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Mechanical properties and microstructures of reaction sintered mullite–zirconia composites in the presence of an additive — dysprosia

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Abstract

Mullite–zirconia composites were prepared from Indian zircon flour and calcined alumina following the reaction sintering route. Zircon flour and calcined alumina with 0–4.5 mol% dysprosium oxide were attrition milled followed by isostatic pressing and sintering at 1400–1650°C for 2 h. Significant densification was achieved after dysprosia addition as an additive. The thermal expansion coefficient values were found to be reduced in the presence of dysprosia. Dysprosia helps in densification by liquid phase formation as well as by stabilisastion in tetragonal zirconia state. The thermo-mechanical and microstructural characteristics of the composites were discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Reaction sintering; Mullite; ZrO_2; Thermal expansion coefficient; Microstructure-final; Composites

1. Introduction

Mullite is one of the basic ceramic materials traditionally used for refractories and is attractive because of its high temperature mechanical properties. Mullite, however, for the development of the structural materials has been delayed since it has a low fracture toughness and relatively low strength at room temperature compared with other engineering ceramics. It is well known that the fracture toughness and flexural strength are improved in zirconia reinforced mullite.[1]

There are many additives that are used to prepare mullite–zirconia ceramics. These are mainly magnesia, calcia, titania, yttria, ceria etc.[2–6]

The objective of the present investigation is to characterise the reaction sintered mullite–zirconia composites, prepared from Indian zircon and calcined alumina in presence of an additive, dysprosia.

2. Experimental

In this investigation, zircon flour was taken as one of the principal raw materials. The other important raw material was calcined alumina. The characteristics of the raw materials are described in Table 1. Dysprosia, as additive, was supplied by Indian Rare Earth Limited, Mumbai, India. Three additive concentrations were selected. The batch composition of the four composites are summarised in Table 2. The experimental procedures followed in this study were described in an earlier publication.[7] Dysprosia (2.5, 3.5 and 4.5 mol%) with respect to the zirconia content was added to the mixture. The sample codes used in the experiment are also described in Table 2. Homogenization and grinding of the batch mix was achieved by attritor milling in isopropyl alcohol for 6 h. After drying and sieving, the powder was compacted by isostatic pressing into discs (35 mm dia.) and bars ($60 \times 6 \times 6$ mm^3) which were reaction sintered at 1400, 1500, 1550 and 1600°C for 2 h soaking time.

Chemical etching of the mirror polished and fracture surface was done by 15% HF + 15% HCl for 5 min followed by ultrasonic cleaning. Thermal etching of the chemically etched polished surface of sintered materials was done at 1350°C/1 h. The rate of heating was maintained at 10°C/min and the rate of cooling was 5°C/min. A few samples were mirror polished and only thermally etched at a temperature 50°C less than the sintering temperature for 20 min. The rate of heating and cooling was the same.

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Table 1
Chemical analyses and physical properties of Indian coastal zircon flour and calcined alumina

Constituents	Zircon flour	Calcined alumina
SiO_2	31.94	0.34
ZrO_2	59.74	–
Al_2O_3	6.76	99.17
Fe_2O_3	0.17	–
TiO_2	Trace	–
HfO_2	0.03	–
CaO	1.03	–
MgO	Trace	–
K_2O	Trace	–
Na_2O	Trace	0.37
XRD analyses (phases)		
Major	Zircon	α-Alumina
Minor	Anorthite	γ-Alumina, β-alumina

Table 2
Batch composition and sample codes used in the experiment

Additive				
mol%	wt%	Zircon flour (wt%)	Calcined alumina (wt%)	Sample code
Nil	Nil	59.00	41.00	MZ
2.5	2.43	57.56	40.00	25 MZD
3.5	3.38	57.00	39.61	35 MZD
4.5	4.30	56.46	39.23	45 MZD

3. Results and discussions

The present study was carried out on two principal raw materials — zircon and calcined alumina. The characteristics of the raw materials were described in an earlier publication.[7] Fig. 1 describes the effect of temperature on the shrinkage of the green composites containing dysprosia. The addition of dysprosia enhanced densification by forming a liquid phase which is identified by EDX study. The additive containing composites started shrinkage at about 1175°C, but the effect of the additive concentration on shrinkage is not significant up to 1300°C. These curves can be considered as typical for the liquid phase sintering process.[2,4] The development of liquid beyond 1375°C was confirmed by the sharp change in the slope of the shrinkage curve.

Sintering in the presence of the liquid phase had received attention because the liquid phase was essential for many practical systems to speed up the sintering process. The sintering process in the presence of a liquid occurred by solution at contact points between the solid particles under the driving force of liquid surface tension.

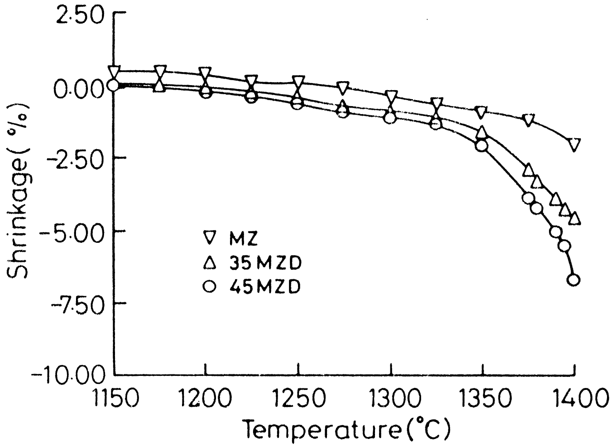

Fig. 1. Shrinkage of mullite–zirconia (MZ) composites as a function of temperature with dysprosia additive. 35 MZD and 45 MZD represented 3.5 and 4.5 mol% of dysprosia (D) in MZ, respectively.

The effects of sintering temperature on the relative density of mullite–zirconia composites are shown in Fig. 2. It was noted that the tetragonal zirconia solid solution field in the zirconia–dysprosia system extended with increase in dysprosia content from 0 to 4 mol%.[8] The relative densification is maximum in 45 MZD at 1550°C followed by a decrease in value with temperature. The addition of dysprosia favoured forward reaction by stabilising zirconia by solid solution formation. But dysprosia was also identified in triangular intergranular spaces. This dual role of dysprosia makes the composite denser. At high temperature, a large portion of dysprosia went into glassy phases which results in low densification in composites with a higher amount of dysprosia.

Thermal expansion of the composites were measured to determine the martensitic start (M_s) temperature. This experiment was carried out using dilatometer from room temperature to 1400°C at 6°C/min rate of heating. On heating, the monoclinic to tetragonal transition was accompanied by a marked contraction followed by an expansion on cooling. A hysteresis effect between the two cycles was thus experienced by all the samples (Fig. 3). The thermal expansion coefficient values of dysprosia containing samples were low compared to that of pure mullite (Table 3). It was observed that dysprosia formed solid solution with mullite. It was assumed that the dysprosium ion occupied the AlO_6 octahedral chains by replacing the Al^{3+} ion. Lattice spacing was increased due to this replacement which causes low thermal expansion coefficient.[9,10]

Dysprosia addition does not significantly decrease the transformation temperature of mullite–zirconia composites. With 3.5 mol% the M_s temperature is 690°C. It was shown that up to 4 mol% dysprosia can reduce the transformation temperature to 500°C in a zirconia–dysprosia binary system.[8] But here the effect of dysprosia in reducing M_s temperature is not significant as a large percentage of dysprosia is used to form the glassy phase.

Mechanical properties of the mullite–zirconia composites are presented in Table 4. The presence of dysprosia increases the room temperature flexural strength, hardness and fracture toughness. The highest strength was observed in 25 MZD due to the presence of a low amount of the glassy phase compared to 35 and 45 MZD. [11] The relative tetragonal zirconia content of the

Table 3
Thermal expansion coefficient, transformation temperature (M_s) and relative tetragonal zirconia content of different composites sintered at 1600°C

Sample code	Thermal expansion coefficient$\times 10^{6}$/°C	Transformation temperature, M_S (°C)	Relative t-ZrO$_2$ (%)
MZ	4.87	725	11.21
25 MZD	3.83	725	26.47
35 MZD	3.84	690	25.00
45 MZD	3.52	725	25.74

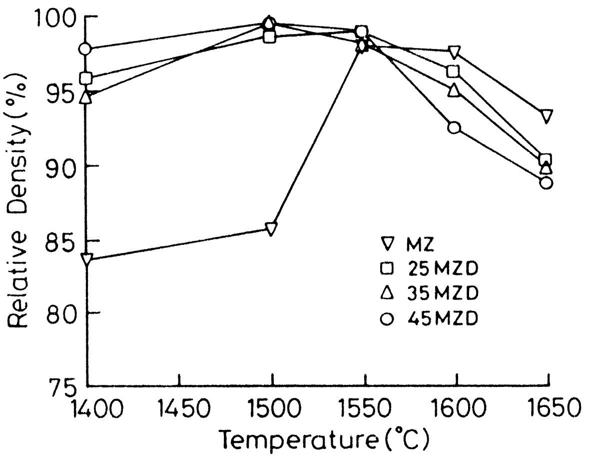

Fig. 2. Relative density as a function of sintering temperature. The numbers represent the mol% of dysprosia in the composite.

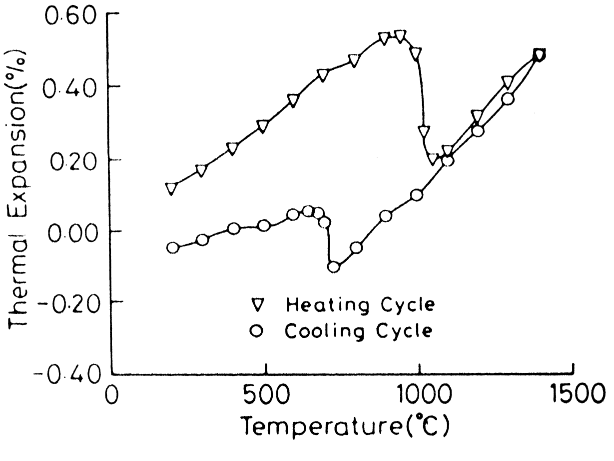

Fig. 3. Linear expansion as a function of temperature of dysprosia containing mullite–zirconia composite (45 MZD).

Table 4
Mechanical properties of mullite–zirconia composites sintered at 1550°C

Sample code	Hardness (GPa)	Fracture toughness (Mpa m$^{1/2}$)	Flexural strength (MPa)	t-ZrO$_2$ content (%)
MZ	5.6	3.69	154	22.2
25MZD	8.2	5.03	328	34.8
35MZD	7.7	4.17	189	34.5
45MZD	7.6	3.53	197	34.2

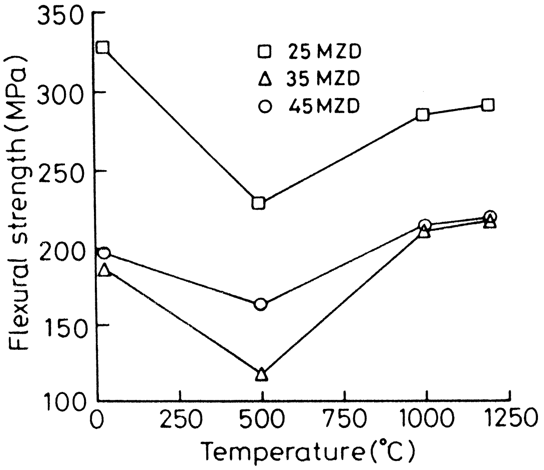

Fig. 4. Effect of temperature on the flexural strength of dysprosia containing mullite–zirconia composites.

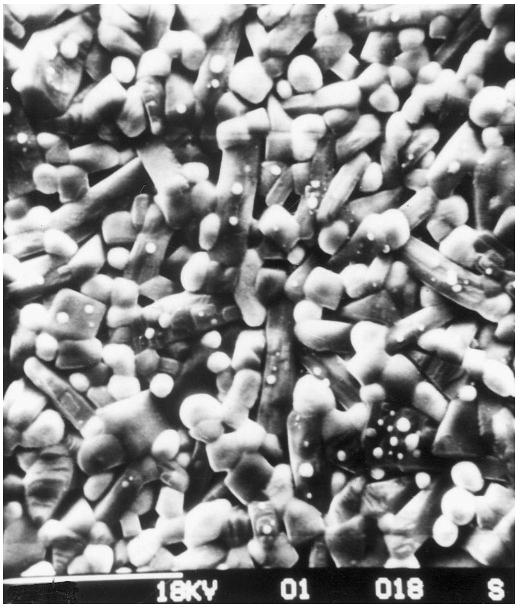

Fig. 5. Secondary electron image of dysprosia containing mullite–zirconia sintered at 1600°C. The fracture surface was chemically etched. Elongated grains are mullite whereas subrounded to rounded grains are zirconia.

three composites are more or less equal, so the amount of glassy phase plays an important role in mechanical properties (Tables 3 and 4).

The high temperature flexural strength was conducted at 500, 1000 and 1200°C, respectively. The strength as a function of testing temperature is presented in Fig. 4. All the composites exhibited the reduction of strength at 500°C. It was anticipated that the disappearance of phase transformation of zirconia and drop in Young's modulus are responsible for the drastic decrease in strength at 500°C. [12]

Table 5
Energy dispersive X-ray analyses in ZrO_2/mullite/Dy_2O_3

Sample code	Phases	Al_2O_3 (wt%)	SiO_2 (wt%)	ZrO_2 (wt%)	Dy_2O_3 (wt%)	CaO (wt%)	Na_2O (wt%)
35 MZD	Mullite	61.43	31.57	5.3	1.65	–	–
	Zirconia	0.28	5.64	88.67	5.41	–	–
	Glassy	44.57	35.29	1.87	17.44	0.35	0.47

All the composites show an increase in strength at 1000°C. A certain amount of grain boundary segregated vitreous phases relax stress concentration and blunt microcracks which lead to a higher strength at 1000°C. [13]

At 1200°C, all dysprosia containing composites show higher strength than that at 1000°C. It is anticipated that the dysprosium ion along with Al_2O_3 and SiO_2 forms highly viscous glass whose transition temperature is high enough. Due to this high viscosity of the intergranular space, this could relax the stress intensity of the crack tip and result in a high strength.

Fig. 5 shows the scanning electron microstructure of thermo-chemically etched fracture surface of dysprosia containing mullite–zirconia composites sintered at 1600°C. The columnar grains are mullite whereas subrounded to rounded grains are zirconia. Most of the

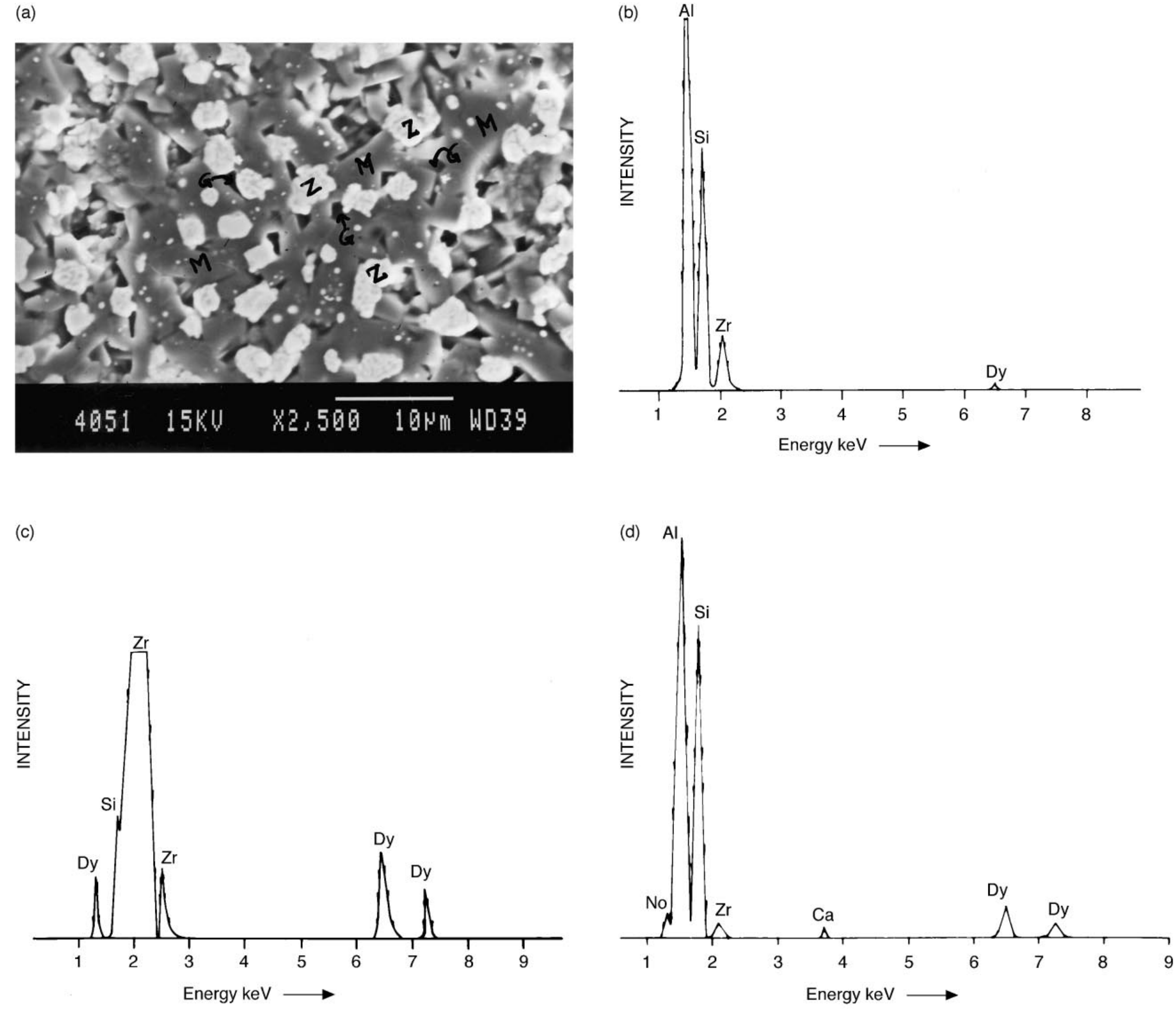

Fig. 6. (a) SEM micrograph of thermally etched polished surface of dysprosia containing sample sintered at 1600°C; (b) EDX analysis of mullite (M) grains; (c) EDX analysis of zirconia (Z) grains; (d) EDX analysis of intergranular region (G).

zirconia is intergranular though a small amount of intragranular zirconia was also found.

The elemental analyses of mullite, zirconia and intergranular phases of dysprosia containing reaction sintered mullite–zirconia composites are displayed in Table 5. Dysprosia was detected in mullite, zirconia and also in triangular pockets. Dysprosia, silica and alumina forms a solid solution with zirconia. The triangular glassy pockets are composed mainly of alumina, silica and dysprosia with a small percentage of zirconia, calcia and soda (from raw materials used). The EDX micrographs are shown in Fig. 6.

4. Conclusion

Mullite–zirconia composites can be prepared by the reaction sintering method of preparation using Indian zircon flour and calcined alumina at relatively low temperature, 1550°C, using dysprosia as a sintering additive. Dysprosia plays a double role — one favouring densification by forming a liquid phase and the other stabilising tetragonal zirconia by solid solution formation. Thermal expansion coefficient values were decreased in the presence of dysprosia. The thermal expansion coefficient and relative t-zirconia of three composites were more or less the same. The 2.5 mol% of dysprosia containing composites shows the best mechanical properties among the three composites with dysprosia. Columnar mullite grains with subrounded to rounded zirconia phase are present in SEM micrograph. Dysprosia forms a solid solution with zirconia and mullite.

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References

1. Claussen, N. and Jahn, J., Mechanical properties of sintered, in situ-reacted mullite–zirconia composites. *J. Am. Ceram. Soc.*, 1980, **63**, 228–229.
2. Pena, P., Miranzo, P., Moya, J. S. and de Aza, S., Mullite component toughened ceramic material obtained by reaction sintering: Part 1 ZrO_2–Al_2O_3–SiO_2–CaO system. *J. Mater. Sci.*, 1985, **20**, 2011–2022.
3. Rincon, J. Ma, Moya, J. S. and Melo, M. F., Microstructural study of toughened ZrO_2/mullite ceramic composites obtained by reaction sintering with TiO_2 additions. *Trans. Br. Ceram. Soc.*, 1986, **85**, 201–206.
4. Pena, P., Moya, J. S., de Aza, S., Cardinal, E., Cambier, F., Leblud, C. and Anseau, M. R., Effect of magnesia additions on the reaction sintering of zircon/alumina mixtures to produce zirconia toughened mullite. *J. Mater. Sci. Lett.*, 1983, **2**, 772–774.
5. Joliet, B., Cambier, F., Dapra, I., Leblud, C. and Leniche, A. Microstructural and mechanical characterisation of mullite–zirconia composites containing Y_2O_3. In *J. de Physique*, ed. P. Odier, F. Cabanes and B. Cales, 1986, Vol. 47, pp. 411–416.
6. Wu, J. and Lin, C., Effect of CeO_2 on reaction sintered mullite–zirconia ceramics. *J. Mater. Sc.*, 1991, **26**, 4631–4636.
7. Das, Kaberi, Mukherjee, B. and Banerjee, G., Effect of yttria on mechanical and microstructural properties of reaction sintered mullite–zirconia composites. *J. Euro. Ceram. Soc.*, 1998, **18**, 1771–1777.
8. Pascual, C. and Duran, P. D., Phase relations and ordering in the dysprosia–zirconia system. *J. Mater. Sci.*, 1980, **15**, 1701–1708.
9. Schneider, H. and Elberhard, E., Thermal expansion of mullite. *J. Am. Ceram. Soc.*, 1990, **73**, 2073–2076.
10. Chaudhury, S. P., Solid solution in mullite. *J. Canadian Ceram. Soc.*, 1989, **38**, 61–76.
11. Miranzo, P., Pena, P., de Aza, S., Moya, J. S., Rincon, J. M. and Thomas, G., TEM study of reaction sintered zirconia–mullite composites with CaO and MgO additions. *J. Mater. Sci.*, 1987, **22**, 2987–2992.
12. Das (nee Roy), Kaberi, Das, S. K., Mukherjee, B. and Banerjee, G., Microstructural and mechanical properties of reaction sintered mullite–zirconia composites in presence of magnesia as additive. *Interceram*, 1998, **47**, 304–312.
13. Mah, T. and Mazdiyasni, Mechanical properties of mullite. *J. Am. Ceram. Soc.*, 1983, **66**, 699–703.