Synthesis of β -SiAlON Whiskers from Pyrophyllite

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ろう石による β -SiAlON の合成

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Beta-SiAlON whiskers were synthesized by heating the admixture of pyrophyllite and resin at 1450 and 1500°C for 3h in N₂ atmosphere. The average diameter and length of the whiskers formed at 1500°C for 3h were about 1 μ m and 35 μ m, respectively. The whiskers were considered to be grown by a vapor-liquid-solid mechanism.

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1. Introduction

SiAlON has been obtained great attention as an engineering ceramic material because of its many excellent mechanical properties. Since Jack's pioneering work,¹⁾ its fabrication and properties have been extensively investigated.^{2),3)} However, concerning the preparation of β -SiAlON whiskers which can be served as a promising reinforcing and toughening phase in fabrication of composites, only the work of Hayashi et al. was available,⁴⁾ in which, β -SiAlON whiskers was grown in the system of the SiO₂-C-Na₃AlF₆ by nitridation process. In the present paper, a new method for the synthesis of β -SiAlON whiskers is presented and the corresponding growth mechanism is discussed briefly.

2. Experimental procedure

The raw materials used in the present study were natural pyrophyllite and liquid resin whose typical chemical compositions are listed in Table 1. 66.66 mass% of pyrophyllite was well mixed with 33.34 mass% of resin. The admixture was formed in a spherical sample (~30 mm in diameter) and then dried at 100°C for 12h. The dried sample was placed in an alumina boat which was inserted into an electric furnace and heated at a rate of 10°C/min to 1450 and 1500°C in a flowing N₂ atmosphere (purity: 99.9%, oxygen content: 3 ppm) at a rate of 0.2 l/min.

The obtained whiskers were observed by optical microscopy (OM) and scanning electron microscopy (SEM), and analyzed by X-ray diffraction (XRD) and energy-dispersed spectrometry (EDS).

3. Results and discussion

3.1 Features of the whisker

Figure 1 shows OM photographs of the whiskers formed at 1450 and 1500°C for 3h, respectively. SEM observation of the whiskers formed at 1500°C for 3h was conducted (see Fig. 2). The whiskers formed at 1450°C were shorter than those formed at 1500°C which have an average diameter

Fig. 1. Optical micrographs of β -SiAlON whiskers formed at 1450 and 1500°C for 3h in N₂, respectively.

about 1 μ m and the length about 35 μ m, respectively. The whiskers were confirmed to be β -SiAlON by XRD.

Figure 3 shows SEM photograph and EDS spectrum of a droplet at tip of the whisker formed at 1500°C for 3h. The droplet was composed of about 56.99 mass% of Fe, 37.09 mass% of Si and 5.92 mass% of Al.

3.2 Growth mechanism

As shown in Fig. 3, the droplet contained impurity Fe was formed at the tip of the whisker, which probably suggested that the β -SiAlON whiskers were grown by the vapor-liquid-solid (VLS) mechanism,⁵⁾ as discussed below.

3.2.1 Formation of liquid droplet

During heating, iron oxide (Fe₂O₃) in pyrophyllite was initially reduced by carbon derived from resin to Fe which further reacted with carbon to form an iron-carbon alloy (Fe_xC_y) which, when the temperature was above its melting point (about 1153°C),⁶⁾ became a liquid droplet under the influence of surface tension.

3.2.2 Dissolution of gases in the liquid droplet

During heating, the Al₂O₃(s) and SiO₂(s) containing in the pyrophyllite would react with carbon, and gaseous species would generate from the sample. According to Ref. 7, the Al- and Si-containing gases were Al(g), Al₂O(g), AlO(g), Al₂O₂(g), SiO(g), Si(g), Si₂(g), Si₃(g) and SiO₂(g), and which could be formed mainly by the following reactions.

Table 1. Chemical Compositions of Raw Materials

Chemical composition	lg.loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	C
pyrophyllite(mass%)	8.53	48.89	41.69	0.17	0.25	0.01	0.01	0.12	0.07	—
resin (mass%)	50	—	—	—	—	—	—	—	—	50

Fig. 2. SEM micrographs of β -SiAlON whiskers formed at 1500°C for 3h in N_2 .

Fig. 3. SEM micrograph and EDS spectrum of a droplet at tip of the whisker formed at 1500°C for 3h in N_2 .

Figure 4, as an example, shows equilibrium partial pressures of these gaseous species at 1700 K as a function of equilibrium partial pressure of $O_2(\text{g})$. Considering the total pressure in the furnace being 1 atm (1.013×10^5 Pa), and neglecting the consumption of nitrogen during reaction process, and assuming the reaction between $\text{C}(\text{s})$ and $O_2(\text{g})$ being in equilibrium, therefore the following equa-

Fig. 4. Equilibrium partial pressures of gases in Al-Si-O system at 1700 K.

tions could be established.

$$p_{N_2} + p_i = 1 \quad (10)$$

i -the gases showed in the Reactions (1)–(8)

$$p_{N_2} = 0.999 / (0.999 + p_{N_2} + p_i) \quad (11)$$

$$K_p = (p_{O_2})^{1/2} / p_{CO} \quad (12)$$

Based on Reactions (1) to (8) and Eqs. (10) to (12), the equilibrium partial pressure of $O_2(\text{g})$ in the furnace could be calculated. In terms of calculation, the partial pressure of $O_2(\text{g})$ in the furnace at 1700 K was about 3.80×10^{-22} atm, at which $\text{Al}(\text{g})$, $\text{Al}_2\text{O}(\text{g})$, $\text{SiO}(\text{g})$ and $\text{Si}(\text{g})$ showed very high partial pressures (Fig. 4). Therefore, once the liquid droplet was formed, these gases (and $N_2(\text{g})$) would dissolve into the droplet.

3.2.3 Growth of β -SiAlON whiskers from the droplet

When the liquid droplet became supersaturated with the gases stated above, the whiskers would grow by precipitation of β -SiAlON from the liquid (according to, for example, Reactions (13) and (14), where $[i]$ indicates i gas dissolved in the droplet)

4. Summary

Synthesis of β -SiAlON whiskers from pyrophyllite was investigated and the growth of the whiskers was explained by VLS (vapor-liquid-solid) mechanism. During heating, Fe_2O_3 in pyrophyllite was reduced by carbon derived from resin to Fe which further reacted with C to form an alloy (Fe_xC_y). When the temperature was above the melting point of the alloy (about 1153°C), the alloy would become a liquid droplet under the influence of surface tension. Once the droplet was formed, the gases such as $\text{Si}(\text{g})$, $\text{SiO}(\text{g})$, $\text{Al}(\text{g})$, $\text{Al}_2\text{O}(\text{g})$ and $N_2(\text{g})$ would dissolve into the droplet. When the liquid droplet became supersaturated with the gases, the whiskers would grow by precipitation of β -

SiAlON from the liquid.

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