



# Effect of different chemical treatments on hydroxyapatite formation of carbon fibers reinforced carbon and SiC dual matrices composites

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## ABSTRACT

In this study, the carbon fibers reinforced carbon and SiC dual matrices (C/C-SiC) composites with 3D needle-punched structure were fabricated by liquid silicon infiltration (LSI). This work focused on the effects of different chemical treatments (aqueous of HF/HNO<sub>3</sub>, aqua regia and CaCl<sub>2</sub> solution) on apatite formation under biometric condition. Samples were characterized by scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR) and so on. The ability of hydroxyapatite formation was evaluated by simulated body fluid (SBF) immersion test. The formation mechanism of apatite layer grown on modified C/C-SiC composites was also revealed. The results showed that modified sample surfaces were consisted of groups –OH, –COOH or/and Ca<sup>2+</sup> ions. These negatively functional groups attracted surrounding Ca<sup>2+</sup> ions to form and anchor the nucleus. The Ca<sup>2+</sup> ions contributed to the apatite nucleation and proliferation by increasing apatite saturation. The SBF results showed that a homogeneous precipitation layer of apatite formed on C/C-SiC after about two weeks under the combined actions of aqua regia and CaCl<sub>2</sub>. This suggested treatments of aqua regia and CaCl<sub>2</sub> solution led to positive results in terms of apatite formation of modified C/C-SiC compared to the native C/C-SiC material.

## 1. Introduction

Carbon and carbon based materials have been extensively used in aviation, brake system, electrochemical capacitors, catalysis, biomedical industry and other fields owing to their special characteristics [1–4]. Carbon/Carbon composite (C/C), which displaying superior biocompatibility, corrosion resistance and mechanical properties was considered as potential material of hard tissue replacement. In particular, its elastic modulus was close to that of human bone [5–7]. However, the C/C composites were biological inert and couldn't stimulate the growth of osseointegration interface. The release of carbon debris around the untreated C/C composites caused a blackening of the tissue and thereby limiting implants widely application [8,9]. Generally, preparing bioactive coating on C/C is a good way to endow surface biological activity and reduce wear debris, like hydroxyapatite (HAp), bio-glass coating etc. HAp showed excellent bioactivity and biocompatibility due to its similar composition and structure to mineral phase of bone [10]. Whereas, the brittleness and solubility of HAp, as well as the much higher thermal expansion than C/C affected the stable

bonding of substrate and coating.

SiC is a kind of stable and high strength bio-ceramic material. The previous studies also illustrated that Si-infiltrated C/C materials, called C/C-SiC composites, showed superior strength, tribological property and mechanical fatigue property in compared with C/C composites [11–13]. In addition, SiC has been proved to be non-toxic, chemical stability and biocompatible for long-term biomedical application but inert in vivo and in vitro [14–16]. Therefore, the SiC was applied into C/C composites as a hard barrier to reduce the shedding of C particles in this paper due to the stability and well adhesion between C/C and SiC phase. In order to deal with the problem of bio-inert, a bioactive coating of HAp was studied. Various functionalization techniques have been proposed to deposit hydroxyapatite on material surface, like plasma-spraying, electrophoretic deposition, pulsed laser depositions, sol-gel [17–19]. In this study, we hope to improve the capability of HAp generation on C/C-SiC by changing its surface properties with simple chemical modification. According to the literature, Ca<sup>2+</sup> ions have been examined in an effort to promote apatite forming [20]. In studies performed by M Tanahashi [21], certain functional sites composed of

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**Table 1**  
The main performance guideline of carbon fiber.

Type	Diameter ( $\mu\text{m}$ )	Carbon content (%)	Volume density ( $\text{g}\cdot\text{cm}^{-3}$ )	Tensile strength (MPa)	Tensile modulus (GPa)	Ductility (%)
T700	7.0	96	1.80	4900	230	2.1
T300	7.0	92	1.76	3530	230	1.5

carboxyl groups played an effective role in the heterogeneous nucleation of apatite. On the other hand, the adhesion and growth of apatite layer might also be affected by material's surface properties. This was partly due to the surface roughness and porosity allowed the bone tissue and capillary to grow inside pores [22].

Considering these aspects, the C/C-SiC composites were modified with different aqueous solution (respectively aqua regia,  $\text{CaCl}_2$  solution, aqua regia +  $\text{CaCl}_2$  solution) after pretreatment of HF/ $\text{HNO}_3$ . The aim of the paper is to evaluate the influence of various composite modifications for inducing apatite formation on specimen surfaces and obtain the optimal treatment to improve bioactivity of C/C-SiC composites.

## 2. Material and methods

### 2.1. Preparation of fabrication

T700 and T300 polyacrylonitrile based (PAN) carbon fibers (12 K, 1 K = 1000 filaments) (as shown in Table 1) were employed and supplied by the Toray, Japan. The particle size and purity of the Si powder were  $\leq 47\ \mu\text{m}$  and 99.3%, respectively, according to information supplied from the manufacturer of Da Zelin-silicon Co., LTD, Beijing, China.

The C/C-SiC composites with a density of 2.0–2.3  $\text{g}/\text{cm}^3$  in this study were prepared by three steps processes including preparation of fiber preforms, densification and siliconization. Fig. 1 is the diagram of fiber preform with sandwich structure. The liquid Si was infiltrated into porous C/C composites using the Liquid Silicon Infiltration (LSI) process during siliconization and further reacted with C as follows [23,24]. The LSI was conducted at range of 1500–1900  $^\circ\text{C}$ , and molten silicon penetrated into the open pores of the residue under the action of capillary forces [25].



Finally, the C/C-SiC composites consisting of carbon fibers embraced by pyrolytic carbon (PyC) and SiC layer outside were obtained [23].

### 2.2. Surface chemical treatments

The schematic of different chemical treatment processes for C/C-SiC composites was shown in Fig. 2. The C/C-SiC composites were washed ultrasonically with ethanol and deionized water before surface modification. After drying, they were etched in HF/ $\text{HNO}_3$  for 30 min at plastic bottle and then carefully rinsed with distilled water until neutral PH was reached. Afterward, specimens were submerged in aqua regia with stirring for 30 min or 1 M  $\text{CaCl}_2$  solution at 80  $^\circ\text{C}$  for 1 d. These specimens were grouped as B1, B2 and B3 based on the three different treatments (as shown in Fig. 2). The HF/ $\text{HNO}_3$  solution was mixed in

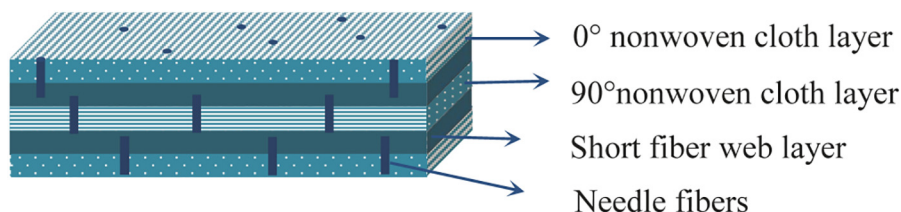


Fig. 1. Structure diagram of carbon fiber preform.

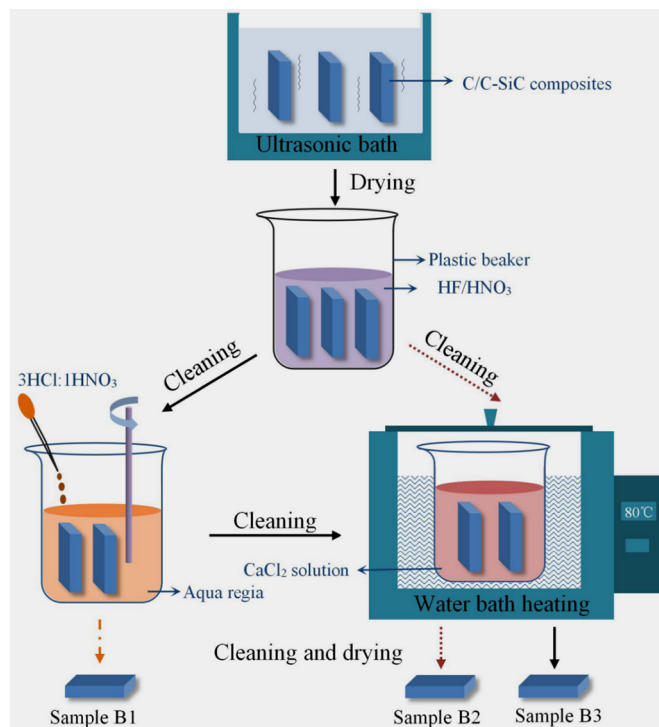


Fig. 2. Schematic representation of different chemical treatment processes for C/C-SiC composites.

plastic vessel by HF (48 wt%) and concentrated  $\text{HNO}_3$  (68 wt%) according to the volume ratio of 1.66:1. After each time of acid treatment, specimens should be immersed in ultrasonic bath and rinsed by distilled water to ensure the acid has been clean out clearly.

### 2.3. Soaking in SBF

The SBF with ion concentrations and pH nearly similar to human blood plasma was (as shown in Table 2) prepared according to procedure developed by Kokubo [26]. The reagents of NaCl,  $\text{NaHCO}_3$ , KCl,  $\text{K}_2\text{HPO}_4\cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , 1.0M-HCl,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  were dissolved in double distilled water one by one following the calculated amounts [27]. This solution was buffered at pH 7.4 at 36.5  $^\circ\text{C}$  by Hydrochloric acid (HCl) and tris (hydroxymethyl aminomethane,  $(\text{CH}_2\text{OH})_3\text{CNH}_2$ ). C/C-SiC composites modified by different treatments were soaked in the SBF at 37  $^\circ\text{C}$  for time periods from 15 to 50 days. To ensure that pH and ion concentration would be stable, the SBF was refreshed every three days. After exposure, the samples were removed from the soaking medium and dried in desiccator at 60  $^\circ\text{C}$  for 24 h.

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