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Ceramics International 29 (2003) 869–873

CERAMICS
INTERNATIONAL

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Role of wollastonite additive on density, microstructure and mechanical properties of alumina

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Received 30 April 2002; received in revised form 5 October 2002; accepted 10 December 2002

Abstract

Wollastonite is a low fusing material and has a considerable effect on the densification of alumina bodies at sintering temperatures ranging from 1300 to 1450 °C. The wollastonite acts as a flux and accelerates the liquid forming process leading to lower temperature densification. The addition of 1.0 wt.% wollastonite alters the microstructure to form well-defined grains with an average grain size in the range of 3.0–5.0 μm. The grains are distributed uniformly and the fracture occurs along the grain boundaries and the microstructure reveals the presence of highly dense and sintered grains. The hardness and bend strength for 0–5.0 wt.% wollastonite increases from 8.5 to 14 GPa and from 119 to 249 MPa respectively at a sintering temperature of 1400 °C.

Keywords: A. Sintering; D. Alumina; Wollastonite; Liquid-phase

1. Introduction

Alumina ceramics are extensively used for structural applications due to alumina's high melting point, chemical stability, corrosion resistance and mechanical properties such as hardness and wear resistance at elevated temperatures. Restrictions to the applications of alumina arise due to the problems related to low thermal shock resistance and low fracture toughness. A successful approach for improving the fracture toughness of alumina ceramics includes second phase additions such as zirconia and SiC [1–3], employing bimodal particle size distribution [4,5] and using grain strengthening agents. Another important approach for improving the performance of alumina comprises of controlling the grain size and their uniform distribution throughout the matrix in the final sintered ceramics. These factors primarily lie in the densification kinetics of the starting alumina.

Densification is the outcome of a combination of numerous parameters during processing, which include the powder characteristics [6], process variables [7] and sintering kinetics. The use of fine starting powder [8] without agglomeration in the green preforms [9,10] may improve densification [11]. Regarding the latter, specific additives such as low melting oxides can be used to enhance the sinterability of powder. Such additives can promote liquid-phase formation at lower sintering temperatures and may considerably increase the rate of sintering. During the sintering process, a viscous liquid may promote an additional diffusion mechanism of dissolution/precipitation [12], particle rearrangement and capillary forces and finally may improve the densification [13,14]. For alumina, as an extreme example of the first approach, Yeh and Sacks [15] used colloidal processing with a specially classified ultrafine powder to achieve a sintered density of 99.2% at 1150 °C in 2.0 h. In another approach, a variety of oxides such as Li_2O, Cr_2O_3, Fe_2O_3, ZrO_2 and MgO were employed as additives for alumina ceramics to enhance the sintering and also modify the microstructures, which leads to the improvement in mechanical properties. It has also been reported that the combined use of simple binary compositions and complex compositions lower the sintering temperature of alumina from 1700 down to 1300 °C resulting in duplex, platelike, equiaxed or elongated microstructures [16–19].

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doi:10.1016/S0272-8842(03)00029-4

However, while employing the liquid-phase additives in ceramic processing, the quantity and extent of liquid formation may influence the thermomechanical properties, which give rise to erosive mechanisms and accelerate grain growth [20]. For this reason, it is preferable to use only a small amount of sintering additives to gain the desired effect without compromising the properties.

The simultaneous application of the two approaches: colloidal powder processing and use of sintering aids or additives has been exploited in the present study for alumina ceramics. Specifically, this paper deals with the role of wollastonite additions on sintering, microstructure and mechanical properties of alumina.

2. Experimental procedure

2.1. Starting materials and processing

Boehmite powder was synthesized by introducing aluminium iso-propoxide into hot water under vigorous stirring [21]. The molar ratio of alkoxide to water was kept at 1:100. Hydrolysis was carried out with triple distilled water by stirring for 1.0 h at 80 °C. Then 0.3 mol of nitric acid/mol of alkoxide was added to the slurry to peptize the system to get clear sol. The peptization was carried out under vigorous stirring for 1.0 h at 80 °C. Both hydrolyzation and peptization were performed under reflux conditions resulting in no loss of material. The addition of acid turned the white dispersion into a transparent sol immediately. This clear sol was poured into a Petri dish, dried at 90 °C and subsequently calcined at 1000 °C for 3.0 h.

The starting materials were sol-gel derived alumina powder derived by calcination at 1000 °C and commercially available wollastonite (Stochem Inc., Mexico). Alumina suspensions containing 0.5–5.0 wt.% of wollastonite were milled in a planetary mill for 1.0 h in aqueous medium in polyurethane bowl and alumina balls; 2.0 wt.% of 60:40 vol.% polyvinyl alcohol (PVA) and polyethylene glycol (PEG) in water were added as binding agents. The mixture was dried and sieved through 200 mesh to obtain soft granules, which were then pressed into pellets of 10 mm dia and rectangular bars ($60\times5.0\times5.0$ mm) using a uniaxial press at a pressure of 100 MPa. The pressed samples were pre-heated to 100 °C for 12 h. The density of the dried samples was about 58% of theoretical density (T.D). A similar procedure was adopted for preparing alumina compacts without PVA/PEG binding agent, to examine the effect of agglomeration of the starting powder. No difference was found in the behaviour of the alumina samples fabricated by the two different routes. The particle size distribution of the powder was determined using a laser diffraction particle size analyzer (Shimadzu SALD 1100, Germany). Sodium hexa-metaphosphate (0.2 wt.%) dissolved in distilled water was used as the dispersing agent, and 0.5 g of powder was dispersed in this solution which was then ultrasonicated for 10 s before measurements were made. The compacts were sintered at various sintering temperatures. Sintered specimen densities were determined by Archimedes' method using water as the immersion medium and the average value of five samples was reported.

2.2. Sintering conditions

The compacts were sintered under isothermal conditions in an electrically-heated quench-type furnace with $MoSi_2$ elements. The temperature was monitored and controlled by a controller with Pt-Rh thermocouples in an atmosphere of static air.

The green compacts were heat treated at a rate of 2 °C/min up to 600 °C and then the heating rate was changed into 5 °C/min till their maximum sintering temperature reached. Then the compacts were soaked for 2.0 h at that sintering temperature. The sintered compacts were cooled to room temperature at a cooling rate of 5 °C/min.

2.3. Microscopy

For microstructural studies, the sintered specimen were mounted in an epoxy resin, ground on silicon carbide paper, down to 1200 grade and polished using diamond paste down to 0.25 μm. Standard ultrasonic bath cleaning was used between each grinding and polishing stage. After the final polishing, they were removed from the resin and specimens were washed in soapy water, rinsed with fresh water and ethanol and then dried. Chemical etching was performed with mixtures of 0.8 N orthophosphoric acid and 0.5 N nitric acid in the volume ratio of 3.0:1.0. The polished surfaces were soaked in the acid mixture for a period of 2.0–3.0 min and again washed, rinsed, dried and examined under optical microscope (Leica, UK).

The etching temperature was below $<70\%$ of the original sintering temperature and the thermal etching time was 10 min and it was found that there was no significant grain growth during the etching time.

Microstructure and fracture surface analysis was characterized by SEM (Leica-Stereoscan 440, UK) and the average grain size were determined from the micrographs using the linear intercept method. Bend strength was measured by three-point bending test (Zwick UTM, Z-7005, Zwick GmbH, Germany) at room temperature. The span length was 30 mm and the crosshead speed was 0.1 mm/min (between 5 and 13, bars were broken for each composition). Hardness was measured (Zwick 3212, Zwick GmbH, Germany) on the polished surface by Vicker's indentation method (at least 10 measurements were made on samples of each composition).

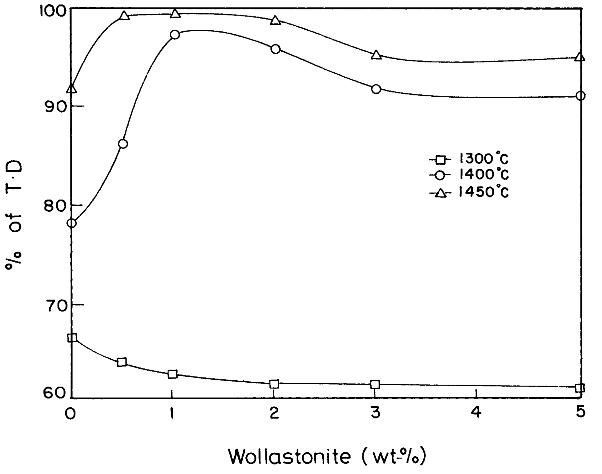

Fig. 1. Dependence of sintered density of alumina on wollastonite content for various sintering temperatures.

3. Results and discussion

3.1. Sintering studies

Fig. 1 shows the density studies of alumina containing wollastonite at various sintering temperatures ranging from 1300 to 1450 °C. The smaller addition of wollastonite in the concentration range of around 1.0 wt.% favours the sintering of alumina whereas further increment of the additive concentration results in decreasing sintered density. The addition of 1.0 wt.% wollastonite enhances the sintering density to near T.D at a sintering temperature of 1400 °C; but for 5.0 wt.% wollastonite, the sintered density decreases to 92% of T.D. This may be due to the higher glassy phase formation [22] and the presence of crystalline phases such as calcium hexa aluminate (CA_6), anorthite (CAS_2) or gehlenite (C_2AS) [22].

The sintering mechanism is governed by generation of a liquid phase. Wollastonite has a melting point of 1125 °C. This lower melting point of the additive produces a liquid-phase, which uniformly spreads among the alumina particles. This ultimately helps in the rearrangement of alumina particles and accelerates the diffusion process at about 1400 °C and hence increases the density to a maximum value.

3.2. Microstructure analysis

Fig. 2 shows the powder morphology of wollastonite and it shows needle-like morphology with an average length and thickness of 15 and 2 μm respectively. Fig. 3a and b shows the microstructure and fracture surface of 0.5 wt.% addition of wollastonite to alumina. It shows large distributions of open pores and voids due to incomplete densification. The average grain size is about 2.0–3.0 μm. There are also small grains distributed locally within the matrix. The addition of 1.0 wt.% wollastonite shows well-defined grains with an average grain size in the order of 3.0–5.0 μm (Fig. 3c). The grains are distributed uniformly and intergranular fracture occurs along the grain boundaries. The microstructure reveals the presence of highly dense and sintered grains. When the amount of wollastonite is increased to 5.0 wt.%, formation of excess liquid-phase is observed. The microstructure shows excess grain growth and the precipitation of second phases along the grain boundaries (Fig. 3d and e). The grain size is about 5.0–8.0 μm.

Fig. 2. Powder morphology of wollastonite powder.

3.3. Mechanical properties

Table 1 shows the Vicker's hardness and three point bend strength of alumina sintered at 1400 °C. The hardness and bend strength increase with increasing additive concentration. For 0–5.0 wt.% addition of wollastonite it increases from 8.5 to 13.6 GPa and from 119 to 249 MPa respectively.

4. Conclusion

The relatively low doping levels of wollastonite as additive (1.0 wt.%) helps to attain 98% of T.D. and form a uniform grain structure at the lowest sintering

Table 1
Vicker's hardness and bend strength for wollastonite doped alumina

Additive concentration (wt.%)	Sintered at 1400 °C			
	Hardness (GPa) (for 2.0 kg load)		Bend strength (MPa)	
	x[a]	s[b]	x[a]	s[b]
0	8.5	0.2	119	26
0.5	10.0	0.4	199	19
1.0	11.3	0.3	231	17
5.0	13.6	0.1	249	21

[a] Mean value.
[b] Standard deviation.

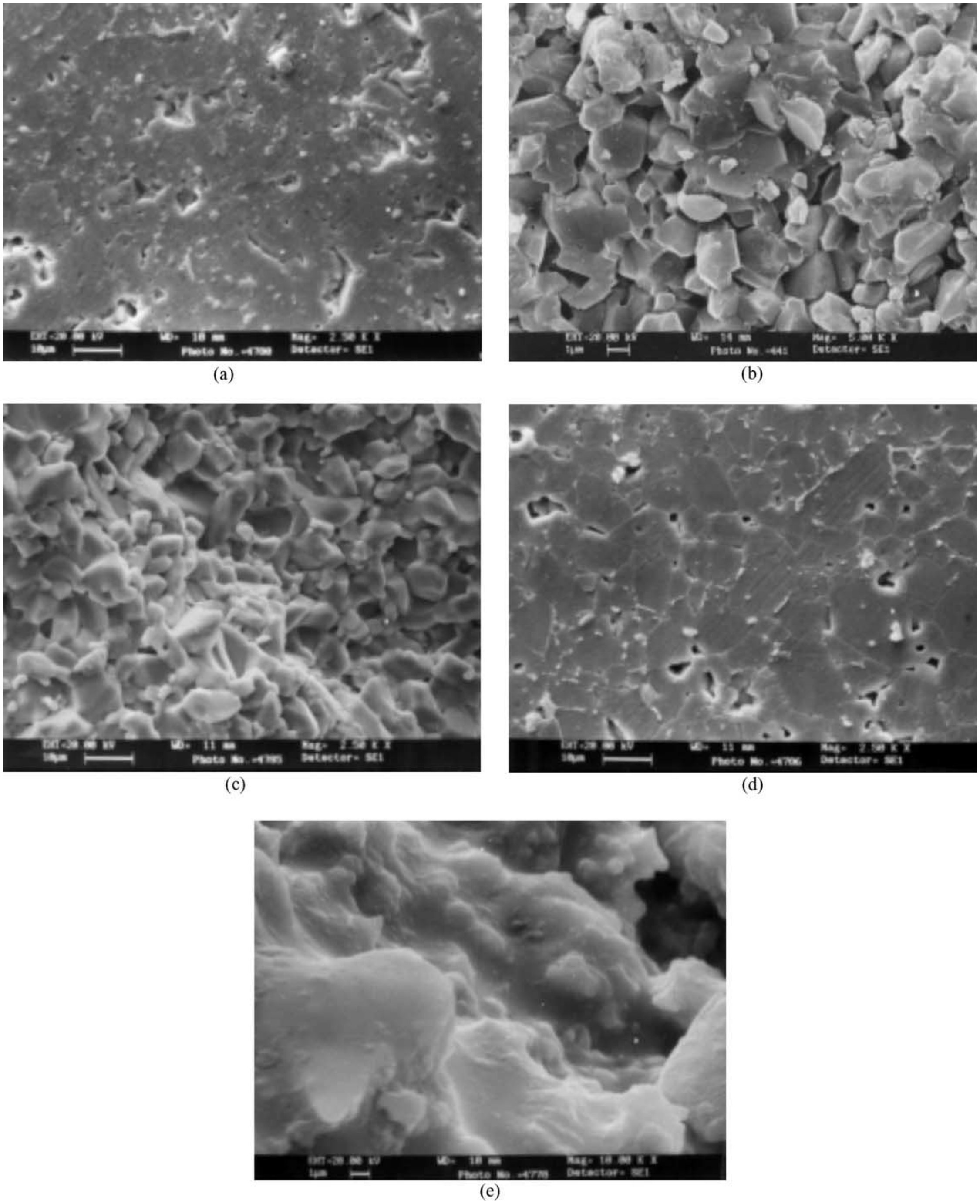
(a) (b) (c) (d) (e)

Fig. 3. Microstructure of alumina sintered at 1400 °C. (a) polished section of 0.5 wt.% of wollastonite, (b) fracture surface of "a", (c) fracture surface of 1.0 wt.%, (d) polished section of 5.0 wt.% of wollastonite, (e) fracture surface of "d".

temperature. Further increment of wollastonite additive reduces the T.D. due to the higher glassy phase formation in the grain boundary. The hardness and bend strength for 0–5.0 wt.% wollastonite increases from 8.5 to 14 GPa and from 119 to 249 MPa respectively at a sintering temperature of 1400 °C.

Acknowledgements

The author thanks CSIR (Council of Scientific and Industrial Research, Government of India), New Delhi, India for providing financial assistance to carry out the work.

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