Fabrication of short carbon fiber preforms coated with pyrocarbon/SiC for liquid metal infiltration

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Abstract A novel method of fabricating short carbon fiber preforms was proposed for liquid metal infiltration. The preforms were shaped by wet forming and strengthened by pyrocarbon (PyC). SiC layers were prepared on carbon fibers by the reaction of SiO and PyC at 1600 °C. X-ray Diffraction, Scanning Electron Microscopy, and Energy Dispersive X-ray Spectroscopy were applied in the characterization of the preforms. Gas pressure infiltration was done to demonstrate the feasibility of the preforms for the liquid metal infiltration. The microstructure analysis indicates that carbon fibers are uniformly distributed in the preforms, and fibers are coated with an inner layer of PyC and an outer layer of SiC. The infiltration experiment proves that the prepared preforms are feasible for liquid metal infiltration under low infiltration pressure and temperature.

Introduction

Compared with metal matrix composites (MMCs) reinforced by continuous carbon fibers, that reinforced by short carbon fibers have received considerable attention due to the low cost and simple fabrication process [1, 2]. Liquid metal infiltration, in the form of squeeze casting, gas pressure infiltration, and vacuum infiltration, is regarded as an economical method for fabricating short fiber-reinforced MMCs [3–7]. However, short fiber preform is necessary for the liquid metal infiltration. A high-quality preform is the base of high-quality MMCs.

Usually, binders are used to stabilize the shape and provide sufficient strength to the preforms [8–11]. However, the excess binder always clusters at the surface of the preform [10, 11]. Clusters were undesirable, as which may block the flow of the melt and decrease the properties of MMCs; therefore, fiber dispersing was one of the problems in the preparation of short carbon fiber preforms. The poor wettability and reactivity of carbon fibers was another problem, which may cause incomplete penetration and decrease the quality of the composites [12–14]. To solve the problem, carbon fibers were usually coated with SiC layer, as which possess a better wettability with molten metals and can control the harmful reaction between fiber and matrix at elevated temperatures [15–17]. Chemical vapor deposition (CVD), a well-known and mature coating technique, has been widely used in processing of SiC coating on carbon fibers. Unfortunately, the precursors gases ($SiCl_4$, CH_3SiCl_3), which are generally used in CVD process, are expensive, toxic, corrosive, flammable, and explosive [18, 19].

In this work, a novel method was proposed for fabricating short carbon fiber preforms coated with pyrocarbon (PyC) and SiC. The carbon fiber preforms were shaped without binders to avoid binder segregation and fiber cluster. After the shaping process, the preform was strengthened by PyC and coated with SiC. The SiC coating was prepared by the carbothermal reduction of SiO and PyC, which was considered as a low cost, nontoxic precursor technology [20, 21]. Finally, the characters of the preform were studied, including the composition of the preform, the fiber distribution in the preform, and the morphology of the fibers. Furthermore, the short carbon fiber-reinforced 2024Al alloy composites were prepared by

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the gas pressure infiltration to prove the feasibility of the preform in liquid metal infiltration.

Experimental

Raw materials

PAN-based short carbon fibers, made in Jilin Carbon Co., Ltd., China, with a length of 3–5 mm and diameter of 5–6 μm, were selected to fabricate the carbon fiber preform. Methane (CH_4) and nitrogen (N_2) were applied in the synthesis of PyC coating. Silicon (99.9%) and silica (99%), produced by Tianjin Chemical Reagent Corporation of China, were used in the synthesis of SiC coating. 2024Al alloy was used in the preparation of metal matrix composites.

Fabrication of short carbon fiber preform

Short carbon fiber preforms coated with PyC/SiC were prepared in a three-step procedure, as shown in Fig. 1. Firstly, carbon fiber preforms were fabricated by a wet-forming process. After immerged in acetone to remove the organic binder, carbon fibers were stirred in a 0.5% aqueous sodium polyacyrlate solution to disperse the fibers. Then the carbon fiber slurry was poured into a mold to shape the preforms and dried at room temperature for 24 h and at 120 °C for 2–4 h. Secondly, the dried preforms were put into an isothermal chemical vapor infiltration (ICVI) furnace to obtain PyC layer by the pyrolysis of CH_4 at 1100 °C. This experiment was carried out in atmospheric pressure with a carrier gas of N_2 for several hours. Finally, SiC coating on carbon fibers was synthesized by the carbothermal reduction of SiO and PyC during the CVR (Chemical Vapor Reaction) process. This process was done in a vacuum-sintering furnace. A graphite crucible with a size fitted with the preform was used as a sample holder containing both carbon fiber preform and mixture powder of SiO_2 and Si, as shown in Fig. 2. The mixture powders were put on the bottom of the graphite crucible and the preform was placed over the mixture powders. The
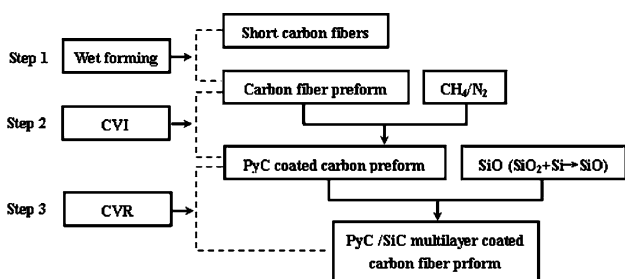

Fig. 1 Schematic illustration of procedures to fabricate short carbon fibers coated with PyC/SiC
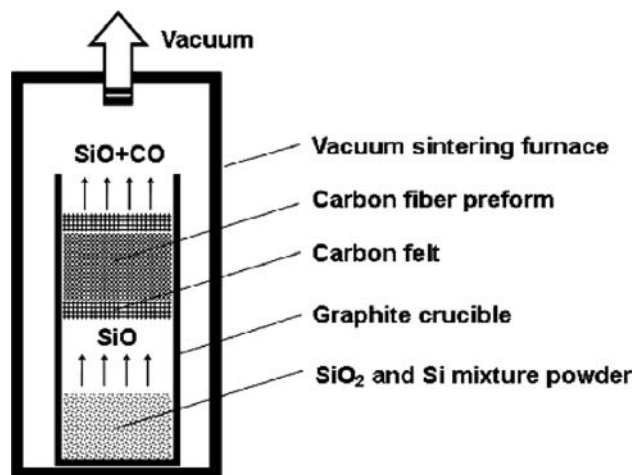

Fig. 2 Schematic illustration of the setting of CVR process

Fig. 3 The profile of the prepared short carbon fiber preform

carbothermal reduction was carried out in vacuum for several hours at 1600 °C. At the elevated temperature, SiO vapor infiltrated into the carbon fiber performs, and reacted with PyC layer to synthesize the SiC layer. The prepared preform was in cylindrical shape with a height of 25 mm and a diameter of 45 mm, as shown in Fig. 3. The fiber volume fraction of the preform was about 15%.

Preparation of MMCs

Short carbon fiber-reinforced 2024Al alloy composites were prepared by a gas pressure infiltration process. The experiment was done by an apparatus designed for this study, as shown in Fig. 4. The apparatus was assembled by two chambers: a melting chamber, in which the alloy is melted under protective atmosphere of N_2; and an infiltration chamber, in which the molten metal infiltrates into the preform by gas pressure. Before infiltration, the melting

Fig. 4 Schematic illustration of the gas pressure infiltration apparatus
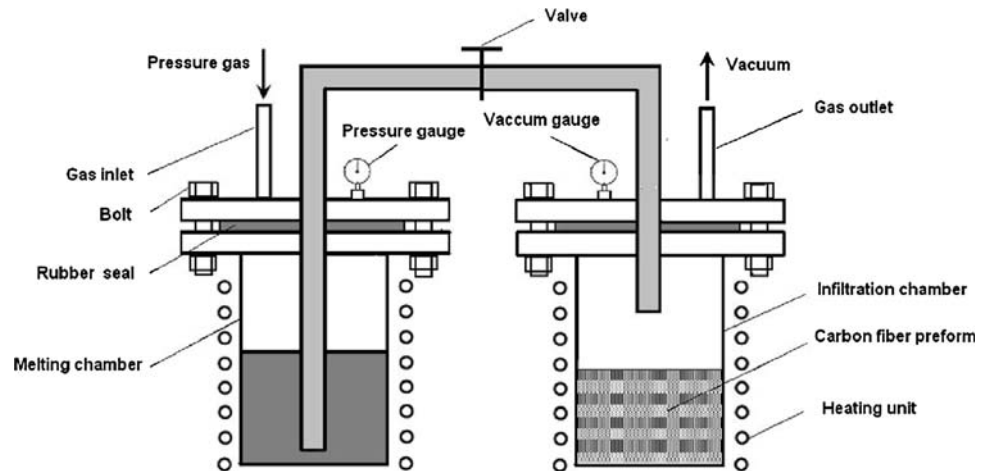
chamber was in a gas pressure of 0.5 MPa and the infiltration chamber was in vacuum. The melting alloy can move from the melting chamber to the infiltration chamber by the pressure difference between these two chambers, when the valve is opened. After that, the melting alloy infiltrates into the carbon fiber preform under gas pressure. The parameters of the gas pressure infiltration were described as follows: the melting temperature of the Al alloy was 800 °C, the pre-heated temperature of infiltration chamber was 600 °C, and the applied infiltration pressure was 0.5 MPa.

Characterization of coated short carbon fiber preform

X-ray diffraction (XRD) was used for phase composition characterization of the preform. Prior to XRD, the preform was ground into powder by ball milling. XRD measurements were performed on Panalytical X-Pert Pro diffractometer with Cu-Kα monochromatic radiation ($\lambda = 1.5406$ Å). The compressive behavior of the preform was tested by INSTRON-1195. The compressive specimen is about 25 mm in height and 20 mm in diameter. The morphologies of the preform and the microstructures of the composites were observed by Scanning Electron Microscope (SEM, JSM-6460). The composition of the layers on fibers was determined by Energy Dispersive X-ray Spectroscopy (EDS, JSM-6460). The microstructures of the coated carbon fibers were observed by Field Emission Scanning Electron Microscope (FESEM, JSM-6700). The porosity of the composites was measured by the Archimedes drainage method.

Results and discussion

Phase analysis of the preform

Figure 5 shows the XRD pattern of the carbon preform coated with PyC/SiC. The diffraction peak of 25.94° is the
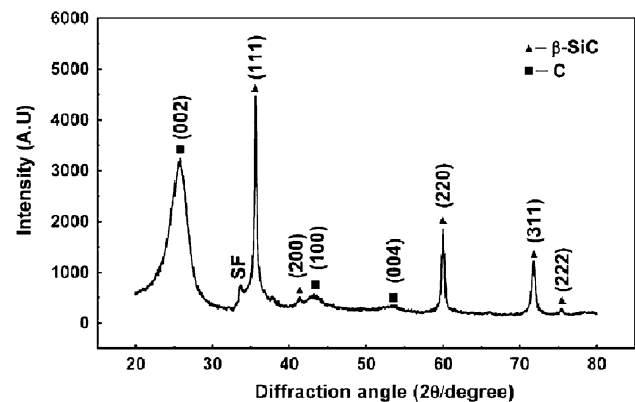
Fig. 5 XRD pattern of the short carbon fiber preform coated with PyC/SiC

(002) peak of carbon. The diffraction peak of 33.5° marked as S.F. is stacking faults in β-SiC, which was also observed in Yang and Wu's researches [22, 23]. The other diffraction peaks in the pattern all refer to the β-SiC. The lattice parameter of β-SiC cubic cell calculated from the XRD data is 4.361 Å, which is in good agreement with the standard value for β-SiC (4.359 Å, JCPDS Card No. 0029-1129).

Compressive behavior of the preform

Figure 6 shows the compressive stress–strain curves of the preform. It can be seen that the curves show the compressive characteristics of the porous materials, that is, the elastic deformation stage at the beginning of deformation, a collapse stage with a small stress increase to large strain, and a densification stage where the stress rapidly increases.

Morphology of the preform and fibers

As seen from the Fig. 7, fibers are arranged at random and no fiber congregation can be found in the preform, which
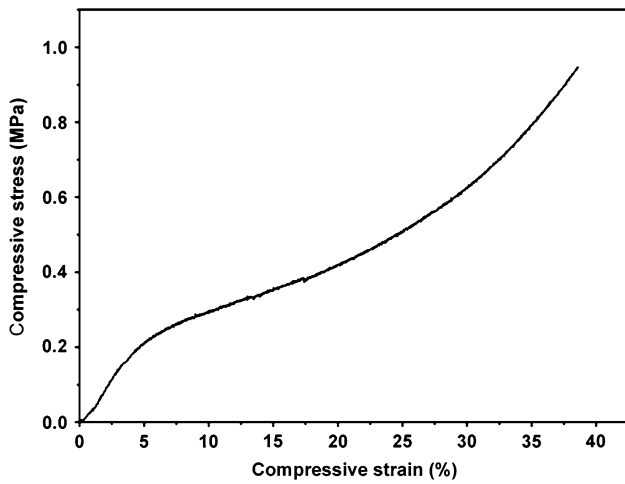
Fig. 6 The compressive stress–strain curves of the carbon fiber perform
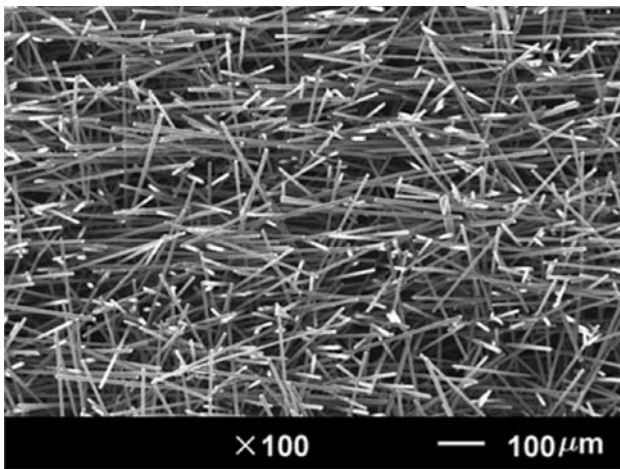
Fig. 7 SEM micrograph of short carbon fiber preform coated with PyC/SiC

indicates that the fibers are uniformly distributed in the preform.

Figure 8 shows the SEM micrographs of short carbon fibers after different steps. According to the morphology of carbon fibers, it can be seen that there is a great change on the fiber surface. As shown in Fig. 8a, the surface is smooth after wet-forming process. As shown in Fig. 8b, the carbon fiber is coated by a thin layer after ICVI process. This layer is smooth with a thickness of about 0.8 μm. As shown in Fig. 8c, the surface of the fiber becomes rough with a double layer structure. EDS analysis shows that the thin film in Fig. 8b is composed of carbon uniquely, and the outer layer in Fig. 8c is composed of silicon and carbon. Associated with the result of the XRD examination (Fig. 5), it can be deduced that the outer layer is β-SiC and the inner layer is PyC. To make clear the details of this multilayer structure, the cross section of the short carbon
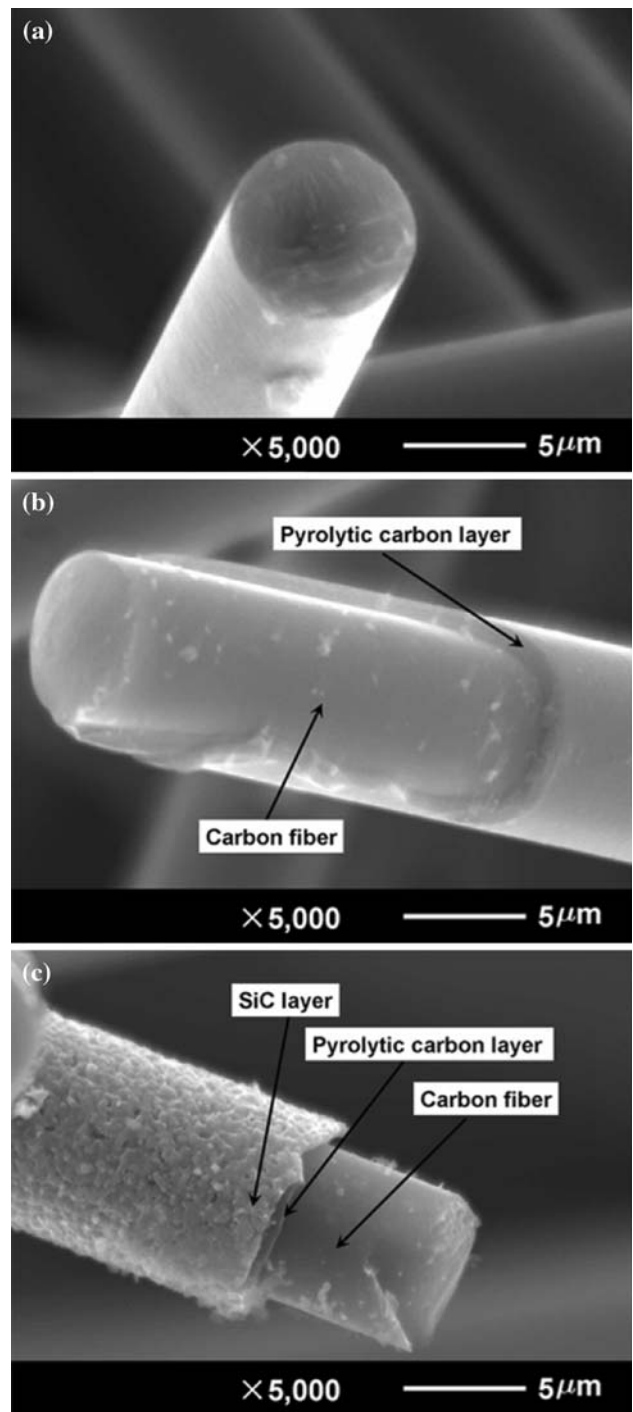
Fig. 8 SEM micrographs of short carbon fibers (a) after the wet formation process, (b) after the ICVI process at 1100 °C, and (c) after the coating process at 1600 °C in vacuum

fibers was observed by FESEM, as shown in Fig. 9. Obviously, there are two layers coated on the fiber. The thickness of the inner layer and outer layer is about 0.5 and 0.3 μm, respectively. Both the layers are continuous and homogeneous. Moreover, the carbon fiber joint can be
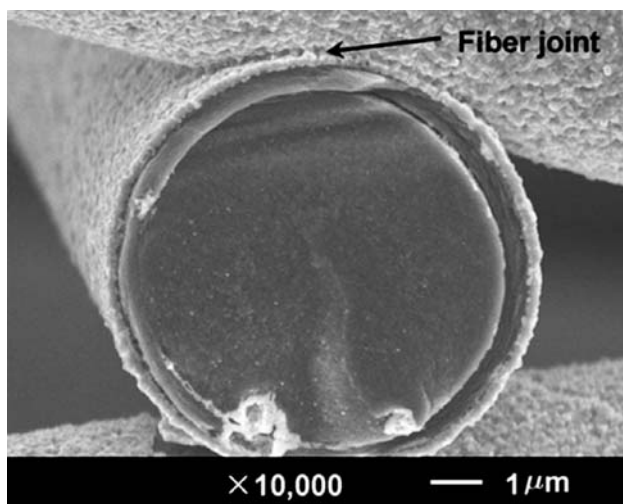
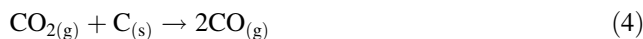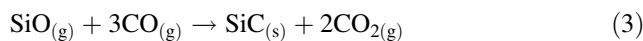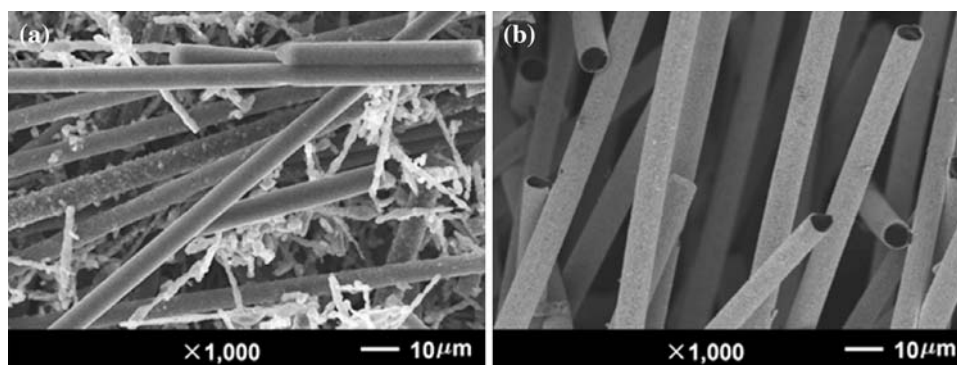**Fig. 9** FESEM micrograph of PyC/SiC-coated carbon fibers on the cross section

found in Fig. 9, which indicates that fibers were connected by PyC and SiC.

From the microstructure of carbon fibers, we can conclude that the PyC plays two important roles in the fabrication of preforms. Firstly, PyC acts as binder to strengthen the preform. It connects the individual fibers to an integral 3-dimensional fibers network. In addition, PyC acts as carbon template and provides carbon source in the synthesis of SiC coating.

Formation of the SiC coating

According to the Si–O–C system in the present experiment, the following reactions are considered. Reaction (1) supplies the SiO vapor for the reactions (2) and (3). Reactions (2) and (3) were the potential reactions to generate SiC. Reaction (3) was stimulated by the CO vapor generated from reaction (2). Once reaction (3) is processed, the CO_2 generated from reaction (3) can react with the carbon in the system and supplies CO for reaction (3). Obviously, reactions (3) and (4) have a positive feedback characteristic to each other [24].

$$SiO_{2(s)} + Si_{(s)} \rightarrow SiO_{(g)} \tag{1}$$

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \tag{2}$$

$$SiO_{(g)} + 3CO_{(g)} \rightarrow SiC_{(s)} + 2CO_{2(g)} \tag{3}$$

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \tag{4}$$

To understand the formation mechanism of SiC coating, the potential reactions to form SiC must be clarified. It is known that reaction (2) is a vapor–solid reaction. The SiC generated by reaction (2) was mainly in the shape of the carbon templates. Besides reaction (2), reaction (3) is another potential reaction to form SiC in the system. Gao [24] indicated that reaction (3) leads to the formation of SiC nanowires and whiskers, when the partial pressure of CO reaches supersaturation condition. Similar results can be found in Vogli and Tang's researches [25, 26]. In the present study, however, no SiC whisker or nanowire was found in the preform. The SiC is only in the form of coating on carbon fibers. The absence of the SiC nanowires might be attributed to the vacuum condition. The lower CO partial pressure under vacuum conditions apparently limits the extent of reaction (3). Once reaction (3) is suppressed, the supply of CO_2 for reaction (4) is terminated and the feedback of the CO for reaction (3) is stopped. Due to the deterioration in the CO supply, the formation of SiC nanowires or whiskers is difficult. To support the above conclusion a further experiment is necessary. The verification experiment was carried out in ambient pressure with Ar as protective gas at 1600 °C. In that case, the CO generated from reaction (2) can hold in the preform and reactions (3) and (4) are feasible. Figure 10a and b shows the carbon fiber preform treated at ambient pressure and vacuum, respectively. It can be seen that many SiC whiskers synthesized in the preform in ambient pressure. Contrastingly, no whisker was found in the preform treated in vacuum. This suggested that the reaction of SiO and CO is restricted in vacuum. Reaction (2) is independent of the pressure according to Le Chaterlier principle. Therefore, the formation of the SiC coating is mainly attributed to the reaction of SiO and PyC layer.

Fig. 10 SEM micrographs of short carbon fiber preforms: (**a**) treated at ambient pressure and (**b**) treated in vacuum
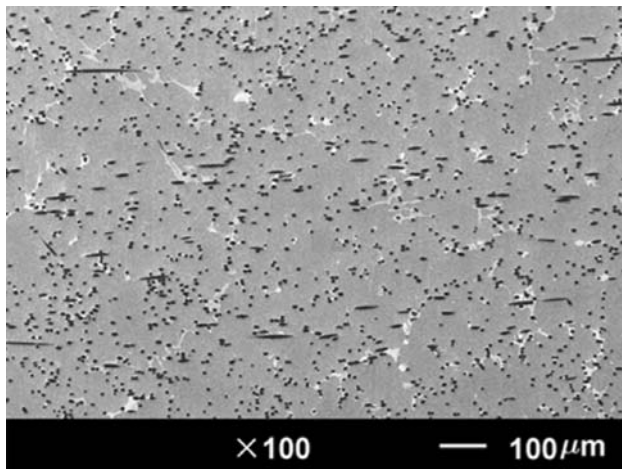
Fig. 11 SEM micrograph of the short carbon fiber-reinforced Al alloy composites

Microstructure of the composites

SEM image analysis of the infiltrated composite samples was made. As shown in Fig. 11, the composites have been successfully fabricated using the 2024Al alloy at an infiltration temperature of 600 °C with an applied pressure of 0.5 MPa. The SEM image shows that the matrix alloy is finely penetrated into the micro-holes of the prepared preform. Furthermore, uniform distribution of carbon fibers is clearly visible in Fig. 11. Additionally, the porosity of the composites was measured by the Archimedes drainage method. It shows that the porosity of the composites is only about 4.5%. Therefore, it is proved that the as-prepared short carbon fiber preforms is feasible for liquid metal infiltration with low infiltration temperature and pressure, which can avoid the fiber damage and fiber inhomogeneous distribution along the infiltration direction [27]. Figure 12 shows the fracture
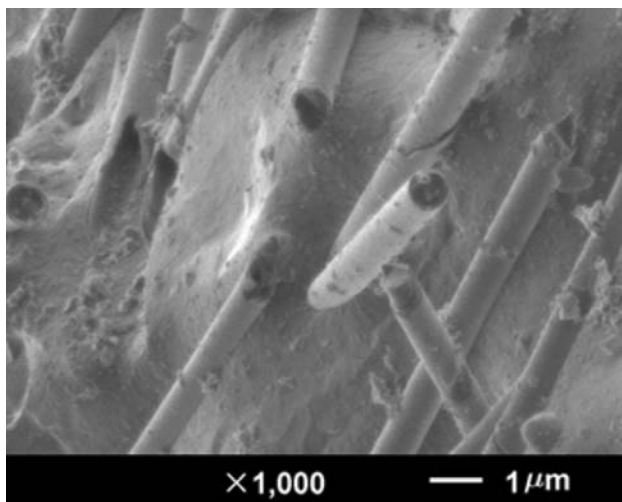
Fig. 12 The fracture surface of the Cf/Al composites

surface of the C_f/Al composites. A modest amount of fibers pull out can be found, which indicates a medium interface bonding between fibers and matrix. It is considered that the appropriate interface bonding is benefited to improve the mechanical properties of the composites [28].

Conclusions

High-quality short carbon fiber preforms for liquid metal infiltration were produced. The preform is of a uniform fiber distribution. Carbon fibers in the preform were coated with an inner layer of PyC and an outer layer of SiC. PyC plays two important role in the fabrication of preforms: as binder to strengthen the carbon fiber preform and as carbon template for the synthesis of SiC layer. The reaction of SiO and PyC layer leads to the formation of SiC coating. Gas infiltration experiment proves that the short carbon fiber preforms fabricated by the present method is feasible for liquid metal infiltration under low infiltration pressure and temperature. Fibers were uniformly distributed in the matrix alloy. The interface bonding of fiber and matrix is appropriate.

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