Low Temperature Synthesis of β -SiC Powder by the Na Flux Method using Fullerene and Silicon

Fumihiko KAWAMURA, Hisanori YAMANE, Takahiro YAMADA, Shu YIN and Tsugio SATO

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai-shi 980-8577

フラーレンとシリコンを用いた Na フラックス法による β -SiC 粉末の低温合成

川村文洋・山根久典・山田高広・殷 シュウ・佐藤次雄

東北大学多元物質科学研究所, 980-8577 仙台市青葉区片平 2-1-1

Silicon carbide (SiC) powder was prepared by heating a mixture of fullerene and silicon powders at 900–1000 K for 24 h with a Na flux. X-ray and electron diffraction revealed that the obtained powder was β -SiC. The agglomerates of SiC particles with a size of a few dozen nm were observed by transmission electron microscopy. The specific surface area and mean particle size of the SiC powder prepared at 1000 K were 12 m²/g and 88 nm, respectively. [Received August 28, 2006; Accepted November 16, 2006]

Key-words : SiC, Low temperature synthesis, Nano-particle, Fullerene, Na flux

1. Introduction

Since SiC has excellent properties of high strength, hardness, corrosion resistance and stability even at high temperatures and in acid solutions, SiC powder and ceramics have been used not only for high temperature structural materials but also for other applications such as catalyst carrier and support.¹⁾ SiC powder has been widely produced by using the Acheson process,²⁾ in which the carbothermic reaction of SiO₂ with carbon powder is carried out at temperatures around 2500–2700 K for several hours. Due to the high reaction temperatures and long reaction times of the process, the prepared powder has a large particle size and mostly consists of α -SiC. It is usually difficult to sinter the SiC powder without sintering aids or pressure due to its covalent bonding.^{3),4)} However, using a fine and high purity powder, well-sintered SiC bodies can be produced with fewer additives under a lower pressure.⁵⁾

Fine SiC powder is synthesized by pyrolysis of organosilicon compounds, such as polycarbosilane and dimethyldichlorosilane, at 1300–1800 K.^{6),7)} Reaction of silane or tetrachlorosilane with hydrocarbons was carried out at around 1400–1700 K for the chemical vapor deposition of SiC powder.^{8),9)} As Hu et al. introduced in their report,¹⁰⁾ SiC powders have also been synthesized by various other techniques such as self-propagating high-temperature synthesis (SHS), sol-gel method, plasma-, and microwave-radiation methods.

Recently, epitaxial β -SiC films were grown on Si (100) substrates at 950–1250 K under ultra-high vacuum conditions by using fullerene (C₆₀ and C₇₀) as an active carbon source.^{11),12)} The nano-size β -SiC powder and nanowires were synthesized at 873–973 K by the reduction of tetrachlorosilane or carbon tetrachloride with Na in a titanium alloy autoclave.^{10),13)} The reactions are represented by the following formulas:

It was expected that Na acts not only for the reducer but also a flux.

In the present study, we prepared β -SiC powder at 900–1000 K by the Na flux method using fullerene and silicon powders instead of the chloride of SiCl₄ or CCl₄ as starting materials, and characterized the obtained powder.

2. Experimental

Si powder (Mitsui Chemicals, 99.999% purity, 200-mesh,) and fullerene powder (Frontier Carbon, C₆₀: 60%, C₇₀: 25%, higher fullerenes: 15%) or graphite powder (Alfa Chemical, 99.9995% purity, 200-mesh) were weighed at a Si:C molar ratio of 1:1, and mixed for about 20 min with an agate pestle and mortar in an Ar-gas filled glove box. About 50 mg of the mixed powder was pressed into a pellet, and placed in a boron nitride crucible (Showa Denko, 99.5%, inside diameter 6 mm, depth 18 mm) with about 150 mg of Na (Nippon Soda, 99.95% purity). The crucible was set in a stainless steel tube (SUS316, external diameter 10 mm, length 100 mm). The tube was sealed with stainless-steel caps in an Ar atmosphere. The sample was heated at prescribed temperatures and maintained the temperatures for 24 h with an electric furnace.

After the heating, the sample was cooled in the furnace by shutting off the electric power to the furnace. The SUS tube was cut in the glove box and the sample in the crucible was taken out from the tube. The Na metal including SiC powder reacted with the 2-propanol and ethanol. A dark gray fine powder suspended in alcohol-Na alkoxides solution was separated with a centrifuge. Distilled water was added to the powder and then the re-suspended powder was centrifuged again to remove any Na alkoxides or NaOH in the sample. This process was repeated 2 to 3 times, until the hydrogen-ion concentration (pH) changed to 7. During these processes, the violent reactivity of Na to water or ethanol, and the strong base of the solution containing Na should be cautioned. Finally, the washed sample was dried at 350 K in air.

The crystalline phases of the as-prepared samples were identified by X-ray diffraction (XRD, RINT2200, Cu K α) using a holder with a polyimide film window in order to keep the samples in an inert atmosphere during the measurement. The XRD pattern of the washed sample was measured in air with a standard powder sample holder.

The observation of the morphology and selected-area electron diffraction (SAD) for the washed powder sample were carried out with a transmission electron microscope (TEM, JEOL, JEM-2000EX). The distribution of the powder size was measured with a laser diffraction particle size analyzer

Table 1. Reaction Conditions and Products

Sample	Temperature (K)	Source materials	Products as prepared	after washing
A	1000	Fullerene, Si	Si >> amorphous	
B	1000	Fullerene, Si, Na	Na, SiC	SiC
C	900	Fullerene, Si, Na	Na	SiC, SiO ₂ , amorphous
D	850	Fullerene, Si, Na	Na, NaSi	SiO ₂ , amorphous
E	700	Fullerene, Si, Na	Na, NaSi, Si	Si, SiO ₂ , amorphous
F	1000	Graphite, Si, Na	Na, NaSi	Graphite, SiO ₂

(Shimadzu, SALD-7000). The powder sample was also characterized with a specific surface area analyzer (Quantachrome, NOVA1000).

3. Results and discussion

Table 1 summarizes the reaction conditions and the results of phase identification by XRD for the as-prepared and washed samples. When the mixture of fullerene and Si powders was heated at 1000 K without Na, SiC was not formed (sample A). The crystalline phase was Si only. A very weak broad diffraction peak was observed around $2\theta = 8\text{--}10^\circ$ and $15\text{--}20^\circ$, which suggests the amorphous phase derived from fullerene. The XRD pattern of the as-prepared sample of B indicated that the crystalline phases were Na and SiC.

The XRD pattern of the washed sample B is shown in **Fig. 1**. All broad diffraction peaks were indexed with the lattice parameter of β -SiC (cubic, $a = 0.436\text{ nm}$). The relative intensities of the diffraction peaks were also consistent with those reported for β -SiC.¹⁴⁾ The crystallite size calculated by Scherrer's equation¹⁵⁾ with the full width at half maximum of the diffraction peaks was about 9 nm.

The TEM image of sample B is shown in **Fig. 2**. It was observed that small particles with a size of 20–40 nm aggregated and formed secondary particles or agglomerates of a few hundred nm. The SAD pattern from the agglomerates consisted of rings with some spots, which corresponded to the diffractions of β -SiC (111), (220) and (311) planes.

The distribution of particle size was measured for the washed sample B dispersed in water by ultrasonic agitation. The mean particle size of the sample was 88 nm, and 10% diameter (D), 50%D, and 90%D are 67 nm, 87 nm, and 116 nm, respectively. The specific surface area of the sample analyzed by nitrogen gas adsorption was $12\text{ m}^2/\text{g}$.

In the XRD pattern of the as-prepared sample of C, diffraction peaks were from Na. After the removal of Na, a small amount of gray powder was obtained. The broad peaks of an amorphous phase and weak peaks of SiC were observed in the diffraction pattern. The formation of SiC at 900 K was confirmed from this result but the yield of SiC was small.

At and below 850 K, NaSi formed in the Na melt. This phase is unstable and probably decomposed into SiO₂ cristobalite during the process of Na removal with alcohol and water. In the XRD patterns of the washed samples of C, D and E, a diffraction peak was observed at $2\theta = 21.5^\circ$, which corresponds to the largest diffraction peak of cristobalite SiO₂. The weak broad diffraction peak was also observed around $2\theta = 10^\circ$ in these XRD patterns. The fullerene probably changed into an amorphous phase at 700–900 K. Unreacted Si was contained in the sample prepared at 700 K.

When graphite was used as a carbon source instead of fullerene, we could not obtain SiC powder at 1000 K by using a Na flux (sample F). The as-prepared sample contained NaSi, and

Fig. 1. XRD pattern of sample B after washing.

Fig. 2. TEM image and SAD pattern of sample B after washing.

after removal of Na, a main peak of graphite was seen at $2\theta = 26.4^\circ$ in addition to the peak of cristobalite in the XRD pattern.

It was reported that an SiC epitaxial layer was formed on the Si substrate by the reaction between Si substrate and C₆₀ or C₇₀ at 900–1000 K in an ultra-high vacuum. However, the formation of SiC powder by reaction of Si and fullerene powders was not detected at 1000 K without Na (sample A). The results of the samples prepared at 700–850 K suggested that Na and Si reacted and formed NaSi at a lower temperature before the formation of SiC. However, graphite did not react with NaSi at 1000 K in the Na flux. Synthesis of SiC by the Na flux method using other reactive carbon sources such as glassy carbon or amorphous carbon is now under investigation.

4. Conclusion

β -SiC powder was prepared by heating the mixture of fulle-

rene and Si powders for 24 h at 900–1000 K in a Na flux. The agglomerates of SiC small particles with a size of a few dozen nm were observed by TEM. It was demonstrated that fullerene was an active carbon source for the synthesis of SiC powder in a Na melt at 1000 K.

Acknowledgements This study was supported in part by Science Research Expenses Subsidy from the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Exploratory Research, 18655083, 2006. The authors thank Dr. Mitsuo Suzuki of the Frontier Carbon Co., Ltd. for his helpful discussion.

References

- 1) Sōmiya, S. and Inomata, Y., "Silicon Carbide Ceramics-2," Elsevier Science (1991).
- 2) Enomoto, R., *J. Ceram. Assoc. Jpn.*, Vol. 17, No. 10, pp. 828–833 (1982) [in Japanese].
- 3) Alliegro, R. A., Coffin, L. B. and Tinklepaugh, J. R., *J. Am. Ceram. Soc.*, Vol. 39, pp. 386–389 (1956).
- 4) She, J. H. and Ueno, K., *Mater. Res. Bull.*, Vol. 34, pp. 1629–1636 (1999).
- 5) Prochazka, S., "Proceedings of the Second Army Materials Technology Conference," Ed. by Burke, J. J., Gorum, A. E. and Katz, R. N., Brook Hill Publishing Co., Chestnut Hill, OH (1975) pp. 239–252.
- 6) Narisawa, M., Shimoda, M., Okamura, K., Sugimoto, M. and Seguti, T., *Bull. Chem. Soc. Jpn.*, Vol. 68, pp. 1098–1104 (1995).
- 7) Krishnan, V., Bindu, R., Chandrasekhar, V. and Murthy, V. S. R., *J. Am. Ceram. Soc.*, Vol. 85, pp. 504–506 (2002).
- 8) Chen, L., Goto, T. and Hirai, T., *J. Mater. Sci.*, Vol. 24, pp. 3824–3830 (1989).
- 9) Kavecky, S., Janekova, B., Madejova, J. and Sajgalik, P., *J. Eur. Ceram. Soc.*, Vol. 20, pp. 1939–1946 (2000).
- 10) Hu, J.-Q., Lu, Q.-Y., Tang, K.-B., Qian, Y.-T., Zhou, G.-E., Liu, X.-M. and Wu, J.-X., *Chem. Mater.*, Vol. 11, pp. 2369–2371 (1999).
- 11) Hamza, A. V., Balooch, M. and Moalem, M., *Surf. Sci.*, Vol. 317, pp. L1129–L1135 (1994).
- 12) Wang, X.-D., Xue, Q., Hashizume, T., Shinohara, H., Saito, Y., Nishina, Y. and Sakurai, T., *Appl. Surf. Sci.*, Vol. 76/77, pp. 334–339 (1994).
- 13) Hu, J. Q., Lu, Q. Y., Tang, K. B., Deng, B., Jiang, R. R., Qian, Y. T., Yu, W. C., Zhou, G. E., Liu, X. M. and Wu, J. X., *J. Phys. Chem. B*, Vol. 104, pp. 5251–5254 (2000).
- 14) International Centre for Diffraction Data, File Card No. 73–1708.
- 15) Cullity, B. D., "Elements of X-ray Diffraction," Addison-Wesley Pub., Reading, Massachusetts (1978).