/C composites after sonoelectrodeposition only and after sonoelectrodeposition in addition to ion exchanges. With Fig1, it can be found that the composition of coatings after sonoelectrodeposition also include a small amount of calcium phosphate besides hydroxyapatite. In the Fig1, the intensity of diffraction peaks (211), (112)and (300) of hydroxyapatite is comparatively weak. The structure of fluorapatite/hydroxyap is the same as that of hydroxyapatite, as well as the diffraction peaks. After sodium fluoride (NaF) – treatment, all of the three diffraction peaks hydroxyapatite have been intensified. Particularly (112) has been largely intensified. On one hand, this proves that sodium fluoride (NaF)-treatment is beneficial to the elevation of the crystallize degree in the coatings; on the other hand, the intensifying of diffraction peak also reveals that fluorine has partly substituted hydroxyl radicals in hydroxyapatite. Fig.1 (B) reveals that after fluoridizing treatment, the diffraction peak of calcium phosphate decreased, which indicates that fluoridizing treatment can speed up calcium phosphate transforming into fluorapatite/hydroxyap [16].

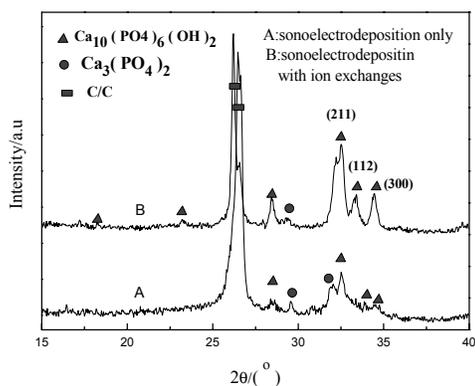


Fig.1 XRD patterns of coating on C/C composites (A)sonoelectrodeposition (B)sonoelectrodeposition and ion exchanges

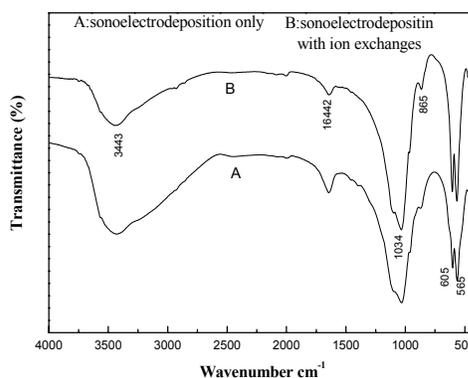


Fig.2 FTIR spectra of coating on C/C composites (A)sonoelectrodeposition (B)sonoelectrodeposition and ion exchanges

sonoelectrodeposition as well as ion exchanges. $565, 605, 1034\text{cm}^{-1}$ are the absorption bands of PO_4^{3-} ; 3421cm^{-1} is the absorption bands of OH^- ; 1646cm^{-1} is the absorption bands of adsorbed water; 865cm^{-1} is the absorption bands of HPO_4^{2-} . According to XRD pattern, there are not other phases. The appearance of HPO_4^{2-} absorption bands confirms that coatings, divided as calcium-deficient apatite $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ [17], $0 \leq x \leq 1$, when $x=0$ are HA; when $x=1$, are $\text{Ca}_3(\text{PO}_4)_2$. Owing to identical structure, their differences can't be found in XRD pattern. It also shows that the intensity of hydroxyl groups and adsorbed water groups has obviously weakened after ion exchanges, which indicates that fluorine has partly substituted hydroxyl radicals in hydroxyapatite and form fluorapatite/hydroxyap.

EDAX was used in quantitative analysis of element content in the coatings by these two methods ((A) sonoelectrodeposition only, (B) sonoelectrodeposition and ion exchanges)). The results can be seen in Fig1. As shown from the Fig, after ion exchanges, fluorine content in the coatings is 4.59%; $n(\text{Ca})/n(\text{P})$ ratio decreases slightly, which perhaps is related with low pH value. The mechanism of ion exchanges is dissolving and deposition. Under the pH of this experiment, there would be a little bit of calcium dissolved in the coat and lost. According to the result of that calcium hydrogen phosphate can be transformed into HA by disposing of sodium hydroxide[18,19]. Therefore raising the value of pH properly can not only transformed the other parts of the coat into HA, but also can keep or even increase $n(\text{Ca})/n(\text{P})$.

3.2 The surface of the Coating

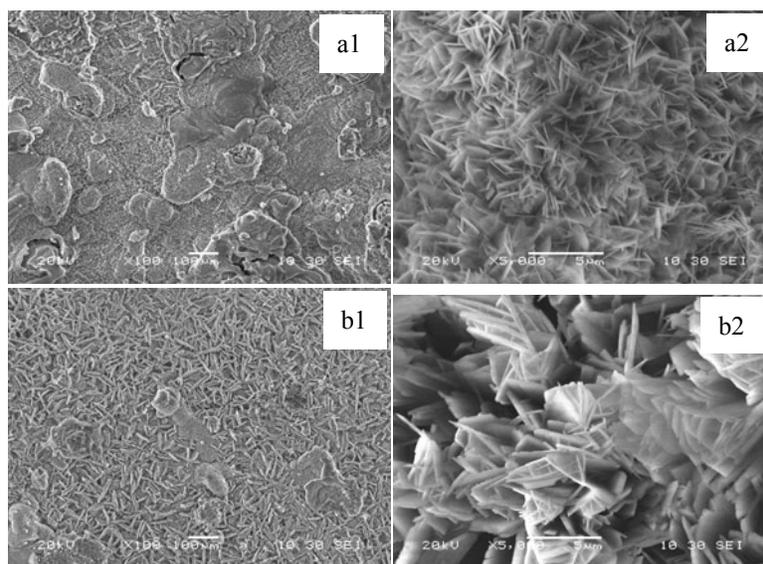


Fig.3 SEM picture of the calcium and phosphorus coating for the carbon composite(a1,a2) sonoelectro-deposition only and (b1,b2)sonoelectrodeposition and ion exchanges)

Fig 3 is SEM micrograph of coating on C/C composites after sonoelectrodeposition and ion exchanges. Plate a1 and plate b1 in the picture 3 are the scanning surface pictures amplified by 100 times. Plates (a2) (b2) are amplified by 5000 times. From plate (a1) and (b1), it can be seen the coat is still fine and close in texture and well distributed with carbon and carbon matrix after the ion exchanges. It can be observed from the plate (a2) (b2) that the shape of the surface underwent changes. The crystal material has become bigger and the lamellar thickness of them has been increased. This

also shows that the process of ion exchange is the mechanism of dissolving-deposition. [20].

Table1 Molar ratios of Ca/P and F/Ca and weight% of F of coating on C/C composites for (A) sonoelectro- deposition only and (B) sonoelectrodeposition and ion exchanges

Processing	A	B
$n(\text{Ca})/n(\text{P})$	1.62	1.58
$n(\text{F})/n(\text{Ca})$		0.303
F(Weight%)		4.59

3.3 The analysis of bonding strength for coating

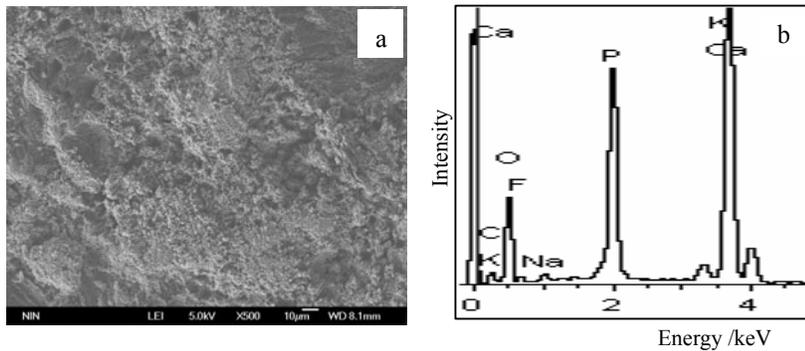


Fig.4 SEM photo (a) and EDAX pattern (b) for the C/C-FHA sample after bonding strength

After sucking and totally solidifying electrodeposited coating on the C/C matrix for steeping the electrodeposited coating and metallic fixture by epoxy resin, to measure the integrate intensity of the coating through the experiment of an electronic stretching test machine. The integrate intensity of coating and matrix is 4.08MPa, which increases a little compared with the sample without immersion (3.85MPa). This result shows that it can not decrease the integrate intensity of coat and matrix after steeping. Study shows that after planting the coating in the body of rabbit for 6 weeks, integrate intensity of HA and bone is 1.594 ± 0.715 MPa [21]. Therefore this kind of coat can be continually planted in the body to make research.

Carbon/carbon composites is a kind of porous material. Applying sonoelectrodeposition can deposit the particles into the porosity of the C/C composites matrix. Through this way the integrated intensity of the coat and matrix can be increased. It can be clearly seen the existence of the coat from the surface of the sample drawn. (Fig 4 (a)).Therefore it is mainly the inside of the coat has lost efficacy. Fig 4(b) is the EDAX surface analysis of Fig 4(a). It is obviously that there is the element of Ca, P, O, F left. So it can be drawn that the coat lost of efficacy primarily caused by the ruining of the cohesion of the coating.

3.3 The exploring of mechanism of ion exchanges

Ion exchanging method can effectively control of part or wholly replaced some OH^{-1} ion in the apatite[22]. This has already been broadly adopted in compounding of apatite mixed with hydroxy. Steeping the powder of HA in the NaF solution, the compounding of the apatite with F hydroxy is realized by exchanging the ion of F and OH. When the pH value of the solution is four, HA will be dissolved and reacted with element F and form CaF_2 . When the pH value is increased to 7, CaF_2 in the

solution will react with other ion and form FHA[23]. So the pH value of the solution we chose is 7, meanwhile we put the buffer of phosphate solution into it to keep the pH value during the steeping process. If the steeping solution is not put the phosphate, experiment shows that the pH value of the solution will be decreased as the time goes on even the prime pH value of the solution is 7, which reflected in Fig 5. The decreasing of the pH value of solution will lead to part of the coating transformed into CaF_2 . XRD has verified under the condition without phosphate, there is some CaF_2 formed by steeping HA coating. (Fig 6)

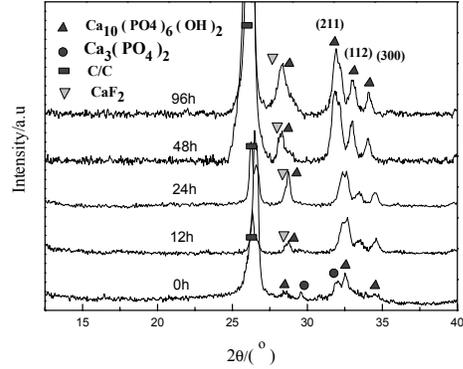
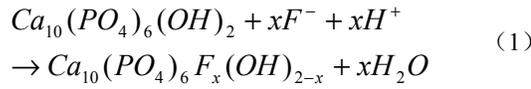


Fig.6 XRD patterns of coating on C/C composites for various immersion time without adding phosphate

Therefore in order to transform HA into FHA, to avoid the reaction of forming CaF_2 , it should put the buffer of phosphate solution to keep the pH value unchanged. The following reactions happened during the process of ion exchanges:



The reaction rate equation of forming FHA is as follow:

$$\frac{d(\text{FHA})}{dt} = kC_{\text{F}^-}^x C_{\text{H}^+}^x \quad (0 < x < 1) \quad (2)$$

Of them, $d(\text{FHA})/dt$ is the speed of the FHA formation, K is the speed constant of FHA formation, CF and CH^+ is the density of F and H in the solution respectively. It is clearly that the higher of the fluorine density is, the higher speed of the FHA formation will be.

When the density of F is high enough ($x \approx 1$), the equation (2) can be written as below:

$$C_{\text{F}^-} = C_{\text{F}_0^-} e^{-Kt} \quad (3)$$

Of them, $K = kC_{\text{H}^+}$, $C_{\text{F}_0^-}$ refers to the prime density of the fluorine ion which put into the steeping solution. It can be seen from the equation that increasing the steeping time will be helpful for promoting the replacing rate of the element F^- .

$$K = kC_{\text{H}^+}, \quad C_{\text{F}_0^-}$$

It can be drawn that from the reaction equations, transforming HA into FHA by applying the ion

exchanging method is influenced by multi- factors. Such as the density of ion fluorine at beginning, pH value of the solution, steeping time, and temperature, etc. we can make use of these factors to control the amount of fluorine in the coat effectively. Therefore when transforming HA into FHA by applying the ion exchanging method, it can not be only operated in the moderate condition, but also can we take advantage of more technological parameters to control the amount of fluorine. All of these can guarantee the stability and biological activity of the coat. This is an effective and proper way to produce FHA. The amount of fluorine in the coat produced in this experiment is 4.59%, the amount of fluorine in the bone organization is between 440 and 800ppm. Being excessive and lacking of the amount of fluorine will bring about pathological changes. Therefore this kind of coating can be provided for research on inserted plantation to study the biological characteristic of it.

4 Conclusion

Being disposed by NaF is good for raising up the crystallizing extent of the coat. The (300) diffraction peak of HA (112) is raising up clearly, while that of calcium phosphate is decreasing. Fluorine replaced part of the hydroxy of HA and formed the FHA coat contained F hydroxy. The amount of fluorine in the coat is 4.59%, the rate of $n(\text{Ca})/n(\text{P})$ is decreased a little. The outside surface has changed after ion exchanging. The crystal has become bigger, and the lamellar thickness of the crystal has been increased. The analysis of integrate intensity of the coat shows that the integrate intensity of coat and matrix has been increased to some extent. The integrate intensity of them is 4.08MPa. Combining the methods of sonoelectrodeposition with ion exchanges can make fluorine replace part of the hydroxy of HA and formed the FHA coating contained F hydroxyl. The amount of fluorine in the coating can be controlled by disposing the following technological parameters: time, temperature, the density of ion fluorine, etc.

Acknowledgements

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