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Synthesis of aluminum borate whiskers via flux method with and without microwaves

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Aluminum borate ($Al_{18}B_4O_{33}$) whiskers have high strength and low thermal expansion coefficient. These properties are similar to those of silicon carbide (SiC) whiskers, but SiC whiskers are costly and sensitive to oxidation at high temperature, resulting in considerable strength and toughness degradation [1–3]. Aluminum borate is estimated to have a high melting point (1950 °C) and is stable in oxidizing environments [4, 5]. Aluminum borate whiskers can be considered as reinforcements for high temperature composites, and may have potential in oxidation-resistant, whisker-reinforced composites [4]. Several methods have been reported for the synthesis of aluminum borate whiskers. For example, Ready [4] has synthesized aluminum borate whiskers having 10–20 μm of length and 2–3 μm of diameter by heating a boric acid-stabilized aluminum acetate. Narita and Iizuka [6] have prepared aluminum borate whiskers with lengths approaching 20 μm and diameter of 0.4–0.8 μm by heating a mixture of $Al(OH)_3$ and H_3BO_3. Wada *et al.* [3, 7] have synthesized aluminum borate whiskers with lengths ranging from 5 to 15 μm via a flux method from aluminum sulphate and boric acid in potassium sulphate flux. The flux method has been reported to be one of the simplest techniques for preparing ceramics with whisker-like, needlelike or platelike morphology [8, 9]. Recently, microwave processing has been employed for chemical synthesis and has been found to have the following attractive characteristics; fast reaction rate, low reaction temperature, and superior structure and properties of the product [10–12]. However, the application of microwave processing for the synthesis of ceramic whiskers through the flux method has received less attention. It is reported that large whiskers are desired to have highly toughened ceramic, metal, and polymer composites [13]. In the present study, we report the synthesis of large aluminum borate whiskers from a mixture of γ-Al_2O_3 and $Na_2B_2O_7 \cdot 10H_2O$ (borax) via flux method using microwave heating, and compare differences in whisker sizes that result from the microwave process and the conventional process.

A covered alumina crucible containing reagent grade γ-Al_2O_3 and borax mixture of 5 g with a molar ratio of 1:0.7 was placed at the center of conventional electric furnace. The furnace temperature was then raised at 15 °C min^{-1} from room temperature to 1100 °C. Following heating at 1100 °C for 1 h, the crucible was furnace-cooled to room temperature. The heated mixture was treated with hot 1 M HCl for 2 h to remove the flux and washed with deionized water. White powders were obtained as the final product. This process and the resultant sample were referred to as "conventional process" and "conventionally treated sample," respectively. Microwave treated sample was prepared following the same procedure as for conventionally treated sample except that the mixture in the crucible was heated in a microwave hybrid furnace. This process was referred to as "microwave process."

A commercial microwave oven operating at 2.45 GHz with power of 700 W was modified for the microwave heat treatments. Its modifications included the attachment of an on-off temperature controller to maintain a consistent temperature and the attachment of a mode stirrer to uniform microwave field. The insulation cavity was composed of alumina fiber board and a SiC

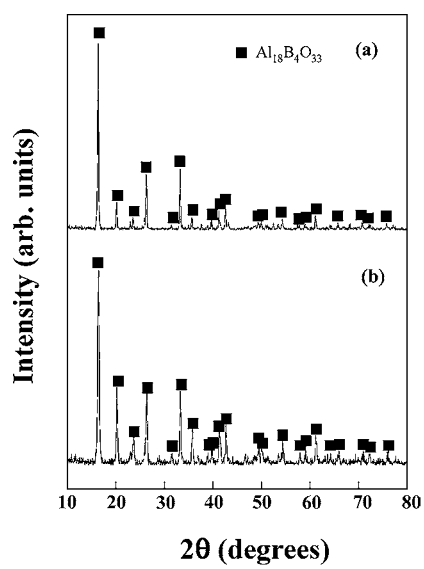

Figure 1 XRD patterns of samples obtained from a powder mixture of γ-Al_2O_3 and borax by (a) conventional process and (b) microwave process.

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sheet. The SiC sheet was used as a preheater [12]. The samples were characterized using X-ray diffractometry (XRD) and scanning electron microscopy (SEM).

Fig. 1 shows XRD patterns of the samples obtained by heating the mixture of γ-Al_2O_3 and borax at 1100 °C for 1 h under both conditions, conventional process and microwave process. The XRD patterns of the samples shown in Fig. 1 confirmed that the samples synthesized in this study had an aluminum borate phase. SEM observations (Fig. 2) show that both samples prepared

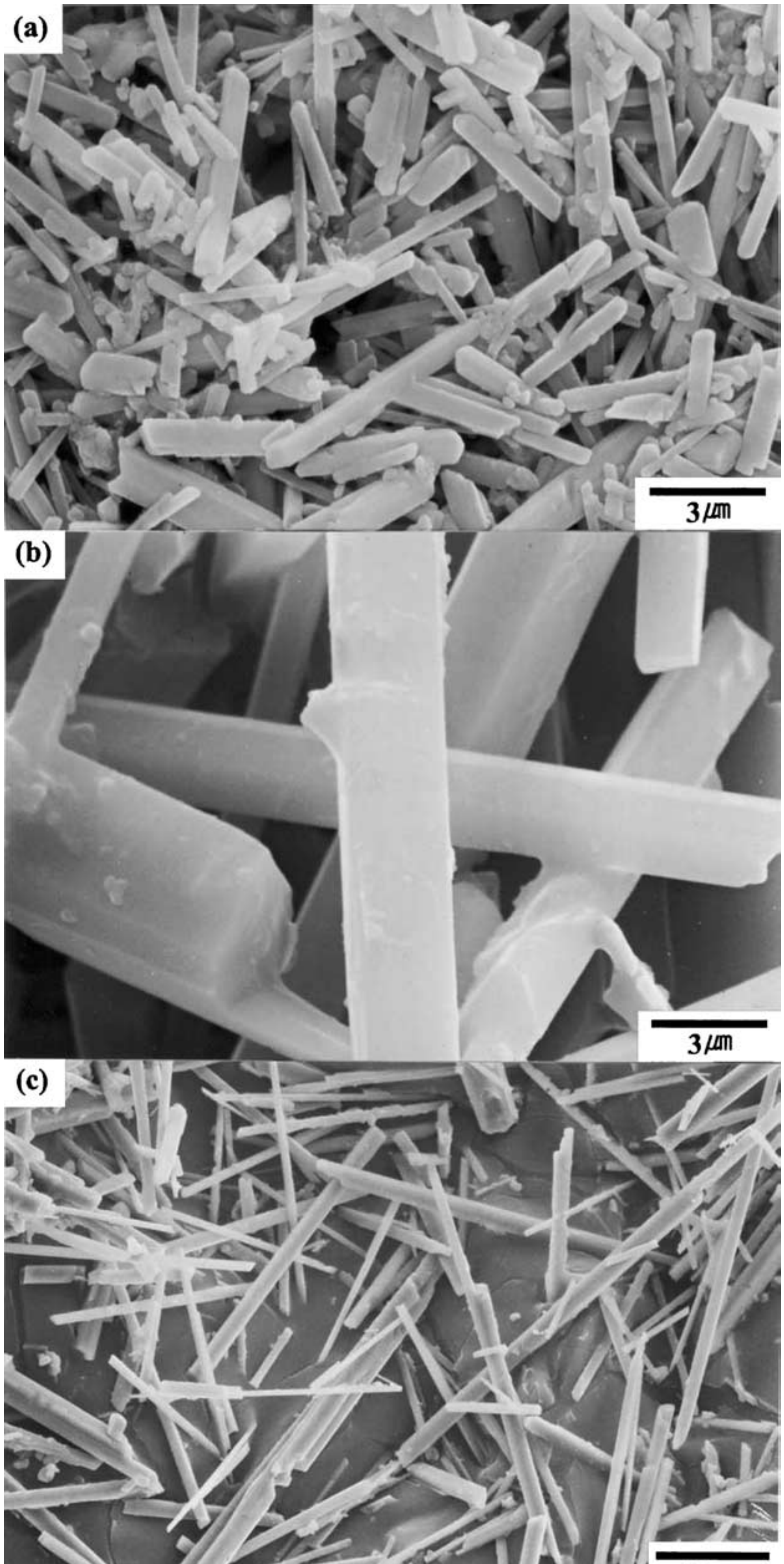

Figure 2 SEM micrographs of the aluminum borate whiskers synthesized from a mixture of γ-Al_2O_3 and borax by (a) conventional process, (b) and (c) microwave process: high and low magnification.

under both conditions are composed of whiskers, but the sizes of the whiskers are different. The sample obtained by microwave process had large whiskers compared with that obtained by conventional process. The lengths of the whiskers obtained by microwave process and conventional process ranged from 30 to 77 μm and from 2 to 8 μm, respectively. It is interesting to note that the whiskers prepared by microwave process and conventional process with the use of the same composition of starting materials and the same heating schedule are identical in crystal phase, $Al_{18}B_4O_{33}$ and morphology, but different in whisker size. Our experimental results imply that the whiskers grow in molten borax through the dissolution-precipitation mechanism [8, 14, 15]. It is known that the power (P) dissipated as heat in a dielectric material with volume V_s is given as [16, 17]

$$P = \frac{1}{2}\varepsilon_0\varepsilon''\omega E^2 V_s$$

where ε_0 is the dielectric constant in a vacuum, ε'' is the dielectric loss, ω is the angular frequency of the irradiated microwave, and E is the electric field strength. The equation suggests that the mixture of γ-Al_2O_3 and borax with high dielectric loss can be heated by dielectric thermal heating. However, simple dielectric thermal heating is not sufficient to explain the larger whisker size obtained by microwave process because both the microwave treated sample and the conventionally treated sample were produced under the same heating schedule with the same composition. It is reported that there is a specific activation effect due to microwave radiation that is acting in addition to the dielectric thermal heating. This effect has been referred to as the non-thermal effect of microwaves [16]. The non-thermal effect will be associated with reaction rate enhancement due to molecular agitation and improved transport properties of molecules [16, 17]. In this study, nucleation and crystal growth of aluminum borate crystal may be enhanced due to non-thermal effect of microwaves through dissolution-precipitation reaction of a mixture of γ-Al_2O_3 and borax flux, resulting in larger aluminum borate whiskers. However, further studies are needed to explain the exact crystallization mechanism that occurs by applying microwave heating.

In conclusion, large aluminum borate whiskers were synthesized by microwave heating a mixture of γ-Al_2O_3 and borax flux. Aluminum borate whiskers with 30–77 μm in length and 1.6–5.2 μm in diameter were obtained by microwave process. The microwave process led to an increase of the whisker size by approximately an order of magnitude, compared to the conventional process.

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