Journal of the European Ceramic Society 20 (2000) 2133–2141

Effect of addition of TiO_2 on reaction sintered $MgO–Al_2O_3$ spinels

Ritwik Sarkar *, Goutam Bannerjee

Refractory Division, Central Glass and Ceramic Research Institute, Jadabpur, Calcutta, India

Received 27 November 1999; accepted 24 February 2000

Abstract

Three different spinel compositions with $MgO:Al_2O_3$ molar ratios 2:1, 1:1 and 1:2 were studied using TiO_2 as an additive up to 2 wt.%. Solid state reaction sintering technique was employed for all the compositions in the temperature range of 1550–1650°C. Attrition milling was done for the reduction of particle size. Sintered products were characterised in terms of densification and shrinkage studies, phase analysis, strength evaluation both at ambient temperature and at elevated temperature, strength retention after different number of thermal cycles at 1000°C, quantitative elemental analysis and microstructural studies.

Keywords: $MgAl_2O_4$; Microstructure-final; Sintering; Spinels; TiO_2

1. Introduction

Magnesium aluminate spinel is an important refractory material for its excellent high temperature mechanical, thermal and chemical properties. Method of fabrication of spinel refractory has been known since 1905[1] and the phase diagram of $MgO–Al_2O_3$ binary system has been well established since 1916[2] but still spinel has failed to get commercial success even up to the mid-eighties, mainly due to complexity in process parameters. Natural availability of magnesium aluminate is rather inconspicuous and so it is prepared synthetically. The limiting factors for spinel preparation are the requirements regarding purity of the raw materials, their reactivity, intermediate calcination temperature, higher sintering temperatures, etc. Cheaper magnesium chromite bodies with similar kinds of properties became popular due to economic advantage. But now, as the refractory practice has changed to high quality items to cope with the sophisticated technologies of higher operating parameters and less down time than practiced earlier, and as people become more conscious about the harmful effects of chrome bearing compounds,[3] magnesium aluminate spinel is gaining importance. Again it has the additional advantage of environment friendliness that also attracts the users.

The major application areas of magnesium aluminate spinel refractories are[4] transition and burning zones of cement rotary kilns, bottom and side walls of steel ladles and checker works of glass furnace regenerators where it is used either as a pure spinel body or as a component in a magnesia rich or alumina rich matrix. Again the use of magnesium aluminate based new generation castables are being used in recent times with much success. Hence, from the application point of view stoichiometric and nonstoichiometric spinels, both the magnesia rich and alumina rich compositions, are important.

The effect of different additives on the development of spinel have been well studied for a long time. Salt vapours were reported[5] to be useful additives for the development and formation of spinel. Fluorine ion (from AlF_3 ar CaF_2) was found[6] to enhance the solid state reaction synthesis of magnesium aluminate spinel when it is incorporated in the lattice by replacing oxygen ions. Addition of LiF was also reported[7,8] to be effective for the improvement in the sintered properties by liquid phase sintering. Better sintered products of magnesium aluminate spinel were also reported by using rare earth oxides like 5 wt.% of Y_2O_3,[9] 4 wt.% of Yb_2O_3 and Dy_2O_3[10] etc. Cr_2O_3, was also reported[11] to improve the thermal shock resistance and slag resistance of the periclase spinel bodies.

* Corresponding author. Fax: +91-33-473-0957.

0955-2219/00/$ - see front matter
PII: S0955-2219(00)00097-2

Addition of Cr_2O_3 was again found[12] to improve the densification of different spinel compositions, specially for the alumina rich spinel. But a higher amount of Cr_2O_3 at higher temperatures was found to be detrimental on the sintered properties due to inhomogeneous growth and pore coalescence.

The effect of addition of TiO_2 on the development of magnesium aluminate spinel is also available in literature. Y. H. Baik[13] worked on the sintering of magnesium aluminate in the presence of TiO_2 and MnO_2 and reported that TiO_2, is more beneficial in improving the densification than that of MnO_2. Yu and Hiragushi[14] worked on the sintering behaviour of spinel with 0.2 to 2 mass% of TiO_2. They found a continuous improvement in the sintered density with an increasing amount of TiO_2 up to a maximum of 1.5 mass%. Above 1.5% of TiO_2, the authors found no further improvement in density and concluded that exsolution of alumina and dissolution of TiO_2 in spinel was probably the reason for better densification.

Literature study does not provide detailed study on the effect of addition of TiO_2 on the sintered properties of stoichiometric and nonstoichiometric spinels. Here a study on the development and properties of three different spinel compositions was undertaken in presence of TiO_2. The study mainly deals with the refractory properties. TiO_2 was added at 0.5, 1 and 2 wt.% to three spinel compositions ($MgO:Al_2O_3$ molar ratio 2:1, 1:1 and 1:2), attritor mill was employed for the reduction of the particle size of the starting materials and single stage sintering was done in the temperature range of 1550 to 1650°C.

Table 1
Physico-chemical properties of magnesia and alumina

Oxides	Magnesia (wt.%)	Alumina (wt.%)
Chemical analysis		
SiO_2	0.5	0.62
Al_2O_3	0.3	97.2
TiO_2	Trace	Trace
Fe_2O_3	0.05	0.19
CaO	1.62	1.26
MgO	97.19	Trace
K_2O	0.04	0.02
Na_2O	0.1	0.22
Physical properties		
Specific gravity	3.59	3.99
Specific surface area ($m^2\ g^{-1}$)	1.8	2.9
Phase analysis	Periclase	Corundum

Table 2
Batch composition and surface area of spinels

	Stoichiometric	Magnesia rich	Alumina rich
Batch code	S	M	A
$MgO:Al_2O_3$	1:1	2:1	1:2
MgO content	28.33	44.22	16.51
$A1_2O_3$ content	71.67	55.78	83.49
Specific surface area ($m^2\ g^{-1}$) (after 4 h milling)	8.1	8.2	8.8

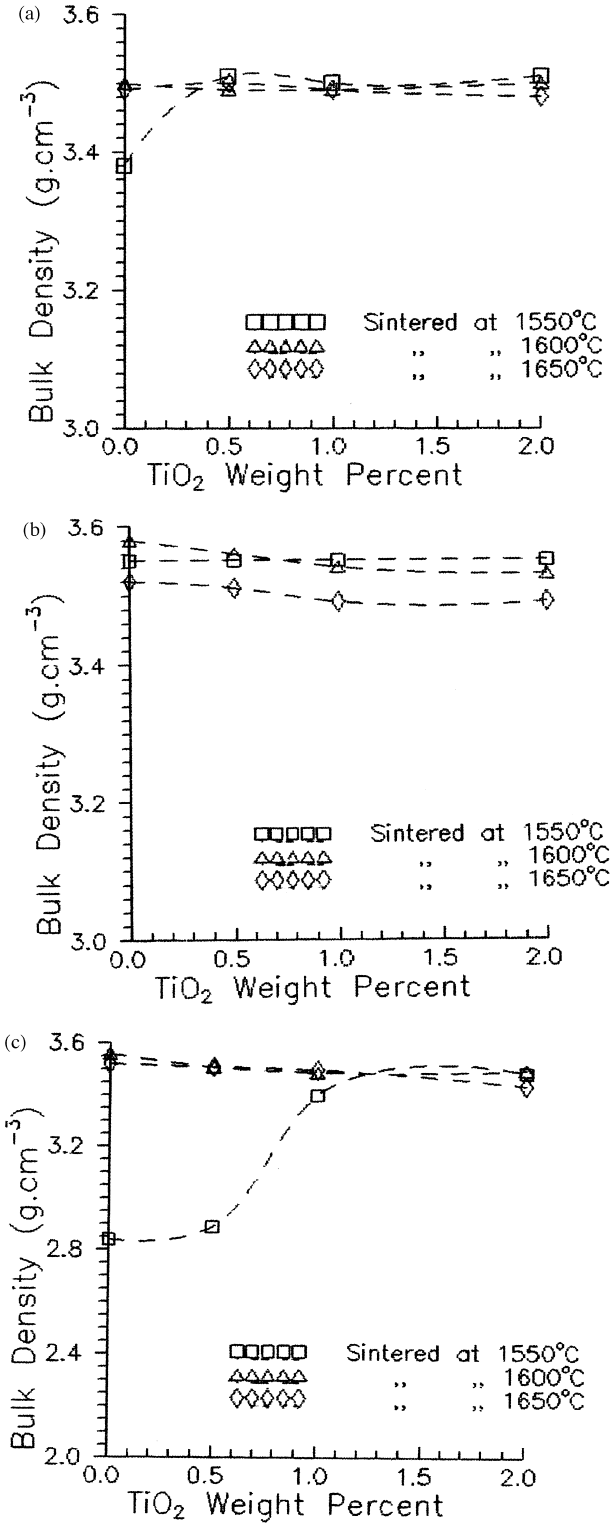


Fig 1. Variation of sintered density of the spinels with TiO_2 content. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

2. Experimental

Starting oxides, magnesia and alumina, were first characterised in terms of chemical analysis, powder X-ray diffraction (using Cu-K_α radiation), specific gravity and specific surface area (applying BET technique) measurements. Physico-chemical properties of the oxides are listed in Table 1. Next the oxides were taken as per the batch composition, given in Table 2 and to each composition TiO_2 (99% pure, supplied by S. D. Fine Chemicals Pvt. Ltd., India) was added at weight percentages of 0.5, 1 and 2. Spinel with stoichiometric composition ($MgO:Al_2O_3 = 1:1$) is termed as S-batch, with magnesia rich composition ($MgO:Al_2O_3 = 2:1$) is M-batch and with alumina rich composition ($MgO:Al_2O_3 = 1:2$) is A-batch. First, all the three batches were preliminary wet mixed in a ball mill for about 15 min and then the mixed powders were attritor milled (Union Process make mill, model 01HD). Optimisation of the milling time was done from previous works[15,16] and 4 h milling was employed. Specific surface area of the milled materials were also measured and are provided in Table 2. Milled powders were then isostatically pressed (Autoclave Engineers make press, model CIP 6-23-30) at 175 MPa to briquettes (25 mm dia × 10 mm) and bars (60 mm × 6 mm × 6 mm) Pressed shapes were dried at 110°C and sintered at 1550, 1600 and 1650°C with a heating rate of 1°C per min and a soaking period of 2 h at the peak temperatures. Phase analysis (by X-ray diffraction method) and densification studies (by measuring the bulk density and linear shrinkage) were done on the briquettes. Bars were used to characterise modulus of rupture (MOR), both at ambient temperature (in an Instron universal testing machine. model 5500R) and at elevated (1300°C) temperature (in a CGCRI, India., developed instrument) and retainment of cold strength after thermal shock (cycles consist of 10 min of heating at 1000°C and 10 min of subsequent air quenching). Microstructural analysis was done in a scanning electron microscope (Leica make model S-430i) attached with electron diffraction X-ray analysis (EDXA) facility for quantitative elemental analysis.

3. Results and discussion

Chemical analysis (Table 1) of both the oxides show that they are more than 97% pure and have a little amount of impurities like lime, silica, iron oxide and alkalies. Again surface areas of the starting oxides and that of the milled materials indicate that 4 h of attritor milling was effective to increase the surface area by about 3–4 times. Little higher surface area is obtained for the A-batch due to the presence of a higher amount of finer alumina in that batch.

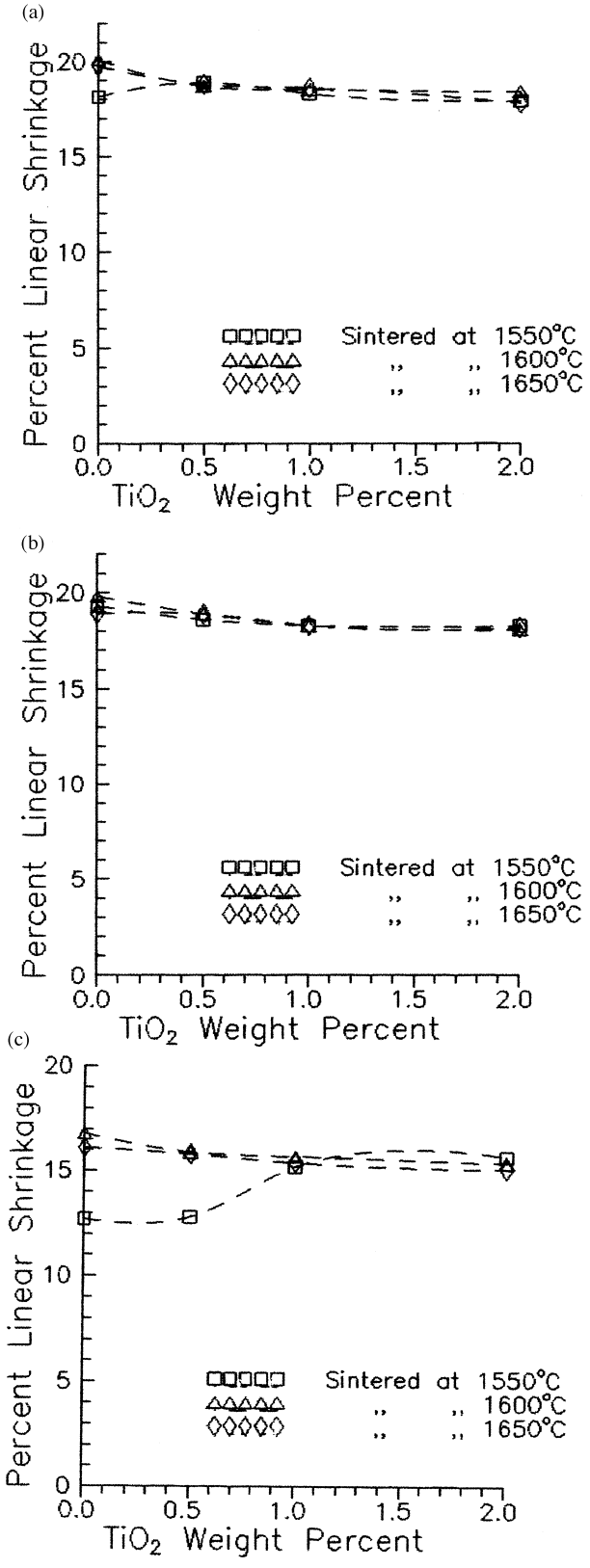


Fig. 2. Variation of linear shrinkage of the spinels with TiO_2 content. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

3.1. Bulk density

Addition of TiO_2 on the sintered density of S-batch (Fig. 1a) shows beneficial effect only for the 1550°C sintering but the amount of the additive has no significant effect. For M-batch, addition of TiO_2 (Fig. 1b) shows a deleterious effect on sintering at 1600°C and at 1650°C may be associated with the grain growth of the batch. For A-batch TiO_2 is highly beneficial at 1550°C. It improves the bulk density from 2.84 to 3.50 g/cm^3 on addition of 2 wt.% of TiO_2 due to dissolution of Ti and exsolution of Al in spinel.[14] But the same amount shows a deteriorating result on sintering at 1650°C, which is associated with grain orientation and increased intergranular porosity (as observed in microstructure).

3.2. Linear shrinkage

Little but gradual fall in linear shrinkage is observed with increasing amount of TiO_2 and increasing sintering temperature for both the S and M-batches (Fig. 2a and b). But the A-batch (Fig. 2c) shows a steep rise in linear shrinkage with increasing amount of TiO_2 on firing at 1550°C due to a much higher extent of sintering; but for higher sintering temperatures no significant variation in shrinkage is observed. Shrinkage patterns support the same trend as that of the density plots.

3.3. Phase analysis

X-ray diffraction study of all the different batches sintered at different temperatures are done for phase analysis and the obtained phases are tabulated in Table 3. S-batch shows only spinel phase for all the conditions of sintering temperature and TiO_2 addition. M-batch shows free periclase along with spinel phase for all the different conditions. But for A-batch free corundum phase is observed along with the spinel phase on sintering at 1550°C, whose intensity is reduced on increasing the sintering temperature to 1600°C but only spinel phase with no free corundum phase is found on sintering at 1650°C. Complete solid solubility of excess alumina in spinel (in a batch containing 83.5 wt.% of alumina) is obtained on sintering at 1650°C and TiO_2 shows no effect on this characteristic. This observation of complete solid solubility of free alumina in spinel phase at 1650°C finds similarity with the work of Bailey and Russel.[17] No TiO_2 bearing phase is obtained in any of the spinel compositions fired at any temperature.

3.4. Strength at ambient temperature (cold MOR)

TiO_2 does not show any drastic change in the cold strength values of the different spinel compositions. Addition of TiO_2 shows only a marginal improvement in the cold MOR values of S-batch (Fig. 3a), with increasing amount of TiO_2 for all the different sintering temperatures. For M-batch (Fig. 3b) the beneficial effect of addition of TiO_2 is found for sintering at 1600°C but at 1650°C a poor strength is always observed; increased roundedness on higher temperature sintering may cause the deterioration. A-batch (Fig. 3c) shows little improvement in strength values with the amount of TiO_2 content for all the sintering temperatures.

3.5. Strength at elevated temperature (hot MOR)

Addition of TiO_2 is found to have (Fig. 4) a deteriorating effect on the hot MOR values of all the three different spinel compositions sintered at different temperatures. A continuous decrease in hot strength is observed with increasing amount of TiO_2 (above 0.5 wt.%) for the S-batch (Fig. 4a). For M-batch, the fall in hot strength values is drastic for the 1650°C sintered products (Fig. 4b). Higher amount of TiO_2 at higher sintering temperatures showed greater deterioration. Increase in

Table 3
Phase analysis of different spinels

Batch	TiO_2	Sintered at		
	(wt.%)	1550°C	1600°C	1650°C
S	0	Spinel	Spinel	Spinel
S	0.5	Spinel	Spinel	Spinel
S	1	Spinel	Spinel	Spinel
S	2	Spinel	Spinel	Spinel
M	0	Spinel and periclase	Spinel and periclase	Spinel and periclase
M	0.5	Spinel and periclase	Spinel and periclase	Spinel and periclase
M	1	Spinel and periclase	Spinel and periclase	Spinel and periclase
M	2	Spinel and periclase	Spinel and periclase	Spinel and periclase
A	0	Spinel and corundum	Spinel and corundum	Spinel
A	0.5	Spinel and corundum	Spinel and corundum	Spinel
A	1	Spinel and corundum	Spinel and corundum	Spinel
A	2	Spinel and corundum	Spinel and corundum	Spinel

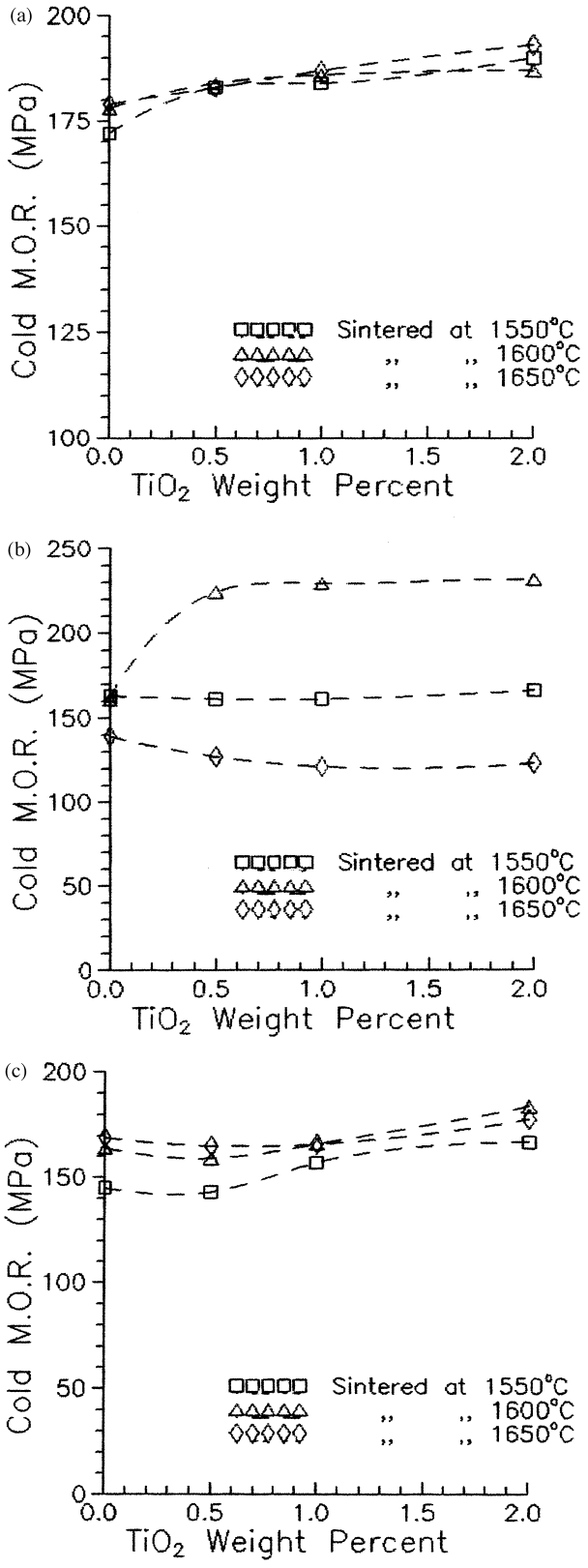


Fig 3. Variation of cold strength (MOR) of the spinels with TiO_2 content. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

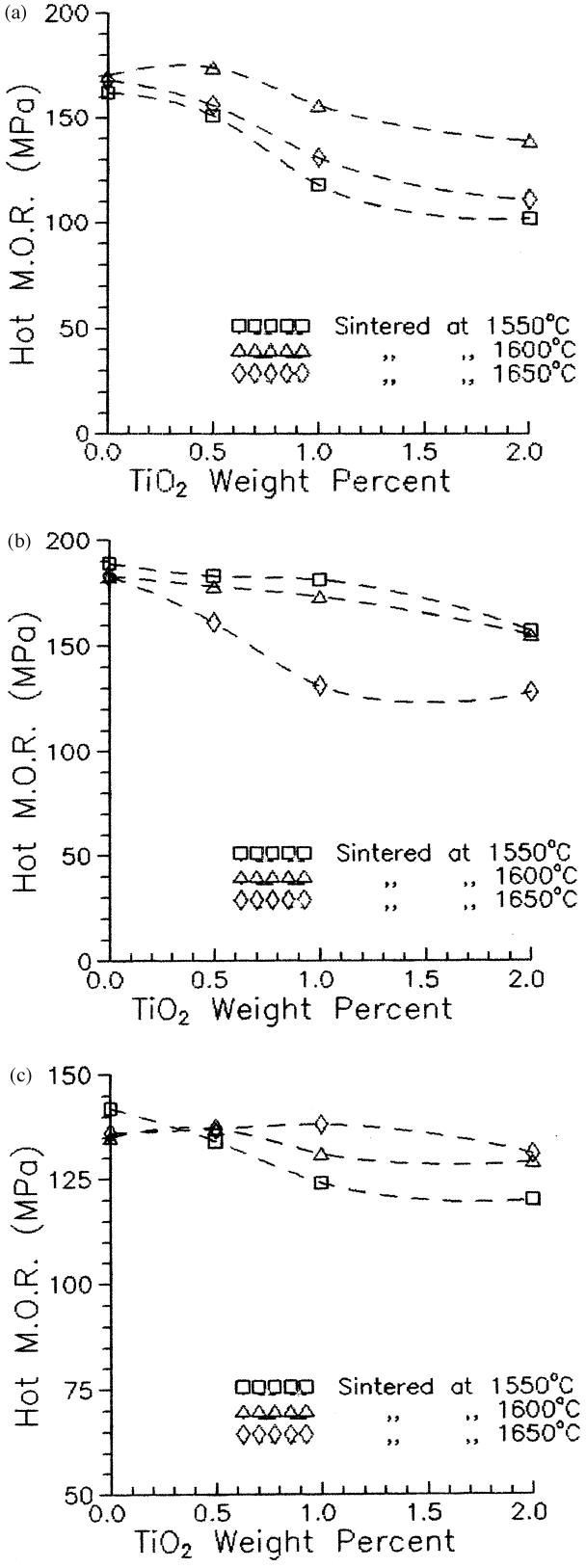


Fig. 4. Variation of hot strength (MOR) of the spinels with TiO_2 content. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

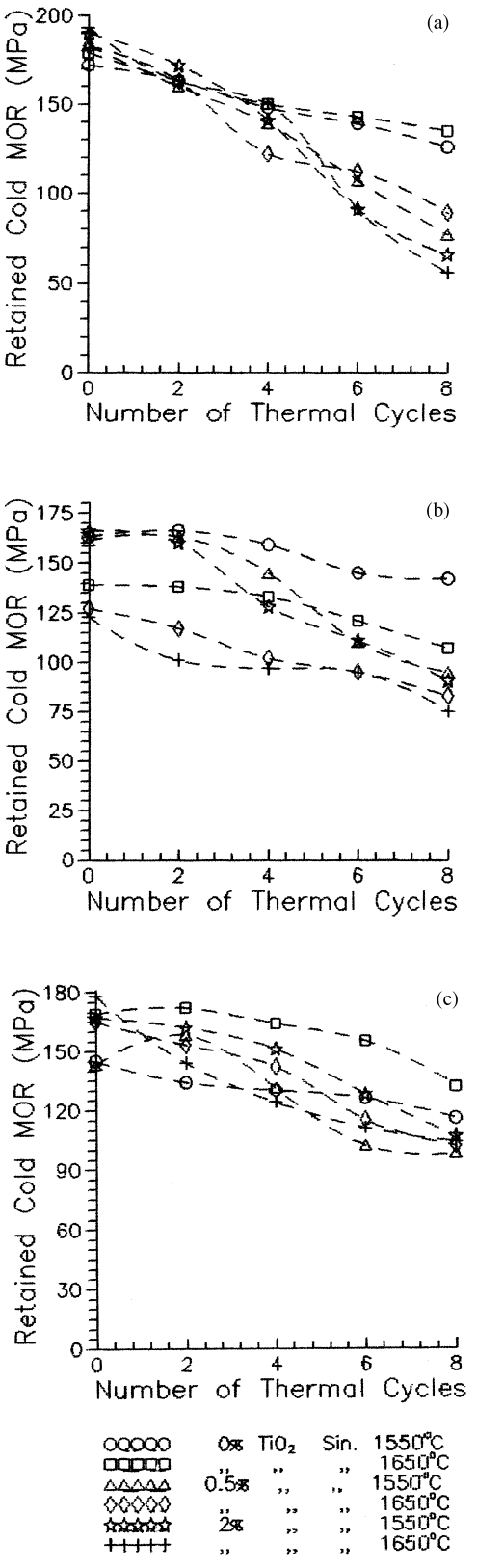
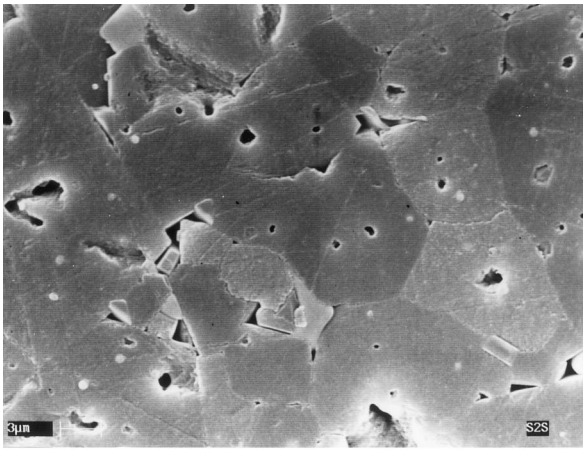
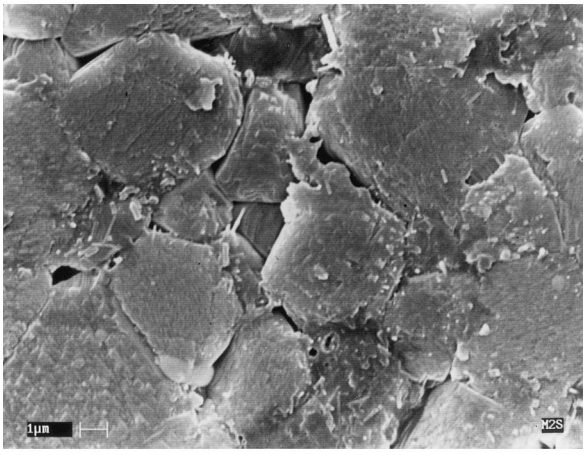


Fig 5. Cold strength retainment study of the spinels after thermal shock. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

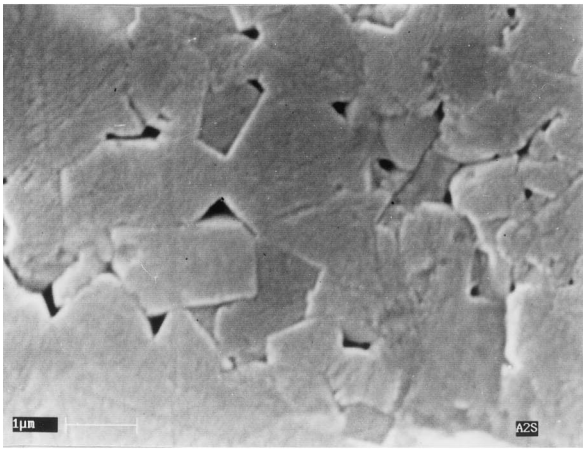
roundedness of the grains (as found in photo micrograph) and presence of higher amount of impurities with TiO_2 at the grain boundaries (confirmed by the EDXA study) are effective to reduce the hot strength values. But A-batch shows much lesser degradation



(a)



(b)



(c)

Fig. 6. Scanning electrton photomicrographs of the without additive containing bodies sintered at 1600°C. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

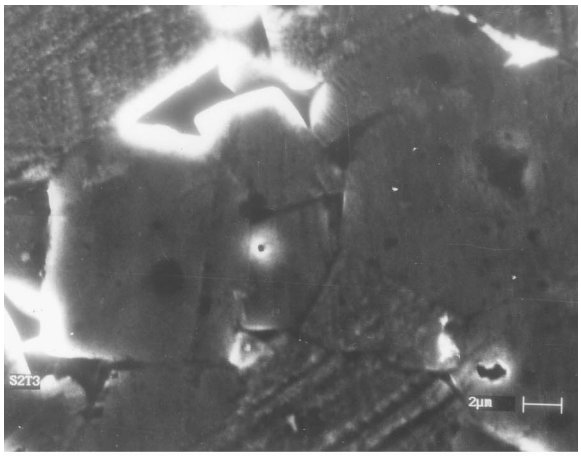
even at the higher sintering temperatures (Fig. 4c). Dissolution of TiO_2 and exsolution of Al_2O_3 from spinel[14] and high alumina containing grain boundary phases (EDXA study) might have restricted the formation of low melting phases that helps in retaining the hot strength characteristics.

3.6. Retained strength after thermal shock

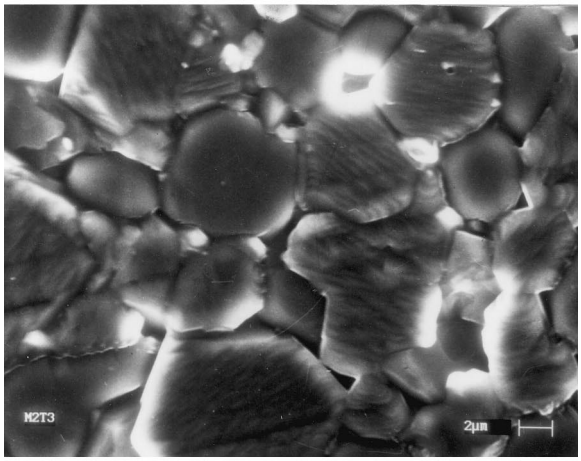
Retained strength after thermal shock at 1000°C shows that presence of TiO_2 in S-batch (Fig. 5a) has a deleterious effect. Retained strength falls slowly and gradually with an increasing number of cycles for S-batch without TiO_2 and about 80% retained strength is found after the 8th thermal cycle. But addition of TiO_2 shows a drastic fall in strength after the 2nd cycle and less than 50% strength values are obtained after the 8th cycle. M-batch (Fig. 5b) also shows similar characteristics to that of the S-batch but the retained strength is higher for this case. Formation of low melting phases at the grain boundaries due to the presence of higher amount of impurities and TiO_2, which has resulted in cracking after thermal shock and gives poor retained strength values. A-batch (Fig. 5c) also shows similar trend as that of the others. But for A-batch the drastic fall in retained strength is found only at a higher number of thermal cycles. In general, addition of TiO_2 was found to be detrimental in retaining the cold strength after thermal shock for all the three compositions.

3.7. Microstructural and elemental analysis

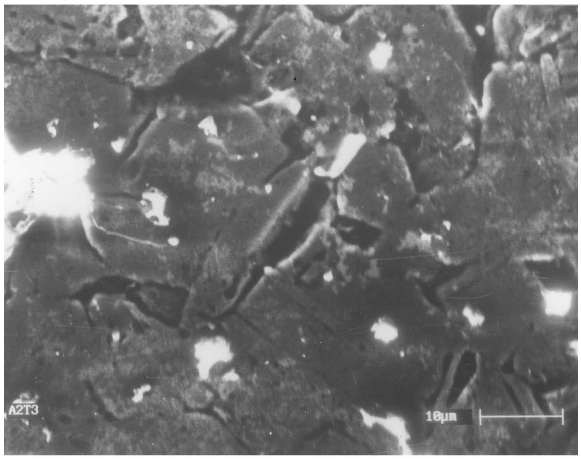
Scanning electron photomicrographs of the with and without TiO_2 containing bodies of all the three different spinel compositions are shown in Figs. 6 and 7 respectively. Results of EDXA study (elemental analysis converted to oxide analysis assuming the valency of oxygen as−2) at different positions of grains and grain boundaries of all the three different spinel batches are shown in Table 4. Addition of TiO_2 in S-batch (Fig. 7a) shows an increase in the grain size and a decrease in the angularity of the grains. These affect the strength values of the sintered products. EDXA study shows near stoichiometric spinel composition for both the grains and grain boundaries (little alumina rich composition is found due to MgO vapourisation at the final stage of sintering[18]) with uniform distribution of TiO_2 at the grains and grain boundaries. M-batch shows more rounded grains in presence of TiO_2 (Fig. 7b) which affects the strength values. The smaller grain size may be due to the presence of small rounded free periclase grains (confirmed by EDXA study) which hinders the grain growth phenomena.[19] EDXA study also shows grain boundary regions higher in amount of MgO, TiO_2 and other impurities which may react to form low melting phases that reduces the hot strength properties. But TiO_2 in A-batch does not strongly affect the grain size and grain angularity (Fig. 7c). Again the grain boundary portions are rich in alumina content which hinders the formation of low melting phases. A



(a)



(b)



(c)

Fig. 7. Effect of addition of 2 wt.% TiO_2 on the microstructure of the spinels sintered at 1650°C. (a) Stoichiometric spinel, (b) magnesia rich spinel and (c) alumina rich spinel.

Table 4
EDX analysis of different spinel compositions

Batch	TiO_2 (wt.%)	Sintered at (°C)	Analysis of	EDX Analysis as wt.% of oxides				
				MgO	Al_2O_3	TiO_2	CaO	SiO_2
S	0	1650	Grain	26.7	73.3			
S	0	1650	Grain boundary	24.4	74.0		1.2	0.4
S	2	1650	Grain	27.2	70.9	1.3	0.4	0.2
S	2	1650	Grain boundary	26.6	70.1	1.4	1.4	0.4
M	0	1650	Grain (larger)	26.4	73.3		0.2	
M	0	1650	Grain (small, rounded and less in number)	95.1	2.8		1.3	
M	0	1650	Grain boundary between larger and smaller grains	48.9	47.9		2.6	0.6
M	0	1650	Grain boundary between larger grains	29.9	67.5		1.1	0.6
M	2	1650	Grain	29.5	69.1	1.1	0.2	0.1
M	2	1650	Grain (small, rounded and less in number)	92.4	4.9	0.3	1.5	0.9
M	2	1650	Grain boundary	29.9	65.8	1.7	1.3	1.3
M	2	1650	Grain boundary between small and big grains	52.3	44.5	1.7	0.9	0.6
A	0	1650	Grain	16.6	82.7		0.2	
A	0	1650	Grain boundary	16.9	79.2		2.4	1.2
A	2	1650	Grain	20.8	77.6	1.2	0.4	
A	2	1650	White portion	7.5	87.1	3.1	2.0	0.2
A	2	1650	Grain boundary	9.7	85.9	1.7	1.3	0.6

separate phase (white in photomicrograph) is also there, at the grain junctions and grain boundaries, containing little higher amount of TiO_2 (higher than in the grains) but presence of high alumina in the same does not affect the batch severely. Thus the strength values do not degrade drastically.

4. Conclusions

TiO_2 was found to improve the density of alumina rich and stoichiometric spinels sintered at 1550°C, but at higher sintering temperatures, higher amount of additive showed a deteriorating effect due to grain growth. Shrinkage study supported the densification behaviour. TiO_2 up to 2 wt.% had no influence on the phase constituents of different spinels, Addition of TiO_2 showed only some marginal changes in cold strength values. But for hot strength TiO_2 showed deteriorating characteristics which is associated with the increased roundedness of the grains and presence of higher amount of impurities and TiO_2 at the grain boundaries. The extent of deterioration was increased with the increase in sintering temperature and amount of additive. All the different spinels showed lower retained strength after thermal shock in presence of TiO_2; formation of low melting compound in presence of higher impurities and TiO_2 at grain boundaries caused cracking during the thermal shock. EDXA study showed that Ti was uniformly distributed through the grains and grain boundaries of all the different compositions. No TiO_2 bearing phase was identified. Photomicrographs marked the increase in the roundedness of the grains in presence of TiO_2 that affected the strength properties.

Acknowledgements

The authors are highly obliged to the Director, C. G. & C. R. I., Calcutta, for his keen interest and kind permission to publish the paper. The authors are also obliged to Dr. S.K. Das, Dr. B. Mukherjee, Mr A. Ghosh, Mr. J.R. Biswas, Dr. A.K. Chakraborty and Dr. S. Sen of the same Institute for their kind help in carrying out different experiments regarding the paper.

References

1. Karisheff A. D., Refractory products and method of fabrication. French Patent No. 350016, Dated August 24, 1905.
2. Rankin, G. A. and Merwin, H. E., Ternary system $CaO–Al_2O_3–MgO$. *Journal of the American Chemical Society*, 1916, **38**(3), 568–588.
3. Bray, D. J., Toxicity of chromium compounds formed in refractories. *American Ceramic Society Bulletin*, 1985, **64**(7), 1012–1016.
4. Maschio, R. D., Fabbri, B. and Fiorri, C., Industrial applications of refractories containing magnesium aluminate spinel. *Industrial Ceramics*, 1988, **8**(3), 121–126.
5. Noda, T. and Hasegawa, S., Effect of addition of salt vapour on the synthesis and crystal growth of spinel. *Journal of the Society for Chemical Industries, Japan*, 1940, **43**(3), 169–172.
6. Kostic, E., Boskovic, S. and Kis, S., Influence of fluorine ion on the spinel synthesis. *Journal of Materials Science Letters*, 1982, **1**(12), 507–510.
7. Stamenkovic, I., Hot pressing of [LiF] doped spinel powder. *La Ceramica*, 1985, **38**(4), 17–22.
8. Huang, J., Sun, S. and Ko, Y., Investigation of high alumina spinel: effect of LiF and $CaCO_3$ addition. *Journal of the American Ceramic Society*, 1997, **80**(12), 3237–3241.
9. Baranova, T. F., Kurskaya, I. and Dabizha, N. A., Sintering of high purity fused MgO and $MgAl_2O_4$. *Ogneupory*, 1981, **46**(3), 54–56.

10. Skomorovskaya, L. A., Magnesia spinel ceramics alloyed with rare earth oxides. *Glass & Ceramics*, 1993, **3–4**, 165–168.
11. Ju, D. S., Fang, G. F. and Xi-ping, C., Effect of Cr_2O_3 on slag resistance of magnesia spinel refractory. *Naihuo Cailiao*, 1994, **28**(4), 189–192.
12. Sarkar, R. and Banerjee, G., Effect of addition of Cr_2O_3 on the properties of $MgOAl_2O_3$ spinels. Paper communicated to *Journal of Materials Science*.
13. Baik, Y. H., Sintering of $MgAl_2O_4$ spinel and its characteristics. *Yoop Hikoechi*, 1985, **22**(6), 29–36.
14. Yu, J. and Hiragushi, K., Sintering behaviour of spinel with added TiO_2. *Taikabutsu Overseas*, 1996, **16**(4), 61.
15. Sarkar, R., Das, S. K. and Banerjee, G., Effect of attritor milling on the densification of magnesium aluminate spinel. *Ceramic International*, 1999, **25**(5), 485–489.
16. Sarkar, R., Banerjee., G., Effect of compositional variation and fineness on the densification of $MgO–Al_2O_3$ compacts. *Journal of the European Ceramic Society*, 1999, **19**(16), 2893–2899.
17. Bailey, J. T. and Russel Jr, R., Preparation and properties of dense spinel ceramics in the $MgAl_2O_4–Al_2O_3$ system. *Transactions and Journal of the British Ceramic Society*, 1969, **68**(4), 159–164.
18. Matsui M., Takashi T. and Oda I., Effects of starting materials and calcining temperature on sintering of spinel ceramics. In *Advances in Ceramics,* ed. W. D. Kingery, The American Ceramic Society, Columbus, OH, 1984. Vol 10, pp. 562–573.
19. Kenya H., Tadashi O. and Zenbee N., Effects of starting materials and calcining temperature on sintering of spinel ceramics. *Rep. Res. Lab. Eng. Mater., Tokyo Institute of Technology,* 1977, No. 2, pp. 85–94.