

## Synthesis of SiC micromembrane tubes by aluminum doping from carbon fibers

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Carbon fiber has become an important material, partly because of its high-temperature strength. However, carbon fiber is so easily oxidized at high temperature that it is impossible to use it in an oxidizing gas environment. As an important high-temperature structural material, silicon carbide (SiC) offers many advantages over traditional materials, such as its suitability as a catalyst support [1, 2] and as a hot-gas filter [3] because of its unique properties, e.g., low thermal-expansion coefficient, good thermal shock resistance, high resistance towards oxidation, high-mechanical strength, and chemical stability. All of these properties are required for good heterogeneous catalyst support materials at elevated temperature [1, 2, 4, 5]. However, in spite of the above advantages, there is still a challenging technical problem in preparing porous SiC materials with a large surface area, because of limitations in the conventional methods. Several methods designed to overcome the major drawback of SiC, namely its very small surface area, have been reported [6–9]. In particular, there have been many attempts to increase the specific surface area of SiC as a catalyst support, using a pack cementation technique [10–13]. The pack cementation technique using a vapor-solid (VS) reaction provides the desired morphology in SiC. The SiC material with carbon residues can be synthesized by the VS reaction based on the following reactions [11]:



in which the gaseous SiO is generated by heating the pack containing a mixture of Si and SiO<sub>2</sub> powders.

In our previous works, SiC microtubes with villus-like morphology on the inner surface have been synthesized from carbon templates using the VS diffusion reaction method (modified pack cementation process) [14–16], resulting in a large specific surface area of 45–63 m<sup>2</sup>g<sup>-1</sup>. The SiC fibers are obtained as a by-product in the synthesis, because of the Fe impurity included in the carbon fiber used as starting material. The reaction for synthesizing the SiC microtubes and the SiC fibers is governed by VS and vapor-liquid-solid (VLS) growth mechanisms, respectively. Therefore, it

has been confirmed that the grain morphology in materials synthesized by the modified pack cementation process is dependent on the impurity. Impurity diffusion is one of the principal methods of doping. Although the effective diffusion coefficients for most of the major impurities in SiC are too small for practical applications, it is nevertheless important to understand the diffusion process in SiC, because the process may take place during bulk and epitaxial growth, as well as during heat treatments. Diffusion coefficients for different impurities in 6H-SiC are well known [17]. Boron (B) and aluminum (Al) diffusions have been used for the fabrication of SiC devices. Boron diffusion has produced yellow and green light-emitting diodes [18], while field-effect transistors are fabricated by aluminum diffusion [19]. However, the effect of an impurity on the products synthesized by the pack cementation process or the modified one has not yet been reported.

In the present study, the VS reaction process has been adopted to convert carbon fibers into SiC micromembrane tubes, and the effect of Al impurity on the synthesis of the SiC micromembrane tubes is described. Carbon fiber (Goodfellow, Cambridge Limited, USA), whose characteristics are summarized in Table I, was used as starting material. Silicon (Daejung Chemicals & Metals Co., Ltd., Republic of Korea) and silica (Junsei, Japan) were used as precursor powders in the VS reaction. Two different pack compositions were used in this study. The first pack composition for the synthesis of the SiC microtubes consisted of 1 mol Si (300 mesh) and 12 mol SiO<sub>2</sub> (325 mesh). The second pack composition for the SiC micromembrane tubes included a small amount of Al impurity ( $\geq 0.75$  wt%) added to the previous composition.

The carbon fibers were heat-treated at 1450 °C for 9 h, with a heating rate of 5 °C/min in a dynamic gas flow of 200 sccm (ml/min) in a pre-carburized tubular alumina crucible, using the first pack composition. Pre-carburization on alumina crucible was carried out to prevent the subsidiary reaction between crucible and carbon fiber at high temperature. This step provides the SiC microtubes with carbon residuals inside the SiC microtubes. As the second step, the SiC microtubes were reheat-treated with the second pack composition containing the Al impurity under the same conditions. The

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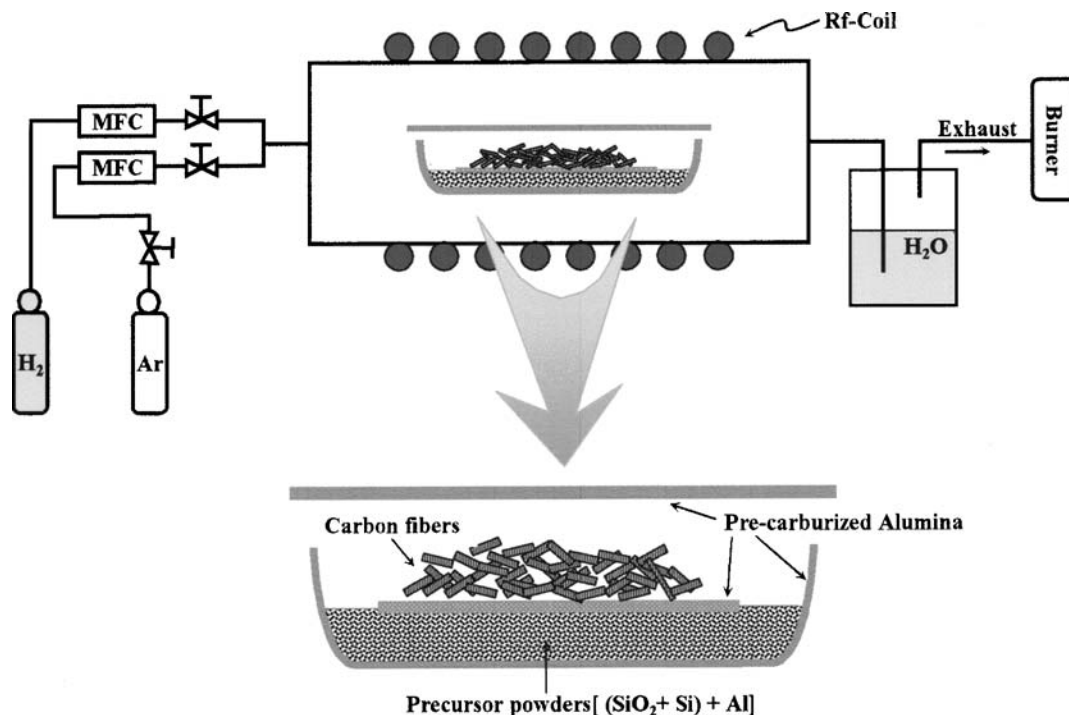


Figure 1 Schematic diagram of the experimental apparatus and vapor-solid (VS) reaction process for the preparation of SiC microtubes and/or SiC micromembrane tubes.

second step yields the SiC micromembrane tubes. The experimental apparatus is shown in Fig. 1. Scanning electron microscopy (SEM, JEOL, JMS-840) revealed the morphological evolution in the SiC microtubes and the SiC micromembrane tubes, with and without the Al impurity, respectively.

Fig. 2 shows the microstructure of the SiC microtube synthesized with the binary gas flow of H<sub>2</sub>/Ar (20/80) at 1450 °C for 9 hr, using the pure precursor powders without the Al impurity. The Si precursor (SiO(g)) reacts with the free surface of carbon fibers to form SiC in the VS reaction. When the surface is covered by the SiC, growth of a further layer into the carbon fibers is permitted by a diffusion phenomenon. The SiC microtube consists of the smooth outer surface and the villus-like inner surface, showing the residual carbon inside the SiC microtube. However, an SiC with radial grain microstructure grows inside the SiC microtubes, as shown in Fig. 3, when the precursor powders with the Al impurity are used in the second step. The SiC grains are synthesized by scarifying the residual carbon of Fig. 2, which grow with the radial morphology to the inward direction marked in Figs 3b and c. Longitudinal cracks have developed at the external surface layer in the SiC micromembrane tubes, which are indicated with arrows in Fig. 3a. They can

be caused by the difference in volume expansion between the synthesized SiC and the consumed carbon fiber.

An Al doping can be expected with the radial SiC grains grown from the SiC/C composite (SiC precursor), which may change the component diffusivities and even the SiC growth mechanism. The diffusivity of SiO(g) with the Al impurity into the SiC precursor would be assumed to be five times greater than that into the pure carbon fiber, on comparing the thicknesses synthesized at each step. In the present study, for the synthesis of the SiC micromembrane tubes, the faster diffusion of SiO(g) with the Al impurity into the SiC precursor increases the growth rate of the SiC grain, showing the radial grain microstructure. More importantly, it improves the morphological quality of the SiC micromembrane tubes through a change in the SiC growth site from the gas-SiC interface to the SiC-C interface. For the growth of pure SiC by the inward diffusion of SiO(g), vacancies must be either annihilated at the SiC-C interface or else cavities are formed [16]. Since the SiC shows significant grain growth, one must expect void creation and detachment of the product SiC from the shrinking carbon core. The very granular internal surface of the SiC grown through the VS reaction is indicative of the SiC layer grown by the inward diffusion at a relatively low reaction temperature (for SiC growth). The inward diffusion of SiO(g) with the Al impurity into the SiC precursor ensures an excellent attachment of the SiC product to the reacted core, although the internal surface of the SiC product is subjected to significant hoop stress, which might be relieved by plastic flow (creep) of the SiC.

In summary, carbon fibers can be uniformly converted to SiC microtubes with improved morphology by the VS reaction process. The uniform SiC layers are achieved for every carbon fiber, from the

TABLE I Characteristics of the carbon fiber used as starting material<sup>a</sup>

Diameter (average)	7 μm
Length	1.0 mm
Specific surface area	0.7–2.0 m <sup>2</sup> g <sup>-1</sup>
Carbon	99.94%
Si	0.04%
Fe	0.01%

<sup>a</sup>Obtained by Brunauer-Emmet-Teller (BET), X-ray fluorescence (XRF), and porosity measurements, statistical observation by S.E.M.

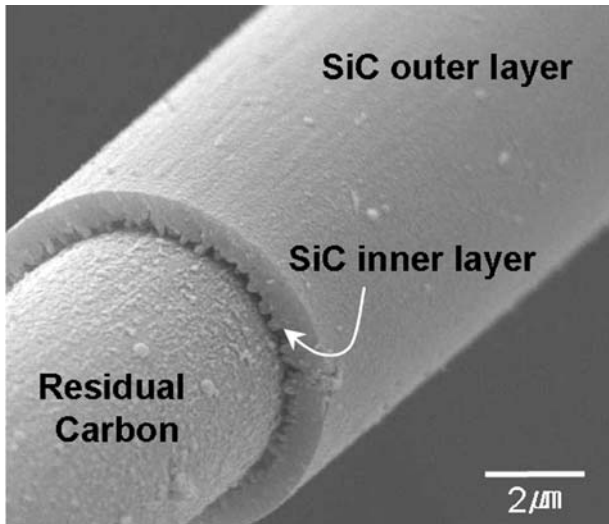


Figure 2 Micrographs of SiC microtube synthesized at 1450 °C for 9 h in a H<sub>2</sub>/Ar (20/80) gas flow of 200 sccm (ml/min) with pure precursor powders without Al impurity.

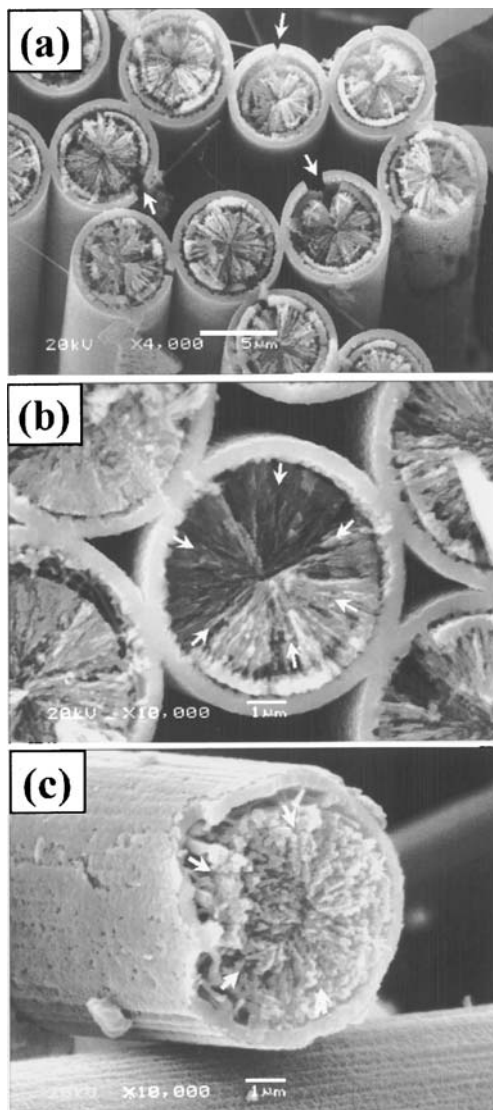


Figure 3 Micrographs of SiC micromembrane synthesized at 1450 °C for 9 h using SiC microtube in a H<sub>2</sub>/Ar (20/80) gas flow of 200 sccm (ml/min) with precursor powders containing Al impurity: (a) and (b) longitudinal surface, and (c) fracture surface of SiC.

surface to the center. The SiC micromembrane tubes can be successfully prepared using the precursor powders containing the Al impurity. The faster diffusion of SiO(g) with the Al impurity into the SiC precursor compared with that in the pure carbon fiber accelerates the growth of the SiC grain, showing the radial grain microstructure. The two-step process for the synthesis of SiC from the carbon fiber provides a core-shell structure with improved morphology.

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### References

1. M. BENAÏSSA, J. WERCKMANN, G. EHRET, E. PESCHIERA, J. GUILLE and M. J. LEDOUX, *J. Mater. Sci.* **29** (1994) 4700.
2. N. KELLER, C. PHAM-HUU, C. CROUZET, M. J. LEDOUX, S. SAVIN-PONCET, J. B. NOUGAYREDE and J. BOUSQUET, *Catal. Today* **53** (1999) 535.
3. R. WESTERHEIDE and J. ADLER, in "Advances in Hot Gas Filtration Technique," Ceramic Materials and Components for Engines, edited by J. G. Heinrich and F. Aldinger (Wiley-VCH Verlag GmbH, Weinheim, Germany, 2001) p. 73.
4. A. ADDAMINO and J. A. SPRAGUE, *Appl. Phys. Lett.* **44** (1984) 525.
5. R. MARCHAND, Y. LAURENT, J. GUYADER, P. L'HARIDON and P. VERDIER, *J. Eur. Ceram. Soc.* **8** (1991) 197.
6. P. W. LEDNOR, *Catal. Today* **15**(2) (1992) 243.
7. M. A. VANNICE, Y. L. CHAO and R. M. FRIEDMAN, *Appl. Catal.* **20**(1/2) (1986) 91.
8. M. BOUTONNET KIZLING, P. STENIUS, S. ANDERSSON and A. FRESTAD, *Appl. Catal. B: Environ.* **1** (1) (1992) 149.
9. R. MOENE, H. T. BOON, J. SCHOOMAN, M. MAKKEE and J. A. MOULIJN, *Carbon* **34**(5) (1996) 567.
10. N. KELLER, C. PHAM-HUU, S. ROY, M. J. LEDOUX, C. ESTOURNÉS and J. L. GUILLE, *J. Mater. Sci.* **34** (1999) 3189.
11. N. KELLER, C. PHAM-HUU, M. J. LEDOUX, C. ESTOURNÉS and G. EHRT, *Appl. Catal. A: Gen.* **187**(2) (1999) 255.
12. K. H. STERN, "Metallurgical and Ceramic Protective Coatings," 1st edn (Chapman & Hall, London, 1996) pp. 1, 194, 74, 152, 169.
13. M. J. LEDOUX, S. HANTZER, C. PHAM-HUU, J. L. GUILLE and M. P. DESANEAUX, *J. Catal.* **114** (1988) 176.
14. W. KIM, S. S. LEE, D. H. PARK, Y. G. JUNG, J. H. LEE and C. Y. JO, *Key Eng. Mater.* **287** (2005) 220.
15. J. W. KIM, S. S. LEE, Y. G. JUNG, B. G. CHOI, C. Y. JO and U. PAIK, *J. Mater. Res.* **20** (2005) 409.
16. J. W. KIM, J. H. YOON, J. H. LEE and Y. G. JUNG, *J. Mater. Res.* (in press).
17. E. N. MOKHOV, Y. A. VODAKOV and G. A. LOMAKINA, "Problems of Physics and Technology of Wide Band Gap Semiconductors" (LIYaF, Leningrad, 1980) p. 136.
18. A. S. BARASH, Y. A. VODAKOV, E. N. KOL'TSOVA, A. A. MAL'TSEV, E. N. MOKHOV and A. D. ROENKOV, *Sov. Phys. Technol. Lett.* **14** (1988) 2222.
19. R. B. CAMPBELL and H. S. BERMAN, *Mater. Res. Bull.* **4** (1969) S211.

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