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Silicon Carbide Whiskers Synthesized from SiO_2-CH_4-Na_3AlF_6 system

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Silicon carbide (SiC) whiskers were synthesized from SiO_2-CH_4-Na_3AlF_6 system. The whiskers obtained were cylindrical in shape, and they had uniform diameter (0.1–5.0 μm) and length (50 μm-10 mm). They were found to have grown by a Vapor-Liquid-Solid (VLS) mechanism since a catalyst droplet was observed on the tip of most of the whiskers. The composition of the Al-Si droplets was determined by means of EDAX. As no researchers have previously reported on Al-Si droplets, we conducted a detailed analysis of them in this study.

1. Introduction

SiC has a high resistance to oxidation, creep and thermal shock at high temperatures, as well as high rigidity and high strength. Therefore, SiC is expected to be applied as a structural material at high temperatures. In addition, SiC is planned to be used as a material for the first wall of a nuclear fusion reactor, since plasma contamination associated with SiC is small and SiC is not damaged easily by radioactive irradiation due to its low atomic number [1]. Very pure, dense and thick SiC is required to analyze its various characteristics. SiC compacts can be obtained through several methods including reaction sintering, recrystallization, hot press and CVD method. Among these methods, CVD is the most appropriate for the synthesis of SiC with high purity and density.

Many researchers have synthesized SiC using CVD; most SiC was synthesized from SiO(g)-CO, SiO_2-C or SiO_2-C-H_2 system by the method of reducing silica [2]. CVD has already been used in practical applications.

The flux method is effective for growing single crystals, whereby seed crystals are immersed in a fused liquid body to promote crystal growth. There have been very few reports on the growth of whiskers using Na_3AlF_6 (cryolite) as a flux; only synthesis from SiO_2-C-Fluoride system by the solid phase method has been reported [3].

In this study, SiC whiskers were synthesized using SiO_2 as the Si source and Na_3AlF_6 as the flux. A large amount of β-SiC whiskers were synthesized when the molar ratio of SiO_2 to Na_3AlF_6 (SiO_2/Na_3AlF_6) ranged from 2 to 8. The effects of the flux on the shape of the whiskers and on the composition of the droplets were discussed.

2. Materials and methods

Fig. 1 shows a schematic drawing of the experimental apparatus, the Lindbergh electrical furnace. SiC whiskers were synthesized as follows: A gas mixture of methane (10 vol %) and argon (90 vol %) was used as the reaction gas. SiO_2 powder and Na_3AlF_6 (Wako Chemical Ltd.) were mixed so the SiO_2/Na_3AlF_6 ratio ranged from 2 to 8. The resulting powder, which was used as the starting material, was crushed to approximately 10 μm particles using a planetary ball mill. The starting material was set on a graphite boat which was, in turn, placed into a graphite tube. The graphite tube was placed in the center of an alumina tube, into which the reaction gas was introduced. After the gas in the tube was replaced by the reaction gas, the reaction gas was supplied at a rate of 180 ml/min, as determined by a preliminary experiment. The temperature within the reaction apparatus was raised at a rate of 5 K/min to 1673 K, which was maintained for 10 h. The temperature was then decreased to 773 K at a rate of 5 K/min, and the samples were allowed to cool freely. A mixture gas was supplied continuously until the temperature fell below 523 K, to prevent oxidation of the reaction products.

The reaction products were identified by X-ray diffraction (XRD) patterns, and the shapes were observed by scanning electron microscopy (SEM). A elemental analysis by EDAX was used for the composition analysis of the products.

3. Results

3.1. Deposition state of whiskers

Fig. 2 shows the deposition states of the whiskers after heat treatment. Table I summarizes the deposition state and the phase of the products identified by XRD. Whiskers were synthesized when the SiO_2/Na_3AlF_6 ratio ranged from 2 to 8. Regardless of the molar ratio, obtained whiskers were β-SiC whiskers and were deposited at three places; on the graphite boat (Fig. 2-No. 1), on the outer surface of the graphite tube (Fig. 2-No. 2) and on the inner wall of the alumina tube (Fig. 2-No. 3, hereafter abbreviated as

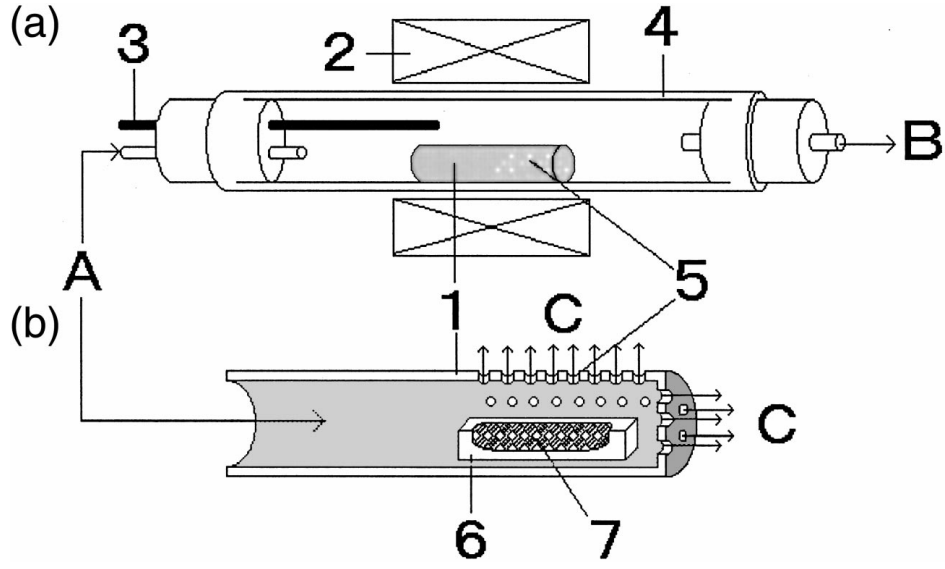


Figure 1 Schematic diagram of the experimental apparatus for SiC whiskers synthesis. (a) whole view, (b) sample holder. A: gas inlet, B: gas outlet, C: gas exhaust. 1: graphite tube (16 mm I.D.), 2: electric furnace, 3: thermocouple (PR), 4: alumina tube (42 mm I.D.), 5: holed part, 6: graphite boats, 7: sample.

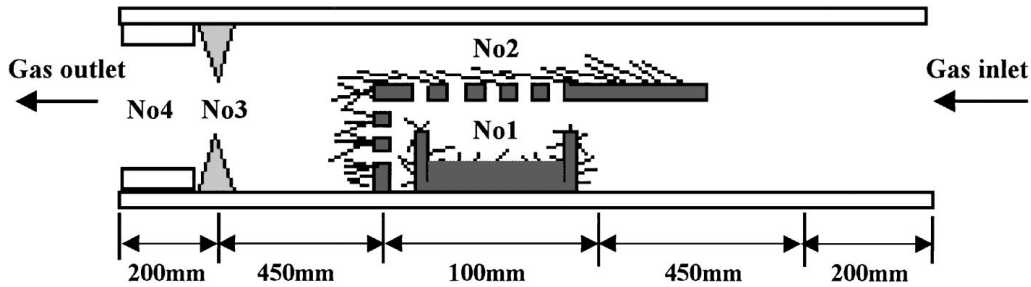


Figure 2 Deposition state of products. No1 and No2 was formed on graphite boat and tube, respectively. No3 and No4 was formed on alumina tube.

outside-whisker). At the bottom of the graphite boat, a glossy melt remained with the product phase which was identified as $Na_2Si_2O_5$. A white coating was formed on the inner wall of the alumina tube near the gas outlet (Fig. 2-No. 4), which was identified as Na_3AlF_6 by XRD.

Whiskers synthesized on the outer surface of the graphite tube and on the inner wall of the alumina tube were wool-like, while whiskers synthesized on the graphite boat were needle-like. The whiskers synthesized on the graphite boat were greenish white and those on the outer surface of the graphite tube and on the inner wall of the alumina tube were greenish white or gray.

Fig. 3 shows X-ray diffraction patterns of the products obtained when the SiO_2/Na_3AlF_6 ratio was 5. At this molar ratio, the greatest amount of product was

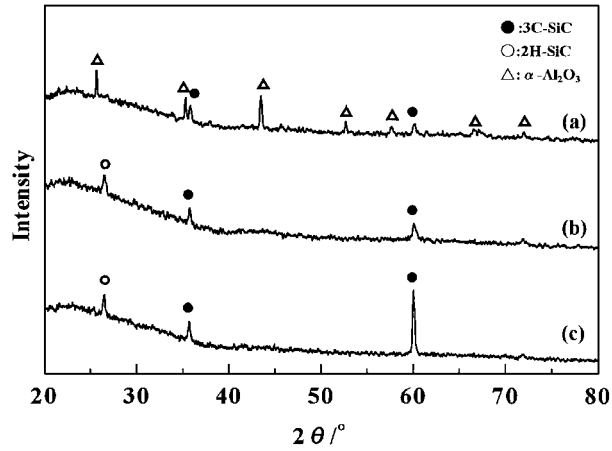


Figure 3 X-ray diffraction patterns of products obtained in the SiO_2/Na_3AlF_6 ratio = 5. (a) on the alumina tube, (b) on the graphite tube, (c) on the graphite boat.

TABLE I Deposition states and phases of products

Places	Deposition states	Phases of products
Graphite boat	W + R	W: 3C-SiC 2H-SiC R: $Na_2Si_2O_5$
Graphite tube	W	3C-SiC 2H-SiC
Alumina tube	W + C	W: 3C-SiC C: Na_3AlF_6

W: whiskers, R: residue, C: coating.

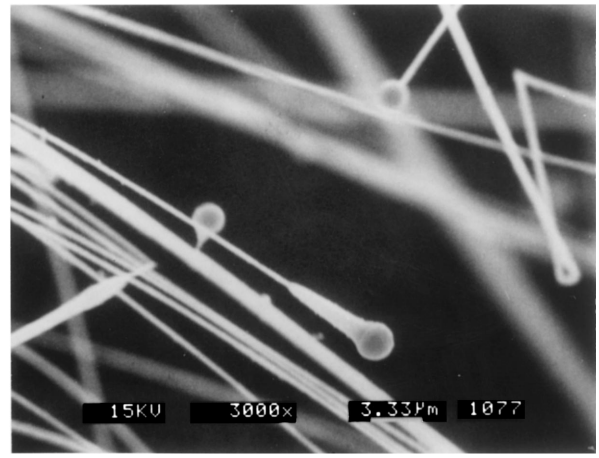
synthesized. In the diffraction pattern of the product obtained on the inner wall of the alumina tube (a), a pattern corresponding to α-Al_2O_3 was detected. Since whiskers were deposited on the inner wall of the alumina tube, it was considered to be mixed whiskers with α-Al_2O_3 when the products were picked out outside-whiskers. As seen in Fig. 3, 3C-phase was observed in the diffraction pattern of the products collected from the three deposited places. The larger the distance between the

synthesis place and the place where the temperature was set at 1673 K, the smaller the relative peak intensity. This is because only the central part of the alumina tube (150 mm) was set at 1673 K, therefore, the degree of supersaturation may vary depending on the deposition place.

3.2. Shape and composition of SiC whiskers

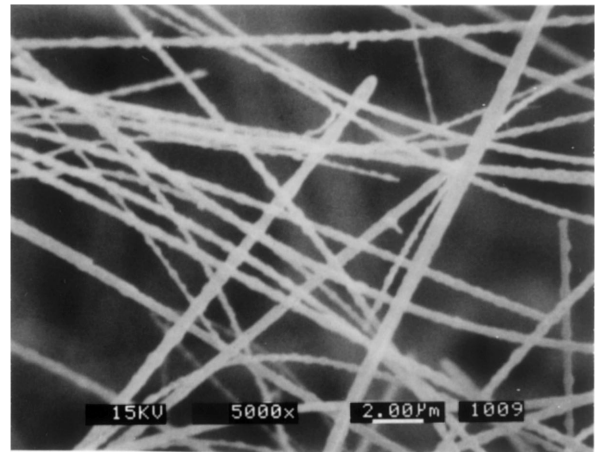
Fig. 4 shows SEM photographs of SiC whiskers. Since whiskers synthesized on the outer surface of the graphite tube, on the graphite boat and on the inner wall of the alumina tube have circular cross sections and droplets on the tips, we assumed the whiskers were grown by a VLS mechanism. With respect to whiskers synthesized on the outer surface of the graphite tube and on the graphite boat, the diameters of the whiskers were smaller than those of the droplets. The diameter of the whiskers synthesized on the inner wall of the alumina tube was the same as those of the droplets, and some of the droplets linked together in a bead-like manner. The diameter of the whiskers did not differ much, with a small range from 0.1 to 5.0 μm. Whiskers, other than SiC whiskers, which grow by a VLS mechanism have Fe-Si droplets on their tips; the well-known composition of these droplets is $Fe/Si = 1 - 0.5$. However, the droplets obtained in this study were composed of Al-Si and this composition has not yet been reported. Therefore, we conducted a detailed analysis of the droplets by EDAX and summarized the results in Table II.

Concerning whiskers synthesized on the outer surface of the graphite tube, as the SiO_2/Na_3AlF_6 ratio increased, the ratio of Al to Si (Al/Si) decreased; specifically, the amount of silicon increased. A similar tendency was observed for whiskers synthesized on the graphite boat and on the inner wall of the alumina tube. However, the Al/Si ratio tends to increase as the SiO_2/Na_3AlF_6 ratio increased when the SiO_2/Na_3AlF_6 ratio is 5 or larger. The ratio of Al to Si for the droplets obtained from the graphite boat, on the outer surface of the graphite tube and on the inner wall of alumina tube ranged from 0.014 to 0.100, from 0.025 to 5.00 and from 0.018 to 0.100, respectively. According to the binary system phase diagram of Al-Si [4], Al-Si forms a liquid phase if the Al/Si value falls in the range stated above. With respect to the color of the whiskers, as the SiO_2/Na_3AlF_6 ratio increased, the amount of silicon increased, therefore, the whiskers were a grayish color. Some of the whiskers were greenish white. According to G. Urretavizcaya et al. [5], SiC whiskers were green when SiO_2 is thermally treated on the graphite substrate in a mixed gas flow which has a composition of $H_2 : CH_4 : N_2 : CO = 80 : 1 : 9 : 10$ (vol %), since N atoms penetrate into the C sublattice. In this study, however, N_2 gas was not used; therefore, the reason for this may be that F atoms in SiF_4(g) (gaseous species) were not completely replaced by C atoms, and F atoms



(a)

(b)



(c)

Figure 4 SEM photographs of SiC whiskers. (a) on the graphite tube, (b) on the graphite boat, and (c) on the alumina tube.

TABLE II The composition of droplet and color of whiskers

SiO_2/Na_3AlF_6		2	3	4	5	6	7	8
Al/Si	Graphite boat	0.100 Wg	0.038 Wg	0.038 Wg	0.014 Wg	0.018 Wg + G	0.019 Wg + G	0.030 Wg
	Graphite tube	5.00 Wg + G	0.125 Wg + G	0.047 Wg + G	0.033 G	0.032 G	0.032 G	0.025 G
	Alumina tube	0.100 W	0.040 Wg	0.039 Wg	0.020 Wg	0.018 Wg + G	0.020 Wg + G	0.031 Wg

Al/Si: Ratio of atomic percent, W: white, Wg: white-green, G: gray.

remained in the C sublattice. This result agrees with the fact that the radius of N and F atoms is similar, as reported by G. Urretavizcaya et al. [5].

4. Discussion

There have been many reports on SiC synthesis using graphite as the synthesis substrate and SiO_2 as the starting material. In this study, the same starting material and substrate as those reported in the references were used. Based on the substrate-dependence of the whiskers, the following reactions could have occurred.

First, methane is decomposed when the temperature is 1273 K or higher.

$$CH_4(g) \rightarrow C(g) + 2H_2(g) \quad (1)$$

Next, $SiO_2(s)$ generates SiO(g) in the presence of graphite.

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g) \quad (2)$$

The obtained CO(g) is then reduced by $H_2(g)$.

$$CO(g) + H_2(g) \rightarrow C(s) + H_2O(g) \quad (3)$$

The gas phase chemicals produced by the decomposition of methane react with SiO(g).

$$SiO(g) + C(g) + 2H_2(g) \rightarrow SiC(s) + 2H_2O(g) \quad (4)$$

Based on the equations from (1) to (4), the following equation is obtained.

$$SiO_2(s) + CH_4(g) \rightarrow SiC(s) + 2H_2O(g) \quad (5)$$

However, if the Gibbs free energy ($\Delta G = 160.19$ kJ/mol) of Equation 5 is considered, this reaction is unlikely to occur. This agrees with the fact that no whiskers were synthesized and that a melt remained on the graphite boat when the starting material without cryolite was thermally treated.

From the results stated above, cryolite is considered, not only to act as a catalyst, but also to participate in the reaction. Saito et al. [6] reported that $Na_2SiO_3(l)$ was produced through a reaction between NaF(l) and $SiO_2(s)$, and, moreover, when the content of $SiO_2(s)$ in the starting material increased, $Na_2Si_2O_5(l)$ was produced. In this study, since the melt that remained on the graphite boat was $Na_2Si_2O_5$ and the SiO_2/Na_3AlF_6 ratio used in this study was greater than the molar ratio in their experiment, the following reaction was considered to be possible.

$$4NaF(l) + 5SiO_2(s) \rightarrow 2Na_2Si_2O_5(s) + SiF_4(g) \quad (6)$$
$$\Delta G = -14.785\,\text{kJ/mol}$$

Continuously, the gaseous species generated in this process, that is, $SiF_4(g)$, reacted with C atom generated by the decomposition of $CH_4(g)$. Also, considering that whiskers grew depending on the substrate, this reaction was shown as follows:

$$2SiF_4(g) + CH_4(g) + C(s) \rightarrow 2SiC(s) + 4F_2(g) + 2H_2(g) \quad (7)$$
$$\Delta G = -38.375\,\text{kJ/mol}$$

It is considered that this reaction is accelerated when the degree of supersaturation is high, and then SiC whiskers grew very well. Moreover, when the free energies of Equation 7 are considered, this reaction is possible according to the equilibrium theory.

5. Conclusions

SiC whiskers were synthesized using SiO_2 as the starting material and Na_3AlF_6 as the flux. The following conclusions have been reached:

1. Whiskers were synthesized when the SiO_2/Na_3AlF_6 ratio ranged from 2 to 8. Regardless of the molar ratio, the obtained whiskers were mainly β-SiC and the whiskers were deposited at three places; on the graphite boat, on the outer surface of the graphite tube, and on the inner wall of the alumina tube.
2. SiC whiskers were formed through the reaction in which $SiF_4(g)$ reacted with C atom generated by the decomposition of $CH_4(g)$. It was concluded that this process is expressed by the following equation.

$$2SiF_4(g) + CH_4(g) + C(s) \rightarrow 2SiC(s) + 4F_2(g) + 2H_2(g)$$

3. Since whiskers synthesized on the outer surface of the graphite tube, on the graphite boat, and on the inner wall of the alumina tube have circular cross sections and droplets on the tips, they are considered to have grown by a VLS mechanism.
4. Al/Si for the droplets obtained from the graphite boat, on the outer surface of the graphite tube and on the inner wall of the alumina tube ranged from 0.014 to 0.100, from 0.025 to 5.00 and from 0.018 to 0.100, respectively.

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