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Densification and Microstructure of SiC_f/SiC Composites Incorporated with In Situ Grown SiC Nanowires

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1. Introduction

Silicon carbide fiber-reinforced silicon carbide matrix (SiC_f/SiC) composites are considered as advanced materials for control rods and other in-core components of high-temperature gas cooled reactors [1]. In general, two-dimensional woven SiC_f/SiC composites have a significant anisotropy in the transverse and in-plane thermo-mechanical properties. Moreover, the composites produced by the chemical vapor infiltration (CVI) technique contain large pores although the technique produces a highly pure SiC matrix. The recently developed 'whisker growing-assisted process,' in which one-dimensional SiC nanostructures with high aspect ratios such as whiskers, nanowires and nanorods are introduced into the fiber preform before the matrix infiltration step, which results in composites with a lower porosity and an uniform distribution of the pores when compared with the conventional CVI [2]. This is expected to increase the mechanical and thermal properties of the SiC_f/SiC composites. In order to take full advantage of the whisker growing strategy, however, a homogeneous growth of long whiskers or nanowires is required.

In this study, we have grown the SiC nanowires within the SiC fiber preform by an atmospheric pressure CVD method without metallic catalysts. The SiC nanowires incorporated in the fiber preform increased the surface area at which a matrix deposition can take place, thus increasing the efficiency of a matrix infiltration and altering the remaining pore structure. We described the densification behavior and microstructure development of the nanowire-grown SiC_f/SiC composites during a matrix infiltration.

2. Experimental Procedure

Plain weave of Tyranno-SA fiber (Ube Industries, Japan) was punched out to make disk-shaped fabrics with diameters of 50 mm. Eleven layers of the fabrics were stacked with a fiber orientation of 0°/90°. Pyrolytic carbon (PyC) interphase with a thickness of 150 nm was deposited on the fiber surface by a decomposition of methane (CH_4) at 1000°C with a deposition pressure of 14.7 kPa for 3 h. Growth of the SiC nanowires and matrix infiltration were carried out using a gas mixture of methyltrichlorosilane (CH_3SiCl_3, MTS) and hydrogen (H_2) in which H_2 acted both as a reducing agent and a carrier gas for the MTS vapor. The SiC nanowires were grown within the PyC-coated fabric preform by decomposing the MTS at 1100°C for 3 h with a system pressure of 101 kPa. The volume ratio of hydrogen to MTS (input gas ratio, α) was varied from 20 to 120. The matrix infiltration process subsequent to the nanowire growth step was performed at 1000°C and α = 10 for various times with the system pressures of 10.7–13.3 kPa. Microstructures of the SiC_f/SiC composites were observed using a scanning electron microscopy (SEM; Model JS-5200, Jeol, Japan). Bulk density and the rate of a weight gain during a matrix infiltration were determined by measuring the dimension and weight of the specimens.

3. Results and Discussion

As described in our previous report [3], the behavior of SiC nanowire growth is largely dependent on the input gas ratio, α. Fig. 1 shows the microstructure of the deposits obtained at α = 20 and 80. At α = 20, one-dimensional but large diameter deposits (average diameter ≈ 0.75 μm) were grown on the SiC fiber and the lengths were limited to less than 10 μm. When the input gas ratio was higher than 80, however, thin and very long SiC nanowires could be obtained in a homogeneous fashion as shown in Fig. 1(b). The average diameters of the SiC nanowires grown at α = 80–120 were less than 60 nm and the lengths were more than several hundreds of micrometers.

Fig. 2 shows the rate of a weight gain during a matrix infiltration for the composites fabricated by the NW-CVI and the conventional CVI processes. In the early

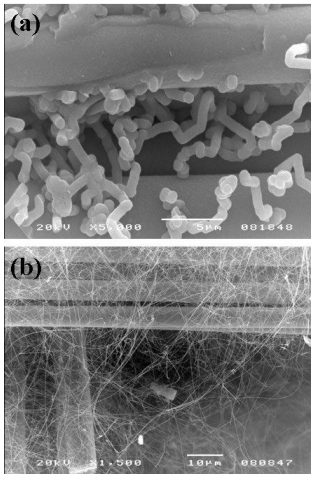

Fig. 1. Microstructures of the deposits grown on the SiC fabric at (a) a = 20 and (b) a = 80.

stage of the infiltration process less than 10 h, the rate of a weight gain of the NW-CVI composite was more than two times higher than that of the conventional CVI composite. This indicates that the efficiency of the matrix infiltration was higher in the NW-CVI process due to the large surface area of the nanowires on which a matrix deposition could take place. The rate of a weight gain of the NW-CVI composite rapidly decreased after the early stage of the infiltration process and it showed a lower value than that of the conventional one after infiltrating for 17 h. This seems to be caused by a decrease of the gas permeability due to the faster infiltration of the NW-CVI composite in the early stage. On the other hand, the conventional CVI composite exhibited only a mild decrease of the rate of a weight gain, indicating a slow infiltration reaction throughout the infiltration process.

The matrix infiltration behavior depicted in Fig. 2 implies that the NW-CVI process would render a higher composite density in a shorter infiltration time than the conventional process. For example, the NW-CVI composite reached a density of 2.6 g/cm^3 within 19 h, while the conventional CVI composite required more than 25 h to attain a similar density. The rapid decrease of the infiltration rate in the NW-CVI composite suggests that a careful control of the concentration of the SiC nanowires and/or a gradient of the concentration through the thickness direction of the composite is required to further increase the maximum attainable density as described in detail in our previous report [4].

Fig. 3 shows the cross-sectional SEM images of the composites fabricated by the NW-CVI and the conventional CVI processes. The void microstructures of the two composites show an obvious difference. While the conventional CVI composite contains interbundle/interlaminar voids being free of any deposit, the NW-CVI composite reveals a lot of rod-like deposits inside the voids. The rod-like deposits originated from the SiC nanowires through the deposition of the SiC films on the nanowires. The modification of the pore structure and the reduction of the macro-pores could be effective for increasing some

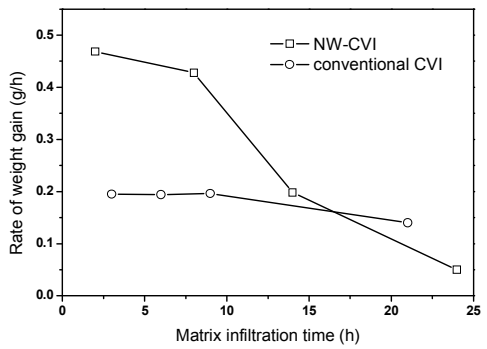

Fig. 2. Rate of weight gain as a function of the matrix infiltration time for the composites fabricated by the NW-CVI and the conventional CVI processes.

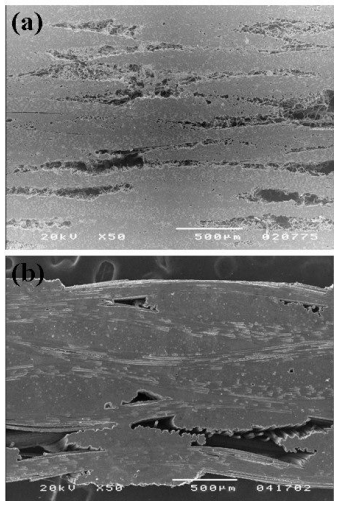

Fig. 3. SEM microstructures for the polished cross-sections of the NW-CVI (a) and the conventional CVI (b) composites after the matrix infiltration.

of the trans-thickness properties of the SiC_f/SiC composites, e.g., interlaminar shear/tensile strengths and transverse thermal conductivity.

4. Conclusions

The SiC nanowires could successfully be grown within the SiC fiber preform by the catalyst-free CVD process through a control of the reactant concentration. The degree of the reactant supersaturation seemed to play an important role in the growth of the SiC nanowires. The incorporation of the SiC nanowires into the fiber perform was clearly shown to be effective for increasing the efficiency of a matrix infiltration, and thus resulted in a higher density in a shorter processing time. The modification of the pore structure and the reduction of the macro-pores in the NW-CVI composite would render enhanced thermo-mechanical properties.

REFERENCES

[1] H. Hoffelner, High Temperature Materials - The Challenge for Future Advanced Gas Cooled Reactors, Proceedings of ICAPP '04, p. 380, Pittsburgh, USA, 2004.

[2] S. M. Kang, J. Y. Park, W. -J. Kim, S. G. Yoon, W. S. Ryu, Densification of SiC_f/SiC Composite by the Multi-Step of Whisker Growing and Matrix Filling, J. Nucl. Mater., Vol. 329-333, pp. 530-533, 2004.

[3] W. -J. Kim, S. M. Kang, J. Y. Park, W. -S. Ryu, Effect of Reactant Concentration on the Microstructure of SiC Nanowires Grown In Situ within SiC Fiber Preforms, Proceedings of the Annual Meeting of the Korean Nuclear Society, May 25-26, 2005, Gangchon, Korea.

[4] W. -J. Kim, S. M. Kang, J. Y. Park, W. -S. Ryu, Effect of a SiC whisker formation on the densification of Tyranno SA/SiC composites fabricated by the CVI process, Fus. Eng. Des., Vol. 81, pp. 931-936, 2006.