Journal of the European Ceramic Society **14** (1994) 45–51

Effect of SrO on Densification and Mechanical Properties of Reaction-Sintered Mullite–Zirconia

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(Received 1 June 1993; revised version received 30 November 1993; accepted 5 December 1993)

Abstract

Reaction sintering of mullite–zirconia ceramic composites using submicron alumina and zircon powders with small additions of strontium oxide was studied. The powder mixture was ball-milled, biaxially pressed into disks and bars and then the samples were sintered at 1450, 1500 and 1600°C for 1, 2 and 4 h in air. Bulk densities were estimated using the mercury displacement method and apparent porosities by boiling the samples in water. Microstructural examinations were performed by SEM and EDAX studies. Flexural strength and fracture toughness values were measured at room temperature by three-point-bending and Vickers indentation techniques respectively. It was found that a certain amount of strontium oxide addition was considerably effective on the densification of the material studied.

In der vorliegenden Arbeit wurde das Reaktionssinterverhalten von Mullit–Zirkoniumoxid-Keramiken, hergestellt aus submikrometer Aluminiumoxidund Zirkonsilikatpulvern und geringer Zugabe von Strontiumoxid, untersucht. Das Pulvergemisch wurde in einer Kugelmühle gemahlen, unter zweiachsigem Druck in Scheiben und Stangen gepreßt und bei 1450, 1500 und 1600°C für 1, 2 und 4 Stunden in Luft gesintert. Die Bestimmung der Dichte und der scheinbaren Porosität erfolgte mittels der Quecksilberverdrängungsmethode bzw. durch Kochen der Proben in Wasser. Das Gefüge wurde mit Hilfe von SEM und EDAX untersucht. Die Biegefestigkeit und die Bruchzähigkeit wurden durch Dreipunktbiegeversuche bzw. Vickershärteeindrücke ermittelt. Die Untersuchungen haben gezeigt, daß die Menge des zugegebenen Strontiumoxids einen beträchtlichen Einfluß auf die Verdichtung des Materials hat.

Le frittage réactif d'un composite céramique mullite–zircone a été étudié à partir de poudres submicroniques d'alumine et de zircon avec une faible quantité d'oxyde de strontium. Le mélange des poudres a été broyé par broyage à boulets, puis pressé de manière biaxiale sous forme disques et barrettes, enfin fritté a 1450, 1500 et 1600°C dans l'air pendant 1, 2 et 4 h. Les densités apparentes ont été estimées par la méthode du déplacement du mercure, et la porosité ouverte par la méthode d'ébullition dans l'eau. Une étude microstructurale a été réalisée par SEM et EDAX. La résistance à la rupture et la ténacité ont été mesurées à température ambiante, respectivement par flexion en trois points et par la technique d'indentation Vickers. Les auteurs ont trouvé qu'une certaine quantité d'ajout d'oxyde de strontium favorisait considérablement la densification du matériau étudié.

1 Introduction

Mullite is the only stable phase in the SiO_2–Al_2O_3 system under atmospheric conditions and is known as an important phase in aluminosilicate refractories. In addition to the traditional uses, it has gained much attention during the last decade as a material for high-temperature structural applications[1] due to its high melting point, low thermal expansion, high creep and thermal shock

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Journal of the European Ceramic Society 0955-2219/94/$7.00

resistance and good bending strength at high temperatures.[2] However, relatively poor mechanical strength and difficulty in sintering high-purity mullite have prevented its more widespread use. Mechanical properties of mullite can be improved by addition of zirconia.[3] Zirconia addition was also found to promote densification and prevent grain growth of mullite.[4] There are two main routes to obtaining zirconia–mullite composites: one route is to obtain mullite and then mix it with zirconia powder;[5] the other is to reaction sinter a zircon and alumina mixture.[6–10] The first method requires high sintering temperatures (higher than 1600°C); the second method requires lower temperatures (still higher than 1500°C) and is comparatively cheaper, owing to the inexpensive raw material zircon.

The production of dispersed zirconia particles in mullite matrix by reaction sintering of zircon and alumina powders is accomplished according to the following reaction:

$$2\ ZrSiO_4 + 3\ Al_2O_3 \rightarrow 3\ Al_2O_3 \cdot 2\ SiO_2 + 2\ ZrO_2$$

This reaction has been studied extensively. Some additives like magnesia, titania and calcia have been used by several researchers[11–14] to get better densification and improve the properties of these composites.

In research on magnesia-partially-stabilized zirconia, Drennan & Hannink[15] have reported the beneficial effect of 0·25 wt% strontium oxide addition. Strontium oxide forms a glass phase with silica which is ejected from the bulk of the ceramic during sintering. This minimizes the retention of the glass phase at the grain boundaries and thus improves the mechanical properties at high temperature.

In the present paper, reaction sintering of an alumina–zircon mixture with strontium oxide addition to get better densification and possible mechanisms responsible for the improvements with the addition of SrO are discussed. Mechanical properties for mullite–zirconia composites were also discussed.

2 Experimental Procedure

The following powders were used as starting materials:

(i) Alumina with 0·35 μm average grain size (A16 SG, Alcoa, USA) with the following impurities in wt% (given by the producer as maximums): SiO_2, 0·07; Fe_2O_3, 0·03; Na_2O, 0·10.

(ii) Fine zircon powder with 0·75 μm average grain size (Zircosil 1, Cookson Ceramics & Antimony Ltd, UK) with the following composition and impurities in wt% (given by the producer): ZrO_2, 61·5; SiO_2, 37·0; Al_2O_3, 0·5; TiO_2, 0·2; Fe_2O_3, 0·1.

(iii) Strontium nitrate, chemical grade, minimum 99% pure (BDH Chemicals, UK).

The powder mixture was prepared to obtain a 3:2

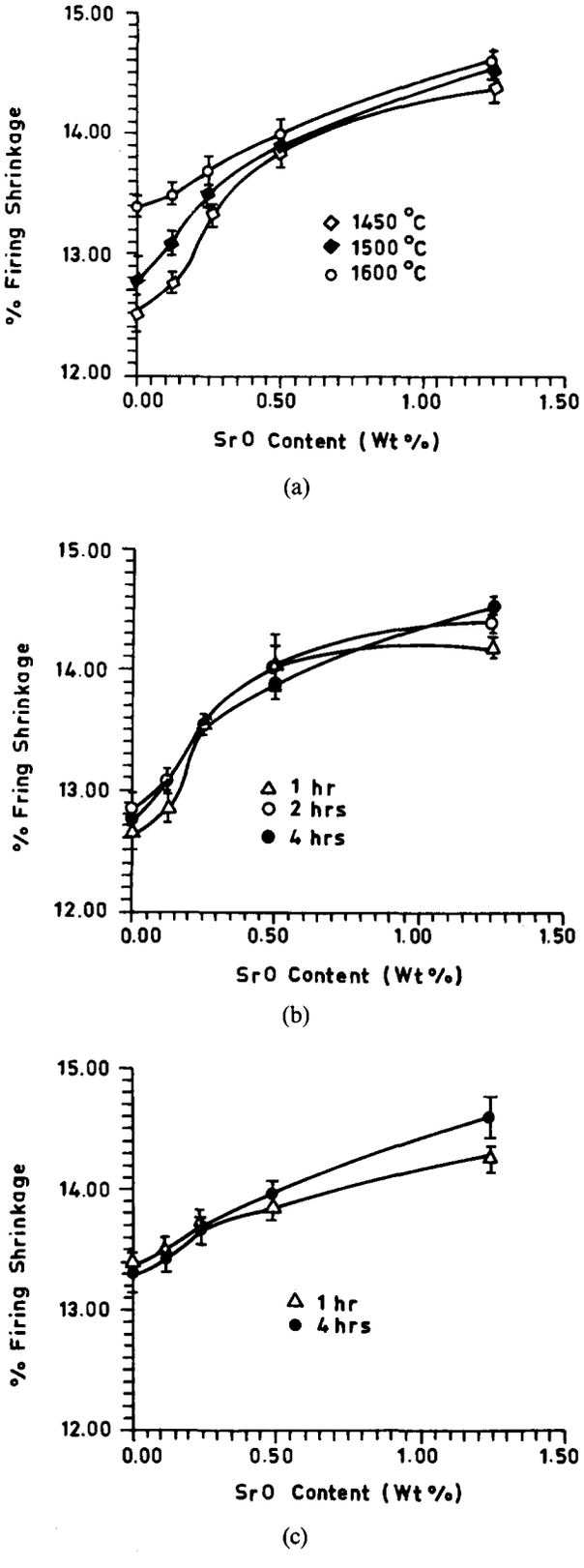
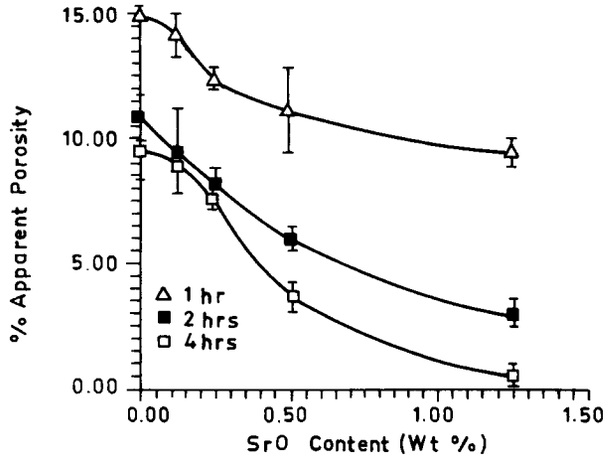


Fig. 1. Firing shrinkage for various SrO additions for (a) 4 h of sintering at all the sintering temperatures, (b) 1 to 4 h of sintering at 1500°C, (c) 1 and 4 h of sintering at 1600°C.

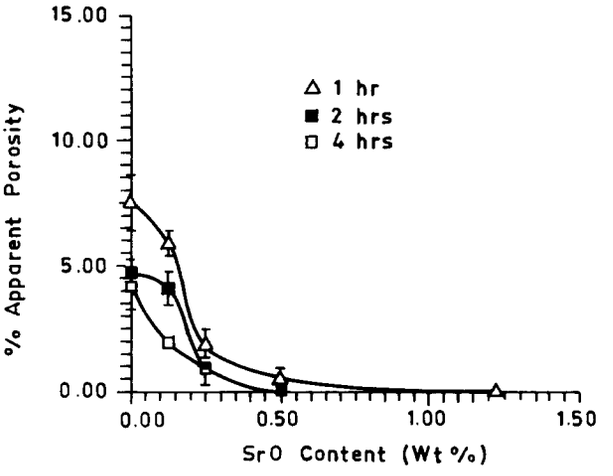
molar ratio for $Al_2O_3 : SiO_2$ and strontium oxide (as strontium nitrate) was added in amounts of 0·125, 0·25, 0·50 and 1·25 wt%. Strontium nitrate was dissolved in water and added to the alumina–zircon mixture in order to have it more homogeneously distributed. Homogenization of the mixture was achieved by ball-milling for 12 h in isopropyl alcohol (20 vol.% powder in alcohol) using zirconia milling media. This alcohol is a suitable milling medium because of its moderate volatility, improved milling rates and reduced wear.[8,16] After milling, the mixture was dried and 1·5% PVA was added as binder by mortar and pestle and then it was granulated through a 355 μm sieve. The samples were biaxially pressed at 100 MPa as disks and bars and sintered at 1450, 1500 and 1600°C for 1, 2, and 4 h, at a heating rate of 300°C/h, in air, in an electrically heated furnace and then allowed to furnace cool.

Bulk densities of the specimens were determined by the mercury displacement method. Apparent porosities were measured by boiling the samples in water and then calculating the absorbed water volume. Least-square average values of 4–6 samples were reported.

The extent of the reaction was followed by X-ray diffraction and microstructural examination was achieved by scanning electron microscopy (SEM) on polished and thermally etched samples.

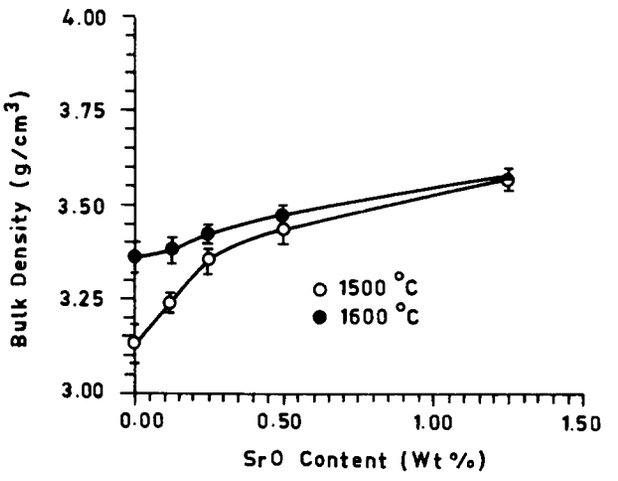


(a)

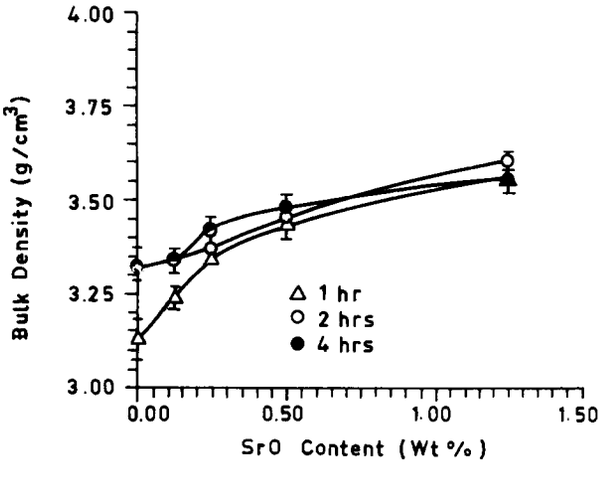


(b)

Fig. 2. Effect of SrO addition on the apparent porosity for sintering for 1 to 4 h (a) at 1450°C, (b) at 1500°C.



(a)



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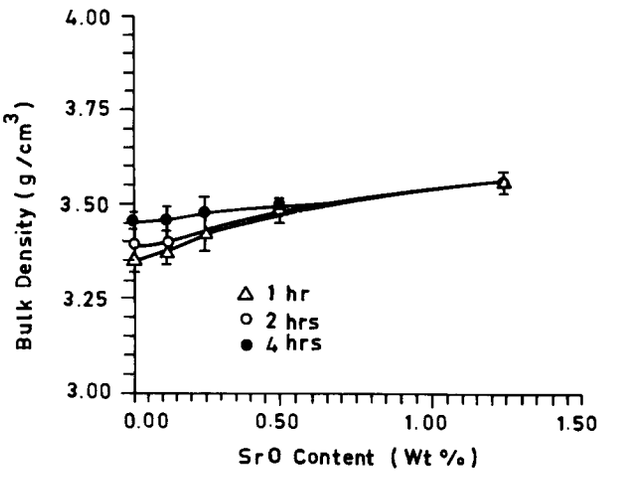


(c)

Fig. 3. Bulk densities for various SrO additions for sintering for (a) 1 h at 1500 and 1600°C, (b) 1 to 4 h at 1500°C, (c) 1 to 4 h at 1600°C.

Thermal etching was performed for each sample at a temperature about 100–150°C lower than the sintering temperature. Energy-dispersive X-ray analysis (EDAX) was used to determine the elemental content at the grain-boundary regions.

Bending strength and fracture toughness values were measured for the samples sintered at 1600°C for 1, 2 and 4 h. Bending strength was measured by three-point-bending test on bars with approximate dimensions of 3 × 6 × 36 mm. The crosshead speed was 0·5 mm/min and 25 mm span was fixed in all cases; 5–6 samples were used for each measurement. Fracture toughness (K_{IC}) values were found by the Vickers indentation technique on metallographically polished samples and calculated by the formula given by Antis *et al.*[17] The applied load was 500 N for all the samples. The specimens were carbon coated to reveal the indents and cracks better. At least 10 indentations were taken for each specimen and least-square average values were used in all the calculations.

3 Results and Discussion

3.1 Firing shrinkage, apparent porosity and bulk density

The firing shrinkages increased with increasing amount of strontium oxide at all sintering temperatures, as seen in Fig. 1(a). The effect of strontium oxide was more pronounced in samples fired at lower temperatures. The influence of sintering time is indicated in Fig. 1(b) and (c).

Apparent porosities decreased with the increase in strontium oxide, as seen in Fig. 2(a) and (b). The samples sintered at 1600°C did not have apparent porosity.

The bulk densities also increased with increase in strontium oxide content (Fig. 3(a)). Free SrO samples sintered for 1 h at 1500 and 1600°C had

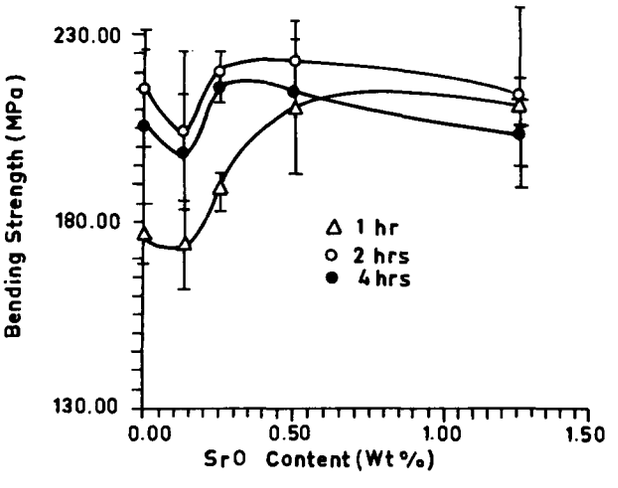


Fig. 4. Effect of SrO addition on bending strength for samples sintered at 1600°C for 1 to 4 h.

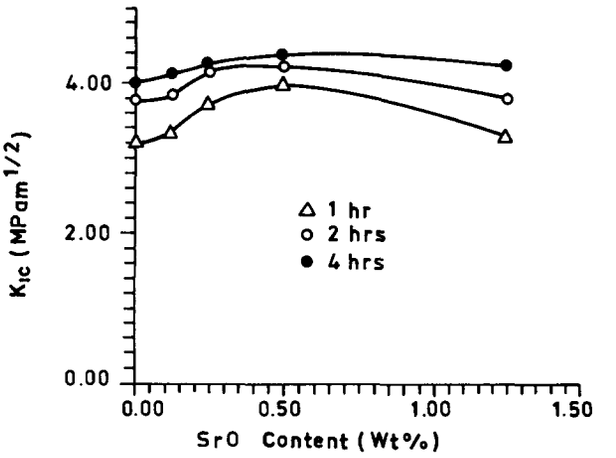
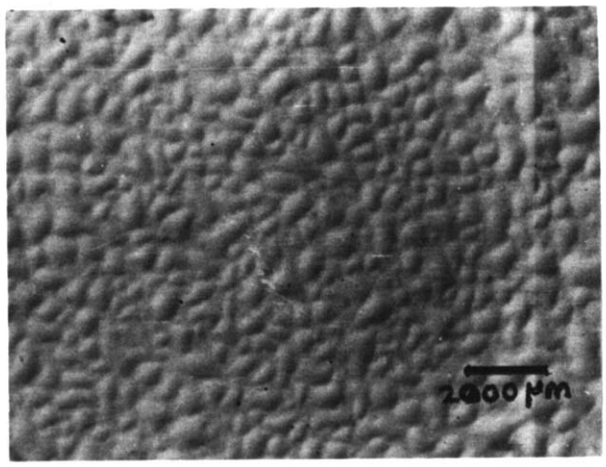
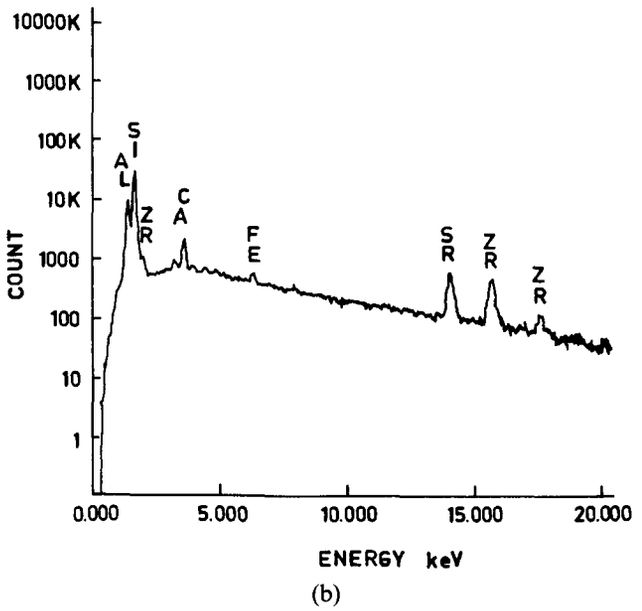


Fig. 5. Effect of SrO addition on fracture toughness for samples sintered at 1600°C for 1 to 4 h.

bulk densities of 3·13 and 3·36 g/cm^3 respectively, whereas the bulk densities of specimens containing 1·25 wt % SrO, sintered under the same conditions, increased to 3·56 and 3·57 g/cm^3. For the samples without SrO, increasing the sintering time

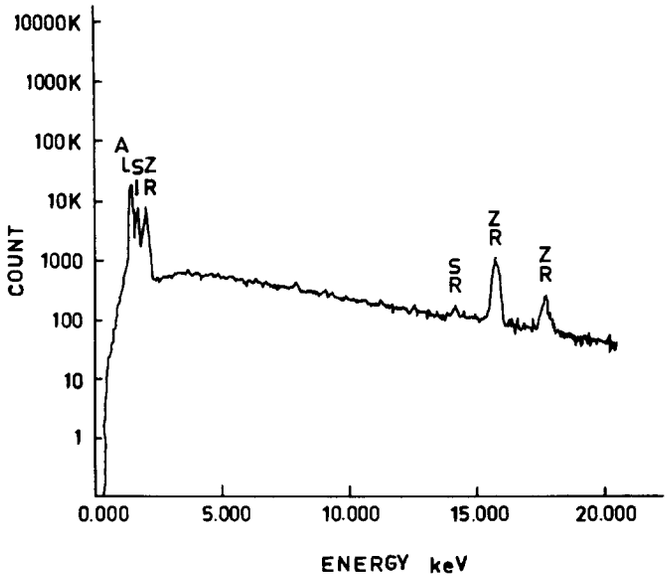


(a)

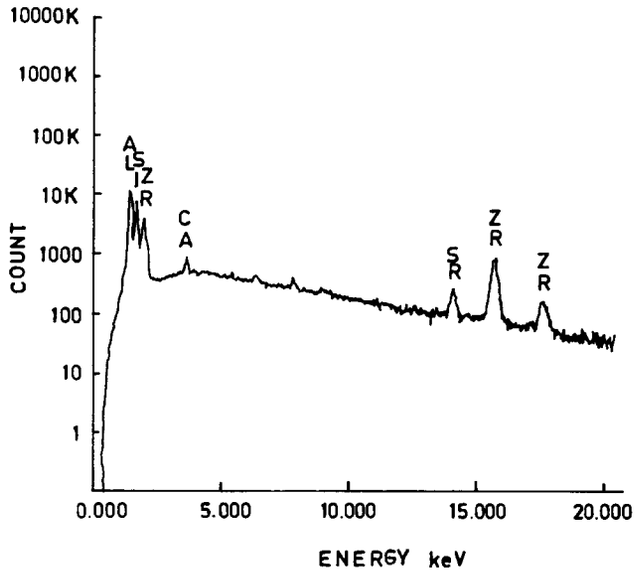


(b)

Fig. 6. (a) Optical micrograph of the surface of the specimen containing 1·25 wt % SrO sintered at 1600°C for 4 h, (b) EDAX spectrum taken from this glassy surface.



(a)



(b)

Fig. 7. EDAX spectra of the sample containing 1·25 wt % SrO sintered at 1600°C for 2 h (a) on the grain (b) at the grain boundary.

from 1 to 4 h at 1500°C resulted in a 6% density increase (Fig. 3(b)); on the other hand, increasing the SrO content to 1·25 wt% caused a density increase of 14% for 1 h sintering at 1500°C. Similar results have been obtained for sinterings at 1600°C (Fig. 3(c)).

3.2 Mechanical properties

Bending strength and fracture toughness values of the samples sintered at 1600°C for 1 to 4 h are shown in Figs 4 and 5 respectively. Maximum strength and toughness values were found for 0.50 wt% SrO addition. The reason SrO was not effective at smaller contents might be due to the titanium oxide impurity of the zircon raw material that reacted with strontium oxide prior to silica at

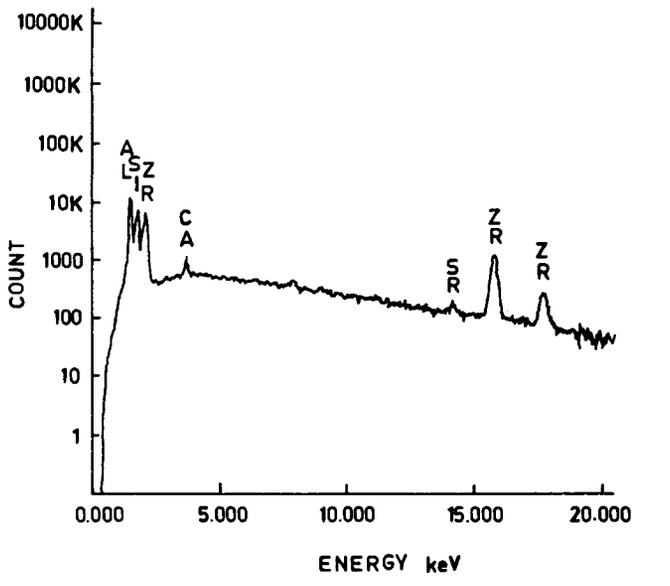


Fig. 8. EDAX spectrum taken at the grain boundary of the sample sintered at 1600°C for 4 h.

the initial stage of sintering.[18,19] Probably $SrTiO_3$ exerted a poisoning effect at the grain boundaries, causing a decrease in the fracture strength. After all the TiO_2 was used up, the remaining SrO became effective in improving the mechanical strength. With larger amounts of SrO, $SrTiO_3$ could be swept to the surface by the glass phase.

As the sintering time was increased to 4 h, a slight decrease in the bending strength might be due to the increased concentration of microcracks resulting from the grain growth of zirconia particles which undergo simultaneous transformation to the monoclinic phase.

3.3 Microstructural properties

EDAX spectra of the phases provided information on the effect of SrO addition. The peak around 1·8 keV is an overlap of $SrL\alpha_1$ and $SiK\alpha_{1,2}$ which are at 1·806 and 1·739 keV respectively. The presence of Sr was confirmed by the $SrK\alpha_1$ peak at 14·14 keV.

The EDAX spectrum taken from the grain boundaries of the samples containing 1·25 wt % SrO, sintered at 1600°C for 1 h, showed no Sr peak, but as the sintering time increased the Sr peak appeared on the spectrum. When the sintering time was 4 h, the Sr peak was smaller again because of the ejection of the glass phase to the surface. A photograph taken of the surface of the sample containing 1·25 wt % SrO sintered at 1600°C for 4 h showed glassy bubbles at the surface (Fig. 6(a)) which was rich in strontium (Fig. 6(b)). As seen from EDAX spectra (Fig. 7(a) and (b)) of the samples sintered at 1600°C for 2 h, SrO stayed preferentially at grain boundaries. However, for 4 h sintering when bubbles rich in SrO appeared at the surface, the amount of SrO at the

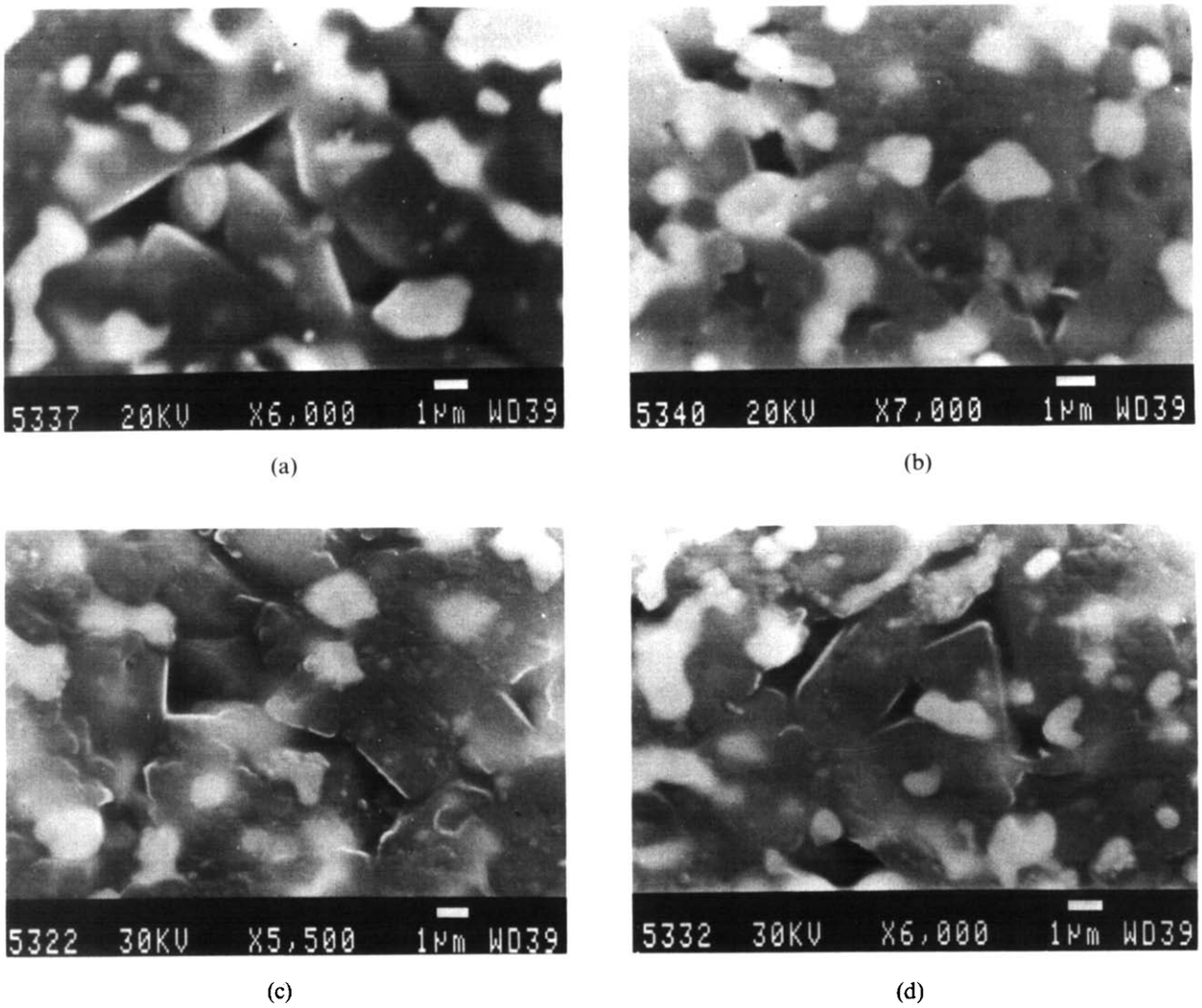


Fig. 9. SEM micrographs of the polished samples sintered at 1600°C without SrO (a) for 1 h, (b) for 4 h, and with 1·25 wt% SrO (c) for 1 h, (d) for 4 h.

grain boundaries decreased (Fig. 8). SEM photographs of the samples sintered at 1600°C for 1 and 4 h with and without strontium oxide addition are shown in Fig. 9(a)–(d).

4 Conclusion

Strontium oxide addition was found to be very effective in densification and in improving the mechanical properties. The glass phase, produced by strontium oxide and impurities present in the raw materials and residual silica, was ejected to the surface when the amount of strontium oxide was above a certain level and when the sintering lasted longer than 2 h. The removal of glass phase from the grain boundaries increased the bending strength and fracture toughness values considerably.

Acknowledgements

The authors are grateful to Prof. R. J. Brook for his kind advice in designing the project. Thanks are also due to Ms Zülal Mısırlı and Ms Sema Onurlu for their help in SEM and EDAX studies.

References

1. Aksay, I. A., Dabbs, D. M. & Sarıkaya, M., Mullite for structural, electronic, and optical applications. *J. Am. Ceram. Soc.*, **74** (1991) 2343–58.
2. Mah, T. I. & Mazdiyasni, K. S., Mechanical properties of mullite. *J. Am. Ceram. Soc.*, **66** (1983) 699–703.
3. Claussen, N. & Jahn, J., Mechanical properties of sintered in situ-reacted mullite–zirconia ceramic composites. *J. Am. Ceram. Soc.*, **63** (1980) 228–9.
4. Wallace, J. S., Petzow, G. & Claussen, N., Microstructure and property development of in situ-reacted in mullite–zirconia composites. In *Advances in Ceramics*, Vol. 12, *Science and Technology of Zirconia II*, ed. N. Claussen, M. Rühle & A. H. Heuer. The American Ceramic Society, Columbus, OH, 1984, pp. 436–42.
5. Moya, J. S. & Osendi, M. I., Effect of ZrO_2 (ss) in mullite on the sintering and mechanical properties of mullite/zirconia composites. *J. Mater. Sci. Lett.*, **2** (1983) 599–601.
6. Di Rupo, E., Anseau, M. R. & Brook, R. J., Reaction sintering: Correlation between densification and reaction. *J. Mater. Sci.*, **14** (1979) 2924–8.
7. Holström, M., Chartier, T. & Boch, P., Reaction-sintered ZrO_2–mullite composites. *Mater. Sci. Eng.*, **A 109** (1989) 105–9.

8. Wallace, J. S., Claussen, N., Rühle, M. & Petzow, G., Developments of phases in in situ-reacted mullite–zirconia composites. In *Ceramics and Ceramic–Metal Interfaces*, ed. J. Pask & A. G. Evans. Plenum Publishing Company, NY, 1981, pp. 155–65.
9. Boch, P. & Giry, J. P., Preparation and properties of reaction-sintered mullite–ZrO_2 ceramics. *Mater. Sci. Eng.*, **71** (1985) 39–48.
10. Anseau, M. R., Leblud, C. & Cambier, F., Reaction sintering (RS) of mixed zircon-based powders as a route for producing ceramics containing zirconia with enhanced mechanical properties. *J. Mater. Sci. Lett.*, **2** (1983) 366–70.
11. Kozmac, T., Wallace, J. S. & Claussen, N., Influence of MgO additions on the microstructure and mechanical properties of Al_2O_3–ZrO_2 composites. *J. Am. Ceram. Soc.*, **65** (1982) C-66–C-67.
12. Melo, M. F. & Figueiredo, M. O., Behaviour of titanium in mullite–zirconia composites. *Mater. Sci. Eng.*, **A 109** (1989) 61–8.
13. Rincon, J. M. & Moya, J. S., Microstructural study of toughened ZrO_2/mullite ceramic composites obtained by reaction sintering with TiO_2 addition. *Brit. Ceram. Trans. J.*, **85** (1986) 201–6.
14. Pena, P., Miranzo, P., Moya, J. S. & De Aza, S., multicomponent toughened ceramic materials obtained by reaction sintering—Part 1. *J. Mater. Sci.*, **20** (1985) 2011–22.
15. Drennan, J. & Hannink, R. H. J., Effect of SrO additions on the grain-boundary microstructure and mechanical properties of magnesia-partially-stabilized zirconia. *J. Am. Ceram. Soc.*, **69** (1986) 541–6.
16. Prochazka, S., Wallace, J. S. & Claussen, N., Microstructure of sintered mullite–zirconia composites. *J. Am. Ceram. Soc.*, **66** (1983) C-125–C-127.
17. Antis, G. R., Chantikul, P., Lawn, B. R. & Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurements. *J. Am. Ceram. Soc.*, **64** (1981) 533–8.
18. Tagawa, H. & Igarashi, K., Reaction of strontium carbonate with anatase and rutile. *J. Am. Ceram. Soc.*, **69** (1986) 310–14.
19. Eitel, W., *Silicate Science*, Vol. III. Academic Press, NY, 1965, pp. 189–92.