Preparation of Thick α - Si_3N_4 Whiskers from Silica Black Ore

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Nishi-8, Kita-13, Kita-ku, Sapporo-shi 060-8628シリカブラック鉱石からの太い α - Si_3N_4 ウィスカーの調製

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α - Si_3N_4 whiskers were grown by heating a mixture of "silica black" ore with additional carbon in a tightly capped crucible (30 cm³ volume) in flowing nitrogen at 1400°C for 40h. The nitrogen flow rate greatly affected the yield and shape of the whiskers. A large mass of whiskers was produced downstream on the outside surface of the crucible when the nitrogen flow rate was 9 cm·min⁻¹. The resulting whiskers had rod- and plate-like forms with an average size of 10 to 40 μm thick and several hundreds μm long. Thin whiskers and fibers were formed downstream on the outside bottom of the crucible and in lower temperature regions, respectively. A droplet containing mainly Fe and Si was formed on the tip of many whiskers, suggesting occurrence of a VLS (Vapor-Liquid-Solid) growth mechanism.

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1. Introduction

Silicon nitride whiskers ($\text{Si}_3\text{N}_4(\text{w})$) are used as a reinforcement material in high strength metal-matrix composites and damage tolerant ceramic-matrix composites, because of their superior properties (high strength, high tensile strength and good thermal shock resistance). $\text{Si}_3\text{N}_4(\text{w})$ can be produced by three methods, similar to those used to prepare SiC whiskers ($\text{SiC}(\text{w})$); carbothermal reduction of silica, decomposition of imide compounds and direct nitridation. Like SiC(w), $\text{Si}_3\text{N}_4(\text{w})$ is very expensive, which restricts their engineering applications in the above-mentioned composites. There have been several studies on the growth of $\text{Si}_3\text{N}_4(\text{w})$ from naturally occurring minerals,¹⁾ wheat husks²⁾ and amorphous Si-N-C powders,³⁾ with the purpose of producing the whiskers at low cost. The former two methods, involving the carbothermal reduction of silica, have the disadvantage of using expensive NH_3 gas and the difficulty of separation of the whiskers from the starting materials, and the latter method does not yield pure Si_3N_4 whiskers.

$\text{Si}_3\text{N}_4(\text{w})$ are usually produced in submicron sizes or ten microns at largest. Very thin whiskers or fibers of SiC or Si_3N_4 ($\leq 1 \mu\text{m}$ in diameter) cause environmental and health problems as do asbestos fibers. If whiskers ≥ 5 to 10 μm in diameter can be prepared, they would solve these problems in engineering applications.

So-called "silica black" ore is a sedimentary siliceous material occurring in black mudstone in the "Kami-no-Kuni" region of south Hokkaido in Japan. Our attention was drawn to it, because it contains the necessary components (silica and carbon) for the formation of SiC and Si_3N_4 whiskers, and also contains iron oxide, a catalyst which promotes the growth of these phases. A previous paper reported that β -SiC whiskers were grown inside a capped graphite crucible by heating powdered silica black ore in argon at 1400°C.⁴⁾ When the atmosphere was changed to high purity nitrogen, α - Si_3N_4 whiskers of 10 to 40 μm in size appeared on the outside surface of the tightly capped graphite crucible, which saved the trouble of separating the whiskers from the unreacted ore. This note describes the successful growth of α - Si_3N_4 whiskers on the outside surface of a tightly closed graphite crucible containing silica

black powder and heated in a pure nitrogen atmosphere. The phases formed inside the crucible are also described.

2. Experimental

The silica black ore was ground to pass through a 5 μm sieve. As previously reported,⁴⁾ it contains free silica (82 mass%) as the major component with minor mass percentages of alumina (6), carbon (5), iron oxide (0.5), sulfur (0.3). Natural graphite powder amounting to one-third of silica black in weight was added, to provide the additional carbon necessary for growing $\text{Si}_3\text{N}_4(\text{w})$. Their mixed powder was contained in a tightly covered graphite crucible of 30 cm³ volume and heated in a 60-mm diameter tube furnace in pure flowing nitrogen at 1400 and 1450°C. Figure 1 shows the experimental arrangement and the temperature gradient in the tube furnace. The position of the lid was located upstream in the flowing gas atmosphere, which varied from 1 to 25 cm·min⁻¹. The whiskers grown on the outside surface of the crucible were examined by optical and scanning electron microscopies (SEM). Chemical analysis of the droplets formed on the tips of the whiskers was carried out by energy dispersive X-ray analysis (EDX).

Fig. 1. Schematic diagram of growth experiment of Si_3N_4 whiskers and the temperature gradients in the tube furnace.

The crystalline phases in the whiskers and the residues from inside the crucible were identified by X-ray diffraction (XRD).

3. Results and discussion

When a mixture of the silica black ore and graphite powder was heated in flowing nitrogen ($7 \text{ cm} \cdot \text{min}^{-1}$) at 1400°C using a small crucible of 5 cm^3 volume, a large mass of whiskers, identified as α - Si_3N_4 , grew on the outside surface of the crucible. Increasing the crucible volume to 30 cm^3 made no difference to the yield of whiskers. Table 1 shows representative experimental results for the growth of $\text{Si}_3\text{N}_4(\text{w})$ at 1400°C and 1450°C , using a crucible of 30 cm^3 volume. At 1400°C , a gas flow rate of $1 \text{ cm} \cdot \text{min}^{-1}$ produced no whiskers on the outside surface of the crucible (Exp. 1), but increasing the flow rate to $4.5 \text{ cm} \cdot \text{min}^{-1}$ produced a small amount of whiskers (Exp. 2). A further flow rate increase to $9 \text{ cm} \cdot \text{min}^{-1}$ produced a large mass of whiskers on the outside surface of the crucible (Exp. 3). The whiskers were identified as α - Si_3N_4 by XRD, and their yield, calculated on the basis of Si recovery, reached about 15%.

Optical microscopy of the whiskers grown on the crucible (Exp. 3) is shown in Fig. 2, illustrating many whiskers grown all over the outside surfaces and bottom of the crucible. The whiskers up to several mm in size could be seen by eye and exhibited rod and plate forms, the former with droplets deposited on the tips (Fig. 3(a)). The whiskers were on average 10 to $40 \mu\text{m}$ in diameter and several hundreds μm long. X-ray analysis showed the crystal faces of the whiskers to be mainly the (110). The form of the whiskers in the vicinity of a droplet was cylindrical, the size varying from several to ten microns long (Fig. 3(b)). Thin submicron sized whiskers in diameter tended to grow downstream on the bottom surface of the crucible. Fibers which were submicron in diameter and up to a centimeter long were also formed downstream at lower temperature regions of 1200 to 1300°C (Fig. 4). These fibers were also found to be α - Si_3N_4 by XRD. Further downstream and in even lower temperature regions (1000 to 1100°C), amorphous sponge-like white masses were formed, which were converted to SiO_2 (cristobalite) when re-heated at 1360°C for 5h in argon. The residue remaining inside the crucible consists mainly of β - Si_3N_4 , with a small amount of sialon and a trace of β -SiC (Exp. 3); relatively short whiskers

Fig. 2. Photograph of whiskers grown on the surface of the crucible. Two separate photographs are combined in the figure.

Fig. 3. α - $\text{Si}_3\text{N}_4(\text{w})$ grown on the surface of the crucible. (a) rod- and plate-like whiskers, (b) a cylindrical whisker with a droplet.

were also present inside the crucible (Fig. 5). By contrast, sialon and unidentified XRD peaks were obtained in the samples when no whiskers were formed (Exp. 1).

Reaction of silica black samples without added graphite (Exp. 4) led to a decrease in the amount of whiskers, by comparing with Exp. 3. At 1450°C , no great change in the amount of whiskers was observed. Increasing the sample size had a negative effect on the yield (Exp. 6), as did an increase in the flow rate of nitrogen to 18 to $25 \text{ cm} \cdot \text{min}^{-1}$ (Exps. 8 and 9). When grooves in the form of an asterisk were provided on the bottom surface of the crucible, the ad-

Table 1. Experimental Results for Growth of α - Si_3N_4 Whiskers

EXP.	S.B. ^{*1} /g	G. ^{*2} /g	N ₂ /cm min ⁻¹	Temp. /°C	yield	residues
1	1.9	0.65	1	1400	non	sialon
2	1.9	0.65	4.5	1400	△	
3	1.9	0.65	9	1400	◎ (about 15 %)	β-Si ₃ N ₄ >sialon, trace of β-SiC
4	1.9	----	9	1400	△	
5	1.9	0.65	9	1450	◎	
6	5.7	1.95	9	1400	○	
7	1.9	0.65	9	1400	◎	
8	1.9	0.65	18	1400	○	
9	1.9	0.65	25	1400	△	

*1 Silica black ore, *2 Graphite

◎ (a lot of whiskers as shown in Fig. 2) > ○ > △ (a small amount of whiskers)

Fig. 4. α - Si_3N_4 fibers grown at the lower temperature locations. Fig. 5. α - Si_3N_4 (w) grown inside the crucible.

ditional sites for whiskers growth promoted a denser formation (Exp. 7).

As described above, cylindrical whiskers had droplets of 1 to 10 μm size on their tips. It was observed that the size of the whiskers was related to the size of the droplet. The droplets on their tips of the whiskers were analyzed by SEM-EDX, which showed them to contain mainly elemental Fe and Si. The composition of the droplet varied from $\text{Fe}_{1.7}\text{Si}$ to $\text{Fe}_{5.8}\text{Si}$; many droplets were in the composition near Fe_2Si . At present, it is not clear where Fe component came from.

On the basis of previous reports,⁵⁾ the growth of α - Si_3N_4 from silica black ore is considered as follows. A rapid initial reaction of SiO_2 with C in silica black ore, probably due to intimate mixing of C with SiO_2 or fine particles of C, produces $\text{SiO}(\text{g})$ and $\text{CO}(\text{g})$, followed by successive reaction of SiO_2 with the added graphite (Eq. (1)),

where C(s) represents the carbon both in the silica black ore and the graphite powder. The SiO and CO gases are emitted from the narrow space between the lid and the crucible. It is assumed that nitrogen gas flowing at 9 ml min^{-1} dilutes the vapor concentration of SiO , reducing the

high partial pressure of SiO to a suitable pressure for a good yield of whiskers. Si_3N_4 whiskers then grow by either Eq. (2) or (3),⁶⁾

$\text{C}^*(\text{s})$ in Eq. (2) represents the carbon of the crucible, which can provide nucleation sites for $\text{Si}_3\text{N}_4(\text{w})$. By the vapor-solid reaction (2), plate-like whiskers were grown.

The droplets occurring on the tip of cylindrical whisker suggest the VLS mechanism, in which SiO and N_2 dissolves in a droplet of Fe-Si, to produce Si_3N_4 whiskers. The component of Fe in silica black ore must be transported to the outside of the crucible to give a droplet of Fe-Si alloy but it is not clear in what form the Fe is transported. It is assumed that the powders and whiskers of Si_3N_4 remaining inside the crucible are formed through reactions (2) or (3) and that sialon powder is formed by dissolution of alumina in the resulting Si_3N_4 .

4. Conclusion

α - Si_3N_4 (w) can be grown by heating a mixture of silica black ore and additional carbon in a tightly capped crucible (30 cm^3 volume) in flowing nitrogen (4.5 to 25 $\text{cm} \cdot \text{min}^{-1}$) at 1400 and 1450°C for 40h. A large mass of rod- and plate-like whiskers of average size of 10 to 40 μm in diameter and several hundreds μm long was formed downstream on the outside surface of the crucible in flowing nitrogen (9 $\text{cm} \cdot \text{min}^{-1}$). Thin whiskers and fibers were also formed downstream on the outside bottom of the crucible and in lower temperature regions, respectively. Si_3N_4 powders and whiskers with a small amount of sialon and a trace of SiC were produced inside the crucible. When cylindrical whiskers were grown, a droplet of composition ranging from $\text{Fe}_{1.7}\text{Si}$ to $\text{Fe}_{5.8}\text{Si}$ was formed on a tip of each whisker, suggesting the VLS growth mechanism.

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