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The synthesis of silicon nitride whiskers from SiO_2-N_2-Na_3AlF_6 system

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Silicon nitride (Si_3N_4) whiskers were synthesized from SiO_2-N_2-Na_3AlF_6 system. Whiskers, which were synthesized when the molar ratio of SiO_2 to Na_3AlF_6 (SiO_2/Na_3AlF_6) ranged from 2 to 8, were prismatic with a stable diameter ranging from 0.1 to 0.5 μm. Therefore, the whiskers were considered to have grown by a VS mechanism. The effect of the addition of iron oxide ($Fe_2O_3 : SiO_2 = 1.5$–$7.5 : 100$) was examined when SiO_2/Na_3AlF_6 was 3, at which the maximum amount of whiskers was obtained. Since some of the whiskers, synthesized when the weight of Fe_2O_3 to that of SiO_2 ranged from 3.0 to 6.25 ($Fe_2O_3 : SiO_2 =$ 3.0–6.25 : 100), have droplets on their tips, they were assumed to have grown by VS and VLS mechanisms. The composition of the droplets were found to be Al-Si by elemental analysis by EDAX. Since droplets composed of Al-Si have never been reported, we performed a detailed analysis of the droplets in this study.

1. Introduction

Si_3N_4 whiskers are expected to be used as a composite material, since Si_3N_4 has high strength at high temperature and high thermal shock resistance, and the whiskers have a tensile strength close to the theoretical value [1].

In general, gas bodies such as $SiCl_4$ or SiH_4 and solid bodies such as Si or SiO_2 are used as Si sources to synthesize Si_3N_4 powders. Compared to gas bodies, solid bodies are more resistant to nitridation, and several kinds of accelerating agents for nitridation have been reported. For example, CaF_2, BaF_2 and Fe are reported as having an excellent accelerating effect for the nitridation of Si, and oxides of alkali metals and transition metals are also reported as having the effect of nitridation in SiO_2-C system [2].

In this study, a powder mixture of SiO_2 pure powder and cryolite (Na_3AlF_6), which is confirmed to be widely present in the natural environment, was used as a starting material. Si_3N_4 whiskers were synthesized by the heating of the starting material under a N_2 gas stream. In the case of studying the fusing effect of cryolite, the amount of cryolite was varied to investigate its effect on the synthesis of Si_3N_4 whiskers. It has been reported that whiskers are grown by VLS mechanism and droplets are formed on their tips when metal oxide is added as a catalyst. For example, whiskers with Fe-Si droplets are synthesized by the addition of Fe_2O_3 [3]. According to [3], whiskers were grown through the VLS mechanism by the addition of Fe_2O_3, ranging in amount from 1.5 to 10.0 ($Fe_2O_3 : SiO_2 = 1.5$–$10.0 : 100$).

2. Materials and methods

Fig. 1 shows a schematic of the experimental apparatus, the Lindbergh electric furnace. Si_3N_4 whiskers were synthesized as follows: SiO_2 powder and Na_3AlF_6 (Wako Chemical, Ltd.) were mixed so that the ratio SiO_2/Na_3AlF_6 ranged from 2 to 8. The obtained powder was ground into particles with an average diameter of approximately 10 μm using a planetary ball mill, and was then used as the starting material. The starting material was set on a graphite boat, and the boat was placed into the graphite tube, one side of which was closed and the hole diameter of 0.8 mm was confirmed at 5 mm intervals along the graphite tube. The graphite tube was placed within an alumina tube. Next, N_2 gas (99.99% purity) was introduced into the alumina tube. After all of the gas in the tube was replaced by N_2 gas, the N_2 gas was supplied at a rate of 180 ml/min (determined by a preliminary experiment). The apparatus temperature was increased at a rate of 5 K/min to 1673 K, which was maintained for 10 h. Subsequently, the temperature was decreased to 773 K at a rate of 5 K/min, and the apparatus was allowed to cool freely. N_2 gas was supplied continuously until the temperature fell below 523 K, to prevent oxidation of the products.

In order to investigate the effect of the addition of Fe_2O_3, Fe_2O_3 powder was added to the starting material

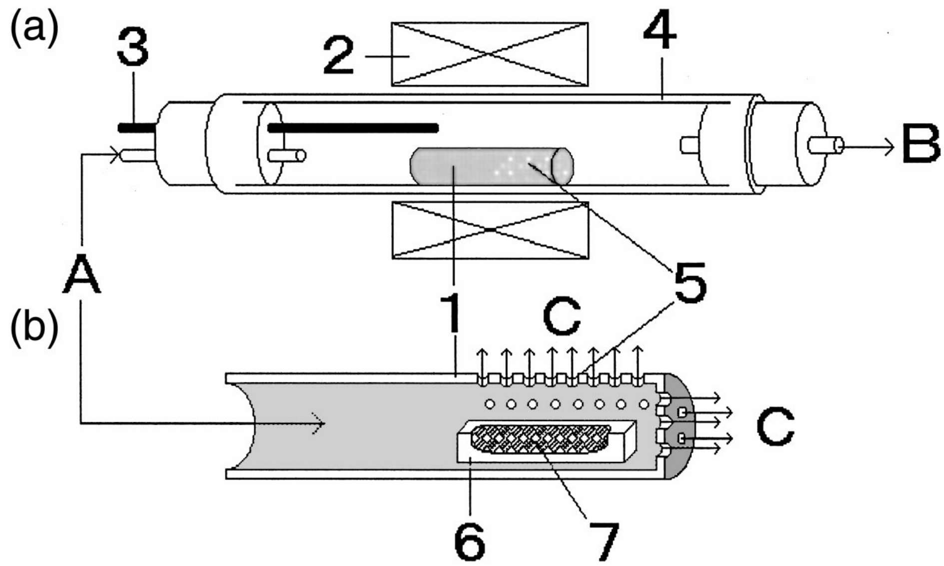

Figure 1 Schematic diagram of the experimental apparatus for Si_3N_4 whiskers synthesis. (a) whole view, (b) sample holder. A: gas inlet, B : gas outlet, C: gas exhaust. 1: graphite tube (16 mm I.D.), 2: electric furnace, 3: thermocouple (PR), 4: alumina tube (42 mm I.D.), 5: holed part, 6 : graphite boats, 7: sample.

so that the weight of Fe_2O_3 with respect to that of SiO_2 ranged from 1.5 to 10.0 ($Fe_2O_3 : SiO_2 = 1.5$–$10.0 : 100$).

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

3. Results
3.1. Deposition state and identification of whiskers
Whiskers were synthesized when SiO_2/Na_3AlF_6 ranged from 2 to 8. The maximum amount of whiskers was synthesized when SiO_2/Na_3AlF_6 was 3. Fig. 2 shows the deposition state of the product when the starting material was heated at 1673 K. At the bottom of the graphite boat, a glassy residue was obtained, surrounded by many deposited wool-like white whiskers (Fig. 2, No. 1). A small amount of whiskers was also deposited on the wall of the graphite boat. A white coating was formed on the inner wall of the alumina tube near the gas outlet (Fig. 2, No. 2). Fig. 3 shows the XRD patterns of the products obtained at 1673 K. The white whiskers were identified as α-Si_3N_4 and the white coating was identified as $NaAlF_4$. With respect to the residue obtained at the bottom of the graphite boat, only the peak of the XRD patterns corresponding to glass was detected. The residue formed at the bottom of the graphite boat was further analyzed by an elementary analysis using EDAX. As a result, the residue was identified as $Na_2Si_2O_5$, since it has a composition of $Na : Si : O = 21.6 : 20.4 : 50.09$.

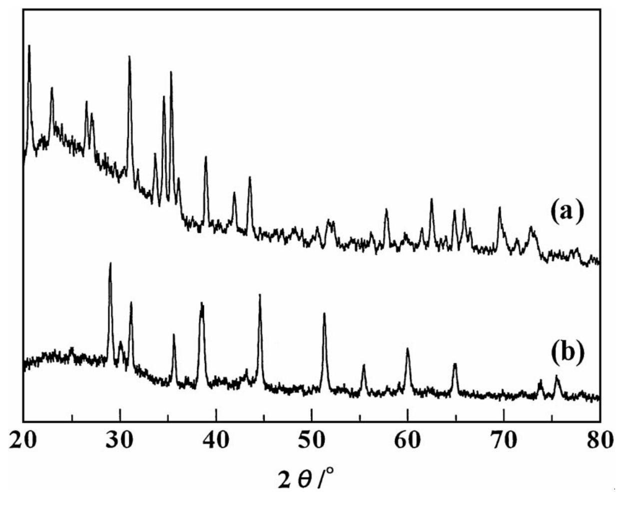

Figure 3 X-ray diffraction patterns of products obtained at 1673 K. (a): Si_3N_4, (b): $NaAlF_4$.

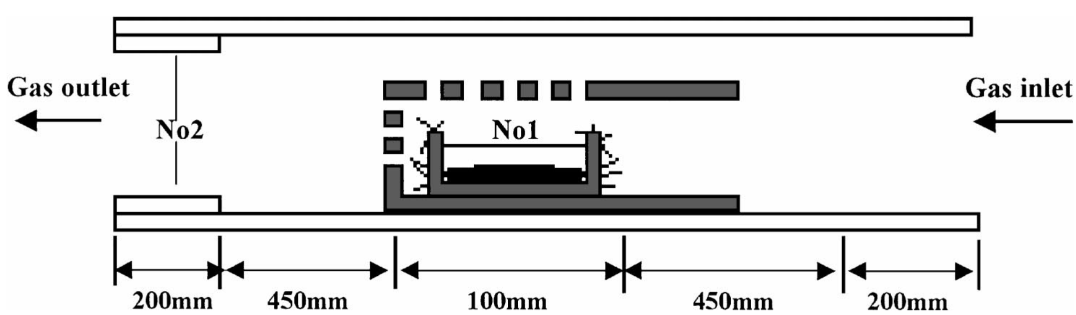

Figure 2 Deposition state of products. No1 was formed on graphite boat. No2 was formed on alumina tube.

3.2. Morphology of whiskers

Fig. 4 shows SEM photographs of the products obtained at 1673 K. In the figure, the nucleus of the wool-like whiskers (a), wool-like whiskers synthesized on the graphite boat (b), needle-like whiskers synthesized on the wall of the graphite boat (c) and droplets present on the tips of wool-like whiskers due to the addition of Fe_2O_3 (d) are shown. The diameter of the whiskers was relatively stable and the diameter was within the range of 0.1 to 0.5 μm, indicating that the size effect can be expected. With respect to the products found in Fig. 4(a)–(c), gaseous species generated on the graphite boat react with cryolite and graphite, and a Si_3N_4 nucleus was formed, then the nucleus was assumed to grow to a certain direction when the degree of supersaturation became high enough. The droplets observed in Fig. 4(d), which are midway between gaseous species and whiskers, generally grow by a VLS mechanism.

Table I summarizes the effect of Fe_2O_3 addition on the growth mechanism and composition of the droplets. Droplets were obtained when $Fe_2O_3 : SiO_2$ ranged from 3.0–4.0 : 100 and 5.0–6.25 : 100. No droplets were obtained for other values. The greatest Al/Si ratio was obtained when $Fe_2O_3 : SiO_2$ was 3.5 : 100 and 5.63 : 100. Interestingly, Fe was not contained in the droplets, although Fe_2O_3 was added to the starting material. At high temperatures such as 1673 K, both Al-Si and Fe-Si droplets can exist. When cryolite is used, Al plays an important role in the synthesis of Si_3N_4 whiskers [2]. In this present study, the Al component contained in the cryolite is considered to participate in the synthesis of the droplets.

4. Discussion

In general, the following reaction equation represents the process of Si_3N_4 synthesis [4]. When the temperature is 1673 K,

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO \qquad \Delta G = 136.153\,\text{kJ/mol} \tag{1}$$

TABLE I Effect of Fe_2O_3 on the mechanism and the droplet of whiskers

Fe_2O_3/mass%	1.5–2.5	3.0	3.5	3.75	4.0	4.5	5.0	5.63	6.25	7.5–10
Al/Si	—	0.25	0.60	0.20	0.076	—	0.36	0.72	0.12	—
Mechanism	VS		VS + VLS			VS		VS + VLS		VS
Diameter/μm					0.1–0.5					

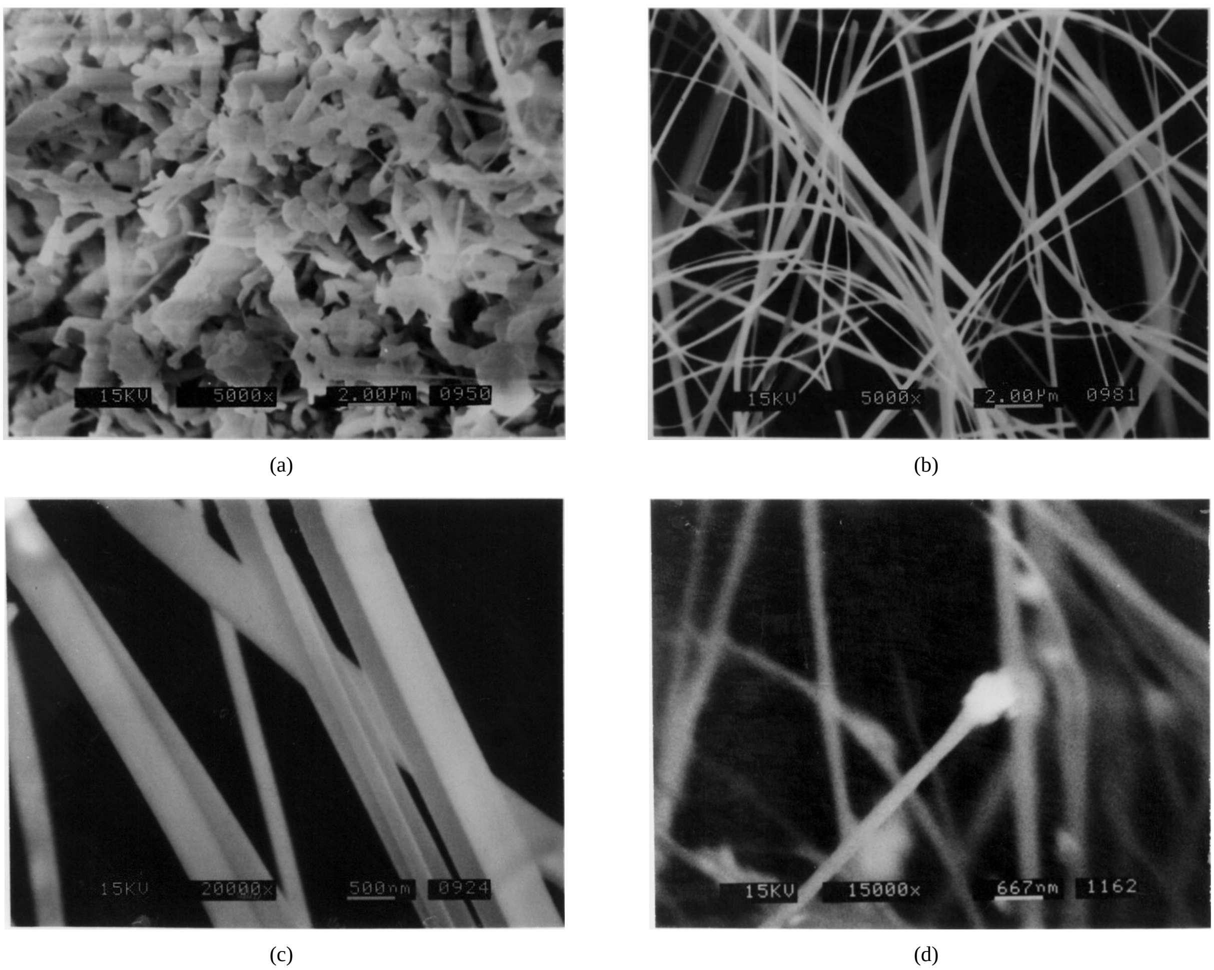

Figure 4 SEM photographs of products obtained at 1673 K. (a): the nucleus of whiskers, (b): wool like whiskers, (c): needle like whiskers, (d): the droplet of whiskers.

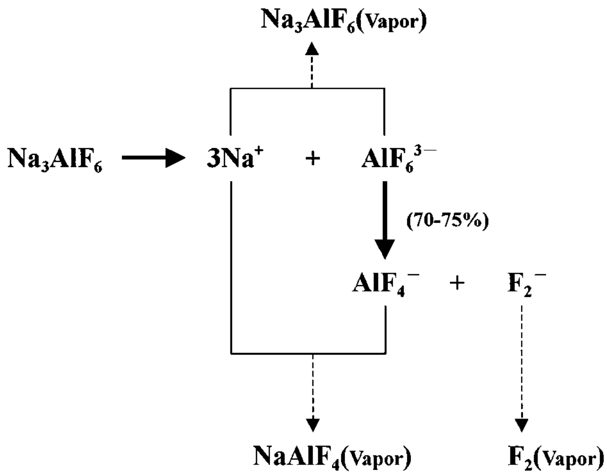

Figure 5 Dissociation mechanism of cryolite (Na_3AlF_6).

In the growth of the whiskers, SiO behaves as an intermediate product, since SiO_2 is not directly reduced and nitrided as in Equation (1), but a gaseous phase reaction is involved. Taking these into account, the following equation is possible.

$$SiO_2 + C \rightarrow SiO + CO \qquad \Delta G = 116.932\,\text{kJ/mol} \tag{2}$$

In this study, cryolite is contained in the starting material. Fig. 5 shows the dissociation mechanism of cryolite clarified so far, when cryolite is melted. The dissociation reaction shown in the following equation might occur.

$$Na_3AlF_6 \rightarrow 2NaF + NaAlF_4 \qquad \Delta G = -3.416\,\text{kJ/mol} \tag{3}$$

Howard confirmed the presence of $NaAlF_4$ by isolating $NaAlF_4$ through quenching cryolite vapor [5]. Solomons *et al*. analyzed the Raman spectrum and confirmed that the cryolite melting body is dissociated into $3Na^+$ and AlF_6^-, and 70–75% of the AlF_6^- is further dissociated into AlF_4^- and F_2^-, when the temperature is high (1303 K) [6].

In this study, both $NaAlF_4$ and Na_3AlF_6 white coatings were deposited on the inner wall of the alumina tube near the gas outlet. Dissociated $3Na^+$ and AlF_6^- were moved to the lower temperature area along the N_2 gas stream and deposited as Na_3AlF_6, while AlF_4^- which was produced as a result of dissociation of AlF_6^- reacted with Na^+ in the low temperature area and $NaAlF_4$ was deposited. A part of the NaF, which became melted states, reacted with SiO_2. As a result, it was considered to generate silicate ($Na_2Si_2O_5$) and SiF_4.

$$5SiO_2 + 4NaF \rightarrow Na_2Si_2O_5 + SiF_4 \qquad \Delta G = -14.875\,\text{kJ/mol} \tag{4}$$

Equation (4) corresponds to the experimental result that the residual by-product obtained on the graphite boat was identified as $Na_2Si_2O_5$ by XRD analysis. Equation (4) is also possible when free energy is taken into consideration. The SiF_4 in Equation (4) can be a Si source in the nitriding reaction as shown in Equation (5).

$$3SiF_4 + 2N_2 \rightarrow Si_3N_4 + 6F_2 \qquad \Delta G = 3966.495\,\text{kJ/mol} \tag{5}$$

Judging from the free energy, the reaction of Equation (5) may be impossible because of the large free energy. Therefore, the SiF_4 is not considered to participate in nitriding reaction.

For the above reasons, the gaseous species which is involved in the synthesis of Si_3N_4 is assumed to be SiO. The following nitriding reaction is possible considering that the growth of whiskers depend on the deposition substrate [7].

$$3SiO + 3C + 2N_2 \rightarrow Si_3N_4 + 3CO \qquad \Delta G = -214.643\,\text{kJ/mol} \tag{6}$$

This equation is possible according to the equilibrium theory. We found that the main and sub-reactions in this study are represented by Equations (6) and (4), respectively.

5. Conclusions

Si_3N_4 whiskers were synthesized using a powder mixture of SiO_2 pure powder and cryolite as starting material, which was heated under the presence of graphite in the flow of N_2 gas. We reached the following conclusions.

1. Whiskers were synthesized when the amount of SiO_2/Na_3AlF_6 ranged from 2 to 8. The maximum amount of whiskers was synthesized when SiO_2/Na_3AlF_6 was 3.
2. Whiskers formed on the graphite boat and on the wall of the graphite boat were wool-like and needle-like whiskers, respectively. Since the diameter of the whiskers ranged from 0.1 to 0.5 μm, it was considered that the values of tensile strength could be explained by the size effect.
3. The composition of the droplets was Al-Si. The Al component contained in the cryolite is considered to play an important role in the formation of the droplets.
4. The following equation is possible to explain the nitriding reaction of SiO_2-N_2-Na_3AlF_6 system in this study.

Main reaction:

$$3SiO + 3C + 2N_2 \rightarrow Si_3N_4 + 3CO$$

Sub-reaction:

$$5SiO_2 + 4NaF \rightarrow Na_2Si_2O_5 + SiF_4$$

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