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Short communication

Preparation of aluminum borate whiskers by the molten salt synthesis method

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Abstract

A molten salt process was used to synthesize approximately single-phase aluminum borate ($Al_{18}B_4O_{33}$) whiskers. The structure and morphology of $Al_{18}B_4O_{33}$ whiskers were characterized by X-ray powder diffraction and scanning electron microscopy. The result showed that high-crystallized $Al_{18}B_4O_{33}$ whiskers with an orthorhombic structure were obtained at 1000 °C. The diameter of $Al_{18}B_4O_{33}$ whiskers synthesized at 1000 °C for 0.5 h was about 1.3 μm, and the lengths ranged from 50 μm to 150 μm. Instead of the well-known vapor–liquid–solid mechanism, a self-catalytic mechanism was used to explain the growth of the $Al_{18}B_4O_{33}$ whiskers.

Keywords: B. Microstructure; In-situ synthesis; Aluminum borate whiskers; Molten salt process

1. Introduction

Aluminum-based composites reinforced with some types of ceramic whiskers have many unique properties, such as high specific strength, modulus, wear resistance, and thermal stability. Examples of ceramic whiskers include silicon carbide whiskers [1,2], silicon nitride whiskers [3], potassium titanate whiskers [4], aluminum oxide whiskers [5], and aluminum borate ($Al_{18}B_4O_{33}$) whiskers [6]. Silicon carbide whiskers are an excellent reinforcement for aluminum-based composites. However, the high cost of silicon carbide limits the commercial application of its composites. Meanwhile, $Al_{18}B_4O_{33}$ whiskers have the advantages of high strength, low thermal expansion coefficient, high melting point, high stability in oxidizing environments, and low cost. Thus, they are widely applied in aluminum-based composites that have potential uses in many fields, such as aerospace, relaxation, and automobile.

Various methods of synthesizing $Al_{18}B_4O_{33}$ nanowires and whiskers have been developed, including catalytic synthesis [7,8], high-temperature solid-state reaction [9,10], the low-heating-temperature solid-state precursor method [11], direct calcination of a precursor powder [12], combustion synthesis [13], the sol–gel method [14,15], the flux method [16], and molten salt synthesis [17]. The composition, morphology, and crystalline phases of $Al_{18}B_4O_{33}$ associated with its properties are reportedly highly dependent on the starting materials, synthesis, and processing methods. For example, Zhou et al. [11] obtained orthorhombic $Al_4B_2O_9$ nanorods with uniform diameters of 20–30 nm and lengths of up to several micrometers by a low-heating-temperature solid-state precursor method using $Al(NO_3)_3 \cdot 9H_2O$, $H_2C_2O_4 \cdot 2H_2O$, and H_3BO_3 as starting materials. Wang et al. [9] synthesized $Al_{18}B_4O_{33}$ whiskers with an average diameter distribution of about 400 nm and lengths ranging from 3 μm to 5 μm by a high-temperature solid-state reaction using H_3BO_3 and aluminum isopropoxide as starting materials. Their results showed that the product obtained at 850 °C was orthorhombic $Al_4B_2O_9$ whiskers, and that obtained at 1250 °C was orthorhombic $Al_{18}B_4O_{33}$ whiskers. Most researchers attempt to obtain high-purity orthorhombic $Al_{18}B_4O_{33}$ whiskers with a large length-to-diameter ratio at the lowest possible cost. However, many $Al_{18}B_4O_{33}$ synthesis methods still harbor impurities such as $Al_4B_2O_9$ and B_2O_3, and are high cost. Therefore, new synthesis methods for $Al_{18}B_4O_{33}$ whiskers are needed to be studied and innovated further.

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This study aimed to prepare single-phase $Al_{18}B_4O_{33}$ whiskers using $KAl(SO_4)_2 \cdot 12H_2O$, H_3BO_3, and K_2SO_4 as raw materials by molten salt synthesis, as well as to study the crystalline phase and morphology of the product. The growth mechanism of $Al_{18}B_4O_{33}$ whiskers was also discussed. Compared with literature [17], $KAl(SO_4)_2 \cdot 12H_2O$ was used as the source of aluminum instead of $Al_2(SO_4)_3$ in our study, the former was decomposed into K_2SO_4 and $Al_2(SO_4)_3$ with molecular-level scale and the uniform mixing when the mixture was heated. Therefore, $Al_{18}B_4O_{33}$ whiskers with higher crystallinity can be obtained at lower temperature.

2. Experimental

2.1. Reagent and apparatus

All chemicals were of reagent-grade purity ($>99.9\%$). X-ray powder diffraction (XRD) was performed using a Rigaku D/Max 2500 V diffractometer equipped with a graphite monochromator and a Cu target. The radiation applied was Cu Kα ($\lambda=0.15406$ nm), operated at 40 kV and 50 mA. The XRD scans were made from 5° to 65° in 2θ with a step size of 0.016°. The morphologies of the synthesis products were observed using an S-3400 scanning electron microscope.

2.2. Preparation of $Al_{18}B_4O_{33}$ whiskers

$Al_{18}B_4O_{33}$ whiskers were prepared by the molten salt synthesis method [17] using $KAl(SO_4)_2 \cdot 12H_2O$, H_3BO_3, and K_2SO_4 as starting materials. In a typical synthesis, $KAl(SO_4)_2 \cdot 12H_2O$ (5.0 g), H_3BO_3 (0.185 g), and K_2SO_4 (3.0 g) were placed in a mortar, and the mixture was thoroughly ground by hand using a rubbing mallet for 35 min. The grinding velocity was about 220 cycles/min, and the strength applied was moderate. The reactant mixture was dried at 150 °C for 3 h to remove crystal water first. Then, the reactant mixture was calcined in air at 1000 °C. The sintered body was washed with hot water to remove K_2SO_4 and B_2O_3. Finally, the precipitates obtained were dried at 120 °C for 3 h. The resulting material was subsequently determined to be orthorhombic $Al_{18}B_4O_{33}$ whiskers.

3. Results and discussion

3.1. Effect of H_3BO_3 dosage on the synthesis products

Fig. 1 shows that the XRD patterns of the samples obtained at different H_3BO_3 dosages are similar except for the diffraction peak intensities. In the four XRD patterns, only several very weak diffraction peaks of $Al_4B_2O_9$ were observed. The other diffraction peaks were in agreement with those of orthorhombic phase $Al_{18}B_4O_{33}$, with space group Pnma (62) and the following cell parameters: $a=1.5008$ nm, $b=0.7685$ nm, $c=0.5309$ nm, $\alpha=\beta=\gamma=90°$, and density $=2.866$ g cm^{-3}

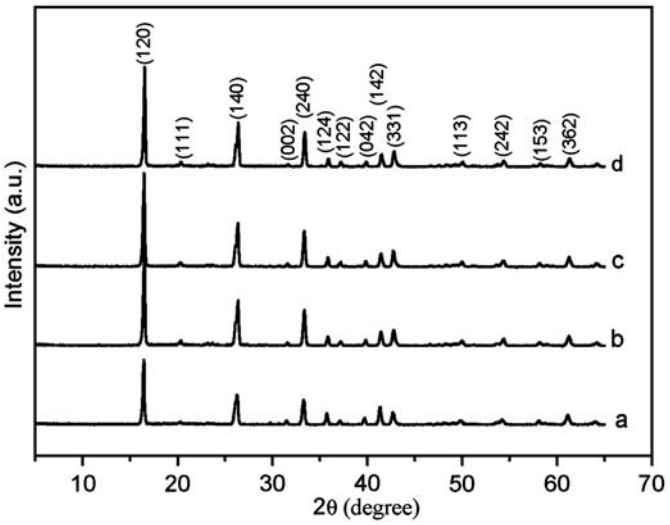

Fig. 1. Shows the XRD patterns of the synthesis products at 1000 °C for 6 h at different H_3BO_3 dosages. (a) 0.145 g, (b) 0.185g, (c) 0.225 g, (d) 0.245 g.

(PDF card 53-1233). This result indicated that the synthesis products had high purity, and that smaller H_3BO_3 dosages caused easier separation of $Al_{18}B_4O_{33}$ whiskers from the sintered body by hot water leaching, which can be attributed that residual B_2O_3 in the sintered body has lower solubility. The crystallinity of orthorhombic $Al_{18}B_4O_{33}$ was evaluated by the MDI Jade 5.0 software [18–20]. Results showed that the crystallinity of orthorhombic $Al_{18}B_4O_{33}$ obtained at the H_3BO_3 dosages of 0.145, 0.185, 0.225, and 0.245 g was 97.30%, 97.48%, 98.12%, and 98.36%, respectively. In other words, the crystallization degree of $Al_{18}B_4O_{33}$ slightly increased with increased H_3BO_3 dosage.

The morphologies of the synthesis products at different H_3BO_3 dosages in air for 6 h are shown in Fig. 2. The synthesis products obtained at the four different H_3BO_3 dosages were very neat and straight, and granular particles were scarce. However, some differences were observed in the whisker lengths obtained from the different H_3BO_3 dosages. Shorter whiskers were obtained at 0.145 g of H_3BO_3; longer whiskers were obtained at 0.185 g of H_3BO_3. These results can be due to the fact that at low H_3BO_3 dosages, the supersaturation degree of B_2O_3 in the molten state was limited. The reaction of B_2O_3 with a large number of fresh Al_2O_3 particles from the thermal decomposition of $KAl(SO_4)_2 \cdot 12H_2O$ initially formed $Al_{18}B_4O_{33}$ particles, which then grew in a one-dimensional direction. Consequently, the $Al_{18}B_4O_{33}$ whiskers formed were more complete but shorter. With increased H_3BO_3 dosage, the degree of supersaturation of B_2O_3 in the molten state increased, thereby providing favorable conditions for $Al_{18}B_4O_{33}$ whisker growth in one dimension. Fig. 2b shows that $Al_{18}B_4O_{33}$ whiskers 30–110 μm long and about 1.3 μm in diameter were obtained at 0.185 g of H_3BO_3. Fig. 2c and d shows that with further increase of H_3BO_3 dosage, the $Al_{18}B_4O_{33}$ whiskers obtained are between 20 and 70 μm long. The shorter whiskers associated with higher H_3BO_3

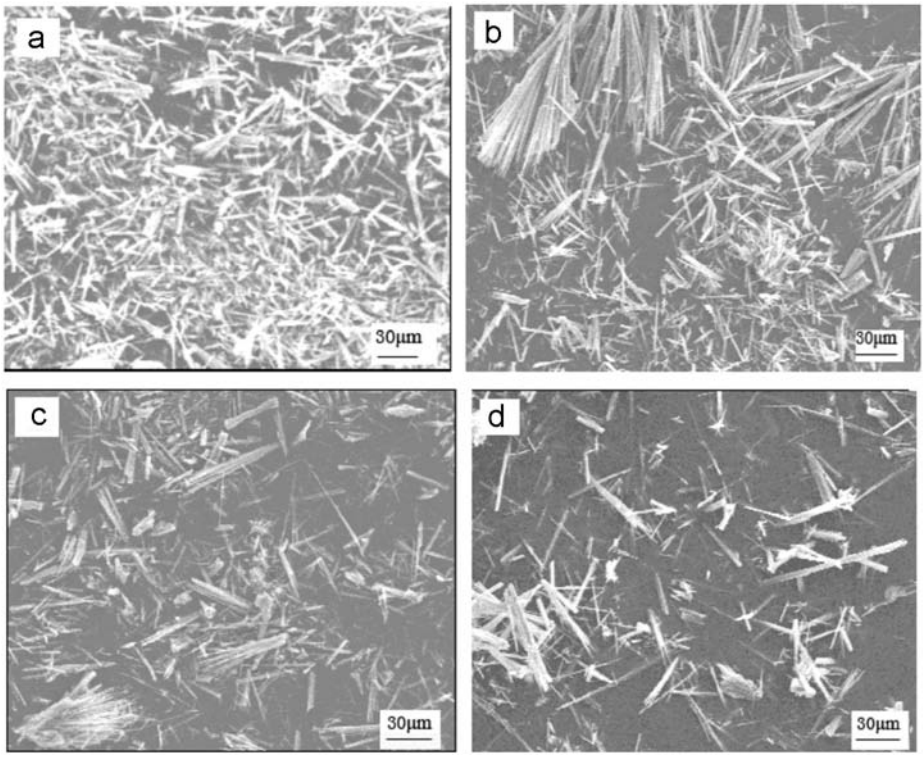

Fig. 2. SEM micrographs of the products synthesized at 1000 °C for 6 h at different H_3BO_3 dosages: (a) 0.145 g, (b) 0.185 g, (c) 0.225 g, and (d) 0.245 g.

dosage than that of 0.185 g can be explained as follow: with the increase of the H_3BO_3 dosage, the degree of supersaturation of B_2O_3 in the molten state increases further, thereby providing favorable conditions for $Al_{18}B_4O_{33}$ whisker growth in width and thickness in addition to one dimensional growth. So $Al_{18}B_4O_{33}$ whiskers are the shorter but thicker. The length-to-diameter ratio of the obtained $Al_{18}B_4O_{33}$ whiskers at 1000 °C significantly differed from other synthesis methods. For example, Wada et al. [17] obtained $Al_{18}B_4O_{33}$ whiskers with lengths ranging from 5 μm to 15 μm and diameters from 0.3 μm to 0.8 μm using the molten salt synthesis method at 1069 °C with $Al_2(SO_4)_3$, H_3BO_3, and K_2SO_4 as starting materials. The cause may be different source of aluminum and synthesis conditions.

In our study, no tips were found at the end of the whiskers. These tips are characteristic of a vapor–liquid–solid (VLS) mechanism [15,21,22]; thus, the VLS mechanism cannot underlie the growth of the as-synthesized $Al_{18}B_4O_{33}$ whiskers. Accordingly, a self-catalytic mechanism was proposed to explain the growth of the $Al_{18}B_4O_{33}$ whiskers. When the precursor mixture was calcined, H_3BO_3 in the mixture decomposed into B_2O_3 at about 250 °C, and then B_2O_3 melted at about 450 °C [15]. With increased temperature, $KAl(SO_4)_2$ decomposed into Al_2O_3 and K_2SO_4 grains, as well as SO_3 at about 700 °C [23]. The reactions are expressed as follows:

$$4H_3BO_3(s) \rightarrow 2B_2O_3(s) + 6H_2O\,(g) \quad (1)$$

$$B_2O_3(s) \rightarrow B_2O_3(l) \quad (2)$$

$$2KAl(SO_4)_2(s) \rightarrow K_2SO_4(s) + Al_2O_3(s) + 3SO_3(s) \quad (3)$$

$$9Al_2O_3(s) + 2B_2O_3(l) \rightarrow Al_{18}B_4O_{33}(s) \quad (4)$$

At 1000 °C, small Al_2O_3 grains dissolved into molten droplets of B_2O_3. All these small Al_2O_3 grains served as nuclei for the growth of $Al_{18}B_4O_{33}$ whiskers, similar to the Au catalysts used in VLS growth [15]. The Al_2O_3 grains first reacted with B_2O_3 into $Al_{18}B_4O_{33}$ particles, and then the $Al_{18}B_4O_{33}$ grains in-situ self-assembled into $Al_{18}B_4O_{33}$ whiskers. K_2SO_4 at 1000 °C changed into a molten state, providing favorable conditions for $Al_{18}B_4O_{33}$ whiskers growth in one dimension by moving in molten state K_2SO_4.

3.2. Effect of calcination time on the synthesis products

The morphologies of the synthesis products at different calcination times in air are shown in Fig. 3. The calcination time had little effect on the whisker morphology. When the mixture was calcined at 1000 °C for 0.5 h, the lengths and diameters of the resulting whiskers were 50–150 μm and about 1.3 μm, respectively, implying a high growth rate.

4. Conclusions

We successfully synthesized orthorhombic $Al_{18}B_4O_{33}$ whiskers by a molten salt synthesis method. XRD analysis showed that orthorhombic $Al_{18}B_4O_{33}$ whiskers were obtained by calcining precursor mixtures at 1000 °C in air for 0.5 h. The $Al_{18}B_4O_{33}$ whiskers were 1.3 μm in

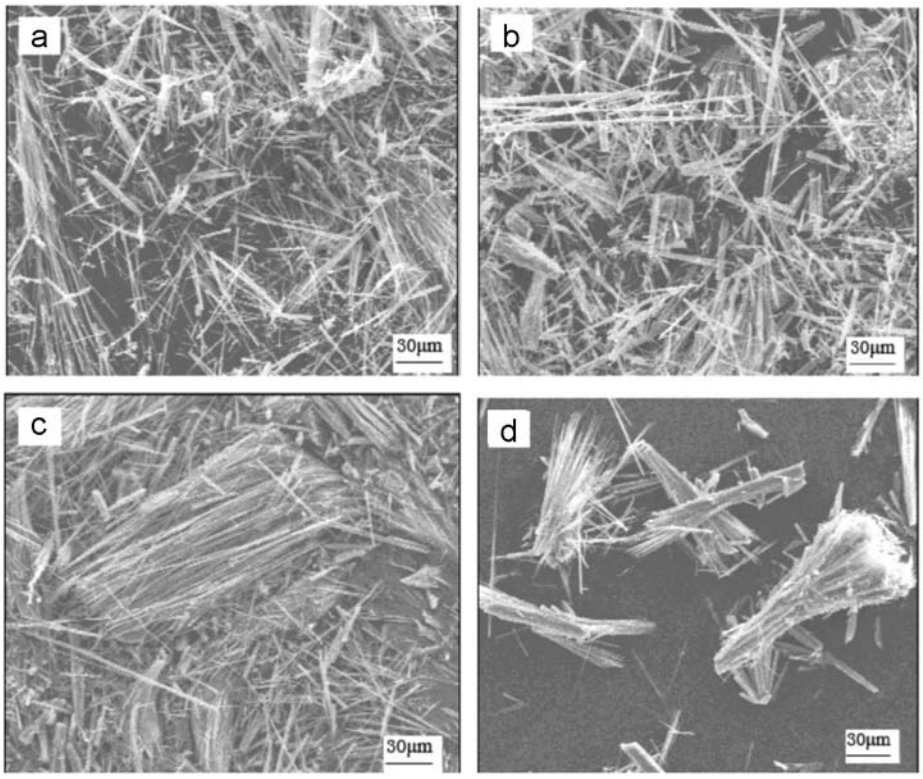

Fig. 3. SEM micrographs of the products synthesized at 1000 °C for different calcination times: (a) 0.5 h, (b) 1.0 h, (c) 3.0 h and (d) 4.0 h.

diameter and 50–150 μm long, implying a high growth rate. The growth mechanism of the whiskers may be a self-catalytic mechanism.

Acknowledgments

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