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## Synthesis Aluminum Borate Ceramic

By

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### Abstract:

Aluminum borates synthesized via a precipitation process. Aluminum nitrate and calcium hexaboride (CaB<sub>6</sub>) as a source of B<sub>2</sub>O<sub>3</sub> were used. Various proportions of aluminum nitrate were mixed with CaB<sub>6</sub> powder and to solution of ammonium hydroxide. The resulting mixtures were evaporated and calcined up to 650°C. Porous ceramic with a framework structure of aluminum borate whiskers was in situ synthesized by firing the green compact bodies up to 1400°C under Ar gas avoiding the oxidation of the CaB<sub>6</sub>. The structure and morphology were investigated by XRD and SEM. The results indicate that whiskers exhibit a well-crystallized structure with an average diameter distribution about 500 nm and lengths ranging from 5 to 8 μm. Porous aluminum borate ceramic consisted of whiskers with a porosity of 9 – 21% for samples sintered up to 1400°C. Increasing the sintering temperature up to 1500°C and CaB<sub>6</sub> addition (15wt.%) deteriorated both the flexural strength and modulus of elasticity of the ceramic bodies.

### Keywords:

whiskers; ceramic; aluminum borate; flexural strength; elasticity

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## 1. Introduction:

Lightweight ceramic materials formed from aluminum borate and/or different proportions of aluminum oxide mixed with either oxides or non oxides are desirable from the standpoint of weight as well as chemical inertness. It was elucidated that ceramic composites could be formulated by reaction of  $\text{Al}_2\text{O}_3$  and  $\text{TiB}_2$  or  $\text{B}_2\text{O}_3$  with aluminum metal. This ceramic material has been found to possess an excellent electrical conductivity and chemical inertness properties even by heating at elevated temperatures.

Because of its hardness, melting point and electronic properties  $\text{CaB}_6$  is used in a variety of industrial applications, where it is known as an abrasive and deoxydation material. It is used in large quantities as a deoxidizing additive for the production of magnesia carbon bricks and for the refinement of pure iron, steel, and copper<sup>(1)</sup>. Furthermore, it is used as a starting material for boron nitride synthesis<sup>(2)</sup>. Numerous papers have been already published on the production  $\text{CaB}_6$  and its characterization<sup>(3, 4 & 5)</sup>. New investigations in the last 15 years are concerned with the electronic structure and magnetism of  $\text{CaB}_6$ <sup>(6)</sup>. According to Kino et al.,<sup>(7)</sup>  $\text{CaB}_6$  has a quasiparticle band structure and is of semimetallic character in bonding. The high temperature oxidation behaviour of hot-pressed and sintered bodies of  $\text{CaB}_6$  have been studied by Matsushita and Komarneni<sup>(8)</sup>. The phase diagram of the Ca–B system was presented in “Binary Alloy Phase Diagram”<sup>(9)</sup> and also by Otani<sup>(10)</sup>.

The formulation of ceramic materials from aluminum and boron oxides would be expected to be some what lighter than aluminum oxide itself, depending on the density difference between the added quantities of boron and the alumina matrix.

$\text{Al}_{18}\text{B}_4\text{O}_{33}$  compound is estimated to have a high melting point and is presumably stable in oxidizing environments<sup>(11)</sup>. With these characteristics,  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  nanowires may have potential in oxidation-resistant reinforced composites<sup>(12)</sup>. Whiskers and fibers composed of  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  have been fabricated by several different techniques<sup>(12, 13)</sup>. Microtubes and nanowires of  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  have been synthesized by direct reaction between alumina and boron oxide<sup>(14, 15)</sup>.

Among all applications of one-dimensional nanomaterials in the fields of nanoelectronics, nanomechanics and nanocomposites<sup>(16)</sup>, aluminum borates are notable ceramic materials with high elastic modulus, tensile strength, and low thermal expansion making them attractive for optical electronics, structure applications, and tribology<sup>(17)</sup>. With these characteristics, one dimensional aluminum borate micro- and nanostructures such as whiskers<sup>(18)</sup>, microtubes<sup>(19)</sup> and nanowires<sup>(20)</sup> may have potential in oxidation-resistant reinforced composites<sup>(21)</sup>, chemical and heat-insulating materials, and filter media<sup>(22)</sup>.

Aluminum borate whisker ( $\text{Al}_{18}\text{B}_4\text{O}_{33}$  denoted by ABOw) reinforced aluminum matrix composites (ABOw/Al) have been widely studied<sup>(1)</sup> due to their relative low cost and good properties. It is expected that aluminum matrix composites with lower coefficient of thermal expansion (CTE) and good mechanical properties can be widely used in many areas, such as electronic encapsulation, precision instruments and so on<sup>(23)</sup>. Low CTE of aluminum matrix composites has attracted significant attention in recent years<sup>(24)</sup>. It was evident that, the effective approach to reducing the CTE of the composite is to increase the

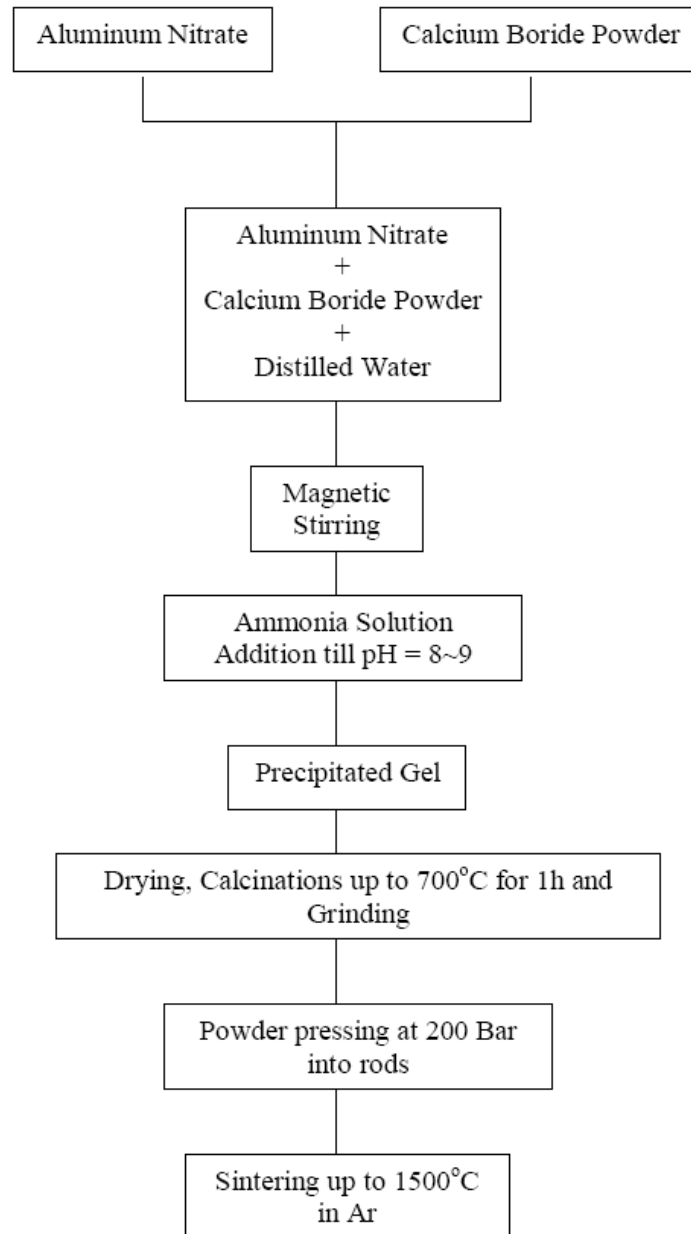
content of the reinforcement. However, high content of reinforcement reduces the plasticity and thermal conductivity of the composite. Wang et al. <sup>(25)</sup> indicated that the addition of  $\beta$ -eucryptite particles with negative CTE into a composite could decrease the CTE of an aluminum matrix composite.

Ceramics are becoming increasingly popular in the field of food industries as corrosive-resistant filter materials and catalysts, due to their exceptional high temperature stability, and superior resistant to chemical attack. Aluminum borate ( $\text{Al}_{18}\text{B}_4\text{O}_{33}$ ) fabricated with characteristics necessary for applicability as a filter with stand the severe conditions required in the area of food filtrations.

Traditionally, whiskers and fibers composed of  $\text{Al}_4\text{B}_2\text{O}_9$ /  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  have been fabricated by different techniques <sup>(4, 5)</sup>. A microtube of  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  has been synthesized via liquid phase reaction between  $\text{NiCl}_2$  and  $\text{NaBH}_4$  solution <sup>(6)</sup>.  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  nanowires could be produced by a direct reaction of alumina, boron oxide and boron in Ar atmosphere <sup>(13)</sup>.  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  nanowires were generated by the same mixture but adding alumina supported  $\text{Fe}_2\text{O}_3$  as catalysts <sup>(7)</sup>. It has been reported that  $\text{Al}_4\text{B}_2\text{O}_9$  nanowires were also successfully synthesized by the direct reaction between Al and  $\text{B}_2\text{O}_3$  in a flow of Ar <sup>(8)</sup>. In this paper, it was developed a convenient, fast and bulk-quantity method to prepare aluminum borate rod-like whiskers using aluminum nitrate as a source of alumina matrix and  $\text{CaB}_6$  as a source of boron in a flow of Ar carrier gas and without impurity doping in the final products.

## 2 Experimental:

The materials used in this investigation were aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) purity (98%), delivered by LOBA Chemie PVT, LTD India. Ammonia solution was used for gel precipitation. Calcium boride powder with a particle size  $>50\mu\text{m}$  as shown in Fig. (1) delivered by elektroschmeltz Werk Kempten Germany. It is revealed that the  $\text{CaB}_6$  particles are coarser equigranular and mainly prismatic and/or rectangular in shape. The alumina-calcium boride batch composites with proportions of 5 - 15 Wt.%  $\text{CaB}_6$  at the expense of alumina were prepared according to the following scheme.



Schematic diagramed of the synthesized alumina-calcium hexaboride composites

## 2.1. Characterization

The microstructure of the final products was examined by SEM (SEM Model XL 30, Philips, Eindhoven, Netherlands). XRD analysis of the samples was carried out using monochromated Cu K<sub>α</sub> radiation (D 500, Siemens, Mannheim, Germany) to identify crystalline reaction products. Apparent porosity of the fired specimens was evaluated using the Archimedes method (ASTM C-20). Bending strength was measured using a three point bending test on a universal testing machine (Model 4204, Instron Corp., Danvers, Mass.) at a crosshead speed of 0.01 mm/Sec. and support distance of 40 mm. At least 10 specimens with the dimensions of 50 mm x 4 mm x 3.5 mm were measured for one data point

### 3. RESULTS AND DISCUSSION

The calcination of the composite powders was carried out up to 700°C for only 1h which is starting temperature for CaB6 oxidation. In general, the evaluation of oxidation resistance of CaB6 was carried out by investigating the weight gain accompanying the following reactions:



During the initial heating between 200 to 600°C, water is removed from the sample corresponding to an initial weight loss of about 3%. This decrease is followed by a limited weight gain starting at 700°C. According to the equation (1) it was suggested that at 700°C a partial oxidation of CaB6 was occurred giving the formation of glassy phase CaB<sub>4</sub>O<sub>7</sub> and boron oxide phase which is responsible for the formation of aluminum borate phase.

It was found that <sup>(26)</sup> the weight gain of the sample oxidized below a temperature of 900°C for 1 h was approximately 1%. However, even if the oxidation time was extended, an additional weight change did not occur. Thus, the sample showed a good oxidation resistance at a high temperature of 900°C. Significant oxidation of samples started at 1000°C, and the weight gain increased with increasing oxidation temperature. The samples oxidized at and above 1000°C also exhibited increasing weight gain with oxidation time.

The above mentioned results were in agreement with the previous study indicated that the sample of CaB6 being oxidized at 600 to 700°C for 25 hours exhibited weight gain with oxidation temperature; the oxidation proceeded in accordance with the parabolic law during the initial oxidation stage. On the other hand, the weight gain of the sample oxidized at and above 800°C for 4 h was approximately 80%; however even if the oxidation time was prolonged, an additional weight change did not occur. Based on the results of the X-ray diffraction analysis, calcium borate (CaB<sub>4</sub>O<sub>7</sub>) was present as glassy phase on the surface of the sample oxidized at 800°C. The sample showed a good oxidation resistance at 1000 to 1100°C because the surface film of calcium borate (CaB<sub>2</sub>O<sub>4</sub>) formed by oxidation acted as an oxidation resistant layer <sup>(27)</sup>.

#### 3.1. Phase composition

XRD measurements of the samples sintered up to 1500°C indicate that the Co-precipitation synthetic route forms the highly crystallized products, no other phases associated with alumina and borate could be observed. This indicates that the use of different proportions of CaB6 on the expense of alumina is suitable for the growth of aluminum borate whiskers. Figures (2 and 3) show the XRD patterns of the product synthesized by co precipitation method. The patterns can be appropriately indexed in peak positions as an orthorhombic structure of aluminum borate with lattice parameters of  $a = 0.774$  nm,  $b = 1.504$  nm, and  $c = 0.567$  nm, which are consistence with the parameters of the bulk Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> (JCPDS 32-0003).

SEM images of the 5-15 Wt.% CaB6 sintered at 1400°C as synthesized products are shown in Fig. 4. All the samples are essentially composed of whiskers but the sizes and the aspect ratio of these whiskers are different. SEM image of the 10% CaB6 in Fig. 4c shows that the whiskers have a relatively large diameter (3.64–0.84 μm) common to all sample prepared when the CaB6 addition content is 5 wt% to the total reactant Aluminum

nitrate. Further increasing the CaB<sub>6</sub> addition content resulted in the increase in the lengths and the uniformity in the diameters of the whiskers Fig. 4, E.

SEM examination established the one-dimensional morphologies of the product, no particles can be observed. This indicates that the coprecipitation procedure assures the structural uniformity. SEM images micrograph in Figs. 4 a, c, and e shows the morphology of the Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> whiskers synthesized by the coprecipitation method. It is clearly shown that the product consists of a relatively short whiskers, usually with an aspect ratio (diameter/length) ranged from 8-15. The morphology is similar to that of the Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> nanowires synthesized by the catalytic growth reaction between boron and alumina<sup>(28)</sup>. The morphologies of these short whiskers should relate to the possible existence of the outgrowth perpendicular to the axis during one-dimensional crystal growth, although axial growth is still preferential. It was postulated that addition of Al-metal obviously increases the aspect ratio of the synthesized whiskers<sup>(28)</sup>.

The EDS analysis of the sintered composites containing 5-15 Wt.% CaB<sub>6</sub> are given in (Fig. 5) and tabulated in Table (1). From table (1) and Fig. 5 it was revealed that each particle contains Al, B and Ca. The phenomenon of particles at the tips of the whiskers strongly indicates that the growth mechanism is vapor–solid–liquid (VLS) growth<sup>(14, 15)</sup>. But to obtain the nuclei which are necessary for VLS growth of whiskers, special catalyst is usually added, such as Fe<sub>2</sub>O<sub>3</sub> supported by Al<sub>2</sub>O<sub>3</sub>.

Recently, some nanowires or whiskers have been synthesized by self-catalytic growth<sup>(16, 17)</sup>. In this growth mechanism, some molten metal, such as Sn and Ga, can serve as liquid nuclei for VLS of the whiskers. Here, it was also considered that the growth of aluminum borate whiskers is a self-catalytic VLS with Al<sub>2</sub>O<sub>3</sub> serving as the nuclei. The possible reaction process could be discussed as follows. In our method, the reaction started during calcinations of the batches at 850°C. During the process, the CaB<sub>6</sub> oxidized producing B<sub>2</sub>O<sub>3</sub> as a by-product which will melt first at about 450°C and Al<sub>2</sub>O<sub>3</sub> powder may be dispersed into the molten B<sub>2</sub>O<sub>3</sub> and will dissociated. It seems that the formation of aluminum borate whiskers could be produced according to the same mechanism suggested by Chun Cheng et al<sup>(29)</sup> who suggested that for the synthesis of the Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> nanowires might be dominated by a local vapor solid (LVS) growth process. For his experiment, before reaching the reaction temperature of 1500°C, B<sub>2</sub>O<sub>3</sub> melted first at about 450°C and the nano-scale Al<sub>2</sub>O<sub>3</sub> particles, dispersed in the reactants beforehand, would be suspended in a liquid B<sub>2</sub>O<sub>3</sub> glass. Therefore, the reactant Al<sub>2</sub>O<sub>3</sub> particles were well isolated from each other. Considering that the boiling point is greater than 2300°C, even at the reaction temperature the B<sub>2</sub>O<sub>3</sub> will be vaporized slowly. The Al<sub>2</sub>O<sub>3</sub> particles reacted with the absorbed boron oxide vapor and yielded the aluminum borate nanowires, which grew along the preferential crystalline direction. With the growth of the nanowires, the Al<sub>2</sub>O<sub>3</sub> particles became smaller and smaller until they reacted completely

The growth process is confirmed by our SEM observations. A typical Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub> whisker that has a spherical end tip is shown in Fig. 5. One side has a slightly larger diameter than that of the whisker, implying an original growth site. In addition, the B<sub>2</sub>O<sub>3</sub> flux formed a glass layer to cover the alumina particles in our experiment, preventing them from further absorbing the reaction vapor. Therefore, the whisker growth was incomplete, resulting in a low whisker yield and a short length.

### 3.3. Physicomechanical Properties

Figure (6) shows the densification parameters of the sintered  $\text{Al}_2\text{O}_3$ -CaB6 bodies as a function of firing temperature as well as the amount of CaB6 present. It is evident that the addition of 5 wt.% CaB6 at the expense of alumina improve slightly the densification at 1400 and 1500°C. Bodies containing 10 wt.% CaB6 and fired at 1500°C give the best densification parameters which the highest bulk density ( $2.55 \text{ g/cm}^3$ ) and minimum apparent porosity. On using 10 Wt.% CaB6 and sintered at 1400°C the bulk density slightly decreased down to ( $2.45 \text{ g/cm}^3$ ). The increase of CaB6 content results in gradual decrease of bulk density and increase of apparent porosity. On rising the firing temperature up to 1500°C the rate of deterioration of densification is slightly lower than the bodies sintered at 1400°C. This may be due to the different rate of oxidation and thermomechanical properties taking place due to the increase of CaB6 content as shown in SEM photos.

It has been reported that<sup>(28)</sup> the nature of the shrinkage and densification curves for the titanium diboride alloys with 5, 10, 20, and 30 wt. % CaB6 show that these materials sinter more rapidly than the initial titanium diboride. The composite  $\text{TiB}_2$ -5 Wt. % CaB6 shrinks and densifies substantially more rapidly at lower sintering temperatures than  $\text{TiB}_2$  powder with a higher concentrations of CaB6. In the alloys with 10, 20, and 30 wt. % CaB6, effects occurring at the two-phase boundaries noticeably affect densification and shrinkage.

The presence of calcium in solid solution evidently activates sintering; the highly active boron atoms that appear in  $\text{TiB}_2$ -CaB6 materials upon reaction of the components also activate sintering. Rapid shrinkage is observed at the very beginning of sintering (15, 30 min); the porosity changes from 50 to -20%. Hence, it can be said that upon reaction of  $\text{TiB}_2$  with CaB6 and subsequent sintering, CaB6 dissolves or redistributes to the grain boundaries of the matrix phase, and accelerates the process of volume or grain boundary diffusion at 1500°C.

Table (2) summarizes the mechanical properties of  $\text{Al}_2\text{O}_3$ -CaB6 composites bodies containing 5-15 wt.% CaB6 after being sintered at 1400 and 1500°C. The mechanical properties expressed as bending strength and elastic modulus are also plotted in Fig. (7) as a function of CaB6 content and firing temperature. It is evident that bending strength and modulus of elasticity of 10 and 15 wt.% CaB6 containing composites are generally less than those of 5 wt.% CaB6 containing composites, regardless the sintering temperature. Increasing the CaB6 as well as increasing the firing temperature from 1400 to 1500°C leads to deterioration of the mechanical properties. However, bodies containing 5 wt. %CaB6 show relatively higher bending strength and higher modulus of elasticity at 1400°C these may be due to the low densification and increasing their porosity. The obtained results were in agreement with those of SEM of these composites Fig. (4 B, D and F).

It was found that individual alumina samples showed better mechanical properties than their composites<sup>(29)</sup>. In general, these results from the defects generated from the internal stresses associated with the incorporation of CaB6. Due to the difference between the thermal expansion coefficient (CTE) of alumina matrix and CaB6 of lower CTE causes a radial compressive stresses and circumferential tensile stresses in the matrix. It was reported that<sup>(15)</sup> the fracture surface of the CaB6 composites resulted from the difference of thermal expansion coefficients (CTE) between the oxide layer and substrate. It was reported that for  $\text{Al}_2\text{O}_3$ /SiC ceramic composites if the particle size of SiC exceeds that of

the matrix, the stress distribution may result in deteriorous radial microcrack formation upon cooling. This leads to decreasing the modulus of elasticity and strength of Al<sub>2</sub>O<sub>3</sub>/SiC composites. By increasing the SiC volume fraction the influence of these stresses on the strength predominates, so that further decrease in strength occurs<sup>(29)</sup>.

## 7. Conclusion:

In conclusion, the single crystalline aluminium borate whiskers with the diameter about 7–17 and 38 nm (Al<sub>4</sub>B<sub>2</sub>O<sub>9</sub> and Al<sub>18</sub>B<sub>4</sub>O<sub>33</sub>) were fabricated by the coprecipitation process followed by sintering at different temperatures. From XRD and SEM results, it is found that the whiskers are polycrystalline solid with slightly uniform diameter. The growth mechanism of the nanowires might be self-catalytic mechanism. The results indicate that whiskers exhibit a well-crystallized structure with an average diameter distribution about 500 nm and lengths ranging from 5 to 8 μm. Porous aluminum borate ceramic consisted of whiskers with a porosity of 9 – 21% for samples sintered up to 1400°C. Increasing the sintering temperature up to 1500°C and CaB<sub>6</sub> addition (15wt.%) deteriorated both the flexural strength and modulus of elasticity of the ceramic bodies

Considering the simplicity of the procedure, the method described here is likely to be of interest to commercial-scale production in order to find application in metal reinforcing materials.

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