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Effect of Reactant Concentration on the Microstructure of SiC Nanowires Grown *In Situ* within SiC Fiber Preforms

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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]. Although the carbon fiber-reinforced carbon matrix (C_f/C) composites are more mature and have advantages in cost, manufacturability and some thermomechanical properties, the SiC_f/SiC composites have a clear advantage in irradiation stability, specifically a lower level of swelling and retention of mechanical properties. This offers a lifetime component for control rod application to HTGRs while the C_f/C composites would require 2-3 replacements over the reactor lifetime [2].

In general, the chemical vapor infiltration (CVI) technique has been used most widely to produce SiC_f/SiC composites. Although the technique produces a highly pure SiC matrix, it requires a long processing time and inevitably contains large interbundle pores. The present authors have 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. This novel method can produce SiC_f/SiC composites with a lower porosity and an uniform distribution of pores when compared with the conventional CVI [3]. This would be expected to increase 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 is required.

In this study, we applied the atmospheric pressure CVI process without metallic catalysts for the growth of SiC nanowires within stacked SiC fiber fabrics. We focused on the effect of the concentration of a reactant gas on the growth behavior and microstructures of the SiC nanowires and discussed a controlling condition for the homogenous growth of long SiC nanowires.

2. Experimental Procedure

Disk shape fabrics with diameters of 50 mm were punched out from a plain weave Tyranno SA SiC fabric (Ube Industries, Japan). Ten layers of the fabrics were stacked and restrained in a perforated graphite fixture to result in an average fiber volume fraction of ~40%. The growth of SiC nanowires was carried out in a horizontal hot-wall CVD system. The stacked fabrics were vertically placed in a graphite tube surrounded by an outer alumina tube. Methyltrichlorosilane (MTS, CH_3SiCl_3, 99%, Aldrich Chemical Co. Ltd.) was used as a source precursor of SiC and H_2 was used as both a carrier and a diluent gas. The growth of SiC nanowires was performed at 1100°C with a system pressure of 0.1 MPa for 3 h. The volume ratio of H_2 to MTS (input gas ratio, α) was controlled from 20 to 120 and the total flow rate was 800 sccm.

Microstructures of the SiC nanowires grown on the SiC fabrics were observed using a scanning electron microscopy (SEM). In order to investigate microstructural differences of the SiC nanowires through the thickness direction, microstructures of the SiC nanowires grown on the 1st, 5th, and 10th layers of the fabrics were observed after separating each layer. The SiC nanowires were also characterized by a transmission electron microscopy (TEM) and a selected area electron-diffraction (SAED).

3. Results and Discussion

Fig. 1 shows the surface microstructures of the SiC nanowire-grown preforms at various input gas ratios from 20 to 120. When the input gas ratio was 20, one-dimensional but large diameter deposits were obtained and the length was limited to several tens of micrometers. At the input gas ratio of 60, clumps of thin and short nanowires were formed. When the input gas ratio was higher than 80, however, thin and very long nanowires could be obtained in a homogeneous fashion.

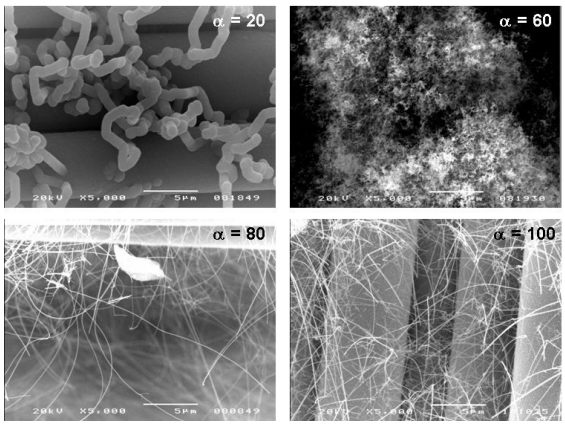

Fig. 1. Microstructures of the SiC nanowires grown on the surfaces of SiC fabrics at various input gas ratios.

It is interesting to note that the diameter of SiC nanowires shows a strong dependency on the stacking

position of fabric layers at the input gas ratios less than 60 (Figs. 2 and 3). Microstructures of nanowires change dramatically at the 5th and 10th layers of the fabric as shown in Fig. 2 when compared with the nanowires grown on the 1st layer (α=20 in Fig. 1). The SiC nanowires become thinner and longer toward the downstream side of the CVI gas. When the input gas ratios were higher than 60, however, the average diameter and the number density of the SiC nanowires were slightly decreased.

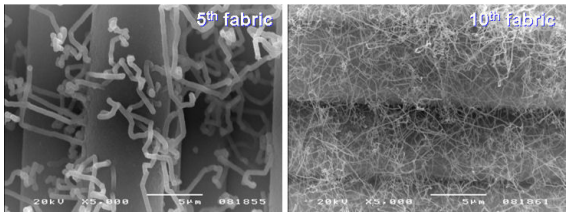

Fig. 2. Microstructures of the SiC nanowires grown on the 1st and 10th layers of the stacked fabric at the input gas ratio of 20.

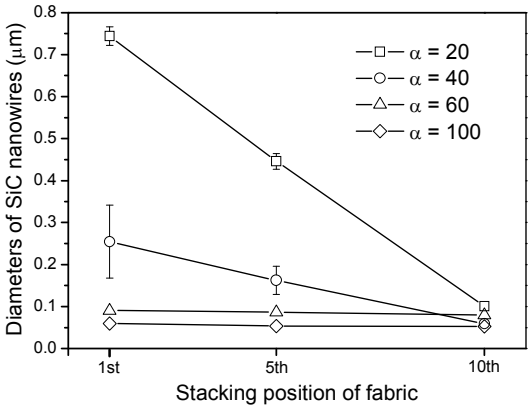

Fig. 3. Variation of the average diameter of SiC nanowires with the stacking position of fabrics at various input gas ratios.

The decrease of the whisker diameter with the stacking position can be explained by a depletion of the reactant gas toward the downstream side of CVI gas. The reactant gas is depleted more and more toward the downstream side of the CVI gas as the CVI reaction proceeds, $CH_3SiCl_3 + H_2 \rightarrow SiC + 3HCl + H_2$. As a result, the progressive depletion of the reactant gas toward the downstream side of the CVI gas leads to a similar effect to an increase of the input gas ratio. These phenomena suggest that the degree of a reactant supersaturation plays an important role in the growth of SiC whiskers.

Fig. 4 shows TEM images and SAED patterns of the SiC nanowires grown at input gas ratios of 60 and 100. The SiC nanowires grown at the input gas ratio of 60 consist of relatively thicker nanowires with diameters of about 100 nm and thin nanowires less than 50–60 nm in diameter. The thicker nanowires had a polycrystalline nature as shown in the SAED pattern of Fig. 4(a) while

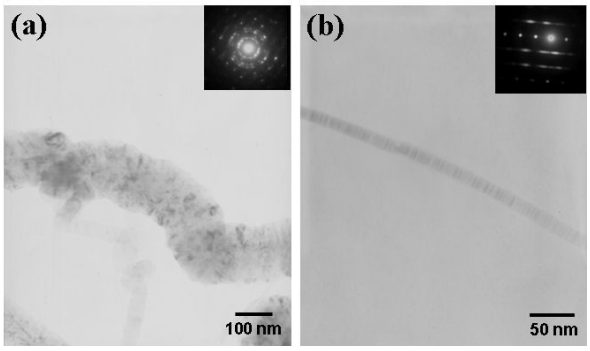

Fig. 4. TEM images of the SiC nanowires grown at input gas ratios of (a) 60 and (b) 100.

the thin nanowires were single crystalline. On the other hands, at the input gas ratio of 100, the deposits exclusively consist of single crystalline nanowires with a growth direction of <111>. When the degree of the reactant supersaturation is low, i.e., at high input gas ratios, the SiC nanowire grows along the <111> direction at the expense of the other higher energy planes because the {111} plane is the lowest-energy plane in a β-SiC crystal. As the degree of the reactant supersaturation increases, however, the higher energy planes can grow and multiple nucleation and growth with random crystallographic orientations can occur. This leads to a significant radial growth as well as an axial growth. As a result, one-dimensional deposits with polycrystalline structures and large diameters were obtained at low input gas ratios (α=20 and 40).

4. Conclusions

The SiC nanowires could be grown homogeneously within SiC fiber preforms by controlling the concentration of the reactant gas. The morphology and growth behavior of SiC nanowires were largely dependent on the degree of the reactant supersaturation. The SiC_f/SiC composites incorporated with the SiC nanowires in the SiC matrix are expected to have enhanced mechanical properties and radiation resistance than the conventional CVI composites.

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