Journal of the European Ceramic Society **19** (1999) 2893–2899

PII: S0955-2219(99)00078-3
0955-2219/99/$ - see front matter

Effect of Compositional Variation and Fineness on the Densification of MgO–Al_2O_3 Compacts

Ritwik Sarkar* and Goutam Banerjee

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

(Received 1 September 1998; accepted 13 March 1999)

Abstract

Single stage densification of magnesia—alumina compacts were studied with MgO to Al_2O_3 molar ratios 1:1 (stoichiometric spinel), 2:1 (magnesia rich spinel) and 1:2 (alumina rich spinel). Attritor milling has been adopted to produce variation in fineness. Milling greatly improved the densification. Densification was found to be easier for the magnesia rich composition and difficult for the alumina rich one. X-ray diffraction patterns showed the expected phases in stoichiometric and magnesia rich spinel. Alumina rich composition showed no free corundum phase on sintering at 1650°C and only spinel phase marks the complete solid solution of excess alumina in spinel at this composition. EDAX analysis also supports the event and also reflects that the impurities are mainly present at the grain boundaries. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: spinels, milling, sintering, solid state reaction, microstructure-final.

1 Introduction

The only compound present in the MgO–Al_2O_3 system is spinel ($MgAl_2O_4$). This magnesium aluminate spinel ceramic offers a unique combination of desirable properties—high melting point, high strength both at room temperature and elevated temperatures, excellent thermal properties, high resistance against chemical attack and low electrical losses. For these excellent characteristics spinel found its major commercial outlet as refractory material. Spinel refractories are used as pure spinel one or as a component in the magnesia rich or alumina rich compositions. The major application areas[1] are transition and burning zones of cement rotary kilns, checker work of the glass furnace regenerators and side walls and bottom of the steel ladles.

As the spinel formation reaction from its constituent oxides, MgO and Al_2O_3, is associated with a volume expansion of about 5%,[2] most fabrication techniques require an intermediate calcination process. Calcining around 1600°C to complete the spinellization reaction, then crushing and milling, followed by shaping and refiring to sintered product was the route to produce dense spinel body. This two stage firing process and a large number of relevant processing parameters influenced the cost of production.

Many works[3–8] have been done on the sintering behaviour of stoichiometric and nonstoichiometric spinels. For stoichiometric spinel, Bailey and Russel introduced[3] a new ‘partial reaction technique’ where a mixture of magnesia and alumina were calcined to complete 55 to 70% of spinellisation reaction, that allowed to overcome the hinderence of 5% volume expansion with retaining sufficient reactivity for greater sintering on a second firing. Teoreanu and Ciocea[4] obtained better densification in a single stage firing with calcined alumina and sintered magnesia, using $MgCl_2$ as a sintering aid. Purer variety of materials with submicron particle sizes and slower rate of heating were found[5] to produce highly sintered magnesium aluminate spinel from sea water magnesia and commercial alumina in a single stage sintering process.

For nonstoichiometric composition, Bailey and Russel[6] studied the system $MgAl_2O_4$–Al_2O_3 using their partial reaction technique.[3] They found a continuous decrease in densification on increasing alumina content up to 85 wt% and only spinel phase in the X-ray studies. Alumina more than 85% was reported to produce free corundum phase and density was also reported to increase. The same author[7] also studied the magnesia rich spinel ceramics and found a little (<10 wt%) excess magnesia to be highly beneficial for improved

---

*To whom correspondence should be addressed.

densification, strength and controlled grain growth. Hing[8] concluded that magnesium aluminate spinel can be sintered to near theoretical density on both sides of the stoichiometry in a hydrogen atmosphere. He pointed out the creation of vacancies in excess alumina or excess magnesia condition helped the sintering.

Literature does not provide any complete study on the densification of stoichiometric and non-stoichiometric spinels by varying the fineness of the starting materials. Here such a study was undertaken and in addition, phase analysis and microstructural characterisation were also included. Three different compositions with $MgO:Al_2O_3$ molar ratios 2:1, 1:1 and 1:2 were studied for single stage densification. Fineness of all the compositions were varied by attritor milling for different hours. The phase diagram of the $MgO–Al_2O_3$ system is shown in Fig. 1. All the three different compositions and the temperature range of densification for this study is marked in the figure.

2 Experimental

Alumina and magnesia were used as the starting materials for the study having physicochemical characteristics as provided in Table 1. Oxides were mixed according to the molar compositions ($MgO:Al_2O_3 = 2:1$, 1:1 and 1:2) and three different spinel batches were prepared, namely, magnesia rich spinel (M), stoichiometric spinel (S) and alumina rich spinel (A). Batch compositions are given in Table 2. All the three different batches were then attritor milled (Union Process make attritor mill, model no. 01HD) for 2, 4 and 6 h. Milled and without milled powders were characterized by specific surface area measurement (applying BET technique) and particle size distribution (applying Stoke's law). Powders were then isostatically pressed (Autoclave Engineers make press model no. CIP-6-23-30) at 175 MPa to briquettes (size 25 mm dia×10 mm). Briquettes were first dried at 110°C and then sintered at temperatures 1550, 1600 and 1650°C. A heating rate of 1°C per min and a soaking period of 2 h at the peak temperatures were used for sintering. Sintered briquettes of different composition and different milling time were then studied for linear shrinkage and densification. All the sintered bodies with 4 h milling were tested for phase analysis (using a Philips make X-ray diffractometer) with Cu – K_α radiation in the diffraction range of 25 to 50°. Microstructural analysis was done in a Leica made scanning electron microscope (model S 440) with EDAX (electron diffraction analysis of X-ray) facility. Grain size measurement was done by lineal intercept method.[9]

3 Results and Discussion

3.1 Milling study

Attritor milling had similar effects for all the three different compositions. Increase in surface area [Fig. 2(A)] was pronounced for the early hours of milling, but the effectiveness was reduced on prolonged milling. The corresponding particle size values of the without-milled and milled powders (obtained from the surface area values by calculation)

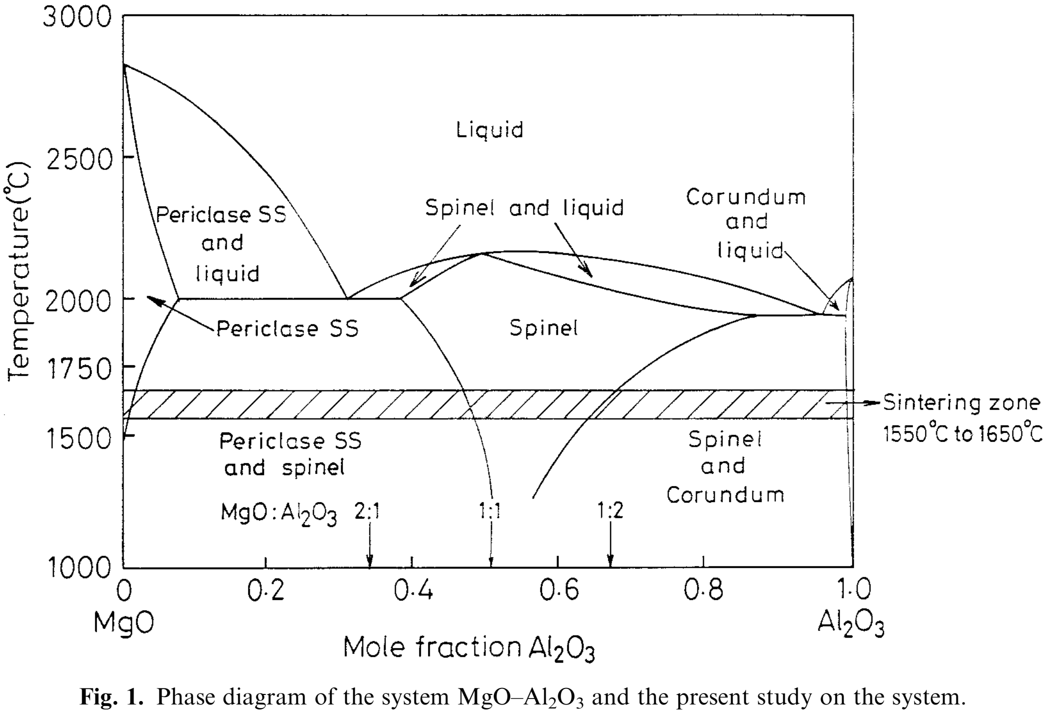

Fig. 1. Phase diagram of the system $MgO–Al_2O_3$ and the present study on the system.

Table 1. Physico-chemical properties of magnesia and alumina

	Magnesia	*Alumina*
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 ($m^2\ gm^{-1}$)	1·8	2·9
Mineralogical phase	Periclase	Corundum

Table 2. Batch composition

	Magnesia	*Alumina*
Stoichiometric spinel	28·36	71·64
Magnesia rich spinel	44·22	55·78
Alumina rich spinel	16·51	83·49

are listed in Table 3. Alumina rich composition showed little higher surface area and lower size than the other compositions due to the presence of higher amount of finer alumina particles. Particle size distribution plot (Fig. 3) of the dried powders showed little difference in sizes for without-milled and 6 h milled materials. Measured size of the powders reflect that they were highly agglomerated. Green density of the pressed briquettes also increased with increasing milling time [Fig. 2(B)] due to reduced particle size (removal of coarser pores) and a maximum density was obtained for the materials having higher milling time.

3.2 Sintering and shrinkage study

Three different compositions are taken separately and discussed for sintering and shrinkage studies. Sintering is evaluated as the bulk density or percent densification and shrinkage is measured as percent linear shrinkage of the sintered compacts.

3.2.1 Compact with $MgO:Al_2O_3 = 1:1$

Materials of stoichiometric composition without milling were densified only up to 91% (3·26 g cm^{-3}). Milling improved the densification [Fig. 4(A)] by increasing the fineness of the starting materials. But prolong milling beyond 4 h and sintering above 1600°C did not show any significant effect on sintered density.

Shrinkage [Fig. 4(B)] was found to increase with increasing sintering temperature and milling time up to 4 h. Milling for 6 h produced lower shrinkage in the sintered body compared to that of the 4 h milling, as sintered density of the materials was similar but the green density was higher for 6 h milled materials, resulting in a lesser shrinkage value.

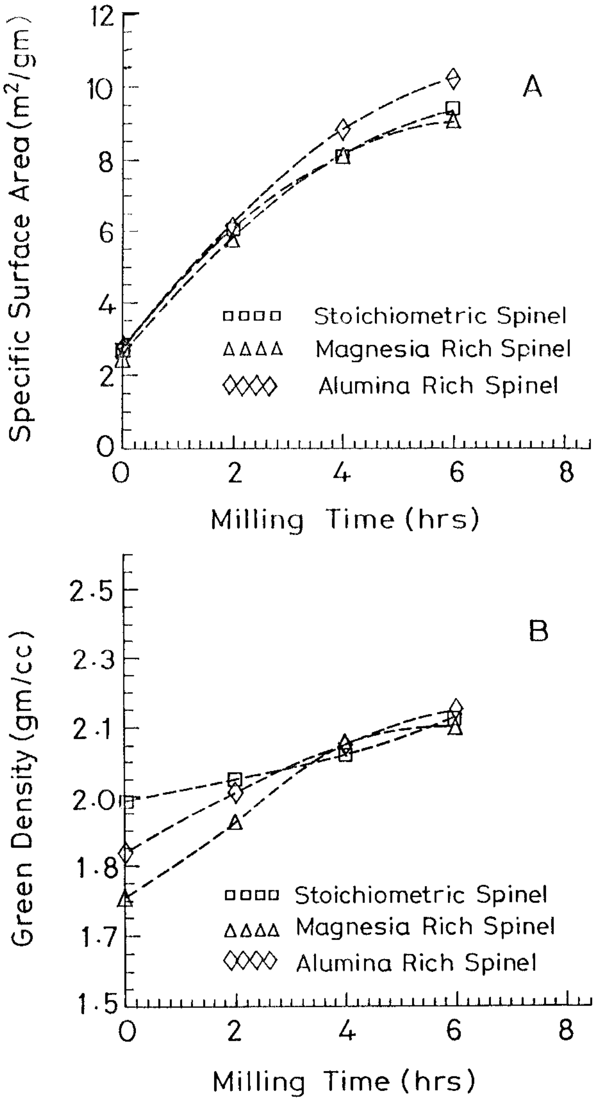

Fig. 2. Effect of milling time on: (A) specific surface area and (B) green density, of the three different spinel compositions.

Table 3. Particle size of the different batches

Milling time	*Particle size* (μ)		
(h)	*Stoichiometric*	*Magnesia rich*	*Alumna rich*
0	0·6	0·63	0·54
2	0·25	0·27	0·25
4	0·19	0·19	0·17
6	0·16	0·17	0·13

3.2.2 Compact with $MgO:Al_2O_3 = 2:1$

Materials without milling were well densified (96·8%) and only a little improvement was found by the incorporation of milling process [Fig. 5(A)]. Increase in surface area by about 4 times for the 6 h milled materials has improved the sintered density only by 3%. Excess magnesia composition

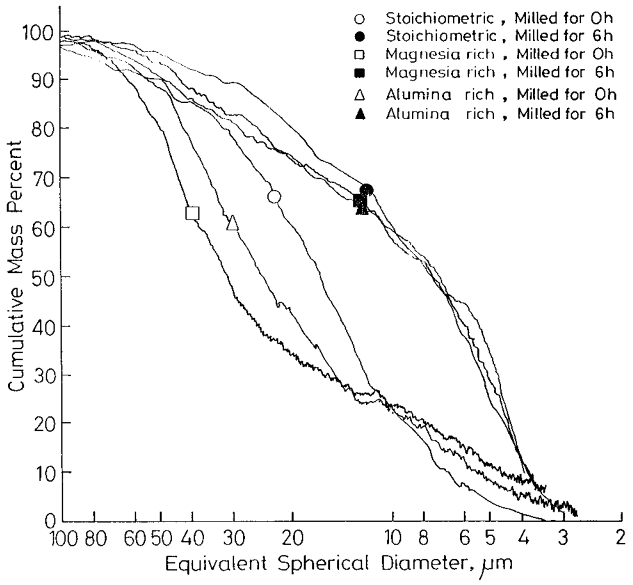

Fig. 3. Particle size distribution plot of without-milled and 6 h milled materials of three different compositions.

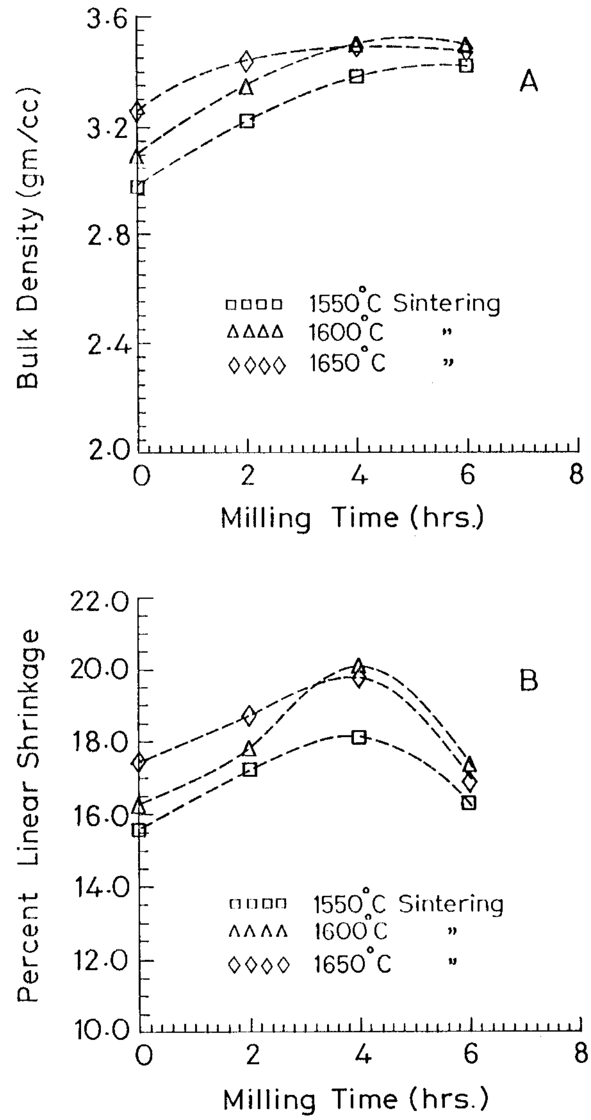

Fig. 4. Effect of milling on stoichiometric spinel: (A) effect on bulk density, (B) effect on linear shrinkage.

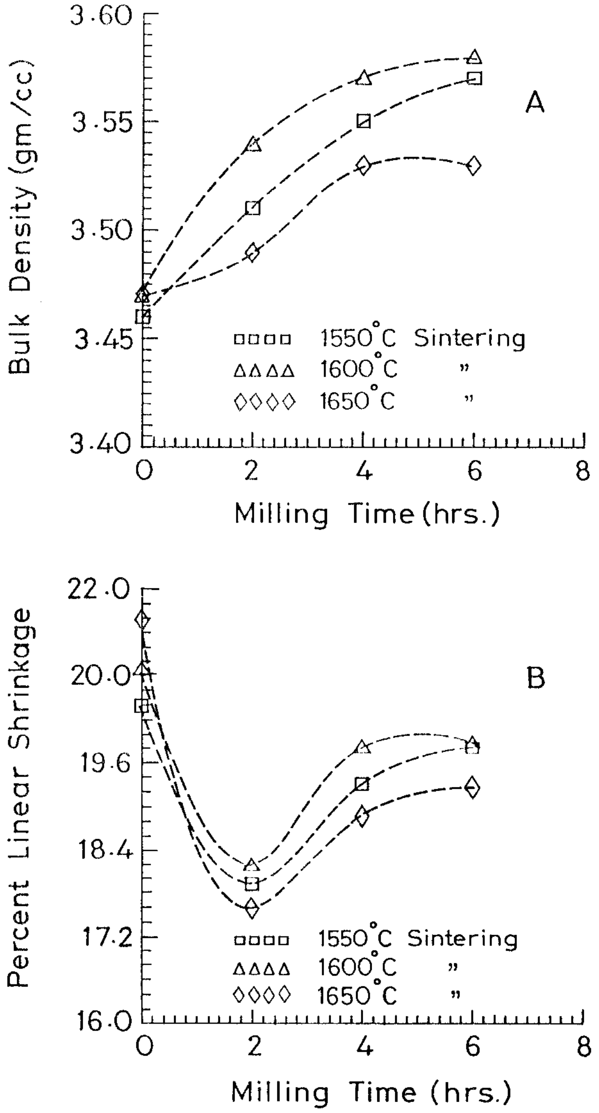

Fig. 5. Effect of milling on magnesia rich spinel: (A) effect on bulk density, (B) effect on linear shrinkage.

is itself very active for higher densification, may be due to the creation of vacancies as suggested by Hing.[8] Again free periclase [as confirmed by phase analysis (Fig. 7) hinders the grain boundary migration and prevents grain growth; which resulted in higher densification.[10]

An interesting pattern for shrinkage [Fig. 5(B)] was found for the magnesia rich composition. Incorporation of milling process had improved the green density of the compacts, but the change in sintered density was very little. This resulted a sharp fall in the shrinkage value of sintered products on introduction of milling process.

3.2.3 Compact with $MgO:Al_2O_3=1:2$

Densification of the alumina rich spinel [Fig. 6(A)] was greatly influenced by the incorporation of milling process. Materials without milling were very poorly densified (66·8%). Milling improved the densification for all the sintering temperatures and a maximum 96·4% true density was observed for

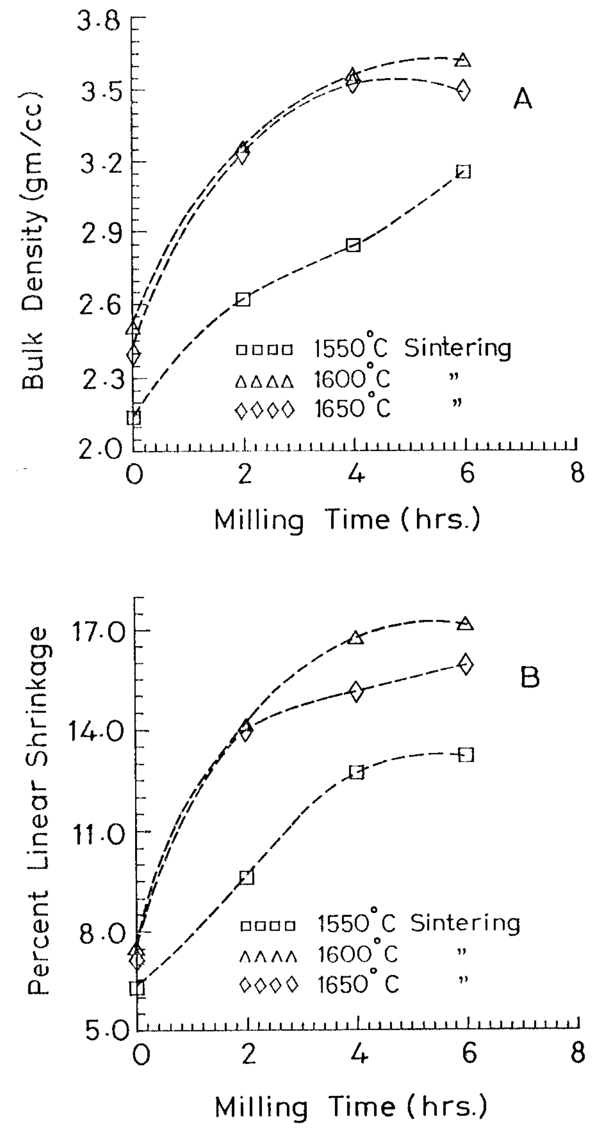

Fig. 6. Effect of milling on alumina rich spinel: (A) effect on bulk density, (B) effect on linear shrinkage.

the 6 h milled material sintered at 1600°C. Effect of temperature is also prominent here besides milling. Sintering at 1550°C was found to be inadequate for this composition.

It was observed that alumina rich composition without milling showed less shrinkage value [Fig. 6(B)]. Milling greatly improved the sintering and a sharp rise in shrinkage was also observed. Shrinkage of 1550°C sintering showed poor values even for 6 h milled materials which also confirms the inadequateness of temperature for densification.

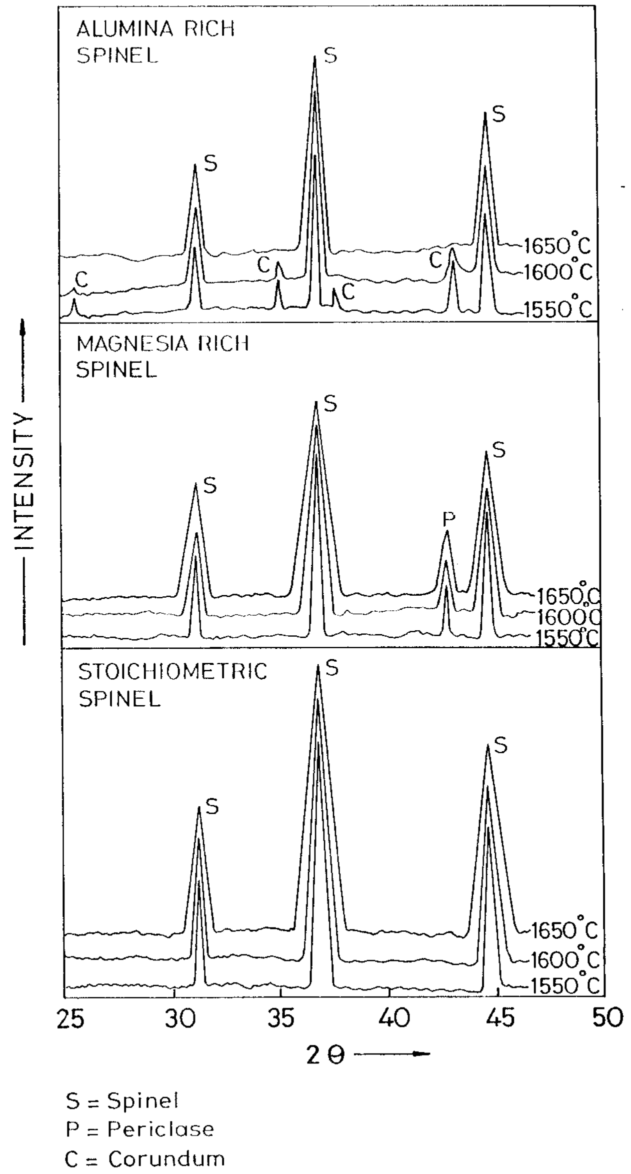

Fig. 7. Phase analysis study of all the three different spinels with 4 h milling time.

Table 4. Cooling schedule of furnace

Cooling time (h)	*Fall of temperature (°C)*
0–1	350–400
1–2	200–300
2–3	200–250
3–4	150–200
4–5	100–150

This single stage densification study of magnesium aluminate spinel is a case of reaction sintering. Now for well densified reaction sintered product it is well established[11,12] to complete the densification process prior to reaction. Here this was followed by the reduction of particle size (by milling), as reaction depends on L^{-1} or L^{-2} and densification depends on L^{-3} or L^{-4}, where L is the size of starting material.[12] But prolong milling of 6 h had no significant benefit on sintering than that of 4 h mined materials, which found similarities of the work of Petkovic and Ristic[13] who reported higher fineness beyond a certain critical value was of no benefit for sintering of alumina powders. Thus control on reaction sintering process of magnesium aluminate helps to avoid the intermediate calcination, that was popular earlier. Always a higher densification was observed for the magnesia rich composition and it was difficult to sinter the alumina rich composition. This observation

Table 5. Edax results (oxide percentages)

	Grain				*Grain boundary*			
	Mgo	Al_2O_3	*CaO*	SiO_2	*MgO*	Al_2O_3	*CaO*	SiO_2
Stoichiometric spinel	26·7	73·3			24·4	74·0	1·2	0·4
Magnesia rich spinel	26·5	73·5			48·9	47·9	2·6	0·6
Alumina rich spinel	21·8	78·2			16·9	79·1	2·4	1·6

also found similarity with some of the previous works.[14,15]

3.3 Phase analysis study

X-ray diffraction study is shown in Fig. 7. Only spinel phase was observed for the stoichiometric composition and a little increase in peak intensity with increasing sintering temperature was also found. For magnesia rich composition free magnesia peaks were observed along with the spinel phase for all the three different sintering temperatures. Most interesting phenomena was observed for the alumina rich composition. For sintering at 1550°C, spinel with free corundum phase were obtained, at 1600°C the intensity of the corundum phase was decreased and that of the spinel phase was found to be increased. But sintering at 1650°C produces only spinel phase with no free corundum peaks. This supports the solubility of excess alumina in spinel phase even at a temperature of 1650°C. This observation found similarity with the work of Bailey and Russel.[6] Exsolution of corundum phase has failed to occur, may be due to the higher rate of natural furnace cooling from the sintering temperatures; cooling schedule is given in Table 4.

3.4 Microstructural studies

Developed microstructure and EDAX analysis (Table 5) of the sintered products were studied on the polished thermally etched samples. Stoichiometric spinel showed close compacted angular grains with intragranular pores; Fig. 8(a) showed a grain size of 3·9 μ on sintering at 1600°C. EDAX analysis shows near stoichiometric composition for both the grains and grain boundaries. Magnesia rich spinel shows less angular grains with intergranular pores; 1600°C sintered product had a size of 2·2 μ [Fig. 8(b)]. A near stoichiometric grain composition with pure magnesia grains was observed in the EDAX analysis. Grain boundaries were rich in magnesia content and associated with the impurities. Alumina rich composition shows less developed microstructure [Fig. 8(c)] with very small grain size (0·6 μ). Both the grains and grain boundaries were rich in alumina content and the impurities were found at the grain boundaries.

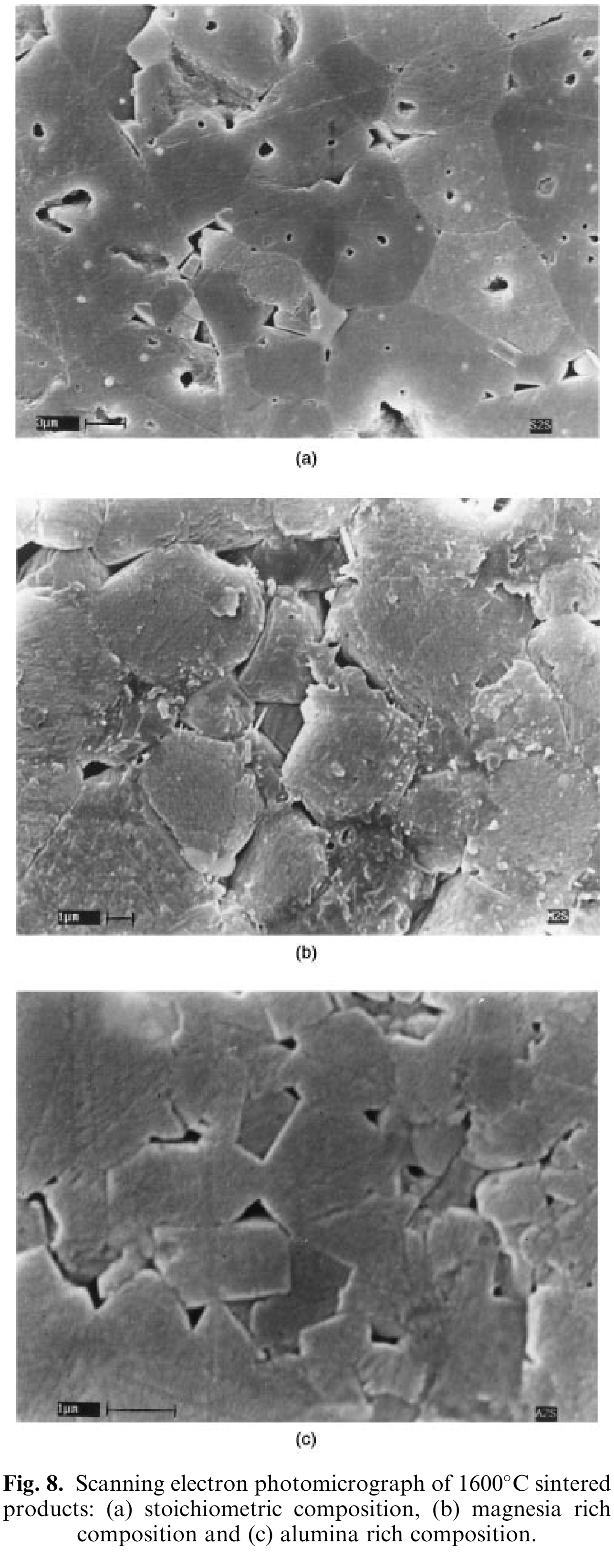

Fig. 8. Scanning electron photomicrograph of 1600°C sintered products: (a) stoichiometric composition, (b) magnesia rich composition and (c) alumina rich composition.

4 Conclusions

1. Very high density can be obtained in a single stage sintering process for all the stoichiometric and nonstoichiometric spinels ($MgO:Al_2O_3$ molar ratios = 2:1, 1:1 and 1:2) by incorporation of milling process.
2. Batch composition has a great effect on the sintering of spinel. Magnesia rich composition showed ease of sintering. Alumina rich composition was found to have less sinterability and milling helps the densification greatly.
3. Attritor milling for 4 h was found to be more effective and economical.
4. Alumina rich composition ($Al_2O_3:MgO$ molar ratio = 2:1) showed only spinel phase on sintering at 1650°C. This signifies the solubility of excess alumina in the spinel phase.
5. Microstructural studies showed well developed compacted structure for stoichiometric and magnesia rich compositions, but less developed small grains for an alumina rich one.
6. EDAX analysis showed near stoichiometric grain composition for both the stoichiometric and magnesia rich compositions. For the alumina rich one grains were little higher in alumina content. Free oxide was found only in magnesia rich composition as magnesia. For all the compositions impurities were found at the grain boundaries.

Acknowledgements

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

References

1. Maschio, R. D., Fabbri, B. and Fiori, C., Industrial applications of refractories containing magnesium aluminate spinel. *Industrial Ceramics*, 1988, **8**, 121–126.
2. Ryskhewitch, E., In *Oxide Ceramics*. Academic Press, New York, 1960, pp. 257–274.
3. Bailey, J. T. and Russel, R., Sintered spinel ceramics. *American Ceramic Society Bulletin*, 1968, **47**, 1025–1029.
4. Teoreanu, I. and Ciocea, N., Magnesia—alumina spinel refractories. *Interceram.*, 1987, **4**, 19–21.
5. Sarkar, R., Das, K., Das, S. K. and Banedee, G., Development of magnesium aluminate spinel by solid oxide reaction. UNITECR-1997, Vol. II, pp. 1053–1058.
6. Bailey, J. T. and Russel, R., Preparation and properties of dense spinel ceramics in the $MgAl_2O_4$–Al_2O_3 system. *Transaction & Journal of the British Ceramic Society*, 1969, **68**, 159–164.
7. Bailey, J. T. and Russel, R., Magnesia rich $MgAl_2O_4$ spinel ceramics. *American Ceramic Society Bulletin*, 1971, **50**, 493–496.
8. Hing, P., Fabrication of translucent magnesium aluminate spinel and its compatibility in sodium vapours. *Journal of Material Science*, 1976, **11**, 1919–1926.
9. Wurst, J. C. and Nelson, J. A., Lineal intercept technique for measuring grain size in two phase polycrystalline ceramics. *Journal of the American Ceramic Society*, 1972, **55**, 109.
10. Kenya, H., Tadashi, O. and Zenbee, N., Effect of starting materials and calcining temperature on the sintering of spinel ceramics. *Rep. Res. Lab. Eng. Mater., Tokyo Ins. Tech.*, 1977, **2**, 85–94.
11. Yangyuan, S. and Brook, R. J., Preparation and strength of forsterite–zirconia ceramic composite. *Ceramics International*, 1983, **9**, 39–45.
12. Bosh, P. and Giry, J. P., Preparation of zirconia–mullite ceramics by reaction sintering. *Science of Sintering*, 1988, **20**, 141–148.
13. Petkovic, J. and Ristic, M. M., The influence of specific surface area on the sintering of alumina powders. *Ceramurgia*, 1973, **1**, 12–14.
14. Kenya, H., Tadashi, O. and Zenbee, X., Effect of starting materials and calcination temperatures on sintering of spinel ceramics. *Rep. Res. Lab. Eng. Mat (Tokyo Institute of Technology)*, 1977, **2**, 85–94.
15. Kanai, T., Effect of composition on sintering and bending strength of spinel ceramics. *Rep. Res. Lab. Eng. Mater (Tokyo Institute of Technology)*, 1988, **13**, 75–83.