ELSEVIER

Ceramics International 29 (2003) 407–411

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Reaction sintered magnesia rich magnesium aluminate spinel: effect of alumina reactivity

Ritwik Sarkar*, Arup Ghosh, Samir Kr Das

Refractories Division, Central Glass & Ceramic Research Institute, Kolkata, India

Received 29 April 2002; received in revised form 7 May 2002; accepted 27 June 2002

Abstract

Reaction sintering of magnesia rich magnesium aluminate spinel (MgO 34 wt.%) was done in the temperature range of 1600–1700 °C. Reactivity of constituent alumina was varied by changing the calcination temperature up to 1600 °C. Thermal expansion curves (through dilatometric study) were used to study the effect of alumina reactivity on spinel formation. Final sintered products were characterized by densification, phase analysis, hot strength measurement and microstructural analysis to evaluate the influence of reactivity of alumina on the sintered characteristics.

Keywords: Magnesium aluminate spinel; Magnesia rich; Reaction sintered magnesia; Effect of alumina reactivity

1. Introduction

Magnesium aluminate spinels are known to offer desirable combination of mechanical, chemical and thermal properties both at ambient and elevated temperatures, but they have not been commercially successful primarily due to the difficulty in sintering. Synthesis of spinel and fabrication of spinel refractories are known since a century [1] but the volume expansion of 5% [2] during spinel formation from the constituent oxides, magnesia and alumina, does not allow the material to densify in the same firing. Hence a two stage firing process was employed, the first one to complete the spinel formation and the second one to densify the formed spinel, which adversely affects the economy. Magnesium chromite refractories having a similar type of properties were in demand due to cheapness. But as the hazardous character of chrome bearing materials is exposed [3], work and use of magnesium aluminate gain momentum. The major application areas of spinel refractories are [4] transition and burning zones of cement rotary kilns, side walls and bottom of steel teeming ladles and checker work of glass tank furnace regenerators.

Formation of spinel from its constituent oxides is a counter diffusion process of Mg^{+2} and Al^{+3} ions [5] and this solid-state reaction depends on large number of parameters. N.A.L. Mansour [6] obtained a maximum spinel formation when the starting materials $MgCO_3$ was calcined at 900 °C and $Al(OH)_3$ was calcined at 1100 °C. Kostic and others [7] found grinding energy increases surface area and structural imperfections and observed spinel formation at lower temperatures after prolong grinding of starting materials. In contrast, Budnikov and others [8] found very fine grinding of alumina had little effect on spinel formation. In an earlier study of the authors it was found [9] calcination of hydroxide sources of constituent materials affects the spinellisation reaction and densification behavior of magnesium aluminate spinel. A separate work on spinel formation [10] from attrition milled materials through dilatometric study reveals that spinellisation reaction starts above 1000 °C for compositions with $MgO:Al_2O_3$ molar ratios 2:1, 1:1 and 1:2. A sharp fall in the expansion curve was found above 1350 °C due to the greater shrinkage rate from sintering than that of expansion from spinellisation reaction.

Magnesia rich spinels are important for various applications and different workers studied the system in depth. Alper and others worked [11] on the phase diagram of the $MgO–MgAl_2O_4$ system and found an

---

* Corresponding author.
E-mail address: ritwiksarkar@rediffmail.com (R. Sarkar).

0272-8842/02/$22.00 © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.
PII: S0272-8842(02)00152-9

eutectic at 1995 °C with 45 wt.% MgO in the MgO–Al_2O_3 binary system. They also reported a solid solubility of MgO in the spinel phase and the solubility was reported to extend up to 39 wt.% MgO and 61 wt.% Al_2O_3. Bailey and Russel found [12] excess magnesia to be extremely beneficial for densification of the spinel. The presence of free periclase as a distinct second phase restrained the grain boundary motion and produced a dense, small grained spinel body. Batrakov and others [13] studied the magnesia rich spinel compositions with MgO content between 100 and 28.33 and reported the best thermo-mechanical properties for compositions containing 72–25 wt.% of periclase (or 28–75 wt.% of spinel). Working on the development of magnesia–magnesium aluminate co-clinker, Cooper and Hudson [14] found magnesia-spinel bricks with 40 wt.% spinel containing magnesia–magnesium aluminate co-clinker resulted in the best combination of properties. The authors also found superior resistance against thermal damage and possible erosion and corrosion for the bricks in many applications.

The present study describes the development of magnesia rich magnesium aluminate spinel (34% MgO) using sea water magnesia and commercially available alumina. Reactivity of alumina was varied by calcinations at different temperatures and an attrition mill was employed for the reduction of particle size of the starting materials. A spinellisation study of each batch was done through a dilatometer. A pressure-less reaction sintering technique was used in the temperature range of 1600–1700 °C. Sintered products were characterized by densification study, phase analysis, hot strength and microstructural analysis.

2. Experimental

The starting materials, sintered sea water magnesia and commercial alumina were first characterized by chemical analysis, specific gravity, specific surface area and phase analysis. Alumina was calcined as loose powders in high alumina crucibles at 800, 1200 and 1600 °C with 1 h soaking time at the peak temperatures. Calcined alumina was characterized by specific surface area measurement. Different batches, containing 34 wt.% MgO, were prepared from sintered sea water magnesia (size less then 150 μ) and uncalcined and calcined aluminas. The batches were mixed in a high alumina lined pot mill for 30 min and subsequently attrition milled [15] for 3 h. Specific surface areas of the milled powders are provided in Table 1. Milled powders were pressed in cylindrical form (10 mm Φ×25 mm) and the green compacts were used for dilatometric study up to 1500 °C with a heating rate of 5 °C per min. Milled powders were then uniaxially pressed to bar shape (size 60 mm×6 mm×6 mm) at 1000 kg/cm^2 and dried at 110 °C for 24 h and sintered at 1600, 1650 and 1700 °C temperatures with 2 h dwelling time at the peak temperatures. Sintered products were tested for bulk density, hot modulus of rupture, phase analysis and microstructural evaluation.

Table 1
Specific surface area of different milled batches

Batch containing alumina calcined at (°C)	Specific surface area (m^2 gm^{-1})
Uncalcined	20.6
800	14.9
1200	8.7
1600	4.6

Chemical analysis of the starting materials was done by the acid dissolution method. Specific gravity was measured by the standard method, using specific gravity bottles with xylene as the test medium. Phase analysis was carried out in an X-ray diffractometer (make Philips, Model PW 1730) at a scanning speed of 2° per minute. Specific surface area was measured by surface area analyzer (make Carlo Ebra, model Sorpty 1750) following the BET method and using nitrogen as the adsorbed gas at the liquid nitrogen temperature. All the calcinations and sintering processes were carried out in an electrically heated programmable furnace (make Bysakh & Co). An attrition mill (make Union process, model 01HD) with zirconia pot, stirrer and grinding media was employed for particle size reduction in a propanol medium. Pressing was done in a hydraulic press (make Fred S. Carver Inc, USA, Model 2698) of 25 ton capacity. Densification study of the sintered products was performed by the conventional liquid displacement method using Archimedes' Principle in xylene medium. Hot strength was measured at 1300 °C as three point bending strength in a CGCRI, India, developed instrument. Microstructure of the polished and thermally etched samples was observed under scanning electron microscope (make Stereoscan model LEO s430i). Grain size measurement was done by the lineal intercept method [16]. Dilatometreic study of the milled powders was done in a high temperature dilatometer (Orton, USA make, model 1600D).

3. Results and discussion

Physico-chemical properties of the starting oxides are shown in Table 2. It shows that both the raw materials are highly pure and contain little amount of SiO_2, Fe_2O_3, CaO and alkalis as impurities. Only oxide phases are present in X-ray diffraction study of the starting materials and the alumina source was quite fine in size.

Fig. 1 shows the effect of calcination on the surface area of alumina. Increase in calcination temperature

Table 2
Physico-chemical properties of the starting materials

Chemical analysis	Magnesia	Alumina
SiO_2	0.06	0.32
Al_2O_3	0.23	97.0
Fe_2O_3	0.05	0.12
TiO_2	Trace	Trace
CaO	0.76	0.21
MgO	98.56	Trace
Alkali	Trace	0.4
Physical properties		
Specific gravity	3.57	3.98
Specific surface area (m^2/gm)	–	35
Phase analysis	Periclase	Corundum

decreases the specific surface area due to agglomeration and coalescence of the alumina particles. The fall in surface area is severe above 800 °C and above 1200 °C the coarsening effect is less prominent.

3.1. Dilatometric study

All the different spinel batches, with alumina calcined at different temperatures, showed (Fig. 2) nearly similar expansion behaviour up to 1100 °C. Above 1100 °C a sudden expansion was observed for all the batches but the nature and extent of expansion were different. The spinel without any calcination showed minimum expansion with sharp shrinkage and showed the highest shrinkage value; the batch with alumina calcined at 800 °C showed nearly similar expansion and shrinkage behaviour. But further increase in calcinaion temperature of alumina increases the extent of expansion and showed a decreasing shrinkage nature. The highest expansion with least shrinkage (up to 1500 °C) was observed for the spinel batch with 1600 °C calcined alumina. Sudden expansion above 1100 °C corresponds to the spinel formation and shrinkage is due to the sintering/densification. Introduction of the calcination process to alumina did not affect the initiation of spinel formation but it reduces the densification process. A higher extent of shrinkage from greater densification in the uncalcined batch resulted in minimum expansion (for spinellisation). The higher the calcination temperature of alumina, the greater the agglomeration of the alumina particles, leading to higher expansion and lesser shrinkage. This also reflects that densification is reduced with increasing calcination temperature.

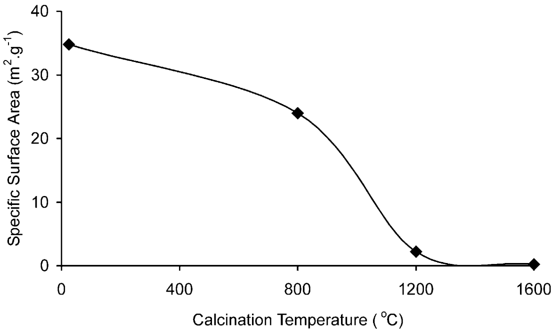

Fig. 1. Variation of surface area of alumina versus on calcination temperatures.

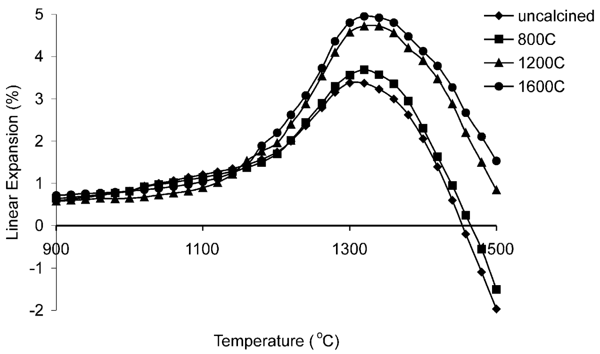

Fig. 2. Dilatometric study of spinels, containing alumina calcined at different temperatures.

3.2. Densification study

Introduction of the calcination process to alumina showed a slight fall in the sintered density of different spinel batches sintered at different temperatures (Fig. 3) and the extent of decrease in density is maximum for the batch with alumina calcined at 1600 °C. Increase in sintering temperature from 1600 to 1650 °C showed an increase in density due to greater densification from higher extent of mass transport, but further increase in sintering temperature slightly reduced the sintered density, which may be associated with coarsening effect. But the spinel batch with 1600 °C calcined alumina showed an increase in sintered density on increasing the sintering temperature to 1700 °C; the higher temperature might have helped to densify the relatively less sinterable batch. However 800 °C calcined alumina containing the spinel batch showed nearly the same densification as that of the without calcined batch for all the sintering temperatures.

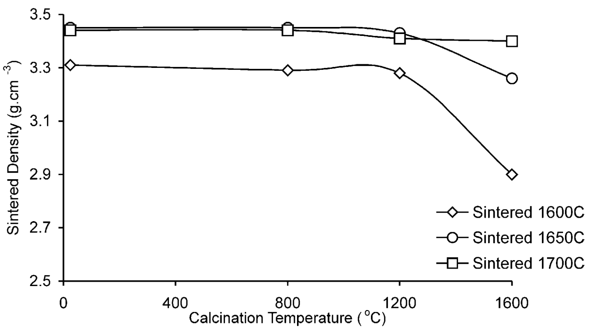

Fig. 3. Variation in sintered density of spinel against calcination temperature of alumina and sintering temperature of spinel.

Table 3
Phase content of different spinel batches

Alumina calcined at (°C)	Sintered at (°C)	Phases present (°C)
Uncalcined	1600	Sp + P
Uncalcined	1650	Sp + P
Uncalcined	1700	Sp + P
800	1600	Sp + P
800	1650	Sp + P
800	1700	Sp + P
1200	1600	Sp + P
1200	1650	Sp + P
1200	1700	Sp + P
1600	1600	Sp + P
1600	1650	Sp + P
1600	1700	Sp + P

Sp stands for spinel phase and P stands for periclase phase.

3.3. Phase analysis study

Variations in calcination temperature of the alumina and sintering temperature of the spinel have no influence on the phases present (Table 3) in the different sintered products. Only spinel and periclase phases were present for all the different conditions. Presence of no corundum phase in all the different batches confirms the complete spinel formation and excess MgO remained as free periclase phase.

3.4. Hot strength study

Increase in calcination temperature of alumina reduces (Fig. 4) the hot strength properties of spinel for all the sintering temperatures. The reduction in strength is gradual with the increase in calcination temperature of alumina and the minimum strength was observed for the spinel batch with 1600 °C calcined alumina, due to its least sinterability. Sintered products at 1700 °C showed the minimum hot strength due to reduced densification associated with grain coarsening.

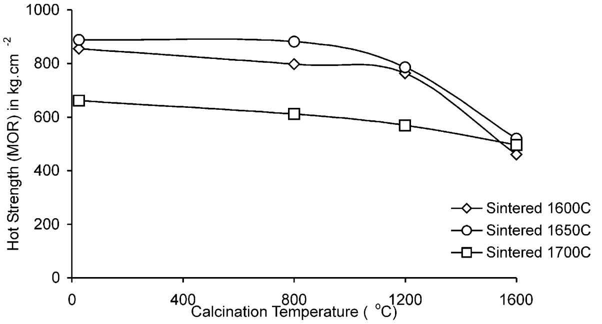

Fig. 4. Variation in hot strength of spinel against calcination temperature of alumina and sintering temperature of spinel.

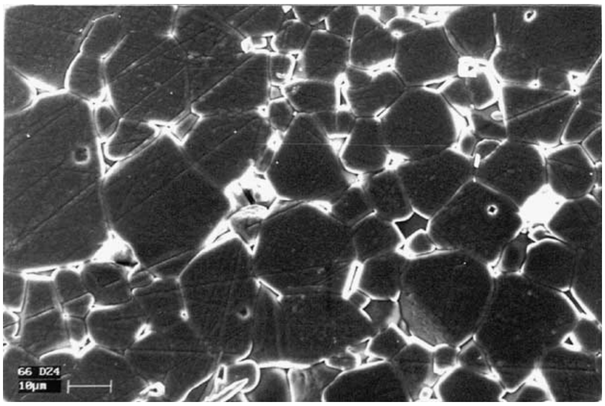

Fig. 5. Scanning electron photomicrograph of 1650 °C sintered MgO rich spinel, with alumina calcined at 800 °C.

3.5. Microstructural analysis

Scanning electron photomicrograph of 1650 °C sintered spinel, with alumina calcined at 800 °C, showed (Fig. 5) compact grain structure with some inter granular porosity. Average grain size measured was 9.2 µ. Compacted grains reflect good strength and densification characteristics of the batch.

4. Conclusion

1. Reactivity of alumina has great influence on spinellisation reaction. Increase in calcination temperature of alumina increases the expansion behaviour in the dilatometer study, due to lesser shrinkage rate resulting from lesser extent of densification for reduced reactivity of alumina.
2. Sintered density does not change greatly with the increase in calcination temperature of alumina up to 1200 °C, but 1600 °C calcination resulted into reduced sinterability due to increased inertness. Increase in sintering temperature increases densification, but a little fall in density is also observed at 1700 °C sintering may be due to grain growth at higher sintering temperature.
3. Calcination of alumina and variation in sintering temperature of spinel have no influence on the phase content of the sintered products.
4. Increase in calcination temperature reduces hot strength and may be due to reduced sinterability. Hot strength of 1700 °C sintered products also showed poor strength, this may be associated with grain growth.
5. Compacted grain structure in microstructural analysis supported better densification and strength properties.

Acknowledgements

The authors are highly obliged to the Director, CGCRI for his kind permission in publishing the paper. The authors are also thankfully acknowledge the sincere contribution of Dr. B. Mukherjee, Dr. M.K. Haldar and Dr. H.S. Tripathi.

References

[1] A. D. Karisheff, Refractory products and method of fabrication, France Patent No. 350016, 24 August 1905.

[2] E. Ryshkewitch, Oxide Ceramics, Academic Press, New York, 1960.

[3] D.J. Bray, Toxicity of chromium compounds formed in refractories, American Ceramic Society Bulletin 64 (7) (1985) 1012–1016.

[4] R.D. Maschio, B. Fabbri, C. Fiori, Industrial applications of refractories containing magnesium aluminate spinel, Industrial Ceramics 8 (2) (1988) 121–126.

[5] R.E. Carter, Mechanism of solid state reaction between MgO–Al_2O_3 and MgO–Fe_2O_3, Journal of the American Ceramic Society 44 (3) (1961) 116–120.

[6] N.A.L. Mansour, Effect of magnesia and alumina characteristics on the formation of spinel, Interceram 27 (1) (1987) 49–51.

[7] E. Kostic, S. Boskovic, S. Kis, Influence of addition of mechanical energy on high temperature processes in solids, Proceedings of the 4th European Ceramic Society Conference 2 (1995) 319–326.

[8] P.P. Buduikov, K.M. Zlochevskaya, Synthesis of magnesia alumina spinel, Ogneupory 23 (3) (1958) 111–118.

[9] Ritwik Sarkar, S.K. Das, G. Banerjee, Calcination effect on magnesium hydroxide and aluminium hydroxide for the development of magnesium aluminate spinel, Ceramics International 26 (1) (2000) 25–28.

[10] Ritwik Sarkar, Goutam Banerjee and Tapan Kumar Pal, Dilatometric study on spinellisation of three different MgO–Al_2O_3 spinels, in: Proceedings of the 63rd Annual Session of the Indian Ceramic Society, 2000, pp. 5–8.

[11] A.M. Alpar, R.N. McNally, P.M. Ribbe, R.C. Doman, The system MgO–$MgAl_2O_4$, The Journal of the American Ceramic Society 45 (6) (1962) 263–268.

[12] J.T. Bailey, R. Russel, Magnesia rich $MgAl_2O_4$ spinel, American Ceramic Society Bulletin 50 (5) (1971) 493–496.

[13] N.A. Batrakov, A.I. Goprindashvili, V.I. Fedotov, Refractories based on the system periclase–spinel, Ognenpory 39 (12) (1974) 40–43.

[14] S.C. Cooper, T.A. Hudson, Magnesia–magnesium aluminate spinel as a refractory, Transaction and Journal of the British Ceramic Society 81 (4) (1982) 121–128.

[15] Ritwik Sarkar, S.K. Das, G. Banerjee, Effect of attritor milling on the densification of magnesium aluminate spinel, Ceramics International 25 (1999) 485–489.

[16] J. Wurst, J.A. Nelson, Lineal intercept technique for measuring grain size in a two phase crystalline ceramics, Journal of the American Ceramic Society 55 (1) (1972) 109.