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Monohydroxy Aluminium Oxide (Boehmite, AlOOH) as a Reactive Binder for Extrusion of Alumina Ceramics

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Abstract

Monohydroxy aluminium oxide (Boehmite, AlOOH) has been used as an extrusion aid along with α-alumina and γ-alumina particulates. Extended ball milling of the mixture using alumina grinding media imparts nucleating seeds to boehmite for an early conversion to α-alumina. The boehmite–γ-alumina mixture appears to result in a denser alumina ceramic accompanied by an enhanced grain growth indicating the higher reactivity at higher temperatures compared to the boehmite–α-alumina system. The reason for this novel behaviour is probably the coating of nanosize boehmite containing nucleating sites on the porous γ-alumina powders resulting in enhanced diffusion reactions. The present study therefore provides scope for low temperature alumina ceramics using boehmite binder along with partly dehydroxylated aluminium hydroxide. © 1997 Elsevier Science Limited.

1 Introduction

Usually binders are employed in the shaping of ceramic materials because of their non-plastic nature. Of the various fabrication processes, extrusion of ceramic–binder mixture has attractions in view of the possibility for continuous processing.[1] Conventional binders are generally organic in origin,[2,3] but recent reports highlight inorganic binders in view of their advantages of fewer binder burnout problems and lower carbon residues.[4] Hydroxy metal oxides produced in the sol–gel method have shown binder characteristics with additional advantages.[5] Monohydroxy aluminium

oxide (Boehmite, AlOOH) was used as an extrusion aid successfully in extrusion of α-alumina.[6,7] The boehmite also is converted to α-alumina above 1100°C. Boehmite has also been reported in applications such as the casting of Al_2O_3 substrates[8] and as intercalants in pillared smectites.[9] The γ-to-α-alumina conversion is a slow process and sometimes leads to porous vermicular network and α-alumina seeds are added to boehmite in order to aid the early conversion[10] and densification. The seed nuclei and their interaction with the transition alumina phase have been widely studied.[11–13] α-Alumina seed nuclei are either introduced as calcined α-alumina fine particles (~0·2 μm) or by extended ball milling of the boehmite in presence of sintered alumina balls.[14] However, use of α-alumina seeds with a mixture of γ-alumina and boehmite for extrusion has not been reported, although the nucleation and growth could be more effective in such systems compared to that containing α-alumina.

Hence, an attempt is made in this work to use boehmite as an extrusion aid for α-alumina and to compare with a mixture of partially dehydroxylated boehmite, rich in γ-alumina phase. The extruded samples were dried and sintered to high densities and characterised. Further, cylindrical samples of diameter 8 mm were made by die compaction and processed in parallel for a comparison with extrusion process.

2 Experimental

The boehmite was prepared by controlled precipitation from aluminium nitrate by ammonium hydroxide as reported earlier.[15] Further characterisation was done by thermogravimetric analysis (TGA-50h, Shimadzu, Japan) and differential
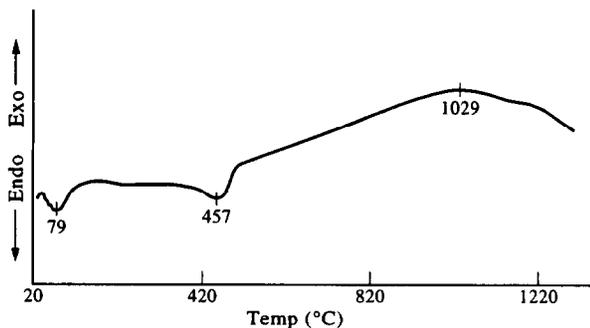
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Fig. 1. Differential thermal analysis curve of boehmite.

Fig. 3. XRD patterns of (a) alumina-A, (b) alumina-G.

thermal analysis (DTA-50h, Shimadzu, Japan) techniques. One batch of boehmite (200 g) was calcined at 1250°C for 5 h (termed as alumina-A). Another batch of boehmite (200 g) was calcined at 400°C for 5 h (termed as alumina-G). Both powders were ball milled in separate PVC containers in propan-2-ol medium with alumina grinding balls for 48 h. Powder was collected and dried at 90 ± 5°C for 24 h in a hot air oven. Both the powders were characterised for surface area (Gemini 2360, Micromeritics, USA), XRD (Rigaku, D/Max 2C, Japan, Nickel filtered Cu K_α radiation) and tap density (Densitometer, India).

Torque rheology of boehmite–alumina-A was carried out in a Brabender Plastograph (Brabender, Germany). The slurries containing 14 wt% boehmite and the A and G alumina powders were then ball milled separately for 50 h using alumina grinding balls in a PVC container, then transferred to a beaker with stirring and flocculated at pH 8·5 by slow dropwise addition of dilute ammonia. The flocculated mass was dried at 80°C to an extrudable consistency and extrusion was carried out in a laboratory scale plunger type hand extruder to 8 mm diameter rods.

All the samples were dried in a humidity-controlled oven (REMI, Environmental Testing Chamber, India) at 65% RH and 45°C for 24 h.

Alumina A and G powders were uniaxially pressed at ~200 MPa to 8-mm diameter pellets in order to compare with the extruded samples.
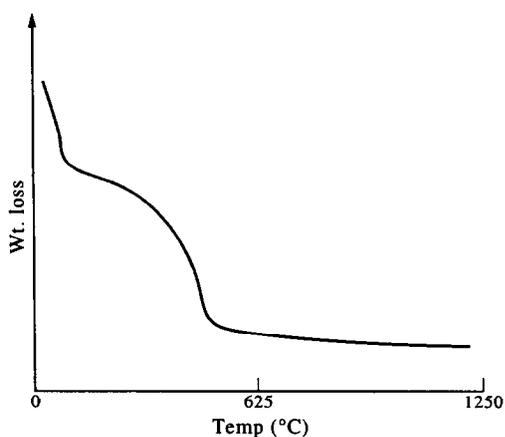
Green densities were calculated by mass–volume method. Thermomechanical analysis of both extruded samples was carried out (TMA-50h, Shimadzu, Japan). Samples were sintered at 1650°C with a soaking of 2 h. Shrinkage parameters and sintered densities were calculated. Sintered microstructures were observed on fractured samples using a scanning electron microscope (S-2400, Hitachi, Japan).

3 Results and Discussion

3.1 Boehmite and the alumina powders

Figure 1 shows the DTA curve for the boehmite used throughout this experiment. The initial endotherm at less than 100°C is due to the evolution of free water in the boehmite. The endotherm at 456·9°C indicates the formation of γ-alumina and the exotherm at 1028·6°C represents transformation to α-alumina. This lowering of the transition temperature may be due to the nucleation effects of the long ball milling. The broad exotherm in the range 500–1000°C is indicative of the formation of various transition alumina phases before conversion to α-alumina. Thermogravimetric analysis of the boehmite binder is presented in Fig. 2. The initial weight loss corresponds to loss of absorbed water. About 80% of the weight loss takes place at below 500°C and the remaining by ~700°C. Thus there are two major steps in the weight loss curve extended up to about 500°C. However, the weight loss takes place over a wide range and hence a comparatively faster debinding schedule can be tolerated for extruded samples. The higher temperature phase formation indicated for α-alumina in DTA at ~1030 is without any weight loss as seen from Fig. 2. Since the binder as such is being converted into α-alumina, which forms part of the ceramic matrix, no contamination including that of carbon usually found in conventional binders, is imported which is a unique advantage. Figure 3
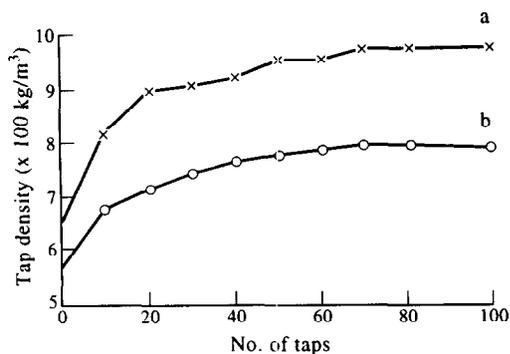

Fig. 2. Thermogravimetric curve of boehmite.

Fig. 4. Tap density curve of (a) alumina-A, (b) alumina-G.

Fig. 6. Compaction response on sintering of (a) alumina-A, (b) alumina-G.

shows the XRD patterns of alumina-G and alumina-A. Alumina-A calcined at 1250°C is fully converted to α-alumina phase whereas alumina-G is still in the dehydroxylated form. BET surface area measurements showed that alumina-A has $11 \cdot 143$ m^2 g^{-1} and alumina-G has $200 \cdot 34$ m^2 g^{-1}, indicating the extremely high surface activity in the case of the latter. Tap densities of both the powders are presented in Fig. 4. The low-temperature alumina is a well-known catalyst material with high porosity and hence possesses poor tap density. Compaction density of alumina-A is higher compared to alumina-G as seen from Fig. 5. Further the compaction density increases linearly with application of pressure. Sintered densities of these powder compacts at 1650°C for 2 h are presented in Fig. 6. Alumina-G showed comparatively higher sintered densities than alumina-A, probably due to the higher surface reactivity. The sintered density indicates a sudden upward jump beyond the compaction pressure of 300 MPa, indicating the break-up of powder agglomerates. There should be the added advantage of introduction of extremely fine seed nucleii into the mixture from the long ball milling in presence of α-alumina grinding media.[14]

3.2 Boehmite–alumina mixture for extrusion

The blending of the boehmite–alumina mixtures was carried out at low pH in the beginning and later condensed by flocculation at pH 7, because
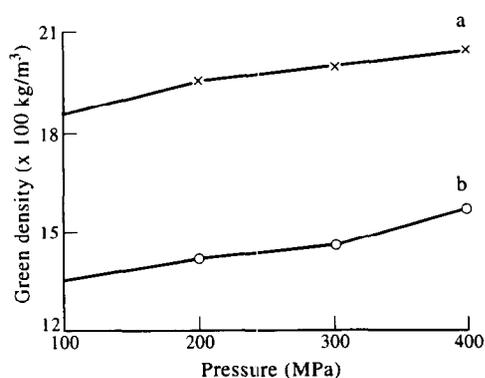
the sol at low pH (3–4) is most effective for blending with alumina and the subsequent gelation of the extrusion mixture will impart sufficient viscosity. There was no remarkable difference observed between the two alumina samples in the preparation of the precursors for extrusion.

3.3 Torque rheology of boehmite–alumina mixture

Figure 7 shows the weight percentage of ceramic loading against torque developed for alumina-A and boehmite at pH ~8·5. Above ~86 wt% of ceramic loading, the torque has a sharp increase (>15 N m) and therefore this value was selected as the critical powder volume concentration (CPVC).[16] The torque behaviour was similar for alumina-G also and hence the CPVC has been fixed at 86 wt%.

3.4 Debinding and sintering

The binder burn-out procedure was derived by comparing the DTA and TGA of boehmite (Figs 1 and 2) and TGA of alumina-G (Fig. 8). The thermogravimetric curve for alumina-A did not show any specific change in the temperature range up to 1100°C as expected. The heating schedule was selected to have a slow rate up to 700°C. Debinding and sintering were conducted in a single schedule as shown below:
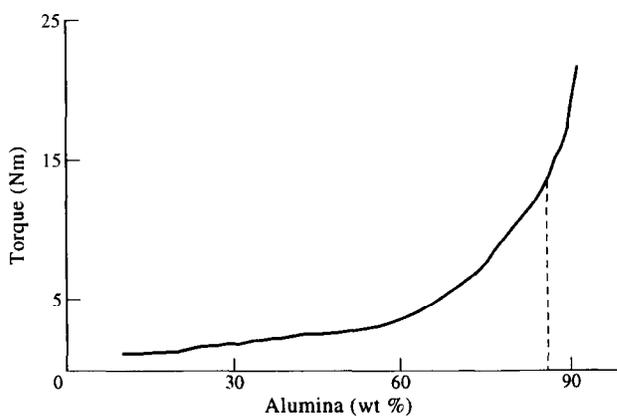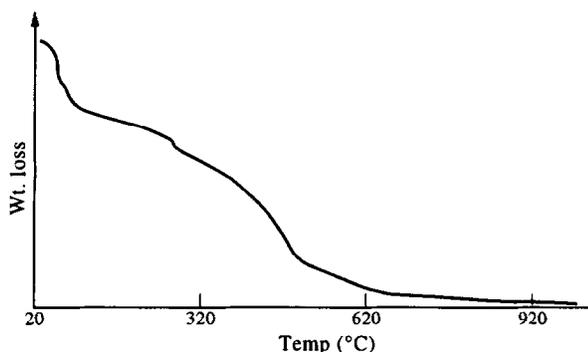

Fig. 5. Compaction response diagram of (a) alumina-A, (b) alumina-G.

Fig. 7. Torque versus ceramic loading curve.

Fig. 8. Thermogravimetric curve of alumina-G.

$$\text{RT} \to 300^\circ\text{C}(2^\circ/\text{min}) \to 700^\circ\text{C}(5^\circ/\text{min}) \to$$
$$1650^\circ\text{C} \ (10^\circ/\text{min}) \ 2 \ \text{h}$$

The TMA corresponding to extruded alumina-A (Fig. 9) has a very small shrinkage near 460°C indicating the initial decomposition of the boehmite binder, in line with the phase change in DTA and also the weight loss in the TGA. However, in the case of alumina-G (Fig. 10), the shrinkage is quite appreciable.

The TMA of alumina-A shows a small shrinkage at about 1050°C corresponding to the DTA of boehmite. Sintering is indicated at 1425°C. On the other hand, the composition containing alumina-G has an appreciable shrinkage around 1050°C (Fig. 10) and further shrinkage as early as 1200°C. This indicates the enhanced reactivity of the binder phase with alumina-G. Precalcined boehmite thus appears to be a better candidate for extrusion along with boehmite. Boehmite appears to catalyse the transformation reaction in precalcined gel. On the other hand, in the case of α-alumina, boehmite should be acting only as an inorganic extrusion aid, since the transformation had already taken place. The boehmite therefore could not only be a binder for alumina, but also enhance sintering in the case of calcined boehmite.

Sintering of the uniaxially pressed (200 MPa) samples was also carried out under identical conditions. Densities and volumetric shrinkages of the
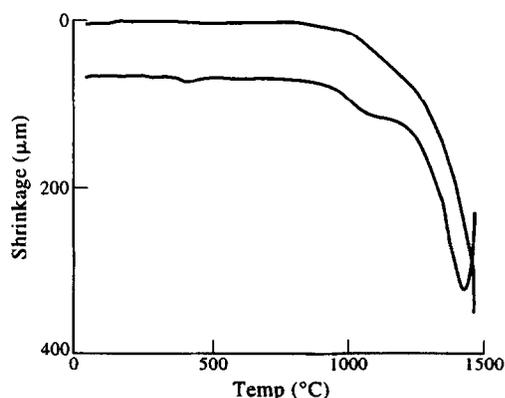

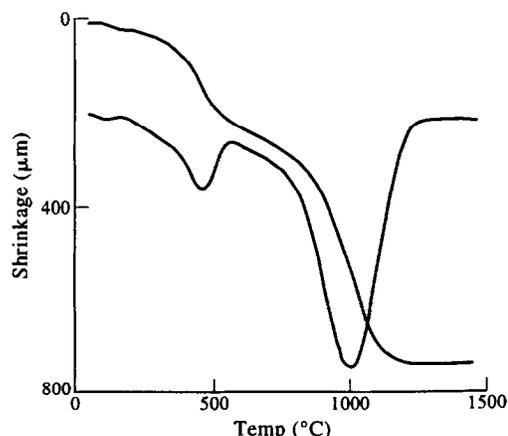Fig. 9. Thermomechanical curve of extruded alumina-A.

Fig. 10. Thermomechanical curve of extruded alumina-G.

various sintered samples are presented in Table 1. Extruded alumina-G has the highest density (98·9%) whereas extruded A has 96%. Uniaxially pressed samples of alumina-G and alumina-A achieved 94 and 92% densities, respectively.

3.5 Microstructural features

The fractographs (Figs 11(a) and (b)), correspond to those of sintered alumina-G and alumina-A. The alumina-G has a higher density with occasional intragranular pores. The average grain size is also large. The grain size distribution appears to be more uniform in the extruded sample compared to the pressed counterpart. The boehmite + alumina-G mixture after extrusion and sintering at 1650°C indicates a very uniform grain size and distribution, having an average less than 10 μm, with sufficiently large intragranular pores and much smaller ones at the grain boundary [Fig. 11(c)]. This fractograph clearly indicates the optimum condition of fabrication and sintering, but the sintering temperatures employed in this case are still higher. This composition should have sintered into a compact at much lower temperatures. The behaviour of alumina-A is quite different in that there is inhomogeneous grain growth varying from >10 μm to as small as 3–4 μm ([Fig. 11(d)]. Most of the pores are in the range less than 1 μm. Hence it appears that the seed nuclei introduced during the ball milling of the gel precursor are compatible with sintering of aluminium oxide.

Table 1. Physical properties of sintered samples

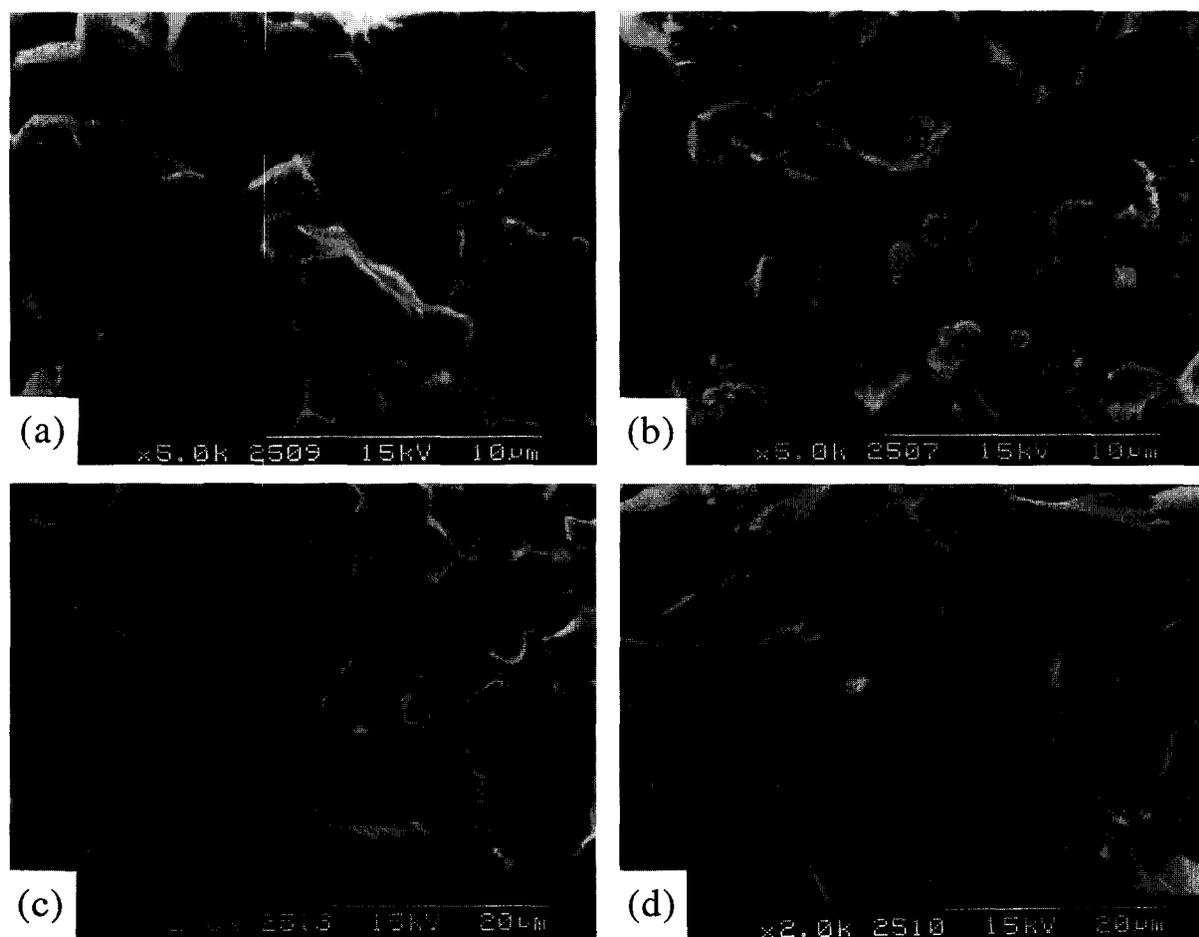| Sample	Method of shaping	Green density (kg m^{-3})	Sintered density (kg m^{-3})	Volumetric shrinkage (%)
Alumina-A	Extruded	2300	3800	46·0
	Pressed	1960	3670	45·2
Alumina-G	Extruded	1600	3930	68·8
	Pressed	1580	3741	68·0

Fig. 11. SEM of the fracture surfaces of (a) alumina-G (uniaxially pressed), (b) alumina-A (uniaxially pressed), (c) boehmite + alumina-G (extruded), (d) boehmite + alumina-A (extruded).

The extrusion procedure is very convenient for fabrication and γ-alumina could be a better source of alumina. The reason for the low temperature densification of γ-alumina could be due to the availability of sufficient nucleation sites developed through extended periods of grinding.

4 Conclusions

Sintered alumina ceramic has been made using boehmite as an extrusion aid and along with two types of alumina powders. The long ball milling in presence of the alumina grinding media introduced sufficient nucleation sites, thus promoting an earlier densification. Between the two forms of alumina, it has been seen that the alumina-G, which is rich in γ-alumina, undergoes much faster densification, but grain growth and intragranular pores occur, due to its enhanced activity. The boehmite binder could hold up to ~86% (by wt) of the alumina powder at the point of critical powder volume concentration. Individual powders made by compaction and sintering at the same temperature showed less tendency for sintering. This study not only highlights the possibility of

boehmite as an inorganic carrier, but also the fact that γ-alumina could be a better source for alumina, when long milling time using alumina grinding media are used.

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