A NOVEL METHOD FOR FABRICATING CARBON FIBRE REINFORCED SILICON CARBIDE COMPOSITES VIA 3D PRINTING TECHNOLOGY

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ABSTRACT

Carbon fibre reinforced silicon carbide (CFRS) composite, are prime candidates for high temperature structural materials in aerospace, nuclear and transportation areas due to their refractory nature, high specific strength, high thermal conductivity and excellent tribology performance at elevated temperature. This research has focused on demonstrating the feasibility of using 3D printing technology to make CFRS composites components. Firstly, short carbon fibre composites were prepared through 3D printing process, which serves as the reinforcing framework. The processing parameters were optimized to obtain the 3D objects with high precision. Secondly, C/C preforms with controllable porosity were generated by infiltrating with phenolic resin followed by carbonization process. Finally, liquid silicon infiltration (LSI) has been performed using the aforementioned C/C porous preforms to convert part of the carbon to silicon carbide. The microstructure evolution and mechanical properties of the CFRS composites were carefully investigated through various characterization techniques. The major advantages of this method over other ceramic processing techniques are the enhanced capability of making near net shape CFRS composite parts with complex structures, full density as well as high performance at a low cost.

1 INTRODUCTION

Carbon fibre reinforced silicon carbide (CFRS) composite has become a promising material in many different areas, especially aerospace, nuclear energy, high-speed trains industries, due to its low density, high strength, superb temperature tolerance and corrosion resistance, etc [1-3]. With the development of key technologies in the above-mentioned area, the demand of the ceramic based composite is continuously increasing and the structures of the components also tend to be extremely complicated [4]. So far, the primary manufacturing methods for carbon fibre reinforced silicon carbide composites contains: pressureless sintering, hot pressing sintering, precursor infiltration pyrolysis (PIP), chemical vapour infiltration (CVI) and liquid silicon infiltration (LSI) [5]. Compared with other methods, LSI has the advantages of low sintering temperature, cost effective and capability of fabricating parts with large scale and complex geometry, which was widely applied in manufacturing telescope mirror blank, brake disc and mechanical seals, etc [6]. LSI basically has two steps: first preparing the carbon fibre reinforced C/C porous preforms, and then infiltrating the C/C preforms with liquid silicon at elevated temperature to form silicon carbide through the reaction between silicon and carbon.

Aiming at manufacturing the carbon fibre reinforced silicon carbide composite parts with complex structure, we propose here a novel compound manufacturing process, combining the additive manufacturing (namely 3D printing) and LSI process together, which overcomes the constrain of shape

complexity and high sintering temperature. Firstly, the carbon fibre composite powder was prepared by coating the carbon fibre with thermoplastic phenolic resin through solvent evaporation method. Then, the porous C/C preform was obtained based on the composite powder by laser selective sintering (SLS) 3D printing process. After the optimization of pore structure, the liquid silicon was infiltrated into the C/C preform through LSI, and the carbon fibre reinforced silicon carbide composite is finally obtained. This research mainly focus on the effects of resin infiltrating times on the bulk density and apparent porosity, and then on the flexural strength and phase constitution of CFRS composites.

2 EXPERIMENTAL PROCEDURE

2.1 Material preparation

In this work, carbon fibre powder (~1.76g/cm^3) with an average diameter of 7 μm and length of 75 μm, and thermoplastic phenolic resin (density: 1.22 g/cm^3, PF2123^{TM}) mixed with hardener methenamine was used as raw materials for the fabrication of phenolic resin coated carbon fibre (phenolic resin/CF) composite powder. The phenolic resin/CF composite powder was prepared by the following procedures: (1) firstly, the phenolic resin powder was completely dissolved in acetone solution with a mass ration of 1:1; (2) then, the CF powder was added into the aforementioned solution and a further ball milling was made to obtain the homogenous suspension; (3) after ball-milling process, the acetone was distilled out and the phenolic resin began to crystallized preferentially taking CF as nuclei; (4) finally, the obtained precipitation was dried in a vacuum oven at 60 ^{o}C and then crushed by universal grinder. The phenolic resin volume in the starting composite powder was 30 Vol%.

The CFRS composite was fabricated by a three-step procedure, and the processing route is shown in Fig.1.

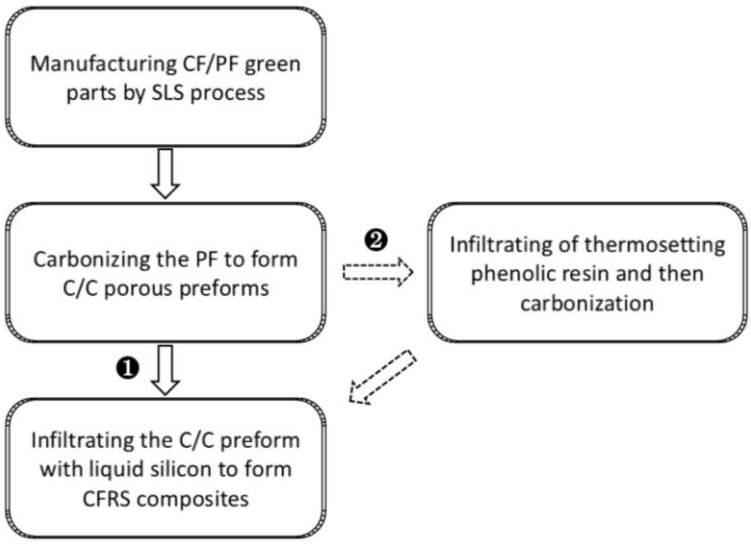

Figure 1: Processing scheme of manufacturing CFRS composites

Step 1: The green part was manufactured by a SLS process. The sintering experiments were conducted on the HK P320^{TM} SLS machine (Wuhan Huake 3D Technology Co.Ltd., China). The SLS system was equipped with a power continuously adjustable CO_2 laser with a wavelength and beam diameter of 10.6 μm and 200 μm, respectively. The processing parameters were set as follows: the laser power was 4 W, the scanning speed was 2000 mm/s, the powder layer thickness was 0.1 mm, the scan spacing was 0.15 mm and the part bed temperature was set as 60°C.

Step 2: The green parts was carbonized into porous C/C preform by decomposing the phenolic resin to pyrolysis carbon. The pyrolysis process was conducted in a tube furnace under the protection of pure argon. First, the green parts were heated to 170 ^{o}C from room temperature and keep for 30 min, to facilitate curing the un-cured phenolic resin under fast laser. Then the temperature was continually increased to 450 ^{o}C at a heating rate of 2 ^{o}C/min and keep for 1h, during which the phenolic resin decomposition and outgassing occurred. Finally, the parts were further heated to 900 ^{o}C for carbonization and followed by nature cooling.

Step 3: The porous C/C preform was infiltrated with melt liquid silicon. The C/C preform was placed in a BN-coated graphic crucible, and the Si particles (industrial grade, average particle size: 1~3 mm) was put on the top and bottom of the C/C preforms. The infiltration was conducted under the vacuum atmosphere at 1500 ^{o}C for 1h.

In order to increase the density of C/C preforms, a soluble thermosetting phenolic resin (THC-400, Shaanxi Taihang Impedefire Polymer Co.Ltd., China, carbon yield: >60%) was used as intermediate polymer to infiltrating the C/C preform, then cured and carbonized to filling the pores. Three different C/C preforms with no infiltration, one infiltration and twice infiltration of resin was prepared, designating C/C-0, C/C-1 and C/C-2. The corresponding CFRS composites parts were labelled as CFRS-0, CFRS-1 and CFRS-2.

2.2 Characterization

The density and apparent porosity of the C/C preforms and CFRS composites were measured by Archimedes method. The morphologies of the powders, fracture surface of the green parts, polished surface of the CFRS composites were examined via a using a field scanning electron microscope (FESEM, JSM-7600F JEOL) and an environmental scanning electron microscopy (ESEM, Quanta 200 FEI). All samples were sputter-coated with platinum to avoid charging before observation. The composition of the specimens was analysed by XRD-7000 X-ray diffractometer (SHIMADZU Corporation, Japan), using Cu Kα radiation in the 2θ range between 10 ^{o} and 90 ^{o} using a scan speed of 10 ^{o}/min. Three point flexural testing was performed in accordance with ISO 14704-2008, using a universal testing machine (Zwick/Roell Z010, Ulm, Germany) at a crosshead speed of 0.5 mm/min.

3 RESULT AND DISCUSSION

3.1 Powder characteristics

Fig.2 shows the SEM micrographs of the raw CFs and the phenolic resin/CF composite powder. As shown in Fig.2 (a), the carbon fibres show a uniform distribution of 10~100 μm in length and 6~8 μm in diameter. It also can be seen that the raw CFs have relatively smooth surfaces but small grooves can still be observed, which can facilitate forming a good surface adhesion with the phenolic resin through mechanical interaction. In Fig.2 (b), the phenolic resin/CF composite powder shows an inherited morphology as that of the CF powder. It can be clearly seen that a thin layer of phenolic resin was uniformly coated on the surfaces of CFs, which serves as the binder to connect the adjacent CF to form a free-standing monolith.

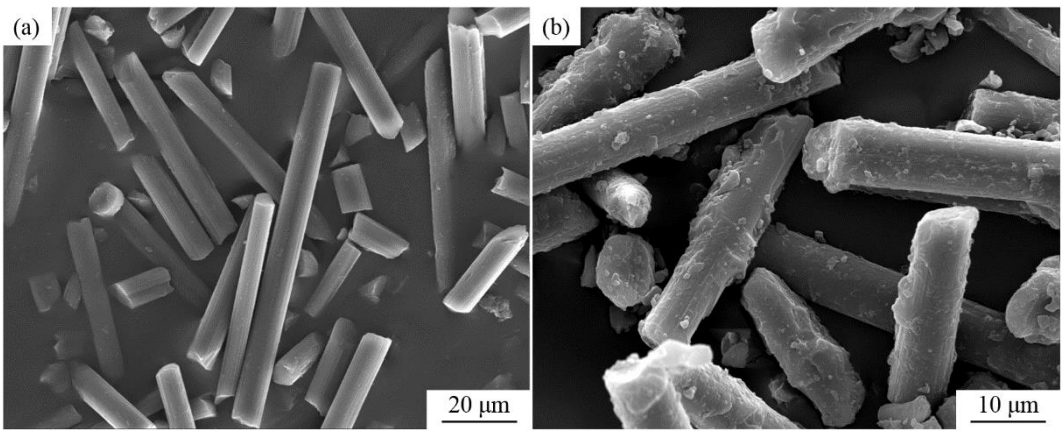

Figure 2: The mophologies of the raw carbon fibres and the phenolic resin coated carbon fibres.

3.2 Morphology analysis

Fig.3 shows representative microstructures of SLS green parts, carbonized parts and resin infiltrated parts. As shown in the Fig.3 (a), the phenolic resin and carbon fibres are easily distinguished, phenolic resin was melt and cured under the radiation of the laser beam, and thus bonded the carbon fibres into a porous but self-standing green parts. It also shows that some un-sintered phenolic resin still exist on the

surfaces of carbon fibres, because that insufficient energy input coming from the fast moving laser can only partially fuse the phenolic resin. During carbonization, the phenolic resin in the green parts undergoes fully curing, outgassing, chemical bond reorganization, shrinkage and formation of structural pyrolytic carbon, so the surfaces of the carbon fibre in carbonized parts show smooth manners (Fig. 3(b)). Due to the transformation of phenolic resin to pyrolysis carbon, the apparent color of the parts change from black to dark gray (Fig.3 (d)), this is because of the different reflectivity of visual light. Fig.3 (c) shows the fracture morphology of the resin infiltrated parts. Compared to the carbonized parts, the pores between the carbon fibres were first filled with liquid resin, after curing and carbonization, the pyrolysis carbon was retained, thus improving the carbon content and meanwhile decrease the porosity in the C/C preform, which is significantly important to the phase constitution and mechanical strength for the final parts. It was also found that there are gaps between carbon fibres and the pyrolysis carbon, which is caused by the shrinkage of liquid resin during solidification.

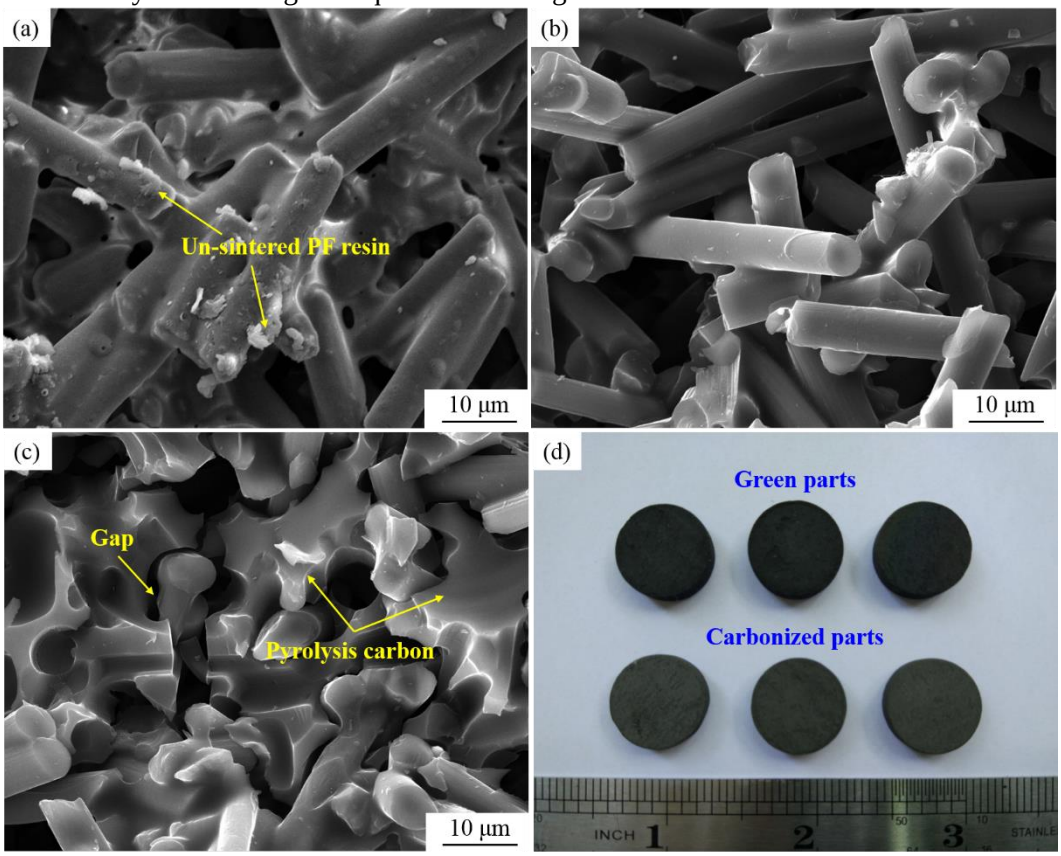

Figure 3: Top surfaces of (a) SLS green parts, (b) C/C-0, and (c) C/C-1, and (d) picture of SLS green parts and carbonized parts.

3.3 Bulk density and apparent porosity of the C/C preform

Bulk density and apparent porosity are important properties of the carbon preform that determine the success of formation of silicon carbide by liquid silicon infiltration (LSI). Singh and Behrendt [7] have reported that for a full conversion of porous carbon preform to SiC product with no residual Si and porosity, the critical preform density is 0.964 g/cm^3. The volume increase can range from about 45 to 140 % according to the different type of carbon [8]. So for preform's bulk density is greater than 0.963 g/cm^3, there is insufficient pore volume to accommodate the volume increase due to the reaction of carbon with silicon to form silicon carbide [9]. This phenomenon is called shock-off [5]. Table 1 shows the evolution of bulk density and apparent porosity of the different C/C preforms. The bulk density and apparent porosity of green parts are 0.476 g/cm^3 and 70.8%, respectively. The bulk densities the C/C preforms vary from 0.458 to 0.81 g/cm^3, and the apparent porosities vary from 54.8 % to 74.9 %.

	Green parts	C/C-0	C/C-1	C/C-2
Bulk density (g/cm^3)	0.476	0.458	0.624	0.81
Apparent porosity (%)	70.8	74.9	64.6	54.8

Table 1: Bulk density and apparent porosity of green parts and different C/C preforms.

3.4 XRD analysis of composite parts

Crystal structure of the CFRS composite was investigated by X-ray diffraction and the results were shown in Fig.4. The composite mainly consist of β-SiC and silicon [10]. Peaks assigned to carbon are not determined in CFRS-0 and CFRS-1, which indicates that carbon had been consumed completely by the siliconization reaction. But for the C/C-2, the peak assigned to carbon was determined. According to the carbon dissolved-precipitate mechanism, the liquid silicon rapidly infiltrates into the pores of C/C preform and dissolves the carbon at the interfaces, then heterogeneous silicon carbide crystallization occurs at the interface, which isolates carbon and liquid silicon thus terminating the direct contact reaction. So when the infiltrated time is increased, the content of pyrolysis carbon increased and become continuously distributed, thus residual carbon can be found in the final composite parts.

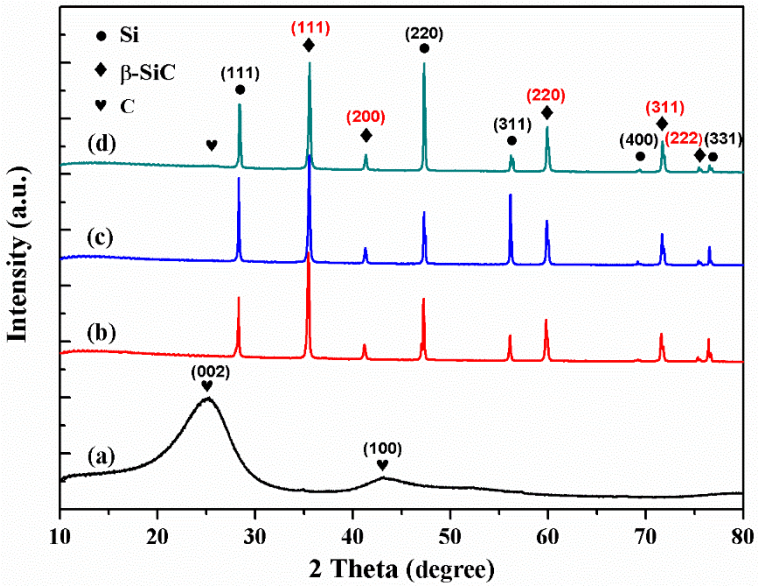

Figure 4: The XRD patterns of: (a) C/C-0, (b) CFRS-0, (c) CFRS-1 and (d) CFRS-2.

3.5 Mechanical properties of the CFRS composite

The flexural strength of the CFRS composite is illustrated in Fig. 5. The flexural strength is varying from 128 to 179 MPa, due to the different resin infiltration times. The variation in the mechanical properties is attributed to the change in microstructure of the parts. As for CFRS-0, the bulk density is too low and the apparent porosity is very high, so the content of residual silicon is high as well. The intrinsic brittleness of silicon give rise to the low strength of the composite parts. CFRS-1 has the maximum flexural strength, which contained the most quantity of SiC phase. With further increasing of infiltrating time, the strength of the parts declines slightly due to the un-complete infiltration of the silicon and the increase of residual carbon.

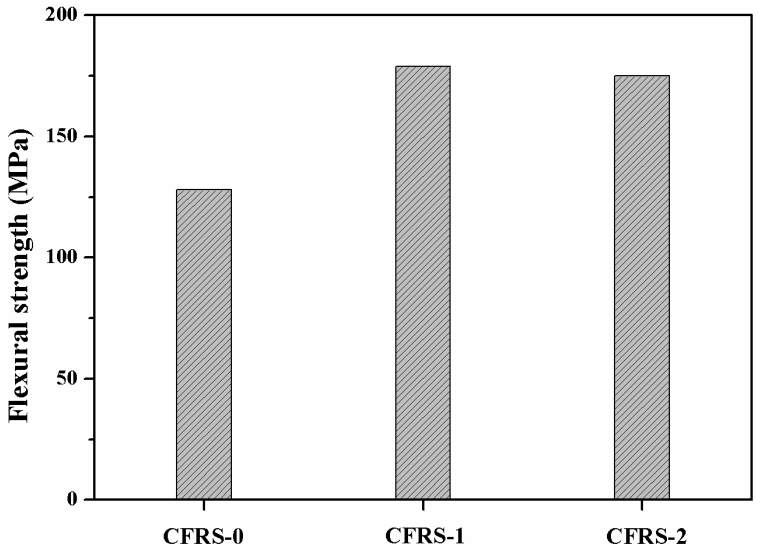

Figure 5: The flexural strengths of CFRS composite parts.

4 CONCLUSIONS

In summary, this study proposed a novel method based on the 3D printing technology and LSI process to produce carbon fibre reinforced silicon carbide composites. The phenolic resin/CF composite powder was successfully prepared, the phenolic resin was uniformly coated on the surface of carbon fibres. The porosity of the C/C preform can be readily controlled by changing the resin infiltrating time. The crystal structures of the CFRS composites parts mainly consist of β-SiC, silicon and residual carbon. The maximum flexural strength of the CFRS composite parts was 179 MPa. Further investigation will be focus on optimize the structure of the C/C preform to achieve better properties of the final CFRS products.

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REFERENCES

[1] Li S, Zhang Y, Han J, Zhou Y. Random chopped fibers in reaction bonded SiC composite: Morphology, etching and reinforcing properties. *Materials Science and Engineering: A*. 2012; 551:104-9.

[2] Zhang Y, Li S, Han J, Zhou Y. Fabrication and characterization of random chopped fiber reinforced reaction bonded silicon carbide composite. Ceramics International. 2012;38(2):1261-6.

[3] Song S, Bao C, Wang B. Effect of the addition of carbon fibres on the microstructure and mechanical properties of reaction bonded B4C/SiC composites. Journal of the European Ceramic Society. 2016;36(8):1905-13.

[4] Cheng L., Zhang L., Mei H., Liu, Y., Zeng, E. and Qing, F. Manufacturing of CMCs by Chemical Vapor Infiltration Process. Journal of Shanghai University (Natural Science), 20 (1), 2014, 15-32.

[5] Xu S, Qiao G, Li D, Yang H, Liu Y, Lu T. Reaction forming of silicon carbide ceramic using phenolic resin derived porous carbon preform. *Journal of the European Ceramic Society*. 2009; 29(11):2395-402.

[6] Lu ZL, Lu F, Cao JW, Li DC, Lian YY, Miao K, et al. Fabricating hollow turbine blades using short carbon fiber-reinforced SiC composite. The International Journal of Advanced Manufacturing Technology. 2013;69(1):417-25.
[7] Singh M, Behrendt DR. Microstructure and mechanical properties of reaction-formed silicon carbide (RFSC) ceramics. *Mater Sci Eng A*, 1994; 187:183–7
[8] Margiotta JC. Study of silicon carbide formation by liquid silicon infiltration of porous carbon structures. 2009.
[9] Wang Y, Tan S, Jiang D. The effect of porous carbon preform and the infiltration process on the properties of reaction-formed SiC. *Carbon*. 2004; 42(8–9):1833-9.
[10] Li S, Zhang Y, Han J, Zhou Y. Effect of carbon particle and carbon fiber on the microstructure and mechanical properties of short fiber reinforced reaction bonded silicon carbide composite. Journal of the European Ceramic Society. 2013; 33(4):887-96.