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Ceramics International 33 (2007) 401–404

CERAMICS INTERNATIONAL

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Properties of Al_2O_3 ceramics consolidated with sulfanilic acid

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Received 29 July 2005; received in revised form 5 September 2005; accepted 29 September 2005
Available online 18 January 2006

Abstract

Al_2O_3 ceramics were prepared through colloidal processing and consolidation process. Initially, Al_2O_3 powder was dispersed in aqueous medium to make 60 vol% suspensions with 1.5 wt% dispersant. After mixing to obtain well-dispersed slurries, a minor amount of sulfanilic acid was added and the slurries were consolidated in a nonporous mould. Al_2O_3 green samples exhibited a homogeneous microstructure with uniform distribution in pore size. After sintering at 1600 °C in air, the microstructure, hardness and toughness were characterized. Toughness as high as 6.40 MPa m$^{1/2}$ was obtained for Al_2O_3 samples with sulfanic acid/Al_2O_3 mass ratio as 5.74 mg/g. Results showed that it was possible to consolidated Al_2O_3 slurries with homogeneous microstructure and high mechanical properties.
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Keywords: D. Al_2O_3; Consolidation; Microstructure; Toughness

1. Introduction

Colloidal processing has been proved to be a practical technique for preparing complex-shaped ceramic parts in term of cost and reliability [1–3]. One of the advantages of colloidal processing is the ability to form ceramic parts with optimal particle packing and homogeneous green microstructures. In recent years, wet processing routes (such as temperature induced coagulation casting (TICC), direct coagulation casting (DCC), slip casting, gel casting, etc.) [4–17], have been extensive studied to forming ceramic green bodies with promising properties [18,19]. However, the consolidation process for these casting techniques is relatively complex [20–22].

In this paper, a simple consolidation method is used to prepare Al_2O_3 green samples. The consolidation process is reported in a previous paper [23]. After consolidation, the resultant sample properties are studied.

2. Experiments

Commercial Al_2O_3 (Sumitomo Chemical Co., Ltd., AKP20, d50 = 0.5 μm) powder was used as starting materials. Sodium polyacrylic acid (PAA-Na, Aldrich Chemical Company Inc. MW ~30,000) was selected as dispersant and 4-aminobenzene sulphonic acid (sulfanilic acid) as consolidation agent. 38 wt% sulfanilic acid solution was prepared for subsequent using with the solution pH adjusted around 7 using $HN_3{\cdot}H_2O$ (Analytical, Osaka Kishida Chemicals, Japan).

60 vol% Al_2O_3 suspensions were prepared in the presence of 1.5 wt% of the dispersant. The suspensions were mixed for 24 h in an Al_2O_3 medium to allow the adsorption of dispersant on Al_2O_3 particle surface. Subsequently, the slurries were poured out into a beak and sulfanilic solutions were added with the mass ratio of sulfanilic acid to alumina powder varied from 0:100 to 1:100. The slurries were mixed quickly in vacuum for removing trapped gas before pouring into moulds for consolidation. The drying of the slurries was conducted in air at room temperature without special care.

Apparent viscosity of Al_2O_3 suspensions under different shear rate was examined under steady shear conditions by ascending and descending shear rate ramps respectively using a viscosity meter (DV-E, Brookfield Engineering Laboratories

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doi:10.1016/j.ceramint.2005.09.023

Inc.). After drying, the porosity was characterized by mercury porosimetry (PoreSizer 9320, Micromeritics). The microstructure of the fracture surface of dried cakes was observed by SEM. After binder removal process, the samples were sintered at 1600 °C for 1 h in air atmosphere. The microstructure of the as-sintered specimens was investigated by SEM. Hardness (HV30) and indentation fracture toughness (K_{IC}) were determined by a Vickers diamond indenter with a 296 N load.

3. Results and discussions

3.1. The consolidation process and the green cake properties

The dispersion behavior of Al_2O_3 slurries using PAA as dispersant is well documented in literature [24–28]. Based on our previous study, Al_2O_3 slurries with high solid content up to 64 vol% can be prepared. However, it is difficult to measure the slurry viscosity at high solid content. In this study, 55 vol% Al_2O_3 slurries were prepared for properties characterization (the dispersant content was 1.5 wt%). As shown in Fig. 1, the slurry viscosity was kept at low level in the shear rate range investigated, indicating that Al_2O_3 particles were in well-stabilized state. This well dispersed Al_2O_3 slurry is prerequisite for the consolidation process.

In this paper, 60 vol% Al_2O_3 slurries were prepared for consolidation. The consolidation process was reported in another paper [23]. After consolidation and drying, the green density of Al_2O_3 suspensions was characterized (see Fig. 2). It is interesting that the green density of Al_2O_3 samples increased initially to a maximum and decreased thereafter. This may suggest that sulfanilic acid act as dispersant at very low concentration, differing from traditional polymer flocculants [25]. This dispersing effect may come from the adsorption of sulfanilic acid molecules on Al_2O_3 surface using $–SO_3H$ as anchoring groups, similar to the adsorption of sodium dodecyl sulfate (SDS) [29]. At low sulfanilic acid content (sulfanilic acid and Al_2O_3 mass ratio <2 mg/g), this adsorption may enhance the stability of Al_2O_3 particles and lead to a well compaction of green samples. With the increase in sulfanilic acid content (sulfanilic acid and Al_2O_3 mass ratio >2 mg/g), more sulfanilic acid will be adsorbed on Al_2O_3 particles surface, so the competing adsorption between sulfanilic acid and PAA-Na become significant. At the same time, the possibility of acid-basic interaction between the dissociated free carboxylic acid groups (COO^-) of PAA-Na and the free $–NH_3^+$ groups of sulfanilic acid molecules will also increase. These interactions might lead to the formation of flocculations due to the bridging or charge neutralization mechanism [26,30,31], which has been evidenced in the previous study [23]. In this region, sulfanilic acid act mainly as a flocculant, and a decrease in green density is resulted (see Fig. 2).

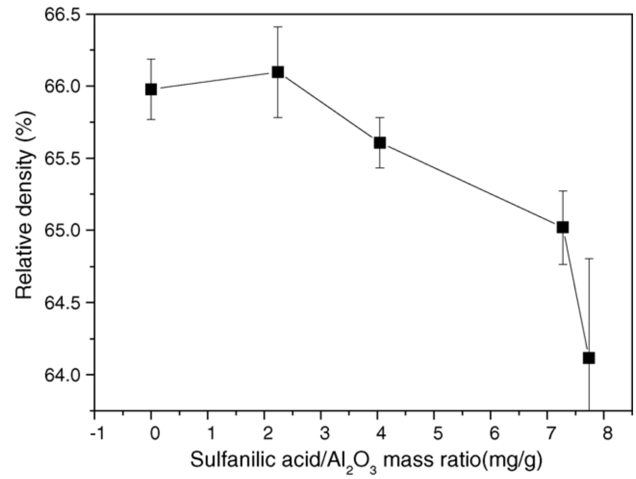

Fig. 2. Influence of sulfanilic acid content on the green density of Al_2O_3 samples.

However, at low sulfanilic acid content (the sulfanilic acid and Al_2O_3 mass ratio $<$ 4 mg/g), though the green density is higher, the Al_2O_3 slurries were more fluidable and could not be practically consolidated. The sulfanic acid started to take effect at the sulfanilic acid and Al_2O_3 mass ratio of about 4 mg/g, where the green density has already decreased. In the following study, the mass ratio between sulfanilic acid and Al_2O_3 is selected in the 4–7 mg/g range, in which the consolidation process could occur effectively without sacrificing much the green density.

The as-consolidated Al_2O_3 samples (the sulfanilic acid/Al_2O_3 ratio is 5.0 mg/g) were characterized by SEM and Hg porosimetry (see Figs. 3 and 4). Al_2O_3 green samples exhibited

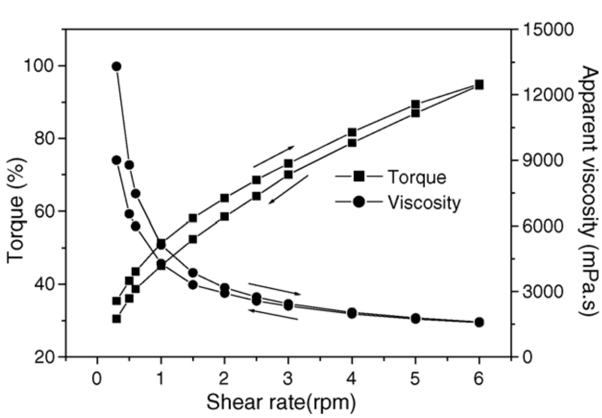

Fig. 1. Properties of 55 vol% Al_2O_3 suspensions.

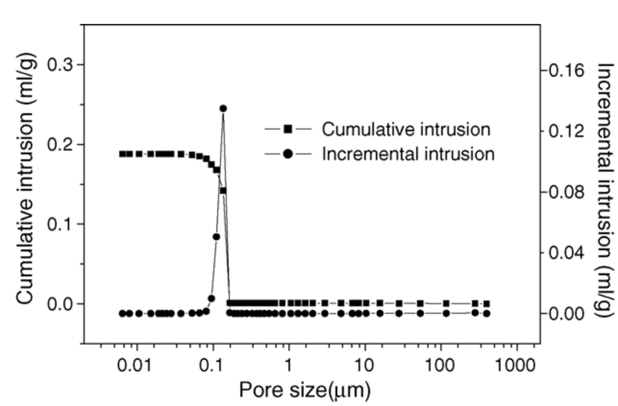

Fig. 3. Pore size distribution of green Al_2O_3 samples (the sulfanilic acid/Al_2O_3 ratio is 5.0 mg/g).

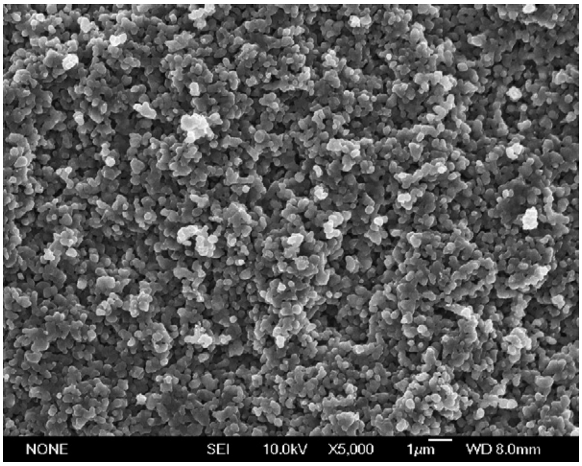

Fig. 4. Microstructure of green Al_2O_3 samples (the sulfanilic acid/Al_2O_3 ratio is 5.0 mg/g).

a uniform distribution in pore size. The relative density, porosity and the median pore diameter of green samples were 65.30%, 34.12% and 0.1256 μm, respectively (see Table 1). This results indicate that the consolidated Al_2O_3 samples were homogeneous. SEM observation also confirmed this result (see Fig. 4).

3.2. Properties of sintered samples

The consolidated Al_2O_3 samples can be easily sintered to high density in air at 1600 °C for 1 h. After sintering, the density, hardness and toughness were tested (see Fig. 5 and Table 1).

Table 1
Properties of green and sintered Al_2O_3 samples

	Green samples	Sintered samples		
Sulfanic acid/Al_2O_3 (mg/g)	5.0	3.64	5.74	7.64
Density (g/cm^3)	2.586	3.85	3.86	3.83
Porosity (%)	34.12	–	–	–
Total pore area (m^2/g)	4.413	–	–	–
Median pore diameter (μm)	0.1256	–	–	–
Relative density (%)	65.30	97.1	97.4	96.7

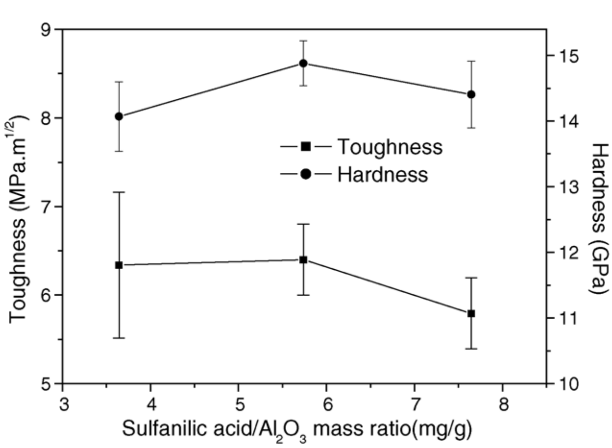

Fig. 5. Hardness and toughness of as-sintered Al_2O_3 samples.

After sintering, all the samples were well densified and no significant difference in density was observed. The linear shrinkage is only between 12% and 13% due to the high green density. A higher toughness and hardness is observed for samples with sulfanilic acid/Al_2O_3 mass ratio as 5.74 mg/g, compared with samples with the said mass ratio as 3.64 and 7.64 mg/g, respectively. At low sulfanilic acid content (sulfanilic acid/Al_2O_3 mass ratio is 3.64 mg/g), though the green density is higher (see Fig. 2), a lower hardness is resulted, which might be due to the low content of sulfanilic acid that are less than required for developing three dimensional network, similar to that in the gel-casting process using less amount of gelatine [7]. As a result, the green samples are not virtually homogeneous and a density gradient might be developed. After sintering, small cracks were observed on the sample surface. The hardness also decreased correspondingly. At higher sulfanilic acid content (sulfanilic acid/Al_2O_3 mass ratio is 7.64 mg/g), due to the low green density (from Fig. 2) and the inhomogeneous microstructure, the decreases in hardness and toughness can be expected. Based on these results, the optimal sulfanilic acid/Al_2O_3 mass ratio was around 5.74 mg/g.

The fracture surfaces of Al_2O_3 samples (with sulfanilic acid/Al_2O_3 mass ratio as 5.74 mg/g) were shown in Fig. 6. After

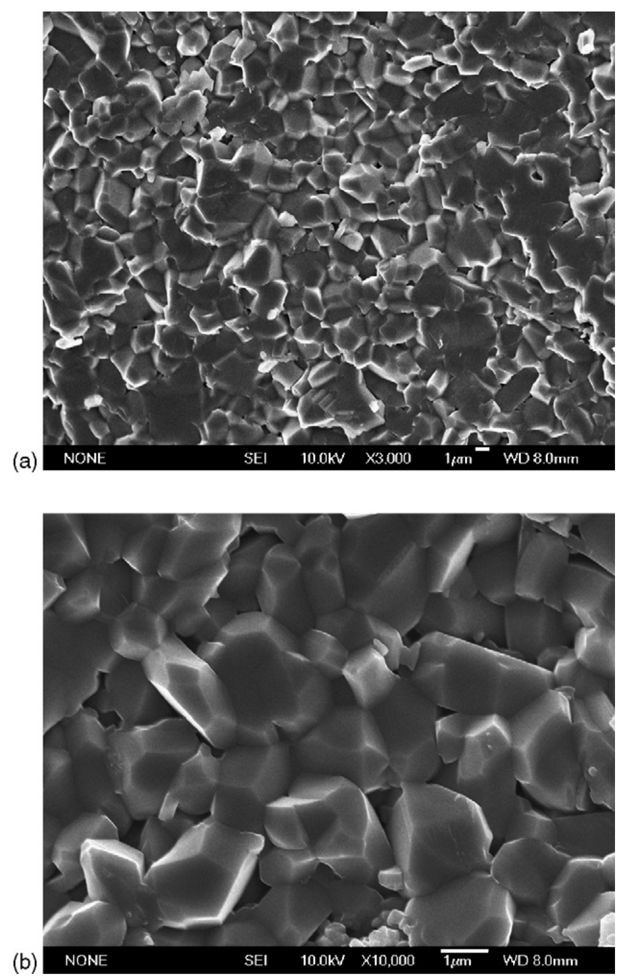

Fig. 6. Microstructure of sintered Al_2O_3 samples (sulfanilic acid/Al_2O_3 mass ratio is 5.74 mg/g). (a) ×3000; (b) ×10,000.

sintering, a homogeneous microstructure is observed. Al_2O_3 grains are equiaxial, with a little increase in grain size. The samples exhibited a mixture of intergranular and intragranular fracture mode, which can be related to the increase in toughness compared to samples formed from dry pressing.

This high toughness of Al_2O_3 samples might result from the wet processing technique. Colloidal processes could help to produce very homogeneous green sheets with limited flaws [19]. For dry pressing, larger defects are inevitably trapped during powder compaction. These defects will inevitably reduce the homogeneity of microstructure and therefore lead to the decrease in toughness.

4. Conclusions

Al_2O_3 ceramics can be prepared through a simple consolidation route using sulfanilic acid as consolidation agent. A homogeneous microstructure was obtained for green samples with the sulfanilic acid/Al_2O_3 mass ratio in 4–7 mg/g range. The relative density and porosity of green samples were 65.30% and 34.12%, respectively (with the sulfanilic acid/ Al_2O_3 mass ratio as 5.0 mg/g). This Al_2O_3 samples can be densified at 1600 °C. The optimal toughness and hardness is 6.40 MPa $m^{1/2}$ and 14.88 GPa respectively for samples with sulfanic acid/Al_2O_3 mass ratio as 5.74 mg/g.

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