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Effect of strontia on the densification and mechanical properties of sol–gel alumina

K. Vishista [*], F.D. Gnanam

Department of Ceramic Technology, Anna University, Chennai 600025, India

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Abstract

Boehmite sol was prepared by hot water hydrolysis of aluminum *iso*-propoxide using nitric acid as the catalyst. Hydrolysis was carried out at 80 °C for 80 min. Calcium nitrate was added and the peptization was complete at 80 °C for 1 h. The sol was precipitated in ammonia, the precipitate was aged for 24 h, dried at 120 °C and calcined at 500 °C for 3 h. The calcined powder was milled at 230 rpm for 6 h. The amount of calcium oxide was varied from 1 to 20 vol.%. The particle size and particle size distribution of the calcined powders were studied. The average particle size was found to increase with calcia content. The powder was compacted into cylindrical pellets using uni-axial press at 180 MPa and sintered at 1600 °C for 6 h. Mechanical properties such as hardness, fracture toughness, diametrical tensile strength and flexural strength for compacts containing various concentrations of strontium oxide was studied. There was a slight decrease in the density with increase in strontia content. Increase in the mechanical properties such as hardness, fracture toughness and diametrical tensile strength was observed with increase in strontia content.

Keywords: C. Hardness; C. Mechanical properties; C. Toughness; C. Toughening; D. Al_2O_3; Strontia

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1. Introduction

The mechanical properties of alumina ceramics depend on the microstructural properties such as grain growth and grain size distribution [1]. These microstructural properties can be controlled by reinforcement through incorporating second phases that contain dispersed particulates. The influence of grain growth on the alumina matrix is dependent on the amount and variety of additive as well as the presence or absence of liquid phase during sintering [2]. Addition of metal as a bonding phase, long fibre or particulate dispersed into ceramics, improves the mechanical properties especially the fracture toughness of the alumina ceramics [3,4]. Platelike grains are produced by the addition of silica and calcia. The sintering properties of alumina by the addition of Cr_2O_3, TiO_2, MnO_2, Co_3O_4, NiO and Nb_2O_5 have been studied [5]. The size of platelike grain in the sintered bodies is important, where toughened ceramics are manufactured. Composites with second phase additions such as whiskers, fibres and platelets are difficult to sinter to high density without hot pressing or hot iso-static pressing [6]. The applications are limited because of the expensive processing routes for these composites. Alumina ceramic composites formed through the sol–gel route with particles or whiskers as reinforcement exhibit fine grained microstructure which leads to high mechanical properties combined with chemical stability [7]. This in situ reacted microstructure has attracted much attention in recent years, mainly due to the mechanical properties of the ceramics that are significantly improved by forming in situ elongate grains. The in situ reacted microstructure of silicon nitride is due to its anisotropic crystal structure [8]. Since the crystal structure of alumina is also anisotropic, it is possible to form large platelets in alumina by applying this in situ-reaction techniques.

Kaysser et al. [9] have demonstrated that the liquid phase of ($CaO\cdot Al_2O_3\cdot 2SiO_2$) anorthite induces grains to grow anisotropically, which is the primary cause of abnormal

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[*] Corresponding author.
E-mail address: vishista@yahoo.com (K. Vishista).

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grain growth. Bateman et al. [10] have demonstrated that alumina containing small amounts of silicate based amorphous grains develops incipient abnormal grains. Handwerker et al. [11] have observed abnormal grain growth in microstructural regions containing high calcium and silicon concentrations. Song and Coble [12] have observed the formation of platelike abnormal grains in alumina containing large amount of liquid forming dopants including silica. Presence of impurities such as sodium, potassium in alumina also promotes grain growth. Introduction of small amount of liquid forming elements such as TiO_2 in $BaTiO_3$ and Bi_2O_3 in ZnO have been considered as the primary cause of abnormal grain growth. Exaggerated grain growth have been observed in Fe doped alumina processed by the in situ technique.

Tsukma and Takahata [13] added a small amount of La_2O_3 to 2Y-TZP/Al_2O_3 to form $LaAl_{11}O_{18}$ platelets. The resultant composite had higher fracture toughness and higher strength at high temperatures as compared to the base 2Y-TZP/Al_2O_3. Cutler et al. [14] used SrO as the additive in forming in situ platelets of $SrAl_{12}O_{19}$ in Ce-TZP to obtain an attractive combination of high levels of strength, toughness and hardness. Chen and Chen [15] have reported the benefits and limitations of in situ-formed aluminate platelets. The platelike morphology of strontium hexaluminate is supposed to increase the mechanical properties of alumina ceramics. Hence this paper deals with the study of the effect of strontia on the densification and mechanical properties of sol–gel alumina.

2. Experimental

Boehmite sol was prepared by hot water hydrolysis of aluminium *iso*-propoxide using nitric acid as the catalyst. Hydrolysis was carried out using double distilled water by stirring for 1 h at 80 °C. Then 0.3 mol of nitric acid/mol of alkoxide was added as the peptizing agent. The peptization was carried out with vigorous stirring for 1 h at 80 °C. Then strontium nitrate was added. Both hydrolysis and peptization were performed under reflux conditions resulting in no loss of the material. Boehmite sol with additives obtained was precipitated in ammonia, aged overnight, vaccum filtered, oven dried at 120 °C for 2 days and calcined at 500 °C for 3 h. The calcined powder was ground in a planetary mill at 230 rpm for 6 h. The amount of strontium oxide was varied from 1 to 20 vol.%. The particle size analysis was performed using Laser particle size analyzer. The powder was compacted into cylindrical pellets using uni-axial press at 180 MPa and sintered at temperatures ranging from 1400–1600 °C for 6 h. The density measurements were carried out using Archimedes method. The pellets were mirror polished using different grades of silicon carbide sheets. The Vickers hardness and fracture toughness were measured using Zwick 3212 hardness tester and the diametrical tensile strength was carried out using the Universal Testing Machine Zwick 1445 model.

3. Results and discussion

3.1. Density studies

Fig. 1 shows the density as a function of sintering temperature for all the four concentrations of strontia. The sintering temperature was varied from 1400 to 1600 °C. The density is found to increase with the increase in the sintering temperature. However, there is a slight decrease in density with increase in strontia content. The slight decrease in the sintered density is due to the formation of strontium hexaluminate plate like grains. Since the pores are trapped within or between the large grains further densification is hindered and hence the decrease in density. Similar densification is reported for calcia by Goswami et al. [16].

When the additive concentration is within the solubility limit, the homogeneous mixing accelerates the densification by diffusion phenomena. Considering the relationship between the Al^{3+} and Sr^{2+}, in the alumina lattice position is the most possible solid mechanism. The majority of the pores remained located at the grain boundaries. Pore boundary separation did occur, but not always within the large abnormal grains.

The strontia added to alumina shows a uniform microstructure of highly homogeneous distribution. The additive shows very fine equiaxed and elongated grains. Large elongated grains are the main features of the microstructure. Fig. 2 shows the optical micrograph of alumina—15 vol.% strontia composites sintered at 1600 °C/3 h.

Polished cross sections viewed under SEM shows an increasing tendency to form plate-shaped grains with increasing SrO additions. This suggests that strontium hexa-aluminate (hexagonal $SrO{\cdot}6Al_2O_3$) density of 3.95 gm/cm^3 is formed in situ during sintering, as would be expected based on phase equilibria between SrO and Al_2O_3. Microstructure shows that the strontium aluminate grains are platelets. The $SrAl_{12}O_{19}$ platelets, which are formed inside are approximately 0.5 μm in thickness and 5–

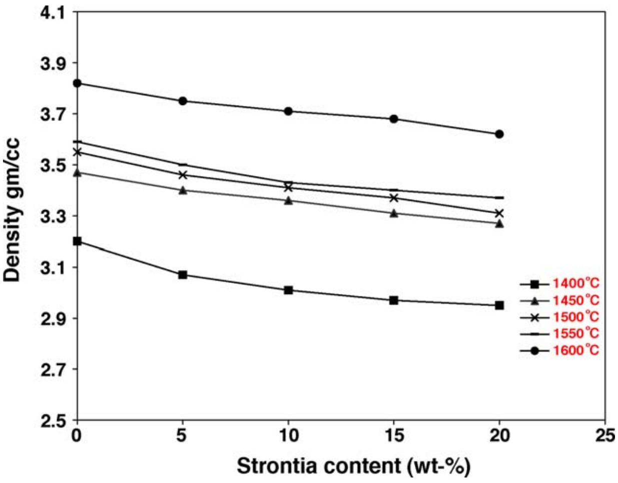

Fig. 1. Dependence of density on concentration of strontia.

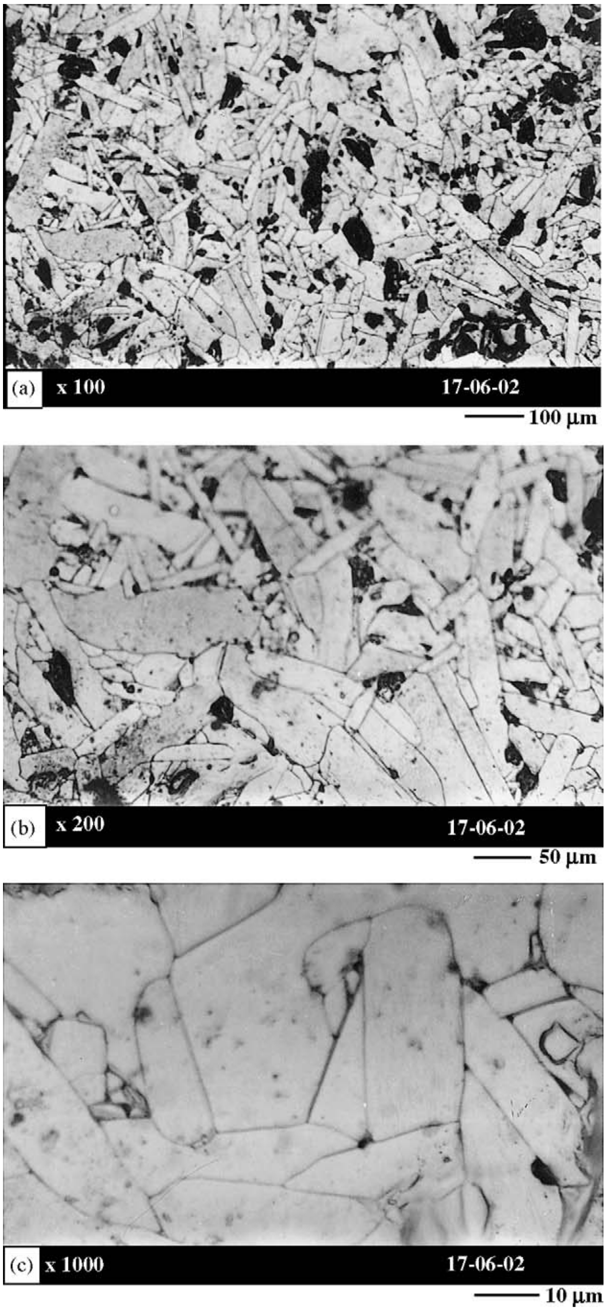

Fig. 2. Optical micrograph (a–c) of alumina-15 vol.% strontia composites sintered at 1600 °C/3 h.

10 µm in length and width. When SrO present in alumina is sintered to a higher temperature, the formation of an excessive liquid phase is observed. During soaking, the evaporation of SrO may take place which forms isolated pores and wrinkles.

3.2. Mechanical properties

3.2.1. Hardness

The highly concentrated stress field at the tip of the intender induces plastic deformation even in macroscopically brittle materials. The analysis of the permanent indent gives the measure of the hardness. Fig. 3(a) shows the dependence of hardness on strontia content for varying loads. The load was varied from 1 to 5 kg. This test was performed for the samples sintered at 1600 °C/6 h. A decrease in hardness with increase in load was observed. Fig. 3(b) shows the dependence of hardness on SrO content for different sintering temperatures. The indentation load was kept constant at 0.5 kg and indentation time was 15 s. The hardness values of strontium hexaluminates are not reported in the literature but are considered to be lower than that of pure alumina [17].

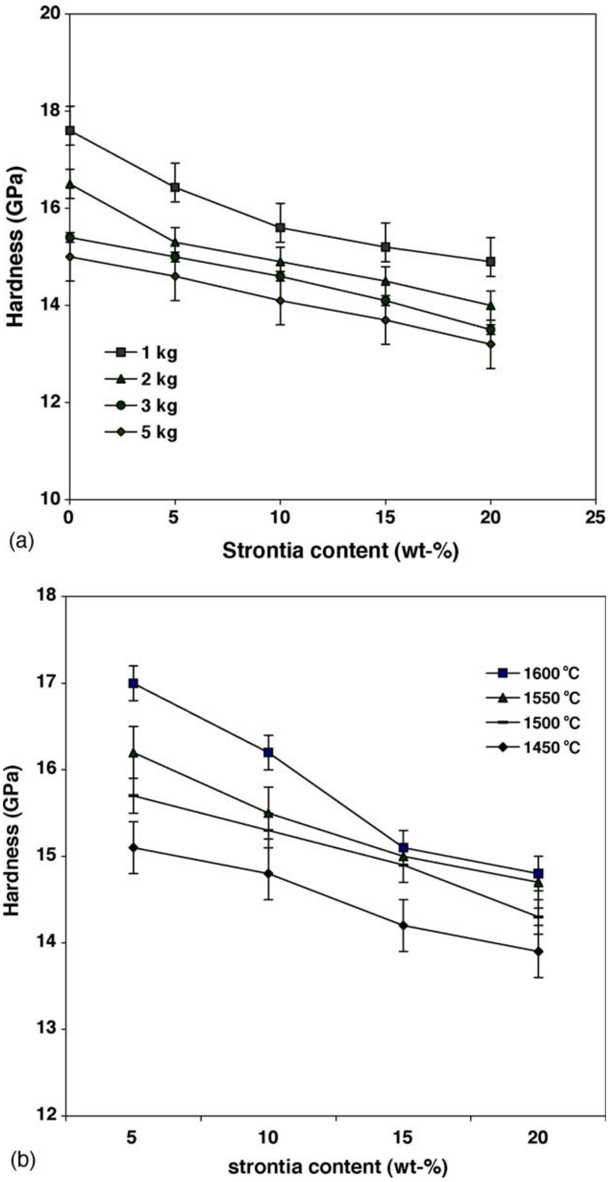

Fig. 3. (a) Dependence of Hardness on concentration of strontia for sintering temperature of 1600 °C/6 h. (b) Dependence of hardness on strontia content for different sintering temperatures at constant load of 0.5 kg.

3.2.2. Fracture toughness

The fracture toughness was measured by indentation fracture technique using a diamond intender. The measure of

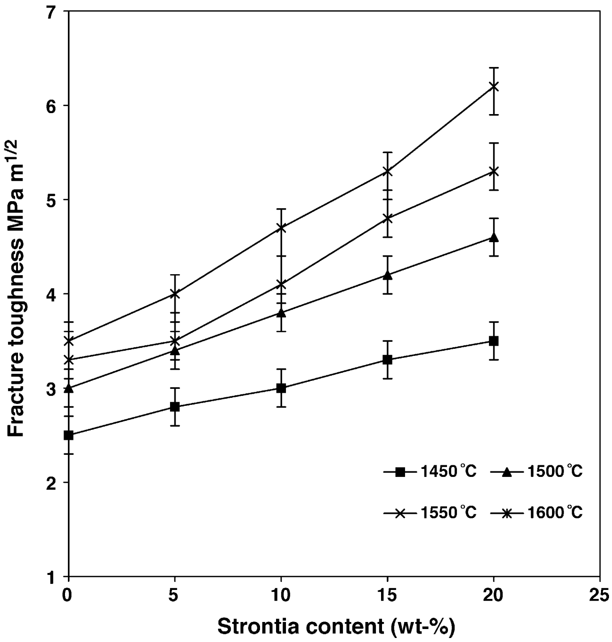

Fig. 4. Dependence of fracture toughness on strontia content.

the crack length gives the information about the fracture toughness (Vickers indentation test parts 1 and 2 [18,19]). Fig. 4 shows the dependence of fracture toughness on the amount of SrO. There was an increase in the fracture toughness from 3.5 MPa m$^{1/2}$ for pure alumina to 7.12 MPa m$^{1/2}$ for alumina with 20 vol.% strontia at the load of 5 kg. The fracture toughness was calculated using the formula

$$K_{1c} = \xi H a^{1/2} \left(\frac{c}{a}\right)^{1/2}$$

ξ is the empirically derived constant equal to 0.16; H is the hardness of the material; a is one half of the average Vickers indentation length; and c is one half of the average crack length.

The increase in fracture toughness can be explained based on the mechanism similar to that of the whisker/fiber-reinforced composites [20,21]. The elongated plate like grains act as the bridging sites in the wake of a crack thus resulting in improved fracture behaviour. The improvements in the strength and toughness of tetragonal zirconia polycrystals/alumina have been achieved by the incorporation of platelet grains of hexaluminate phase namely $LaAl_{11}O_{18}$ and $SrAl_{12}O_{19}$ [14]. The evidence for crack bridging has also been discussed.

3.2.3. Diametrical tensile strength

The results of the diametrical tensile tests with the varying concentrations of strontia, sintered at different temperatures are shown in Fig. 5(a). The diametrical tensile strength is found to increase with increase in the sintering temperature and concentration of strontia. The dependence of diametrical tensile strength on porosity of the sintered samples is shown in Fig. 5(b).

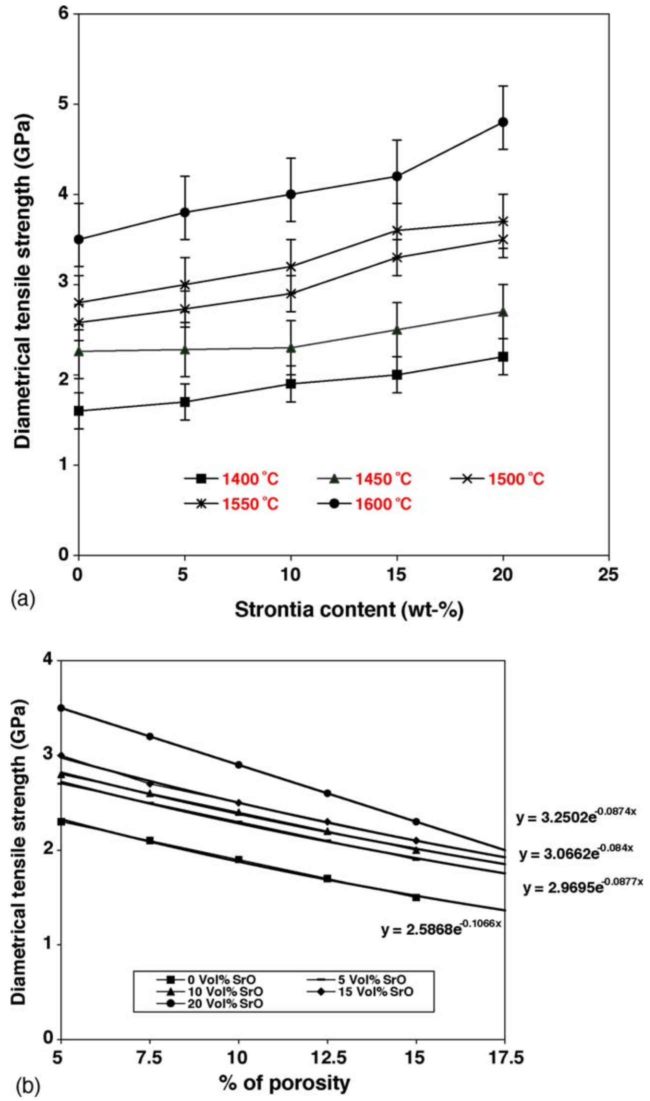

Fig. 5. (a) Dependence of diametrical tensile strength on strontia content. (b) Dependence of diametrical tensile strength on % of porosity.

3.2.4. Flexural strength

Fig. 6 shows the dependence of flexural strength on the amount of SrO for samples sintered at different temperatures. An average of 6–10 bars were used for each concentration. The increase in flexural strength with increase in strontia content was observed. The flexural strength was found to increase with the increase in the sintering temperature. The flexural strength was calculated using the formula

$$\text{Flexural strength } (\sigma) = \frac{1.5FL}{bh^2}$$

where F is the force in Newton; L is the span length in mm; b is the breadth of the specimen in mm; and h is the height of the specimen in mm.

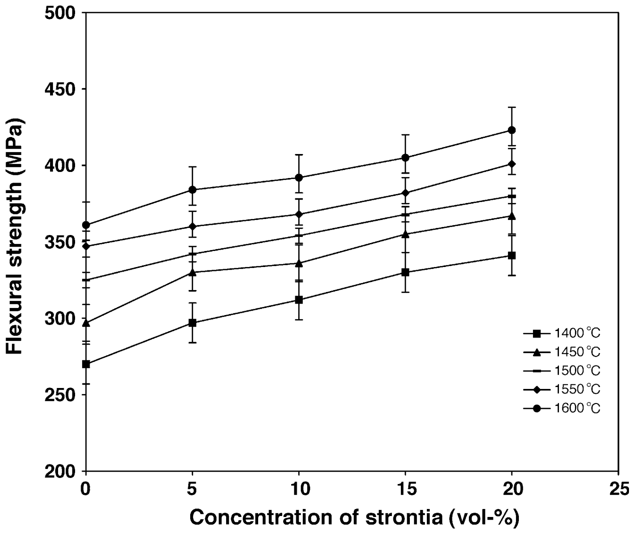

Fig. 6. Dependence of flexural strength on concentration of strontia.

SA_6 platelets grow in situ during sintering and thus, the processing is not hindered by the typical problems of whisker and fiber reinforced ceramics. Maity et al. [22] suggested a role of crack deflection. If the microstructural features are developed after the densification process is completed, i.e. via in situ formation of a second phase which has a highly anisotropic growth habit, then a tough ceramic composite can be obtained. Hori et al. [23] reported that the in situ composite of TiO_2 matrix with dispersed corundum platelets had anisotropic growth. A toughness of 7 MPa $m^{1/2}$ was reported for that system. Liquid phase sintering provides kinetic and thermodynamic conditions favourable to anisotropic grain growth [24]. In situ formation of elongated, rod like grains of Si_3N_4 in alumina matrix under nitrogen gas pressure resulted in improved toughness of 10 MPa $m^{1/2}$.

The toughness enhancement was reported for 3Y-TZP/mullite composites in which elongated mullite grains could be formed in situ [25]. Alumina is compatible with many layer composites such as $LaA1_{11}O_{18}$ and $LaMgA1_{11}O_{19}$ as well as others in the same structural family of hexaluminates. Chantikul et al. [26] observed a strong enhancement in the flaw tolerance of alumina with increase in grain size. Russo et al. [27] and Padture et al. [28] have observed that the incorporation of coarse grained regions in alumina/aluminium titanate composites improved the toughness and a homogeneous fine grained composite was obtained. In the present study, it has been observed that the formation of elongated grains results in an increase in the fracture toughness. The in situ growth of elongated grains did not lower the flexural strength as many second phases do. The changes of flexural strength and fracture toughness with respect to different temperatures were studied. The flexural strength and fracture toughness increased with strontia content.

4. Conclusions

Alumina–strontia composites were synthesised through sol–gel technique using aluminium *iso*-propoxide and strontium nitrate as the precursors. Density studies were performed using Archemedes method, a slight decrease in density with increase in strontia content was observed. Mechanical properties such as hardness, fracture toughness and strength were studied. Vickers hardness decreased with increase in strontia content, fracture toughness increased with increase in strontia content, diametrical tensile strength and flexural strength increased with increase in strontia content. Microstructure reveals the presence of alumina and plate-like strontium-hexaluminate grains.

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