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Polygonal Single-Crystal Aluminum Borate Microtubes

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In this paper we report the synthesis of polygonal single-crystal aluminum borate microtubes by the direct calcination of alumina and boron nitride powders in air. The diameters of the obtained tubes vary between 1 and 15 μm; and the lengths are in the range of tens to hundreds of micrometers. The cross-sections of the microtubes are in the shapes of rectangular, hexagonal, and quasi-circle. A new solid–liquid–solid growth mechanism was proposed to account for the formation of microtubes instead of whiskers.

I. Introduction

The discovery of carbon nanotubes in 1991[1] has attracted extensive research interests in micro- and nano-scaled tubular structures over the last decade. This new class of structures offers a unique opportunity for studying geometrically confining effect on such phenomena as electron and phonon motions and light emission, as well as the transportation of liquids and gases. In addition, the interior hollow structure has a great potential for many applications, including sensors, drug delivery, microfluidic processes in microelectromechanical systems (MEMS), optical resonance cavities, and waveguides. The successful synthesis of micro- and nanotubes in a number of materials, such as SiO_2, TiO_2, InGaSa/GaAs, WS_2, MoS_2, NbS_2, NaV_3O_7, V_2O_5, VO_x, BN, SiC, Si_3N_4, AlN, mullite, and sialon has been reported.[2–20]

Aluminum borate ceramics are of particular interest due to their high elastic modulus and tensile strength, excellent resistance to oxidation/corrosion, and thermal properties, and are thus promising for applications such as high-temperature structural components, optical electronics, and tribology.[21–25] Aluminum borate has been well known to grow into needle-like whiskers in the presence of liquid phase. Such whiskers have been synthesized for oxidation-resistant whisker-reinforced composites using either direct high-temperature sintering of the mixture of Al_2O_3 and B_2O_3 [21] or the so-called molten salt flux synthesis technique.[26–28] With the assistance of catalysts, the diameter of the whiskers can be reduced to nanometer scale by confining growth to form nanowires.[29,30] Besides these solid whiskers/nanowires, Gogotsi *et al.*[31] and Schneider *et al.*[32] reported the formation of hollow aluminum borates with square or tetragonal cross-sections in oxide layers containing B_2O_3, Al_2O_3, and SiO_2 when oxidizing the composites of B_4C–SiC–AlON. Recently, Ma *et al.*[33] reported the synthesis of single-crystal $Al_{18}B_4O_{33}$ microtubes by calcining aluminum borate particles in the presence of nickel powders. However, the mechanism that governs the growth of microtubes rather than whiskers/nanowires is not clear.

In this communication we report the synthesis of $Al_{18}B_4O_{33}$ microtubes via simply high-temperature calcining the mixture of alumina and boron nitride in air without catalyst additives. The characterization of the morphology and crystalline structures of the obtained microtubes revealed that the microtubes are single crystal with cross-section of polygonal geometries. The thickness of the wall can be as thin as 50 nm. A possible growth mechanism based on solid–liquid–solid (SLS) is proposed.

II. Experimental Procedure

Commercially available alumina (Henan Xinyuan Aluminium Co. Ltd., Henan, China) and BN powders (Beijing Bei Hua Fine Chemicals Co. Ltd., Beijing, China), both at micrometer scale, were used as starting materials. The two powders were mixed together by ball milling for 12 h. The mole ratio of Al_2O_3 to BN powder was about 9:5. The powder mixture was then placed in a high-purity alumina crucible and heat treated in air using a conventional tube furnace. The powder mixture was first heated to 1200°C at 10°C/min and then to 1700°C at 3°C/min and held there for 2 or 4 h followed by slow furnace-cool. The morphology, structure, and composition of the synthesized products were characterized using field emission scanning electron microscopy (SEM, JSM-6301, JEOL, Tokyo, Japan), X-ray diffraction (XRD, Automated D/Max-RB, Rigaku, Akishima-shi, Japan) with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å), sequential X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan), and transmission electron microscopy (TEM, 200C X, JEOL, Japan). To prepare TEM samples, the microtubes were first dispersed in ethanol in an ultrasonic bath for 20 min, and the suspension was then dropped onto a copper grid.

III. Results and Discussion

Figure 1(a) shows a typical SEM image of the as-synthesized microtubes after calcining at 1700°C for 4 h. It can be seen that the whole surface of the mixed powder is covered by tubular structures. While most of tubes have hollow structures with open ends, some of the tubes have filling and/or blockage (examples are indicated by arrows). Besides rectangular, hexagonal- and quasi-circle-shaped cross-sections are also observed. The widths of the tubes with polygonal geometries vary between 1 and 15 μm, and the lengths are in the range of a few to hundreds of micrometers. SEM observations at higher magnification (Figs. 1(b) and (c)) show that the wall thickness of the tubes is in the range of 50–300 nm. Both the surface and inner parts of the microtubes were flat and clear (Figs. 1(b) and (c)). The tubes that have a uniform completely hollow structure without filling or blockage are ideal structures for transporting fluid or gas. The sharp knife-shaped edges and tips are very useful for penetrating biological tissues for drug delivery and injection and

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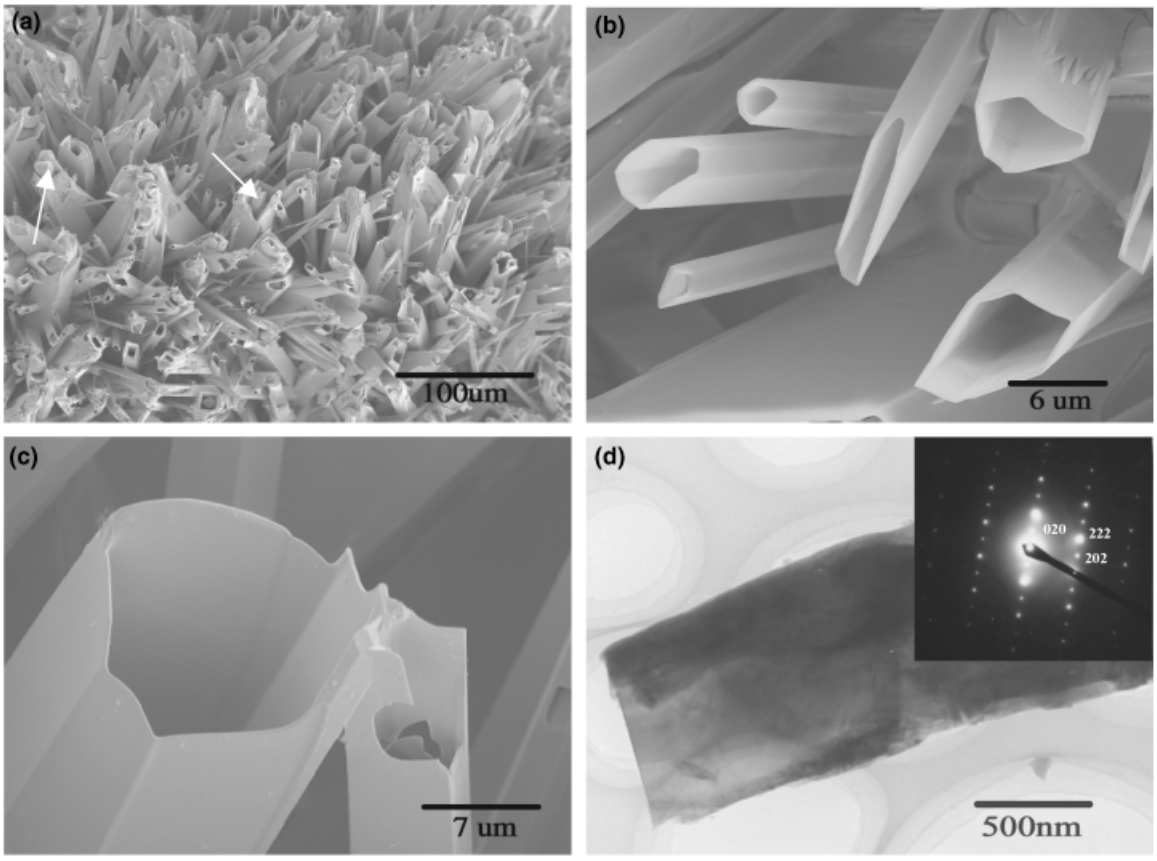

Fig. 1. (a) Scanning electron microscopy (SEM) micrograph of $Al_{18}B_4O_{33}$ microtubes synthesized via simply high-temperature calcining the mixture of aluminum and boron nitride at 1700°C for 4 h; (b) higher magnification SEM image shows that the microtubes take on several different geometries such as rectangular, hexagonal, and quasi-circle; (c) SEM image shows microtubes with polygonal and rectangular cross-section; and (d) transmission electron microscopy image and select area electron diffraction of a typical microtube.

extraction of bio-fluids. Figure 1(d) shows a TEM image of the microtube with select area electron diffraction (SAED) pattern (inset). In order to obtain the SAED pattern, the thickness of the tubes was reduced with high-energy ball milling. The ball milling resulted in surface damage as can be seen from Fig. 1(d). The SAED pattern was taken from the tip edge. The pattern can be indexed as an orthorhombic $Al_{18}B_4O_{33}$ single crystal with lattice constants of $a = 0.77$, $b = 1.50$, and $c = 0.57$ nm, which are consistent with those of bulk $Al_{18}B_4O_{33}$ reported in JCPDS (32-0003). The SAED also suggests that this particular tube grows along the [222] direction.

The XRD pattern (Fig. 2) of the products suggests that orthorhombic aluminum borate is the only crystalline phase without any impurities present in the products. The positions and relative intensities of the peaks are in good agreement with those reported in JCPDS (32-0003). The composition of the tubes was quantified by X-ray fluorescence analysis. The weight ratio of Al:B:O is about 11:1:13, which is approximately equal to the stoichoimetric ratio of $Al_{18}B_4O_{33}$.

In order to understand the mechanisms that govern the formation of microtubes instead of whisker/nanowires, the materials obtained at the early stage of the calcination were observed. Figure 3 shows a representative SEM image of the microtubes

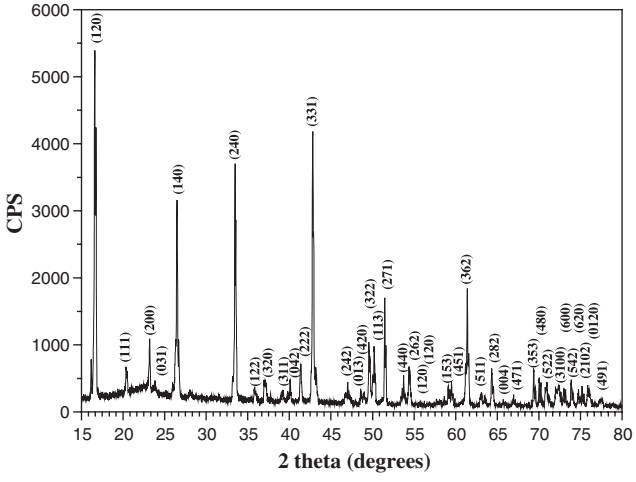

Fig. 2. X-ray diffraction pattern of as-synthesized microtubes showing that orthorhombic $Al_{18}B_4O_{33}$ is the only crystalline phase.

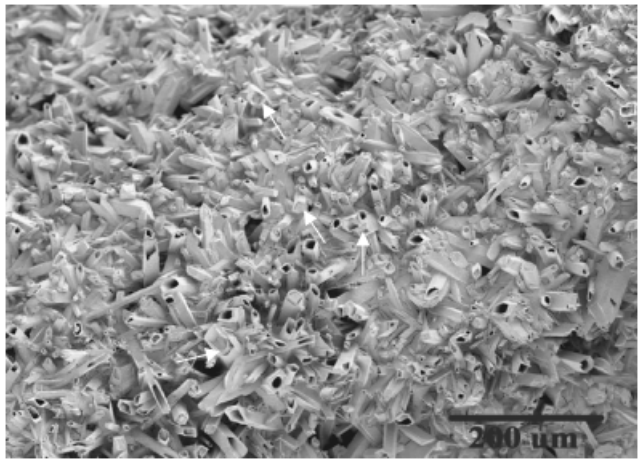

Fig. 3. Scanning electron microscopy micrograph of $Al_{18}B_4O_{33}$ microtubes synthesized via simply high-temperature calcining the mixture of aluminum and boron nitride at 1700°C for 2 h.

obtained at 1700°C for 2 h. By comparing Figs. 3 and 1(a), it can be seen that (i) the average length of the tubes in Fig. 3 (calcine for 2 h) is significantly shorter than that in Fig. 1(a) (calcine for 4 h), suggesting the continued growth of the tubes formed at an early stage; and (ii) the percentage of tubes with filling/blockage in Fig. 3 (examples are indicated by arrows) is much higher than that in Fig. 1(a), suggesting that the filling/blockage was cleaned during the growth of the tubes.

Consequently, we propose following the SLS growth mechanism to account for the growth of microtubes rather than whiskers in the present study. When calcining at high temperatures, BN powders first reacted with O_2 in air to form B_2O_3, which became liquid at temperatures higher than $\sim$450°C according to the phase-diagram.[26] The liquid B_2O_3 reacted with Al_2O_3 on the surface of the alumina to form $Al_4B_2O_9$ and liquid aluminum borate phase at temperatures between 450° and 1035°C[26], according to reaction Eq. (1). At higher temperatures, the $Al_{18}B_4O_{33}$ became more stable[26] and can be formed through reaction Eq. (2) and (3), and $Al_4B_2O_9$ formed at lower temperatures took place peritectic decomposition and decomposed into $Al_{18}B_4O_{33}$ and liquid aluminum borate (reaction Eq. (3)). The chemical reactions involved are expressed below:[22]

$$2Al_2O_3 + B_2O_3 \rightarrow 2Al_2O_3 \cdot B_2O_3 \quad (1)$$

$$9Al_2O_3 + 2B_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3 \quad (2)$$

$$9(2Al_2O_3 \cdot B_2O_3) \rightarrow 2(9Al_2O_3 \cdot 2B_2O_3) + 5B_2O_3 \quad (3)$$

The formation of $Al_{18}B_4O_{33}$ prevents direct contact between nonreacted Al_2O_3 and B_2O_3; thus further reaction between the two can only occur through the following sequence: (i) first unreacted Al_2O_3 and B_2O_3 were dissolved into the aluminum borate liquid to form supersaturated liquid and (ii) then $Al_{18}B_4O_{33}$ was precipitated. During this SLS reaction, the $Al_{18}B_4O_{33}$ frames formed on the surface of alumina at an earlier stage served as seed sites for the precipitation. The Al_2O_3 within $Al_{18}B_4O_{33}$ frame was dissolved so that a cavity was left behind to form hollow, tube-like structures. The above growth mechanism is purely speculative at this moment, and further validation is ongoing.

The proposed SLS mechanism can also be used to explain the formation of $Al_{18}B_4O_{33}$ microtubes reported in Gogotsi *et al.*,[31] Schneider *et al.*,[32] and Ma *et al.*[33] The formation of $Al_{18}B_4O_{33}$ whiskers instead of tubes in Readey[26] and Li *et al.*[27] Rohmund and Smalley[28] could be due to the use of small sizes of fumed alumina or aluminum hydroxide and boric acid, which allow complete reaction between alumina and boron oxide without residual Al_2O_3.

IV. Summary

In summary, single-crystalline $Al_{18}B_4O_{33}$ microtubes were successfully synthesized by directly calcining Al_2O_3 and BN powders in air without catalysts. The cross-sections of the tubes are in the shapes of rectangular, hexagonal, and quasi-circle. The widths of the tubes vary between 1 and 15 μm, and their lengths are in the range of tens to hundreds of micrometers. The microtubes' growth is attributed to an SLS mechanism. $Al_{18}B_4O_{33}$ microtubes synthesized here could be potentially useful for applications in a number of fields such as fluid/gas transportations in MEMS, biomedical drug delivery systems, optical resonance cavities and waveguides, and nanocomposites.

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