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Fabrication and characterization of SiC_f/SiC composite by CVI using the whiskering process

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Abstract

The chemical vapor infiltration (CVI) process is an effective method for fabricating SiC fiber-reinforced SiC matrix composites but it is slow with an inherent drawback of substantial residual porosity. To obtain the dense SiC_f/SiC composite by the CVI process, in situ whisker growing and matrix filling (called whiskering process) was applied. The process was designed to reduce the canning effect during the CVI process and may serve to divide the large natural pores between fibers or bundles by the grown whisker and then fill the matrix inside the modified pore structure. This process was performed using MTS (CH_3SiCl_3) as a source gas and H_2 or N_2 as a diluent and the amounts of the whiskers into the matrix phases were changed by controlling the whiskering cycles. The infiltration effects, that is, increasing of the density of the SiC_f/SiC composite were investigated. And the improved SiC_f/SiC composites were fabricated using this process.

1. Introduction

The use of ceramics in high-temperature structural applications has been severely limited by their low fracture toughness and lack of predictable service life. Any flaw in the ceramic can lead to catastrophic failure. However, by using long fibers to reinforce the ceramic matrix, fracture toughness has been significantly improved. SiC_f/SiC is one of the typical continuous fiber reinforced ceramic composites. In addition to the thermomechanical advantages of SiC_f/SiC composites, the low induced activation by neutron and good irradiation resistance have also made them quite attractive for fusion reactor applications [1–5].

Several fabrication processes for SiC_f/SiC composites, such as chemical vapor infiltration (CVI) process [6], polymer impregnation and pyrolysis [7,8], reaction sintering process [9], etc. have been under investigation for more than 10 years. The CVI process is an effective method for fabricating SiC fiber-reinforced SiC matrix composites but this process is slow with an inherent drawback of substantial residual porosity [1]. As the infiltration process proceeds, the growing matrix obstructs the infiltration of vapor reagents, decreasing the infiltration efficiency [6,10]. Because of this canning phenomenon, large closed pores are left into the interior of the fiber preform. In a previous work [11], we proposed a new method, the so-called whiskering process (in situ whisker growing and matrix filling process), to obtain a dense composite in the C_f/SiC system by the CVI process. This process consists of two steps: a whisker growing step and a matrix filling step. In the first step, the grown SiC whiskers may serve to divide large natural pores between fibers or bundles into smaller ones and modify the void structure. In addition the grown whiskers offer new deposition sites for SiC. Therefore, matrix filling may be efficiently performed, in the next step, inside the whisker grown composites.

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In this study, the whiskering process was applied to the SiC_f/SiC system to obtain a dense composite. The matrix filling behavior was investigated using multi-layered preforms of 2D plain-weave Nicalon™ fiber cloth. Additionally, the possibility of making a dense SiC_f/SiC composite by the multi-step whiskering process was confirmed using only one layer of Nicalon™ cloth.

2. Experimental procedure

All the experiments were performed in a hot-wall horizontal reactor as previously described [11]. Acetylene (C_2H_2) and methyltrichlorosilane (CH_3SiCl_3, MTS) were chosen as source precursors of pyrolytic carbon and SiC, respectively. MTS was chosen because it has an equivalent atomic content of Si and C and shows a relatively low thermal decomposition temperature. Hydrogen was used as a carrier gas to transfer source precursor through the bubbler to the main reactor. Hydrogen or nitrogen was used as a diluent gas to regulate the concentration of the mixture involving MTS vapor and carrier gas. Diluent gas and carrier gas containing MTS vapor were mixed together before being introduced into the reactor. The flow rate of MTS vapor was controlled by adjusting the bubbler pressure and the flow rate of the carrier gas (H_2), maintaining the temperature of the bubbler containing liquid MTS at 0 °C. The pressure in the reactor was monitored with capacitance nanometer and controlled with throttle valve located between the reactor and a mechanical pump.

Fibrous preforms were fabricated by depositing a thin pyrolytic carbon layer of about 0.1 μm thick in a stack of 2D plain-weave Nicalon™ cloth. The whisker growing of the first step in the whiskering process, was performed at 1100 °C for up to 6 h and the matrix filling step was carried out at 1000 °C for 5 h to observe an intermediate step of pores (or voids) filling behavior. The input gas ratio of diluent plus carrier gas to MTS, $\alpha = F_{(\text{diluent+carrier})}/F_{\text{MTS}}$ was 5–15 and total flow rate was 500 sccm. A cyclic whiskering process, a repetition of a whisker growing and a matrix filling, was then performed to densify the SiC_f/SiC composite. Crystalline phases were detected and characterized by the X-ray diffraction (XRD) method. The microstructure of the SiC_f/SiC composites was observed using scanning electron microscopy (SEM; Model JS-5200, Jeol, Japan).

3. Results and discussion

Fig. 1 shows the microstructures of the SiC_f/SiC composites prepared by different processes. Fig. 1(a) is

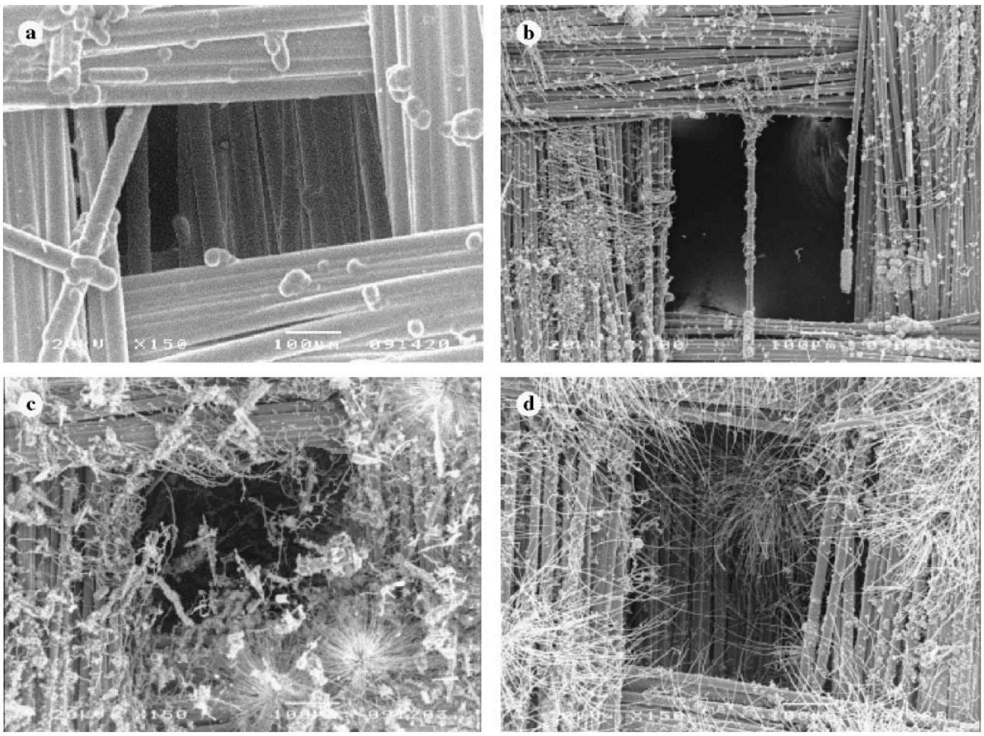

Fig. 1. Microstructures of SiC_f/SiC composites (a) infiltrated at 1000 °C for 5 h without whisker growing, and only grown whiskers at 1100 °C for (b) 2 h, (c) 4 h and (d) 6 h, respectively.

the microstructure of the SiC_f/SiC composite only infiltrated at 1000 °C for 5 h without whisker growth and Fig. 1(b), (c) and (d) are microstructures of the specimens after the whisker growing step at 1100 °C for 2, 4 and 6 h, respectively. After only infiltration of the SiC_f perform, the structure and the size of a large void between the fiber bundles did not change, but the whiskers grown in the large voids as well as on the fibers were observed in the whisker growing step. There are three types of whiskers: a short spike-like type (Fig. 2(b)), a long vine-like type (Fig. 1(b)) and a thread-like type (Fig. 1(d)). As the size of the voids and the reaction time increased, the thread-like type was predominantly observed. But the short spike-like type predominantly existed in the small voids between the fibers. As shown in Fig. 2(b), the short spike-like whiskers grew dividing the voids between the fibers and leaving the open channels for matrix filling. Additionally, these grown whiskers were expected to act as new sites for the deposition of SiC. Therefore, the infiltration is more efficiently performed in the matrix filling step. On the other hand, if only the infiltration process was applied without the whisker growing step, SiC was circumferentially deposited on the fibers (Fig. 2(a)). As the circumferential deposition of SiC proceeded, the grown SiC layers met each other and stopped further deposition into the closed porosity formed inside the junction of the deposited SiC. Therefore, the CVI process using whisker growing process suggests the possibility of an effective matrix filling by dividing the size of voids into smaller ones and increasing the sites for SiC deposition. The phases of the grown whiskers were detected by X-ray diffractometry. Fig. 3 shows XRD patterns of SiC_f/SiC composites after whisker growing for up to 6 h and as-received Nicalon™ cloth. Crystalline phases were not clearly detected in the as-received Nicalon™ cloth but the crystalline β-SiC was observed in the specimens subjected to whisker growing.

To understand the intermediate stage of the matrix filling, the specimens shown in Fig. 1(a) and (d) were further infiltrated for 5 h. Fig. 4 shows the microstructures of SiC_f/SiC composites after partial matrix filling of both specimens for 5 h. As shown in Fig. 4(a) and (c), large voids between the fiber bundles can be observed in the infiltrated specimen without the whisker growing step. On the contrary many whiskers (arrow marks) are present in the voids between fiber bundles and some filling of SiC through the whiskers is also observed in the whisker grown specimen (Fig. 4(b) and (d)). Furthermore each bundle of the whisker grown specimen seems to be more porous than that of only the infiltrated specimen, which will assist the densification in the further filling step by offering more paths to reactant gases. This suggests that whisker growing is a more effective method of making a dense composite.

Fig. 5 shows the microstructures of the SiC_f/SiC composite with only a single layer of the 2D Nicalon™

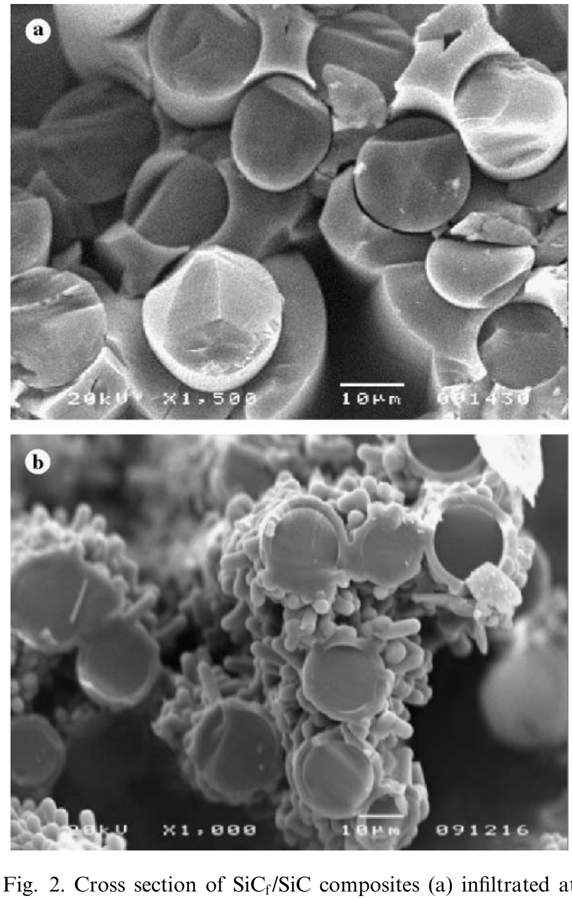

Fig. 2. Cross section of SiC_f/SiC composites (a) infiltrated at 1000 °C for 5 h without whisker growing and (b) only grown whiskers at 1100 °C for 4 h.

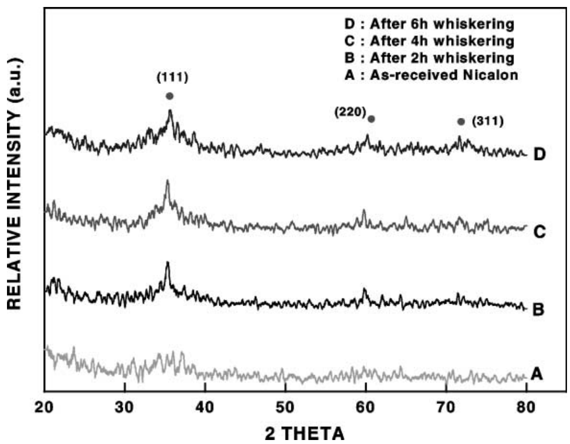

Fig. 3. XRD patterns of as-received Nicalon™ fabric and SiC_f/SiC composites infiltrated with the whisker growing step at 1100 °C.

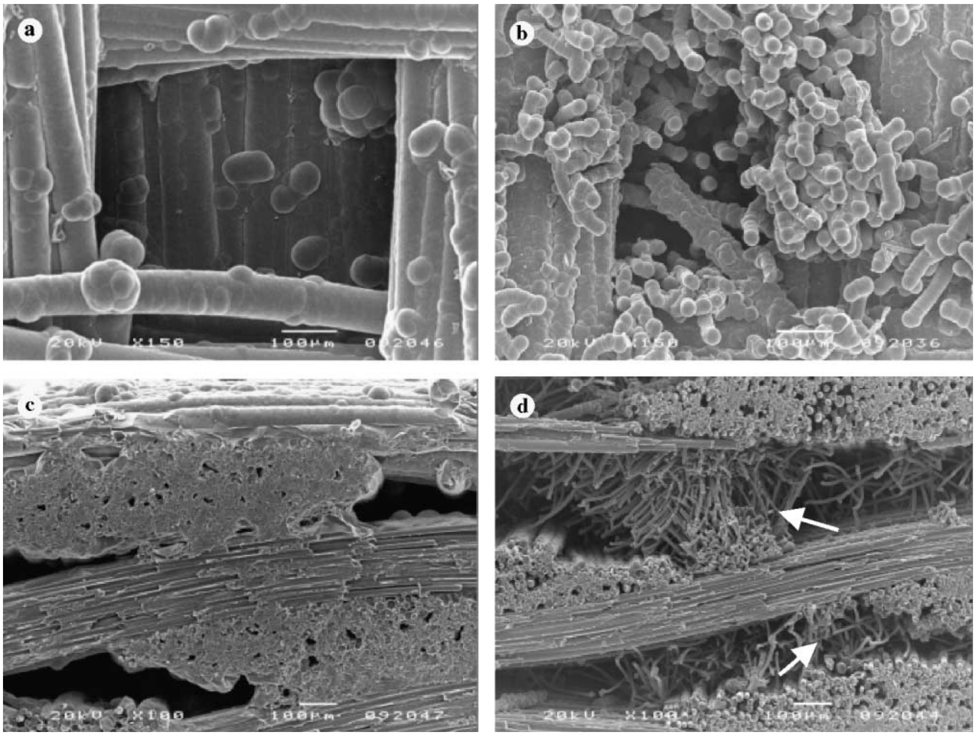

Fig. 4. Microstructures of SiC_f/SiC composites prepared by (a) 5 h + 5 h matrix filling and (b) 6 h whisker growing + 5 h matrix filling. (c) and (d) are the cross sections of (a) and (b), respectively.

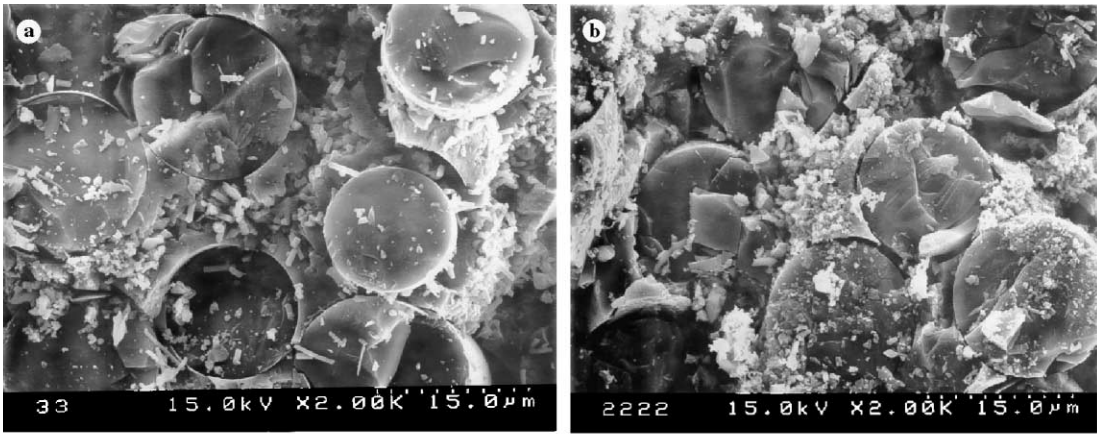

Fig. 5. Microstructures of SiC_f/SiC composites which were prepared using (a) one cycle of in situ whisker growing and matrix filling and (b) two cycles of the two-step process.

cloth that has been prepared using only one cycle of whiskering process (a whisker growing for 3 h and a matrix filling for 3 h) and two cycles of whiskering process (a whisker growing for 2 h and a matrix filling for 2 h), respectively. A comparison of the densification degree of the two types of specimens based on the microstructures is difficult, but dense SiC_f/SiC composites can be easily obtained.

4. Summary

β-SiC whiskers can be grown in the voids of the SiC_f preforms by the whiskering process. These whiskers are expected to modify the pore structure of SiC_f/SiC composite and act as new SiC deposition sites for further matrix filling. Therefore, dense SiC_f/SiC composite can be easily fabricated by the whiskering process. And the cyclic whiskering process seems to be an alternative method for enhancing the density of the SiC_f/SiC composite.

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References

[1] A. Hasegawa, A. Kohyama, R.H. Jones, L.L. Snead, B. Riccardi, P. Fenici, J. Nucl. Mater. 283–287 (2000) 128.
[2] R.H. Jones, L.L. Snead, A. Kohyama, P. Fenici, Fus. Eng. Des. 41 (1998) 15.
[3] R.H. Jones, C.H. Henager, J. Nucl. Mater. 233–237 (1996) 26.
[4] A.G. Evans, J. Am. Ceram. Soc. 73 (1990) 187.
[5] D.W. Freitag, D.W. Richerson, Opportunities for Advanced Ceramics to Meet the Needs of the Industries of the Future, DOE/ORO 2076, 1998.
[6] T.M. Besmann, B.W. Sheldon, R.A. Lowden, D.P. Stinton, Science 253 (1991) 1104.
[7] R. Jones, A. Szweda, D. Petrak, Compos. A 30 (1999) 569.
[8] A. Kohyama, M. Kotani, Y. Katoh, T. Nakayasu, M. Sato, T. Yamamura, K. Okamura, J. Nucl. Mater. 283–287 (2000) 565.
[9] A. Sayano, C. Sutoh, S. Suyama, Y. Itoh, S. Nakagawa, J. Nucl. Mater. 271&272 (1999) 467.
[10] N.H. Tai, T.W. Chou, J. Am. Ceram. Soc. 73 (1990) 1489.
[11] B.J. Oh, Y.J. Lee, D.J. Choi, G.W. Hong, J.Y. Park, W.J. Kim, J. Am. Ceram. Soc. 84 (2001) 245.