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Densification of SiC_f/SiC composite by the multi-step of whisker growing and matrix filling

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Abstract

The whisker growing and matrix filling process was applied to reduce the canning effect during the CVI process. Grown whiskers may serve to divide the large natural pores between fibers or bundles and then matrix filling may be efficiently carried out through the modified pore structure. In this study, the multi-step of the in situ whisker growing and matrix filling process were performed to investigate the densification behaviors of SiC_f/SiC composite. MTS (CH_3SiCl_3) and H_2 were used as source and diluent gases, respectively. The process cycles were repeated three times. The whisker growth and densification behaviors with the number of the process cycles were evaluated. SiC whiskers were grown in the SiC fiber preforms at the input gas ratio of 60 and the total reaction pressure of 5 Torr. As the number of process cycles increased, the maximum size of the large voids decreased and homogeneity of the voids distributions increased.

1. Introduction

SiC_f/SiC is one of the typical continuous fiber reinforced ceramic composites. By using a long fiber to reinforce the ceramic matrix, fracture toughness has been significantly improved [1,2]. In addition to the thermo-mechanical advantages of SiC_f/SiC composites, the low induced activation by neutrons and a good irradiation resistance have also made them quite attractive for fusion reactor applications [3,4]. Chemical vapor infiltration (CVI) is one of the main processes commonly used to fabricate SiC_f/SiC composites but it is a slow process with an inherent drawback of a substantial residual porosity [5,6]. To obtain a dense SiC matrix fiber reinforced composite by the CVI process, the whisker growing process was applied prior to the conventional I-CVI process [7,8]. Before matrix filling of the SiC preform, SiC whiskers are grown on SiC fibers. These whiskers may serve to divide the large natural pores between fiber bundles into smaller ones and modify the void structure. Therefore, matrix filling may be efficiently performed inside whisker grown composites.

In this study, the multi-step of the in situ whisker growing and matrix filling process were performed to fill the matrix phase inside whisker grown composite. The process was repeated three times to investigate the densification behaviors of SiC_f/SiC composite. Density and the weight gain rate were measured at each processing step, respectively. Additionally, microstructures of grown whiskers and the matrix phases were analyzed.

2. Experimental procedure

Preparation of SiC whiskers was carried out using a gas mixture of methyltrichlorosilane (CH_3SiCl_3, MTS,

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Aldrich Co., 99%) and purified H_2 (purity: 5 N) where H_2 acted both as a reducing agent and a carrier gas for MTS vapor. The whisker growing was performed at 1100 °C and the total pressure of 5 Torr with the input gas ratio of H_2 to MTS, $\alpha\,(=F_{\text{diluent}+\text{carriergas}})/F_{\text{MTS}}$) of 60 in a hot wall chamber. The flow rate of MTS vapor was controlled by adjusting the bubbler pressure and the flow rate of the carrier gas, maintaining the temperature of the bubbler containing liquid MTS at 0 °C. The pressure in the reactor was monitored with a capacitance manometer and controlled at 5 Torr with a throttle valve located between the reactor and the mechanical pump. A plain weave fabric of Tyranno-SA™ was used as a reinforced substrate. Ten layers of the fabric with the diameter of 50 mm were stacked as a green preform. Before whisker growth, the preforms were coated with pyrolytic carbon using methane gas (CH_4) at 950 °C for 2 h. The matrix filling process was performed at the filling temperature of 1000 °C and the total pressure of 100 Torr for up to 29 h.

Microstructures of SiC_f/SiC composites were observed using scanning electron microscopy (SEM; Model JS-5200, Jeol, Japan). Bulk densities and the weight gain rate were determined by measuring the dimension and weight of the specimens.

3. Results and discussion

SiC whiskers were grown on a SiC preform for up to 6 h to investigate the growing behaviors in the SiC fabrics. Fig. 1 shows the variations of the density and the weight gain rate of SiC_f/SiC composites with the whisker growth time. After growing whiskers, the amounts of the weight changes were not large and the increment of the density was small. These were caused by SiC whiskers which only grew in the diluent concentration of MTS. In this study, SiC whiskers were

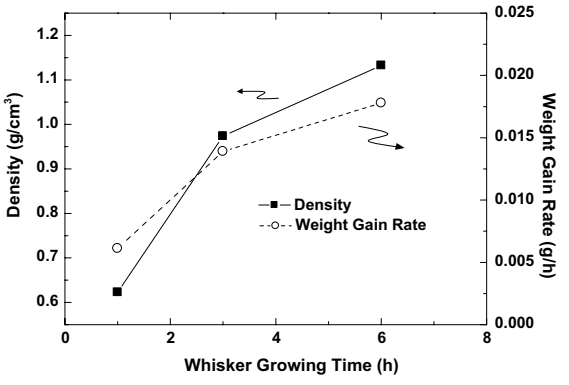

Fig. 1. Variations of density and the weight gain rate of SiC_f/SiC composites with the whisker growth time.

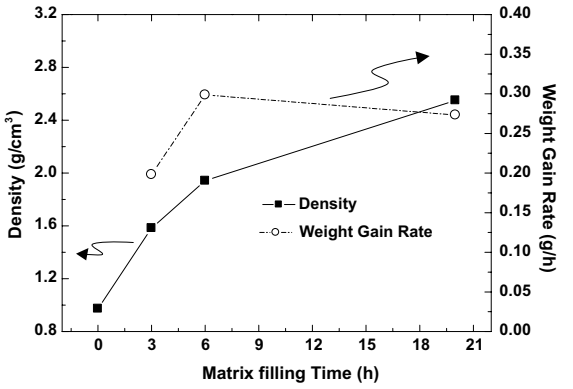

Fig. 2. Variations of density and the weight gain rate of SiC_f/SiC composites with the matrix filling time after whisker growth for 3 h.

grown well at the input gas ratio of 60 and the total reaction pressure of 5 Torr as will be shown the microstructures in Fig. 3. Densities of the specimens were 0.97 and 1.13 g/cm^3 only after a whisker growth for 3 and 6 h, respectively. This meant that more than 80% of whiskers were grown in the early growth time of 3 h. And the slope of the increment of the weight gain rate was decreased to about a half after 3 h. Therefore we chose the whisker growth time as 3 h.

Using SiC composites grown whiskers for 3 h, the SiC matrix phases were filled by the conventional CVI process for up to 20 h to investigate the densification behaviors. Fig. 2 shows the variations of the density and the weight gain rate of SiC_f/SiC composites with the matrix filling time. Density of SiC_f/SiC composite increased to 2.54 g/cm^3 as the matrix filling time was extended to 20 h. But the weight gain rate increased till the matrix filling time of 6 h. After that, it had a small amount of decreased tendencies. Density of SiC_f/SiC composite prepared by matrix filling for 6 h was 1.94 g/cm^3, which corresponded to the remaining porosity of about 40%. For the multi-step of whisker growing and matrix filling, a proper amount of voids had to exist. Therefore, we chose the matrix filling time as 6 h for the next step of whisker growing and matrix filling. Based on the above results of the whisker growth and densification behaviors, we determined the process cycle of the whisker growth to be 3 h and the matrix filling to be 6 h as one step.

Three SiC_f/SiC composites were prepared by different numbers of the process cycles to investigate the whisker growing behaviors. Fig. 3 shows microstructures of SiC whiskers grown at the each whisker growth step. We could easily observe SiC whiskers with a high aspect ratio in all specimens. As shown in Fig. 3(b) and (c), we could distinguish whiskers (black arrow mark) grown during the whisker growth step from the deposits (white

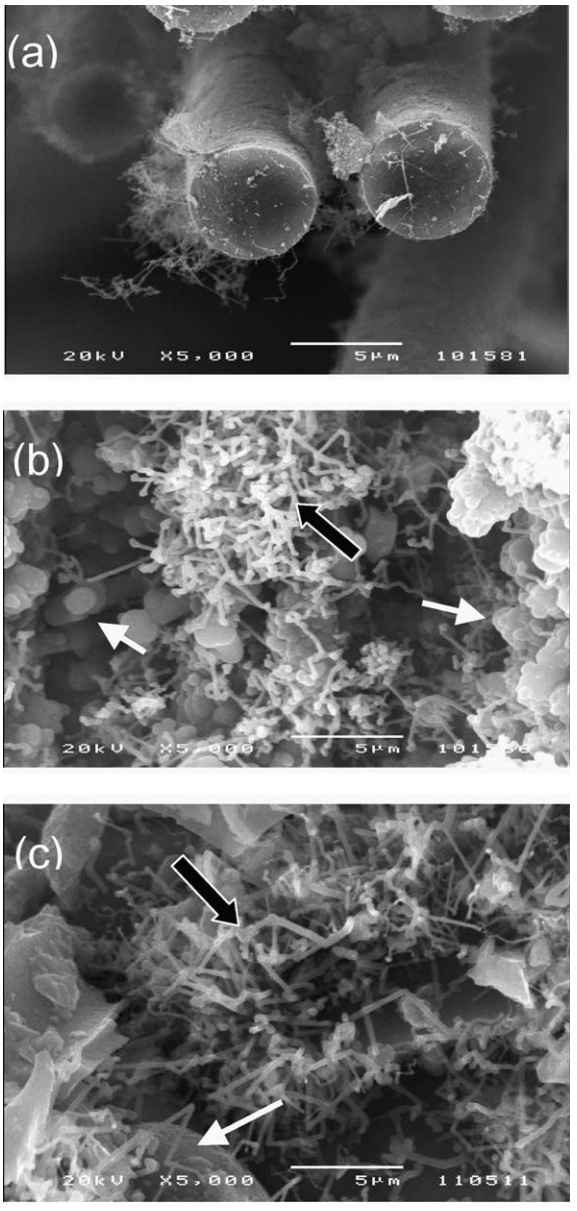

Fig. 3. Microstructures of grown whiskers in SiC_f/SiC composites: (a) after 1st WG for 3 h, (b) after 2nd WG for 3 h + 1st step and (c) after 3rd WG for 3 h + 1st step + 2nd step. (WG: whisker growth, step: whisker growth + matrix filling).

arrow marks) grown during the previous matrix filling step. The previous grown deposits with two types of morphologies were observed. One was the spike-like deposits with a low aspect ratio (white arrow marks) as shown in Fig. 3(b) and the other was the film-type deposits with the round-top morphology (white arrow mark) as shown in Fig. 3(c). The film-type deposits resulted from deposition onto the original SiC fibers or bundles by the same matrix filling process as that of the conventional CVI. The spike-like deposits seemed to result from deposition onto the previously grown whiskers. These spike-like deposits may be divided the large

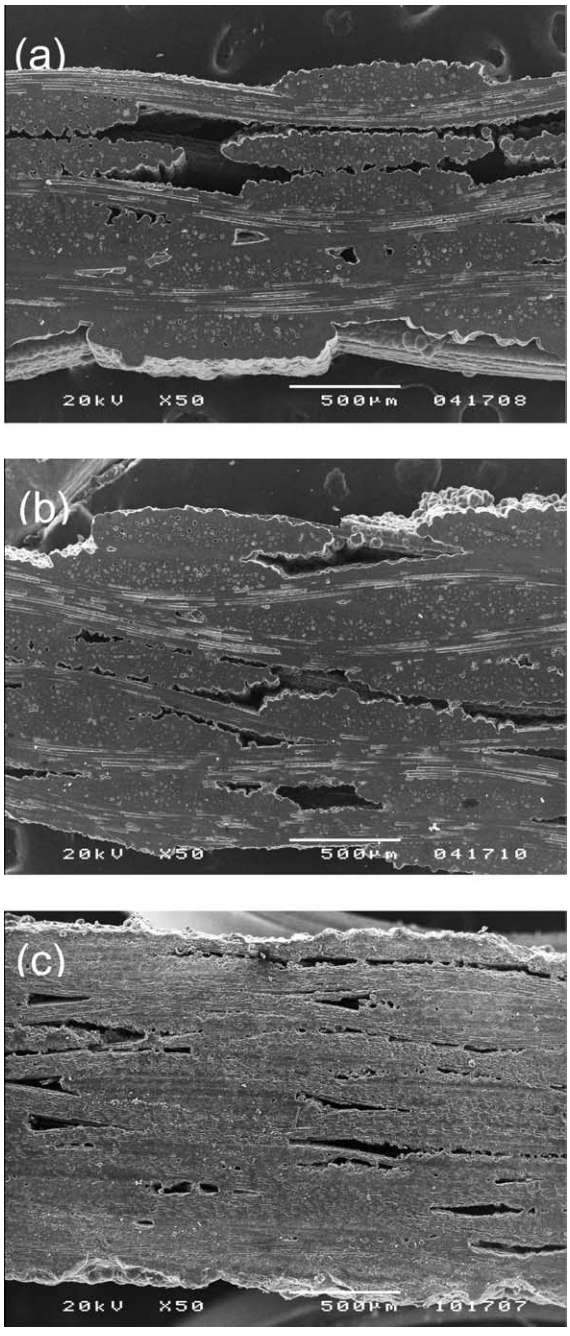

Fig. 4. Microstructures of SiC_f/SiC composites prepared by the different numbers of the process cycles: (a) one cycle, (b) two cycles and (c) three cycles.

voids into small ones to enhance the densification at the next matrix filling steps.

To compare the densification behaviors with the number of the process cycles, three SiC_f/SiC composites were prepared by different numbers of the process cycles with an extending of the last matrix filling time to more than 25 h. Fig. 4(a)–(c) show microstructures of the cross sections of each composite prepared by one cycle of the process (whisker growth (WG) for 3 h + matrix filling (MF) for 25 h), two cycles of the process (1st WG for 3 h + 1st MF for 6 h + 2nd WG for 3 h + 2nd MF for 21 h), and three cycles of the process (1st WG for 3 h + 1st MF for 6 h + 2nd WG for 3 h + 2nd MF for 6 h + 3rd WG for 3 h + 3rd MF for 17 h), respectively. The density of each specimen was 2.67, 2.54 and 2.60 g/cm^3, respectively. Three composites had a small amount of density differences but showed a large difference in the size and distribution of the voids with the number of the process cycles. As the number of the cycles increased, the maximum size of large voids decreased and the homogeneity of the voids distribution increased. These changes of the size and distribution of the voids could have resulted from the modifying of the void structures by whisker growing.

4. Summary

SiC whiskers were grown in the SiC fiber preforms at the input gas ratio of 60 and the total reaction pressure of 5 Torr. After three cycles of the process (1st whisker growth (WG) for 3 h + 1st matrix filling (MF) for 6 h + 2nd WG for 3 h + 2nd MF for 6 h + 3rd WG for 3 h + 3rd MF for 17 h), the composite had a density of 2.6 g/cm^3 and a improved microstructure with a smaller size and a more homogeneous distribution of the voids. As the number of the cycles increased, the maximum size of the large voids decreased and homogeneity of the voids distribution increased.

Acknowledgements

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