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Characterization of the matrix phase of whisker growing-assisted CVI-SiC_f/SiC composites

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The matrix phases of conventional CVI and whisker growing-assisted CVI (WA-CVI) SiC_f/SiC composites were compared to analyze the effects of the whiskers grown in the matrix of WA-CVI composite on the properties. Microstructures of the matrices and fracture surfaces were observed and the hardness and elastic modulus were measured. The whiskers in the matrix as well as on the fibers acted as deposition core sites in WA-CVI composite. The whiskers remained on the pulled-out fibers after fracture resulted in the improved mechanical properties in WA-CVI composite.

Key words: SiC_f/SiC composite, Whisker, Chemical vapor infiltration, Microstructure, Hardness, Elastic modulus.

Introduction

SiC_f/SiC composites are typical continuous fiber reinforced ceramic composites. The fracture toughness is significantly improved by complicated mechanisms for crack propagation in fiber reinforced composites [1]. SiC_f/SiC composites produced by a chemical vapor infiltration (CVI) technique contain large pores although the technique produces a highly-pure SiC matrix. We have developed a 'whisker growing-assisted CVI process (WA-CVI),' in which one-dimensional SiC nanostructures with high aspect ratios such as whiskers, nanowires and nanorods are introduced into the SiC fiber preform before the matrix infiltration step [2-6]. In this process, SiC deposits with a high aspect ratio may change the structure of large voids existing in the inter-bundles and inter-fibers and supply the new deposition sites. Therefore, SiC_f/SiC composites fabricated by the WA-CVI have a lower porosity and a uniform distribution of pores when compared with composites prepared by the conventional CVI process, which results in better properties. The crystal structure of the grown whiskers, the faster weight gain rate and an improved bending strength of WA-CVI SiC composites were reported in our previous study [4]. This investigation suggested that the whiskers could act as reinforcements in the matrix of a SiC_f/SiC composite similar to fibers in conventional CVI composites.

In this study, the characteristics of the matrix phases prepared by the CVI and WA-CVI processes are compared. Microstructures were observed by a transmission electron microscope (TEM) and the hardness and elastic modulus were measured by a nanoindentation method. Additionally, the fiber pull-out behaviors were observed using the tensile-tested specimens.

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Experimental Procedures

Preparation of SiC whiskers was carried out using a gas mixture of methyltrichlorosilane (CH_3SiCl_3, MTS, Aldrich Co., 99%) and purified H_2 (purity: 5N) where H_2 acted both as a reducing agent and a carrier gas for the MTS vapor. The whisker growth was performed at 1100 °C under a total pressure of 0.74 kPa with an input gas ratio of H_2 to MTS, α ($= F_{(diluent+carrier\ gas)}/F_{MTS}$) of 60 in a hot wall chamber. The flow rate of the MTS vapor was controlled by adjusting the bubbler pressure and the flow rate of the carrier gas, and maintaining the temperature of the bubbler containing the liquid MTS at 0 °C. The pressure in the reactor was monitored with a capacitance manometer and controlled at 0.74 kPa with a throttle valve located between the reactor and the mechanical pump. A plain weave fabric of Tyranno-SA^{TM} was used as a reinforced substrate. Ten layers of the fabric with a diameter of 50 mm were stacked as a green preform. Before the whisker growth, the preforms were coated with pyrolytic carbon using methane gas (CH_4) at 950 °C for up to 3 h with a deposition pressure of 14.7 kPa. The matrix filling process was performed at 1000 °C with a total pressure of 14.7 kPa for up to 24 h.

A focused ion beam (FIB) milling system (Model NOVA200, FEI Co., Netherlands) was used to prepare the specimens for TEM observations. The microstructural examinations were carried out using a TEM (JEM-2000FX, JEOL) operating at 200 KeV. The evaluations of the hardness and elastic modulus were carried out with a nano-indentation tester (Nano Indenter XP, MTS Ltd.) and a Berkovich diamond tip. The tensile specimens were machined from the disk in a direction of 0°/90°.

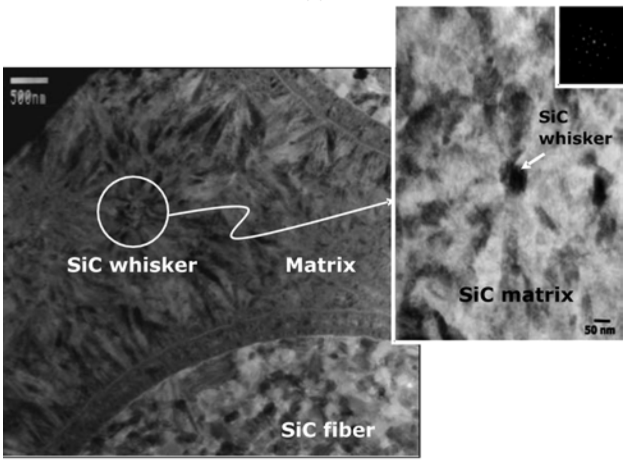
The plate-shaped specimens for the tensile tests had an overall length of 40 mm and a thickness of 3.1 mm. The tensile tests were conducted on a servo-hydraulic testing machine (INSTRON 8861S, Instron Co.) with a laser extensometer in an Ar atmosphere at room temperature and 1300 °C. The crosshead displacement rate was 0.5 mm/minute and the heating rate to 1300°C was about 20 K/minute^{-1}. The fracture surfaces of the tensile tested specimens were observed with a 3D digital microscope (VHX-200, KEYENCE) for an evaluation of the fiber pull-out behaviors.

Results and Discussion

Microstructure evaluation

Fig. 1 shows microstructures of the matrix phase in SiC$_f$/SiC composites prepared by the different CVI processes. Fig. 1(a) is a typical microstructure of the matrix phase in conventional CVI composite which shows a radial growth of fine columnar SiC grains without any other deposition core sites (e.g. fibers) in the matrix. However, in the matrix of WA-CVI composite, a complicated microstructure with fine columnar and fine equiaxed grains was observed as shown in Fig. 1(b). Radially grown SiC grains with a columnar shape were also observed in WA-CVI composite as shown in conventional CVI composite (Fig. 1(a)). On the other hand, several fine equiaxed grains were additionally existed in the matrix of WA-CVI composite. These grains seemed to be whiskers which were grown intentionally before the matrix filling process. As shown in an enlarged micrograph of Fig. 1(b), these fine equiaxed grains acted as another deposition core sites for the growth of fine columnar SiC grains. This means that the matrix phases were deposited on the whiskers as well as on the fibers during matrix filling in WA-CVI composite. Therefore, a matrix filling rate of WA-CVI composite could be relatively faster than that of conventional CVI composite as reported previously [4]. We can reduce the process time for the fabrication of a SiC$_f$/SiC composite using the WA-CVI process.

(a)



(b)

Fig. 1. Transmission electron micrographs of the matrix of SiC$_f$/SiC composites prepared by (a) the conventional CVI and (b) the WA-CVI process.

Mechanical Properties

The whiskers grown in the matrix are expected to act as reinforcement which may improve the mechanical properties of SiC$_f$/SiC composites. The hardness and elastic modulus of SiC$_f$/SiC composite were measured by a nanoindentation tester and the ultimate tensile strength (UTS) was measured by a servo-hydraulic testing machine. Fig. 2 shows the hardnesses and elastic moduli of SiC$_f$/SiC composites prepared by the conventional CVI and WA-CVI process. WA-CVI composite had a slightly higher hardness and elastic modulus. However, the UTS values were clearly different from each other. The average tensile strength of conventional CVI composite was 135 MPa irrespective of the test temperatures (RT or 1300 °C). On the other hand, those of WA-CVI composites were 165-238 MPa depending on the existence of the whiskers coated with a PyC layer. In WA-CVI composites, the average tensile strengths were similar irrespective of the testing temperatures as measured in conventional CVI composite. The similar values measured at room and high temperatures indicate that CVI SiC$_f$/SiC composite has a very high purity. Generally, sintering aids or additives are added for a densification of monolithic SiC or SiC$_f$/SiC composites.

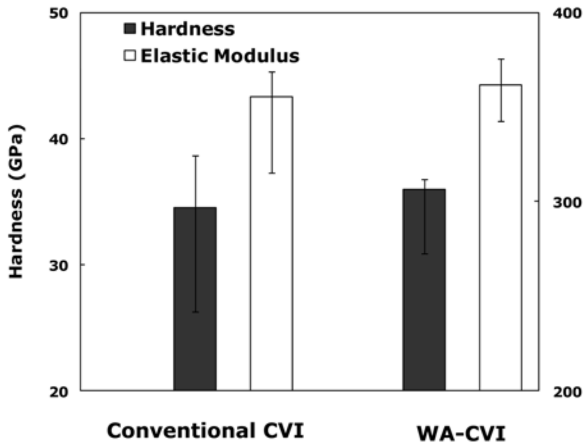
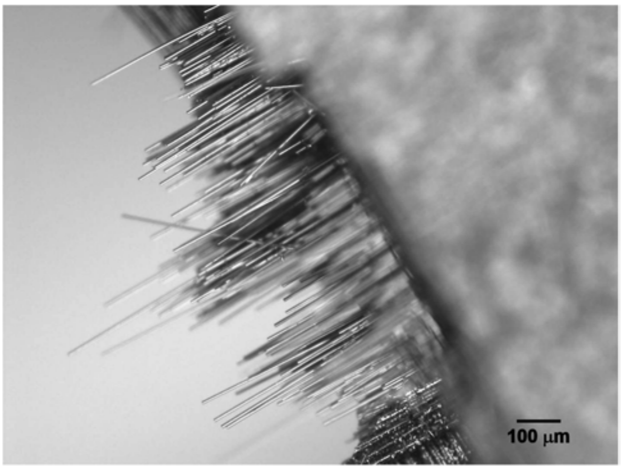
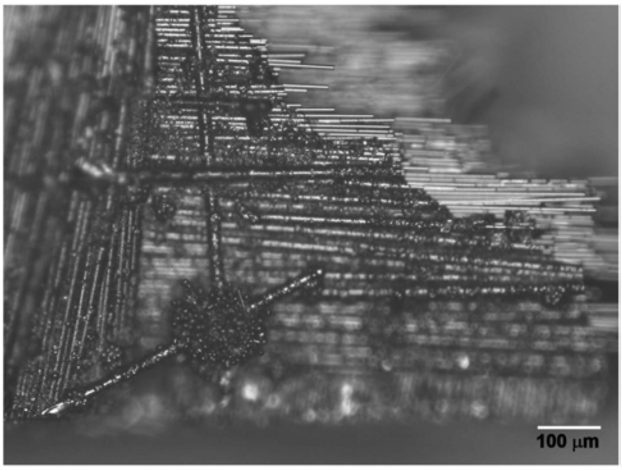


Fig. 2. Hardness and elastic modulus of SiC$_f$/SiC composites prepared by two different CVI processes.



(a)



(b)

Fig. 3. Three dimensional micrographs of SiC_f/SiC composites showing the different pull-out behavior between (a) conventional CVI composite and (b) WA-CVI composite.

However, these additives cause a degradation of the high temperature mechanical properties. In CVI composites, no additives and sintering aids were added during the infiltration process. Therefore, CVI composites had a high purity and no degradation of their mechanical properties occurred even at a high temperature. When compared with the UTS values of conventional CVI composites, those of WA-CVI composites were increased by 20-75%. To understand the enhancement of the UTS in WA-CVI composites, the pull-out behaviors of the fibers were evaluated by observing the microstructures of the fracture surfaces. Fig. 3 shows the microstructures of the pulled-out fibers of SiC_f/SiC composite. The typical pulled-out fibers were observed in both CVI composites as usually found in fiber reinforced composite. However, the surface morphologies of the pulled-out fibers were different. As shown in Fig. 3(a), the pulled-out fibers from conventional CVI composite had a clean surface without any obstacles. On the other hand, many obstacles were found on the surface of the pulled-out fibers from WA-CVI composites (Fig. 3(b)). These obstacles seem to be the whiskers that had remained on the fiber surface without a de-bonding when applying a tensile stress. These obstacles might disturb the pull-out behavior of the fibers and result in an increase of the tensile strength.

Summary

Whiskers were observed in the matrix of WA-CVI composite. Fine columnar SiC grains were radially grown on the whiskers as well as on the fibers of WA-CVI composite. It is suggested that the whiskers played an important role in increasing the infiltration rate of the matrix phase and improving the mechanical properties of WA-CVI when compared with those of conventional CVI composites. Differences of the hardness and the elastic modulus of WA-CVI and conventional composite were not large while the tensile strengths of WA-CVI composites (165-238 MPa) were significantly higher than that of conventional CVI composite (135 MPa).

Acknowledgments

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References

1. A.G. Evans and F.W. Zok, J. Mater. Sci., 29 (1994) 3857-3896.
2. B.J. Oh, Y.J. Lee, D.J. Choi, G.W. Hong, J.Y. Park and W.-J. Kim: J. Am. Ceram. Soc. 84 (2001) 245-247.
3. J.Y. Park, H.S. Hwang, W.-J. Kim, J.I. Kim, J.H. Son, B.J. Oh and D.J. Choi, J. Nucl. Mater., 307-311 (2002) 1227-1231.
4. J.Y. Park, S.M. Kang, W.-J. Kim and W.S. Ryu, Key Eng. Mater., 287 (2005) 200-205.
5. W.-J. Kim, S.M. Kang, C.H. Jung, J.Y. Park and W.-S. Ryu, J. Crystal Growth 300 (2007) 503-508.
6. S.M. Kang, W.-J. Kim, J. Y. Park, S.G. Yoon and W.-S. Ryu, Solid State Phenomena. 124-126 (2007) 711-714.
7. D. Lara-Curzio, Properties of CVI-SiC matrix Composite, in Comprehensive Composite Materials, Vol. 4, Ch. 4.18, Published by Elsevier Science, Netherlands (2000).