

Letter to the editor

Three dimensional printing of carbon/carbon composites by selective laser sintering

A B S T R A C T

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A novel three dimensional (3D) printing method is developed to fabricate complex carbon/carbon (C/C) composite components. The C/C composites with the high mechanical performance are achieved by combining the selective laser sintering and the chemical vapor infiltration-thermal treatment process. The C/C composites with a maximum density of 1.5 g/cm^3 and bending strength of 100 MPa are obtained. Complex C/C composite parts with the minimum thickness of 0.5 mm are accurately fabricated with the computer-aided design technique. This developed 3D printing method can be well applied to the production of complex C/C composite parts with high precision and good mechanical performance.

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Carbon/carbon (C/C) composites have been widely used in high-temperature fields because of their low density, good electrical property, high thermal stability, high specific strength, high module, and reasonable bioactivity [1]. On the basis of different carbon fibers (CFs) used, two types of C/C composite materials can be distinguished: continuous CF reinforced carbon composites (CFRCs) and discontinuous CF reinforced carbon composites (SCFRCs). The CFRCs with superior performance have been rapidly developed in recent decades. However, they are usually prepared by unidirectional or multidirectional CF weave, in which the complex braiding process and high cost have severely restricted their further application in manufacturing of sophisticated instruments and complex parts. Guo L et al. [2] used molding technique to shape SCFRCs; Cai D et al. [3] prepared SCFRCs with the improved strength by hot pressure sintering. SCFRCs cannot exhibit so good properties as those of CFRCs, but they use lower quality CFs and only need a simple preparation technique, indicating better material reutilization efficiency and lower energy requirement. Their methods showed the feasibility of fabricating C/C composites using short CFs as reinforcement materials. However, these methods are still difficult to fabricate complex parts and also need corresponding mold.

Three dimensional (3D) printing is one of the solid freeform fabrication methods. 3D printing makes it possible to shape complex composite parts that cannot be achieved by the traditional powder metallurgy techniques. Currently, 3D printing is well applied to prepare composite materials, especially the polymer-based composites. When carbon nanofiber [4], silicon carbonate [5], aluminum powders [6], nanosilica [7], hydroxyapatite [8], and carbon black [9] are added to the resin matrix, the mechanical properties, bioactivity, thermal stability and electrical conductivity of polymer have been increased accordingly. But the polymer-based

composites still cannot meet the rigorous requirement of complex environment and new 3D printing materials are urgently needed.

In this paper, a typical 3D printing method—selective laser sintering (SLS) was used and a multi-step procedure combining the SLS printing and chemical vapor infiltration (CVI) thermal treatment was developed to prepare C/C composites. The preparation process is schematically shown in Fig. 1. CFs were first treated by oxidation method to etch the surface of CFs in concentrated nitric acid (67 wt.%). The etched CFs were then mixed with the phenolic resin 2123 (PF2123) powders by 4:6, 5:5, 6:4 (wt/wt) respectively in acetone solution. After removing the acetone, CF/PF powders with 40 wt.%, 50 wt.%, and 60 wt.% CFs can be respectively obtained by mechanical crush (more details see Supporting information (S.I.)). C/C composite green body was fabricated by 3D SLS printing with a laser power of 30 W, a scanning speed of 280 inch/s, and a scanning space of $100 \mu\text{m}$ (parameter selection see S.I.). To cure the PF2123, C/C composite green body was heated to 180°C in a CVI furnace from RT and kept there for 2 h. After that, it was further carbonized by heating up to 1100°C . When the temperature reached 1100°C , the natural gas was introduced into the furnace and the gas pressure was kept at 1.0–1.5 KPa to perform the CVI reaction. The density of 3D printing C/C composite parts can be increased upon prolonging reaction time during the densification. As a result, the 3D printing C/C composites with density of 1.3 g/cm^3 , 1.4 g/cm^3 , 1.5 g/cm^3 were obtained (details see S.I.).

As shown in scanning electron microscopy (SEM) image of Fig. 2a, the chemically etched CFs show a uniform distribution of $200\text{--}400 \mu\text{m}$ in length and good dispersion. A high magnification SEM image in Fig. 2b shows that CFs have a rough and active surface. The X-ray diffraction (XRD) pattern (Fig. 2c) exhibits a high crystallinity of CFs. Energy-dispersive X-ray spectroscopy (EDS) analysis (Fig. 2d) confirms existence of oxygen, which comes

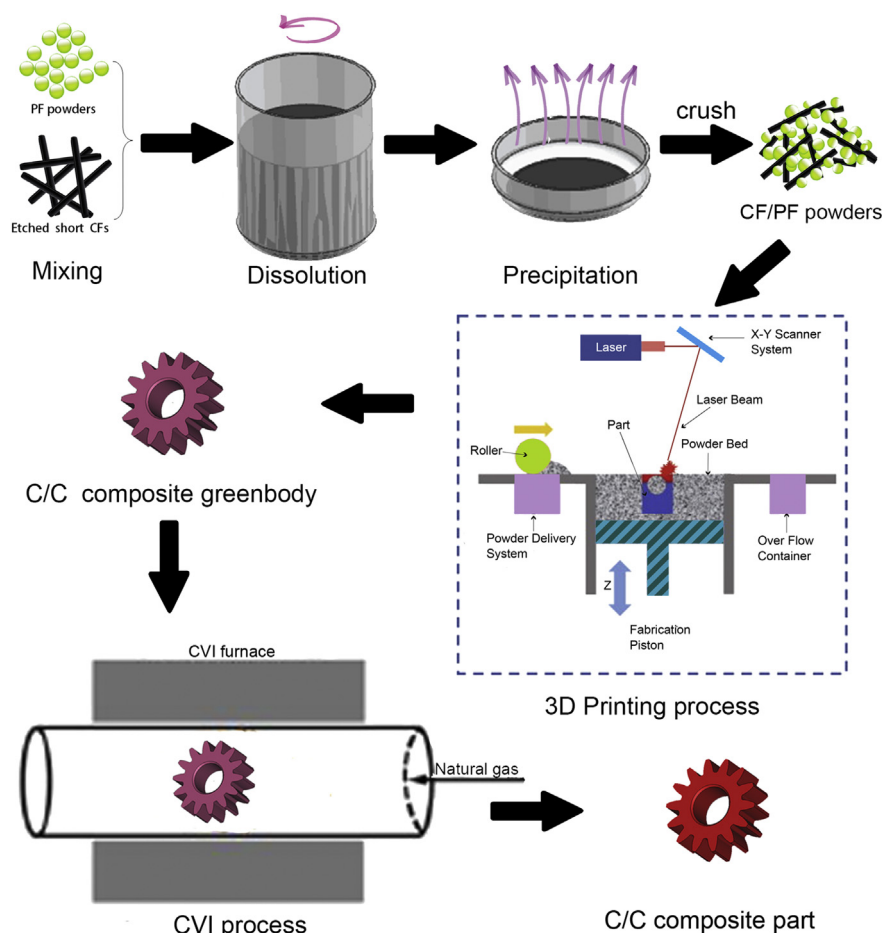


Fig. 1. Overview of preparing carbon/carbon composites complex part. (A color version of this figure can be viewed online.)

from oxygen-containing functional groups on the surface of etched CFs and can facilitate forming a good surface adhesion with the PF2123. In Fig. 2e, the 3D printing powders exhibit the similar morphology as that of the CF powders (Fig. 2a). Fig. 2f shows that the surface of CFs was uniformly coated with the PF2123. The coated CF (Fig. 2g) has good interface adhesion with PF2123. It demonstrated that the surface oxidation treatment of CFs and dissolution-precipitation method played an important role in preparing 3D printing powders with good fiber dispersion and interfacial adhesion. Fig. 2h shows the detailed flexural properties of C/C composites under a three-point bending test. It is shown that the flexural strength of specimens at a certain density rises with increasing CFs. Specifically, the flexural strength of specimens with 60 wt.% CFs is increased by 235.9%, 237.5%, and 238.1% at the densities of 1.3, 1.4 and 1.5 g/cm³, respectively, compared with those without CFs. When 60 wt.% short CFs are added into the green body of C/C composites, the maximum flexural strength of 100 MPa is achieved with a density of 1.5 g/cm³. Meanwhile, it is showed that C/C composites with a certain ratio of CFs displayed an increasing flexural strength along with the increase of densities.

Fig. 3 shows the SEM and polarized light microscopy (PLM) images of the fracture surface of the C/C composites of 60 wt.% CFs after three-point bending test. As shown in the Fig. 3a and b, the surface of C/C composite is rugged, and most of CFs are pulled out of the fracture surface due to the de-bonding phenomenon, indicating a good adhesion between CFs and pyrolytic carbon matrix. The as-formed crack has been restricted or deflected at the CF/pyrolytic carbon interface by dissipating fracturing energy. In

the Fig. 3c and d, the pyrolytic carbon around the CFs has a low texture, and cylinder pyrolytic carbon sheets parallel to the CF surface can be clearly observed. It will bring the same reinforcing effect as that of fibers against the cracks. With more CFs added, the CF/pyrolytic carbon interface and cylinder pyrolytic carbon sheets increased. As a result, the carbon fiber reinforcing effect will be much stronger along with increase of CFs (Fig. 2h). Meanwhile, there are a number of pores among the CFs in the C/C composites (Fig. 3a). When the pyrolytic carbon matrix near the pores starts mechanical deformation, it will be prone to get brittle fracture. The redistribution of stress and crack propagation then happened. The cracks are easily extended, resulting in a rupture of C/C composites. However, the densification of C/C composites is an essential process to eliminate the pores and restrict the brittle fracture. Therefore, the flexural strength of the C/C composites is improved (Fig. 2h). The fracture surface observation and property analysis reveal that the 3D printing powders prepared by dissolution-precipitation method can be well used to prepare C/C composites with solid interfacial combination and good mechanical properties.

Fig. 4a and b shows the complex C/C composite parts with different shapes and sizes by combining 3D printing of 50 wt.% CF/50 wt.% PF mixed powders and carbonization as well as densification treatment. The inner and outer diameter of typical composite gear (Fig. 4a) is 20 and 30 mm, respectively. Furthermore, a minimum thickness of 0.5 mm in the complex part of Fig. 4b can be achieved. It is shown that the deformation of the specimen is less than 0.5%, compared with CAD models (Fig. 4c and d). The density of the specimens is 1.4 g/cm³. The method combining carbon

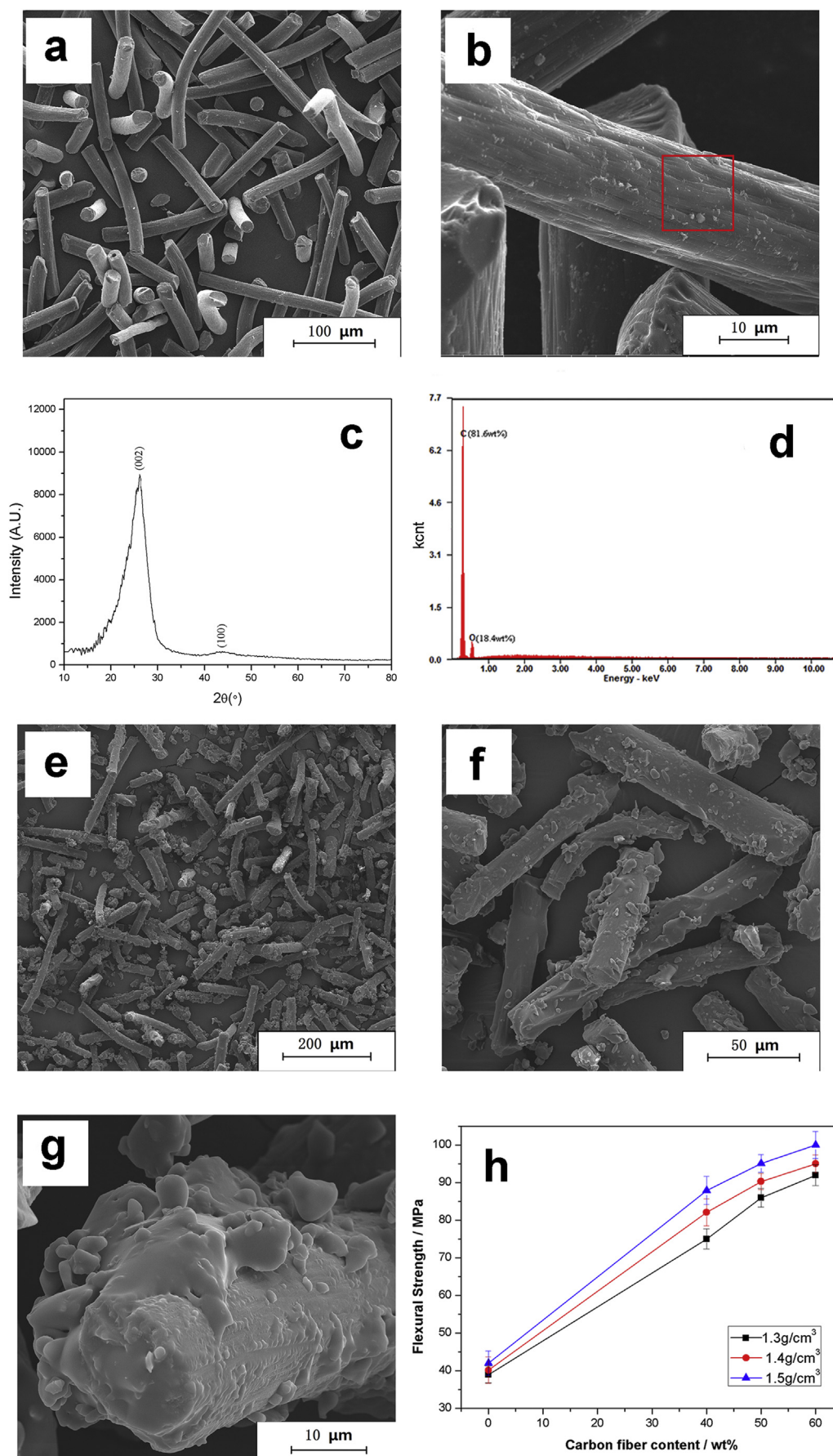


Fig. 2. SEM images of the surface modified carbon fibers at the magnifications of (a) 300 \times , (b) 5000 \times . The XRD (c) and EDX (d) results of the modified fibers. The SEM images of 60 wt.% CF/PF composite powder at the magnification of (e) 300 \times , (f) 1200 \times , and (g) 5000 \times . (h) Variations of the flexural strength of the 3D printing C/C composite parts with different carbon fiber content and density. (A color version of this figure can be viewed online.)

fiber needling and CVI [10] could be used to prepare C/C composites with high density and good mechanical performance. What's more, when it comes to prepare the complex C/C composite parts, the continuity of the fibers can be maintained to ensure high mechanical performance. However, the complex braiding and subsequent machining process are complicated. Although molding technique only need low cost raw material and simple preparation process for SCFRC, the corresponding mold of the parts should be prepared, and it is difficult to change the shape and prepare special components, such as hollow parts. All those drawbacks can be eliminated in 3D printing for C/C composites. It could fabricate composite components from powders in any shapes with computer-aided design without any machining and complex fabrication process. Moreover, it is also a facile way to realize automation of synthesis of highly precise C/C composite parts.

To summarize, it is demonstrated that C/C composite complex components with high mechanical performance can be prepared by combining the 3D printing and the CVI-thermal treatment process. Complex C/C composite parts of 60 wt.% CFs with a density of 1.4 g/cm³ and the minimum thickness of 0.5 mm were fabricated, which indicated that the developed 3D printing method can be well applied to the production of complex C/C composite parts with high precision and good mechanical performance. 3D printing is a more practical way to fabricate highly dense C/C components with complex shapes and structures.

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Appendix A. Supporting information

Supporting information related to this article can be found at <http://dx.doi.org/10.1016/j.carbon.2015.09.110>.

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