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Effect of B_2O_3 Addition on the Sintering of α-Al_2O_3

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Abstract: Boron-containing alumina materials in the Al_2O_3–B_2O_3 binary phase system have attracted special attention recently due to the stable, whisker-like crystalline compound aluminum borate ($9Al_2O_3.2B_2O_3$). Hence in this study, the effect of the addition of B_2O_3 up to 1·5 wt% on the sintering characteristics of α-Al_2O_3 has been investigated in the sintering temperature range of 1450–1650°C. The effect of B_2O_3 addition on the bulk density and porosity, on the mechanical properties and on the microstructure of α-Al_2O_3 have been elucidated. The formation and the stability of the aluminum borate phase was also investigated in the range of sintering temperatures studied.

1 INTRODUCTION

High boron-containing alumina materials in the Al_2O_3–B_2O_3 binary system have attracted special attention in recent years due to the stable crystalline compound aluminum borate ($9Al_2O_3.2B_2O_3$ or $Al_{18}B_4O_{33}$). The compound has an orthorhombic crystalline structure and a density of $2{\cdot}93 \times 10^3$ kg/m^3. When it is synthesized from the end members of the binary system by the conventional ceramic processing technique, a porous material of a low bulk density having whisker-like grain morphology is obtained. Furthermore, the compound $Al_{18}B_4O_{33}$ has a high melting point ~1950°C at which it melts incongruently and it is quite stable in oxidizing environments up to 1700°C. Such properties along with easy and cheap processing means make this material a potential candidate for metal–ceramic and for ceramic–ceramic composites as ceramic preforms. It has also been proposed that the aluminum borates containing 8–25 wt% B_2O_3 have a potential use as a catalyst for high-temperature chemical conversions, particularly for exhaust-gas conversions.[1,2]

Readey[2] has synthesized the compound $Al_{18}B_4O_{33}$ from boric-acid-stabilized aluminum acetate at 1000°C, in a whisker-like grain morphology. He reported that the size of the whiskers increased dramatically on sintering to 1500–1700°C, achieving a length of 20 μm and a diameter of 2–3 μm. He found that the four-point bend strength of the sintered material fell with the sintering temperature from 50 MPa at 1500°C to about 25 MPa at 1700°C.

2 EXPERIMENTAL

Alpha Al_2O_3 (A16, Alcoa Industrial Chemical, Bauxite, AR) slips containing 30% alumina by volume and calculated amounts of boric acid to yield 0, 0·5, 1·0, 1·5 wt% B_2O_3 were prepared by mechanical mixing in distilled water, at pH 2 using HCl as the pH controlling acid. The slips were spray-dried in a Niro Atomizer (Mobile Minor, Denmark) using ϕ~1 mm nipple at 100°C nipple and ~250°C chamber temperatures.

Bar-shaped specimens (50 mm in length, ~5 × 5 mm cross-section) were preformed for the three-point flexure strength test by die-pressing the granules obtained from spray-drying. Then pressing was carried out in a floating die assembly at a pressure of 100 MPa. The preformed samples were then isostatically cold pressed to 350 MPa for better compaction. The samples were sintered at 1450,

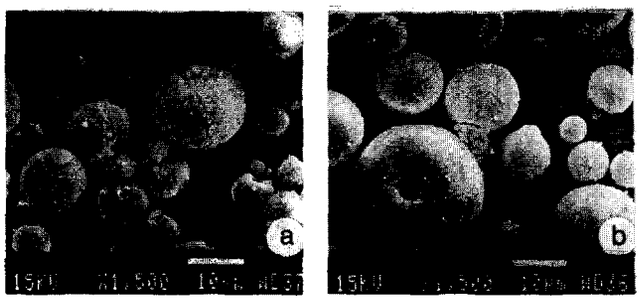

Fig. 1. SEM micrographs of spray-dried granules. (a) Alcoa alumina, (b) 1·5 wt% B_2O_3 added alumina.

1550, 1650°C for 1 h in air, using 10°C/min heating and cooling rates.

The green densities of the pressed samples were calculated from the weight and volume measurements. The bulk density and open porosity of the sintered samples were determined according to the Archimedes' method (ASTM C 373-72). The microstructure examinations were carried out by SEM (JEOL 840). The X-ray diffraction and thermal analysis were carried out in a Philips diffractometer (PW-1050) and Netzsch STA-429, respectively. The three-point strength testing was done in a universal testing machine (model 1115, Instron Corp. Canton MA) using a rig with 5-mm support diameter, 25-mm support height and a span of 25 mm between the supports. A machine crosshead speed of 0·5 mm/min was employed in the strength testing.

3 RESULTS AND DISCUSSION

3.1 Formation of the phases

The SEM study of the powders obtained from spray-drying showed spherical granular formations in all samples. The pure alumina granules had the finest size distribution in the range of 2–10 μm (Fig. 1(a)). The samples with boric acid gave larger size granules (5–30 μm) and they had sharper definition in their spherical shapes (Fig. 1(b)). The variation in boric acid content did not affect the size distribution. This indicated that the boric acid acted as a binder. This was also supported by the excellent compaction behaviour observed in the powders during the die-pressing operation. Most of the granules also had a single dimple formation on the surfaces which is usually referred to as 'doughnut-like morphology' in spray-drying technology.

The X-ray diffraction study, using CuK_α radiation, of the sintered samples revealed the presence of the aluminum borate ($Al_{18}B_4O_{33}$) phase along with the main phase of α-Al_2O_3 in the B_2O_3-containing samples. The borate phase was easily detected even at the lowest B_2O_3 concentration. The most intense diffraction peak for this phase occurred at 2θ=16·25 degrees, indicating the $d_{(120)}$=5·37 A planes. As expected, the intensity of this peak was affected by the B_2O_3 content and not by the variations of the sintering temperatures

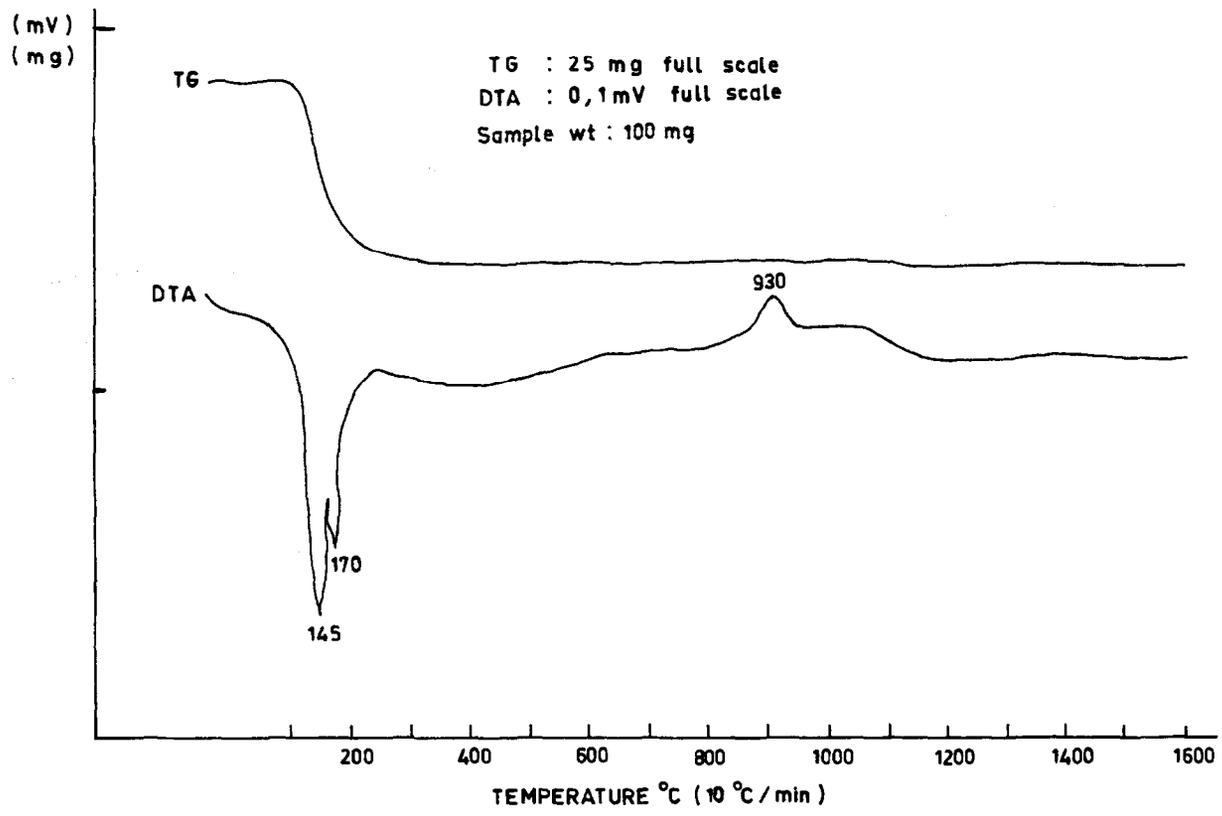

Fig. 2. DTA/TG analysis of 15·16 wt% B_2O_3 added alumina.

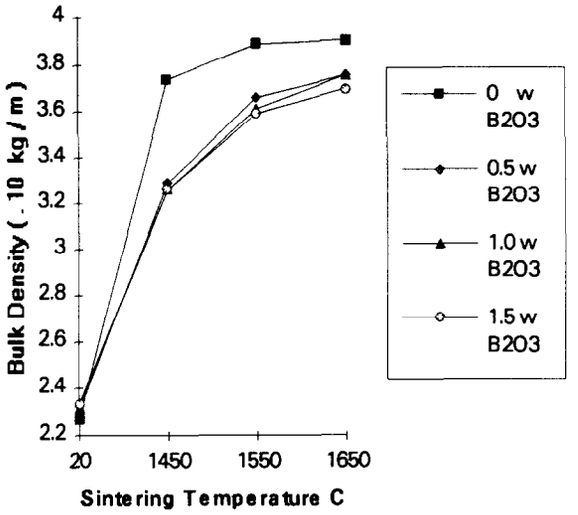

Fig. 3. Variation of bulk density with temperature.

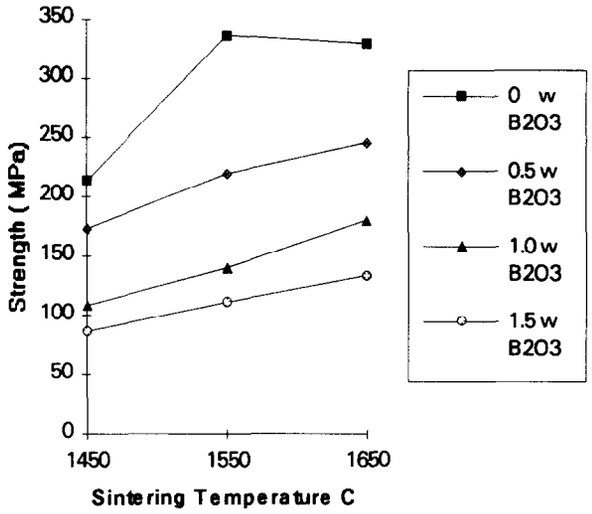

Fig. 4. Variation of strength with temperature.

which indicated that the formation of the aluminum borate phase had been completed at a lower temperature than employed in this study.

In order to investigate this point, simultaneous differential thermal analysis (DTA) and thermal gravemetric analysis (TG) were carried out on the highest B_2O_3 (1·5 wt%) sample which revealed a very slight exothermic reaction around 900°C. To elucidate this point further, a sample was specially prepared having a 15·16 wt% B_2O_3 addition in order to yield a stoichiometric aluminum borate phase. The DTA/TG analysis of this sample (Fig. 2) showed double endothermic peaks at 145 and 170°C due to the dehydroxylation of the boric acid and a broad exothermic reaction between 780 and 960°C with a peak temperature of 930°C. This result is similar to the findings of Marono,[3] who also observed two-stage dehydroxylation below 200°C and an exothermic peak between 700 and 800°C in his DTA study of boric acid for which he used α-Al_2O_3 in 1 : 4 proportion as a sample dilution reference material. He attributed the exothermic peak observed either to the reaction of B_2O_3 with the alumina or to the reaction of B_2O_3 with the quartz crucible he used, but not to the formation of the aluminum borate phase.

In a study of the preparation and the characterization of aluminum borate, Ray[1] proposed two-stage reactions for the formation of the $Al_{18}B_4O_{33}$ phase. He showed that no reaction took place between B_2O_3 and alumina below 800°C. Between 800 and 900°C, he observed the formation of the $2Al_2O_3.B_2O_3$ phase which above 900°C reacted gradually with excess alumina to form the $Al_{18}B_4O_{33}$ phase. The reaction was found to be complete at 1100°C. The broad exothermic peak observed in the DTA curve between 780 and 960°C supports Ray's findings. Also, from the SEM microstructure studies, it is believed that the formation of the $Al_{18}B_4O_{33}$ phase is completed before 1000°C and the fibrous-like grain growth occurs between 1000 and 1100°C resulting in a complete fibrous microstructure typical of this phase. Furthermore, TG analysis carried out up to 1600°C both in the 1·5 wt% and 15·16 wt% B_2O_3 samples did not reveal any loss of B_2O_3 from the composition which also supports Readey's findings that the aluminum borate phase is stable up to 1700°C. This is contrary to the dissociation temperature quoted as 1400°C in the earlier studies.[4–6]

3.2 Physical properties of the sintered samples

The physical properties of the sintered samples (bulk density, open porosity, three-point flexural strength) are given in Table 1 below and shown graphically in Figs 3 and 4. When sintering the

Table 1. Physical properties of the sintered samples

Sintering temperature (°C)	B_2O_3 (wt%)	Bulk density[a,b] ($\times 10^3$ kg/m^3)	Open porosity (%)	Three-point flexural strength[b]
1450	0	3·74	1·47	213
	0·5	3·29	12·33	173
	1·0	3·26	16·28	108
	1·5	3·26	17·30	87
1550	0	3·89	0·9	336
	0·5	3·66	6·10	219
	1·0	3·61	6·17	140
	1·5	3·59	7·14	111
1650	0	3·91	0·01	330
	0·5	3·76	1·33	245
	1·0	3·71	1·37	180
	1·5	3·70	1·69	133

[a]Green densities of samples varied between 2·27 and 2·33 $\times$ 10^3 kg/m^3, ~57% theoretical density.
[b]Standard deviation was less than 2% in bulk density and less than 10% in strength measurements.

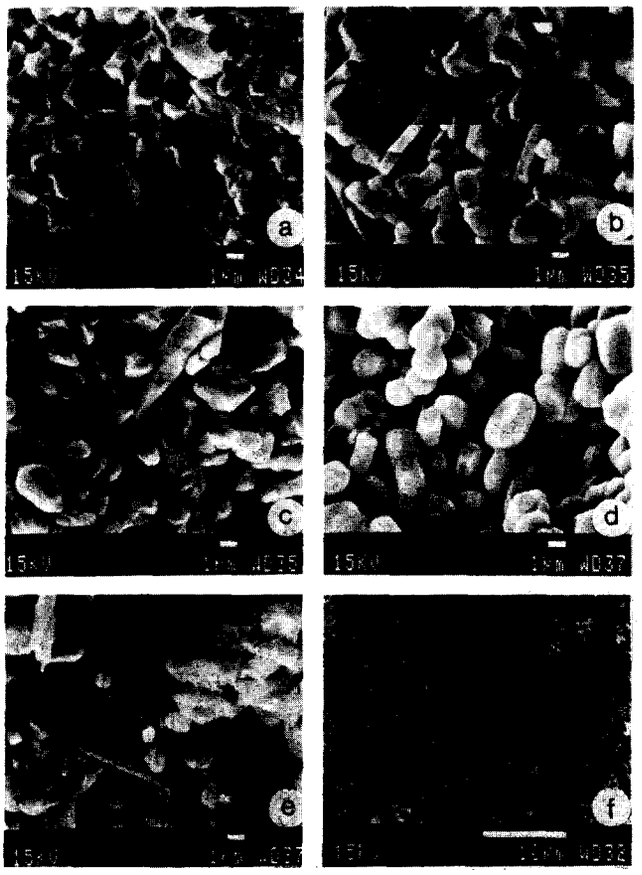

Fig. 5. SEM micrographs of the fracture surfaces of (a) pure alumina, (b) 0·5 wt%, (c) 1·0 wt%, (d),(e) 1·5 wt% B_2O_3 added alumina sintered at 1550°C and (f) 15·16 wt% B_2O_3 added alumina sintered at 1100°C.

Alcoa A16 alumina at 1450°C, 94% theoretical density is achieved giving a strength value of 213 MPa. Increasing the sintering temperature to 1550°C, resulted in 97·5% densification, giving a fine and uniform-grained microstructure and an optimum strength value of 336 MPa (Figs 3–5(a)). Although a further rise in sintering temperature to 1650°C increased the densification to 98% of the theoretical value, a slight lowering in strength to 330 MPa was observed due to grain growth.

The addition of B_2O_3 to Alcoa alumina has a pronounced effect in lowering the bulk density which, in turn, results in porous microstructures and lowers the strength values of the sintered samples (Figs 3–5(b)). An addition of B_2O_3 between 0·5 and 1·5 wt% results in a narrow spread in the bulk density values, whereas it shows a much more marked difference in strength at the same sintering temperature. The higher the B_2O_3 content, the lower the strength. It should be noted that an increase in sintering temperature results in a more pronounced rise in the bulk density than in strength. These results can be explained by the formation of the aluminum borate phase which has chemical and physical properties incompatible to that of the α-Al_2O_3 matrix. These properties are the lack of solid solubility between the two phases, the low theoretical density ($2{\cdot}93 \times 10^3$ kg/m^3) of the aluminum borate phase which results in a volume expansion during its formation and the low strength value of this phase compared to that of the α-Al_2O_3 (according to Readey, 50 MPa for the 1500°C-sintered samples in a four-point bend testing).

In Figs 5(a)–(f), a series of SEM micrographs of the fracture surfaces are shown for the samples sintered at 1500°C for 1 h. As stated above, the pure alumina sintered at this temperature gives small and uniform-grained microstructure with an average grain size of 5 μm (Fig. 5(a)). When 0·5 wt% B_2O_3 is added, the alumina grains lose their sharp definitions and a discontinuous grain growth is observed within the microstructure. This addition level, which corresponds to the presence of 3·3% of the aluminum borate phase within the matrix, gives rise to a porous microstructure due to the volume expansion of this phase during its formation. This phase is randomly distributed within the α-Al_2O_3 matrix as small ($\leq$ 0·5 μm) rounded grains (Fig. 5(b)). In increasing the B_2O_3 addition to 1 wt% level, the discontinuous grain growth in α-Al_2O_3 becomes more pronounced and the aluminum borate phase is easily recognized by its round shapes (Fig. 5(c)). The B_2O_3 addition level of 1·5 wt%, which corresponds to ~10 wt% of the aluminum borate phase, results in the formation of clustered areas of this phase within the matrix, along with areas having again the areas of the discontinuously grown α-Al_2O_3 grains (Fig. 5(d)). The tendency of the aluminum borate grains to grow into fibrous shapes can be observed within clustered areas. The occurrence of such clustered areas in the high-boron-containing sample indicates chemical inhomogeneties within the sample. This probably results from the migration of the water-soluble boric acid to the surface of the granules during the spray-drying process, which results in boron-rich surface layers. This also explains the sharp definitions obtained in the spherical shapes of the boric-acid-containing granules and their easy compaction behaviour during the die-pressing operation. The micrograph given in Fig. 5(f) shows the fully developed fibrous form of the aluminum borate phase in the 15·16 wt% B_2O_3 addition level at 1100°C.

The results show that the Al_2O_3–$Al_{18}B_4O_{33}$ portion of the Al_2O_3–B_2O_3 binary phase system offers the possibility of production of an interesting ceramic–ceramic composite material that might have potential use as ceramic filters and as ceramic preforms for ceramic–metal composites.

4 CONCLUSIONS

The spray-drying technique gives good results in the preparation of uniform-sized alumina granules from alumina slip having boric acid as the B_2O_3 additive. The boric acid also acts as a binder both for the granulation and for the die-pressing process. The formation of the aluminum borate phase is found to be complete at 1000°C and the fibrous microstructure which is characteristic of this phase is developed between 1000 and 1100°C. The addition of B_2O_3 between 0·5 and 1·5 wt% to alumina results in a discontinuous grain growth in the sintered samples. The incompatible characteristics of the aluminum borate phase to those of the α-Al_2O_3 result in a porous microstructure which in turn reduces the strength of the sintered material. The porosity level can be controlled by the B_2O_3 addition levels. The porous structure and reasonable strength values make the material a potential candidate to be used as ceramic filters and for ceramic–metal composite preforms.

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