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Effect of spinel content on the properties of magnesia–spinel composite refractory

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Abstract

Magnesium aluminate spinel was synthesized by solid oxide reaction route at 1400 °C and then added to magnesia refractory brick compositions in the range of 0–30 weight percentages. Optimum firing temperature of the magnesia–spinel refractory composites was determined from densification study and phase analysis. Final refractory products were then characterized by thermal expansion, refractoriness under load, cold strength, retainment of cold strength after thermal shock, hot strength at different temperatures and micro-structural analysis. Spinel (20 wt.%) containing magnesia composition was found to have superior properties.

Keywords: Composite; MgO; $MgAl_2O_4$; Thermo-mechanical properties; Thermal expansion; Microstructure; Refractories

1. Introduction

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

Magnesia–magnesium aluminate compositions are important for various applications and different workers studied the system in depth. Alper and others[6] worked on the phase diagram of MgO–$MgAl_2O_4$ system and found an eutectic at 1995 °C with 45 wt.% MgO in MgO–Al_2O_3 binary system. They also reported a solid solubility of MgO in spinel phase and the solubility was reported to extend up to 39 wt.% MgO and 61 wt.% Al_2O_3. Bailey and Russel found[7] that excess magnesia was extremely beneficial for densification of spinel. The presence of periclase as a second phase restrained the grain boundary motion and produced dense, small grained body with superior mechanical characteristics. Working on the development of magnesia–magnesium aluminate co-clinker, Cooper and Hudson[8] found magnesia–spinel bricks with 40 wt.% spinel containing magnesia–magnesium aluminate co-clinker resulted in best combination of properties. The authors also found superior resistance against thermal shock damage and possible erosion and corrosion for the bricks in many applications. Gonsalves and others studied[9] various magnesia–spinel bricks for cement rotary kiln applications. They found bricks manufactured from natural magnesite and fused spinel grain exhibit higher resistance to hydration, carbonation, alkali and sulfate

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attack than the similar product made from sea water magnesia and sintered spinel. The former combination was also reported to perform better in the presence of higher liquid phase and unstable coating conditions. Eusner and Hubble developed[10] a basic refractory using 92% pure periclase and 8% pure alumina as the starting materials. They found that during firing or in service fine fractions of periclase and alumina react to form spinel that acts as bond in the brick. They also obtained outstanding resistance against load deformation, slagging and spalling for the developed products.

The addition of spinel in periclase bricks has been again reported[11,12] to improve the thermal shock resistance, and it is also claimed that two to three times longer service life can be obtained in cement rotary kilns compared to conventional magnesite-chrome bricks. The reason for the improved thermal shock resistance has been linked[13,14] to the large difference in the thermal expansion behaviour between magnesia and spinel. Thermal expansion mismatch leads to large tensile hoop stresses and microcrack development around the spinel grains, which prevent propagation of crack generated by thermal shock. Aksel and others concluded[15] that microcracking and grain boundary separation originating at periclase–spinel interface in a hot pressed dense magnesia–spinel composite body resulted from thermal expansion mismatch and crystallization of secondary spinel during cooling. They also reported the cracks as critical defects causing failure on loading and loss in strength and modulus with increasing spinel content and its size due to increased extent of local tensile stress field, but a marked increase in the work of fracture values with the addition of spinel is considered to be a major factor to increase the resistance of further shock damage of magnesia spinel materials.

In the present work stoichiometric magnesium aluminate spinel was prepared from calcined magnesia and calcined alumina at 1400 °C, then milled for increased fineness/reactivity. This fine spinel was then added to sintered magnesia grain composition, replacing finer fraction of magnesia, at an amount of 10, 20, and 30 wt.%. Phase analysis and densification study of the sintered products were carried out to select the optimum firing temperature. The fired spinel containing various compositions were compared against pure magnesia composition for different characteristics like thermal expansion, cold strength, hot strength at different temperatures, refractoriness under load, strength retainment capacity after thermal shock and microstructural analysis.

2. Experimental

Calcined magnesia (supplied by Nedmag Industries, The Netherlands) and calcined alumina (supplied by Indian aluminium Company, India) were first evaluated for chemical analysis, phase analysis, specific gravity and specific surface area measurement (Table 1). The oxides were then intimately mixed for stoichiometric spinel composition in an alumina lined pot mill for 30 min. The mixed batch was fired as loose powder in high alumina crucible at 1400 °C for 2 h. The fired spinel composition was then milled for 3 h in a propanol medium using pot, stirrer and grinding media made of zirconia. Milled spinel was characterized for various physico-chemical properties (Table 2).

Milled spinel was finally mixed with sintered magnesia grains (supplied by Nedmag Industries, The Netherlands) for brick making. Various physico-chemical properties of the sintered magnesia are provided in Table 1. Four different batches were prepared, named A, B, C and D containing 0, 10, 20 and 30 wt.% of milled spinel respectively. Spinel replaces the finest

Table 1
Physico-chemical properties of the starting materials

	Calcined MgO	Calcined Al_2O_3	Sintered MgO
Chemical analysis			
SiO_2	0.16	0.08	0.13
Al_2O_3	0.27	99.2	0.06
Fe_2O_3	0.52	0.12	0.48
TiO_2	Trace	0.04	Trace
B_2O_3	0.01	Trace	0.01
CaO	0.7	0.08	0.6
MgO	98.1	Trace	98.5
Na_2O	0.04	0.3	0.08
K_2O	0.05	0.05	0.04
Physical Properties			
Sp. surface area (m^2g^{-1})	4.6	1.8	
Specific gravity	3.56	3.96	3.57
Phase analysis	Periclase	Corundum	Periclase
Bulk density (g cm^{-3})			3.43
Apparent porosity (%)			4.0

Table 2
Physico-chemical properties of milled spinel

Chemical analysis	
SiO_2	0.11
Al_2O_3	71.42
Fe_2O_3	0.26
TiO_2	Trace
ZrO_2	Trace
B_2O_3	Trace
CaO	0.22
MgO	27.61
Na_2O	0.22
K_2O	0.04
Physical properties	
Specific gravity	3.60
Phase content	Spinel
Specific surface area (m^2gm^{-1})	4.0

fraction of magnesia grain in the grain composition. Granulometric compositions of the batches containing different amounts of spinel are shown in Table 3. Batches were then mixed with 6% PVA solution (5% concentration) and pressed uniaxially at a specific pressure of 125 MPa to standard brick shape, 230 mm×115 mm×75 mm. The green bricks were air dried for 1 day, and subsequently dried in an oven at 110 °C for 1 day. Next the bricks were fired at 1600, 1650 and 1700 °C with 2 h soaking time. Phase analysis and densification study was carried out on the sintered products to select the optimum sintering temperature. All the compositions were fired at the optimum sintering temperature and the sintered products were characterized by linear thermal expansion up to 1400 °C, cold strength as modulus of rupture (MOR), refractoriness under load (RUL), hot strength (as MOR) at temperatures of 1000, 1200 and 1400 °C after a soaking period of 30 min at the test temperature, retainment of cold MOR after thermal shock (thermal cycles consist of 10 min of heating at 1000 °C and 10 min air quenching) and microstructural study by scanning electron microscope.

Chemical analysis of the samples was done as per the conventional acid dissolution method. Specific gravity was measured by the method of using specific gravity bottles and with xylene as the liquid medium. All the phase analyses were carried out by X-ray diffraction study using an X-ray diffractometer (make Phillips, model PW 1730) with Cu–Kα radiation in the diffraction range of 20–60°. Specific surface area was measured applying BET principle (make Carlo Ebra, model Sorpty 1750) using nitrogen as the adsorbed gas at the liquid nitrogen temperature. Milling of the fired spinel was done in an attrition mill (make Union process, model 01HD) and pressing of the batches was performed in a heavy-duty hydraulic press (make Laeis, Germany, capacity 1200 t). All the firing was carried out in an electrically heated programmable furnace. Densification study was done by conventional liquid displacement method using Archimedes's principle in xylene medium. High temperature dilatometer (make Orton, model 1600D) was used to study the thermal expansion behavior. All the cold MOR values were determined in a universal testing machine (make Instron, model 5500R) and hot MOR was measured in a Netzsch make instrument. RUL was tested in a conventional instrument by measuring the temperature of appearance (Ta) with 6% deformation from the maximum expansion. Microstructural analysis was done by a scanning electron microscope (make Leica, model S430i).

Table 3
Batch composition (%)

Constituents and average size	A	B	C	D
Sintered MgO				
2500 μm	30	30	30	30
1100 μm	20	20	20	20
375 μm	5	5	5	5
175 μm	15	15	15	15
<100 μm	30	20	10	0
Milled spinel	0	10	20	30

3. Results and discussion

Physico-chemical properties of the starting raw materials show that they are more than 98% pure. Calcined MgO contains lime and iron oxide as major impurities and has very little B_2O_3 content. Calcined alumina has alkali as a major impurity. Specific gravity and phase analysis of the raw materials for spinel also reflect the higher purity and specific surface area indicates submicron size of the starting materials. Sintered MgO has also lime and iron oxide as major impurities with very little B_2O_3 content and sintered to above 96% of true density. Specific gravity and phase analysis also reflect the high purity of the material.

X-ray diffraction pattern of the fired and milled spinel shows (Fig. 1) only spinel phase and no free constituting oxide, which marks the complete spinellisation reaction for the batch. Milled spinel powder shows (Table 2) its stoichiometric composition with trace amount of ZrO_2 content (which nullifies the possibility of ZrO_2 contamination during milling). Surface area of the milled powders indicate sub-micron particle size of the material.

3.1. Phase analysis

Phase analysis study shows the presence of spinel phase in addition to periclase phase on incorporation of spinel in the composition and a gradual increase in spinel phase peak intensity and a decrease in periclase phase have been observed with increasing spinel content. Nearly no effect of sintering temperature was observed on the phase content of different batches. X-ray diffraction pattern of 20 wt.% spinel containing magnesia batch sintered at 1650 °C is shown in Fig. 2 as a representative one.

3.2. Densification study

Bulk density plot of the batches (Fig. 3) shows a little but gradual increase in density value with increasing spinel content up to 20 wt.%. Increase in sintering temperature is also beneficial up to 1650 °C, but further increase in temperature does not show any further improvement. For all the compositions a sintering temperature of 1650 °C was found to be optimum. Apparent porosity study (Fig. 4) also supports the phenomenon. Little increase in density value of the sintered products on incorporation of spinel may be

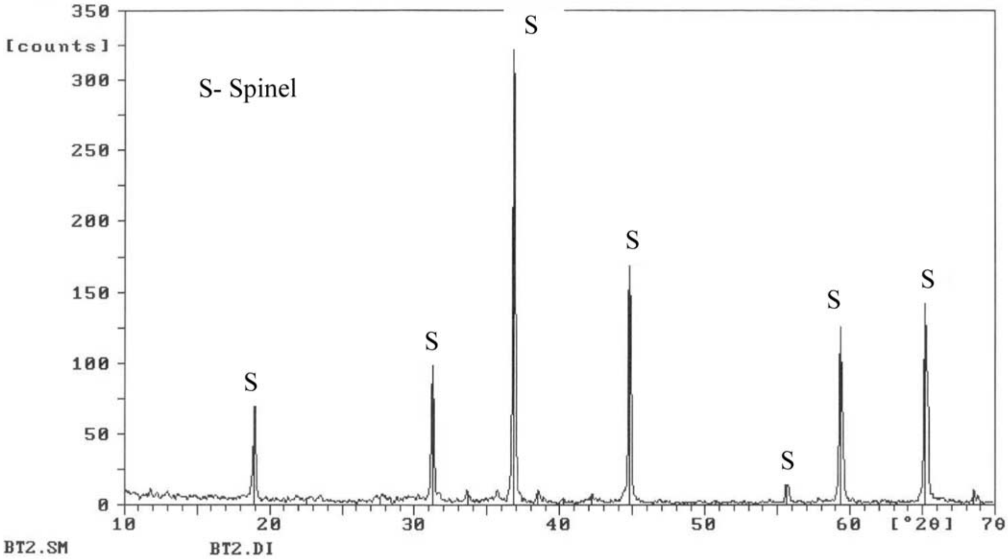

Fig. 1. X-ray diffraction pattern of the milled spinel.

associated with better sintering of the body due to the presence of fine/reactive spinel phase and better compaction of the body on filling up of the intergranular voids between magnesia grains by finer spinel phase, as observed in scanning electron photomicrograph (Section 3.7). However the densification study does not show any significant difference among the batches, which may be due to the similar true density values for both spinel and periclase phases.

3.3. Thermal expansion study

Percentage of linear thermal expansion of the different batches shows (Fig. 5) a gradual decrease in thermal expansion value with increasing amount of spinel. This is due to much lower thermal expansion behaviour of spinel phase than magnesia. An expansion value of 1.66% for the no spinel containing A batch has reduced to 1.36% at 1400 °C in the presence of 30 wt.% spinel

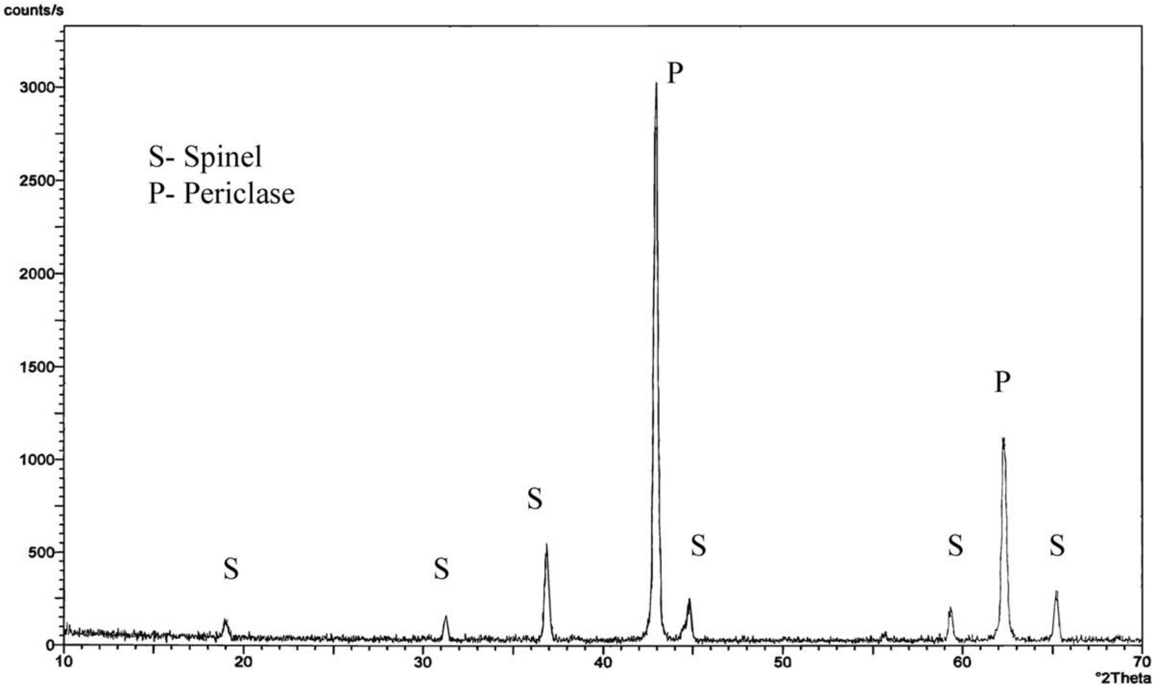

Fig. 2. X-ray diffraction pattern of the 20 wt.% spinel containing batch sintered at 1650 °C.

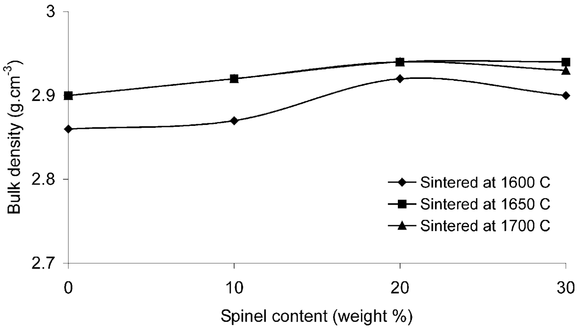

Fig. 3. Variation of bulk density against spinel content of the magnesia–spinel composites.

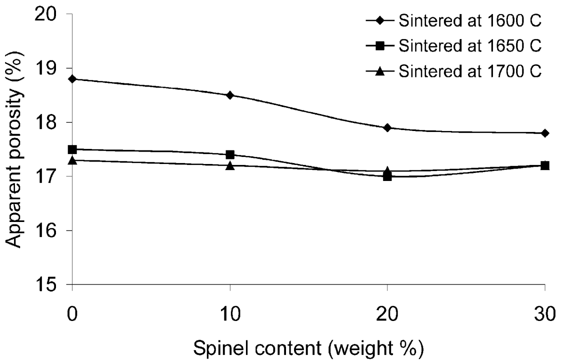

Fig. 4. Variation of apparent porosity against spinel content of the magnesia–spinel composites.

(D batch). Coefficient of linear expansion values of the composite refractory batches are given in Table 4, which shows a gradual reduction of values with increasing amount of spinel content.

3.4. R U L Study

Fig. 6 shows that incorporation of spinel in pure magnesia composition greatly improves the RUL value (temperature of 6% deformation). However an increase in spinel content above 20 wt.% shows a marginal decrease in RUL value. Use of spinel powder replacing fine magnesia reduces the chances of low melting phase formation from impurities and spinel can also absorb Fe_2O_3 (major harmful impurity in magnesia) in its structure. Thus incorporation of spinel reduces the chances of deterioration and increases the strength against deformation. Again deformation by slip mechanism for pure magnesia body [face centered cubic structure with $\{111\} < 110 >$ slip system] is restricted by the presence of second phase spinel in the batch containing spinel. Thermal expansion mismatch between magnesia and spinel phases results in microcracking in the body that helps to restrict the crack propagation by interlinking during failure. Again the extent of microcracking enhances with higher amount of spinel. This also improves the mechanical characteristics of the body. But at the very higher extent of microcracking, strength deteriorates due to propagation of the existing cracks present in large numbers, which is observed for 30 wt.% spinel containing body.

3.5. Retained strength after thermal shock

Cold strength (MOR) of the batches show (Fig. 7) nearly similar strength values for the compositions containing up to 20 wt.% spinel. The relatively lower value of 30 wt.% spinel containing D batch may be due to the large population of microcracks, which can propagate to failure at a comparatively lower stress level. Introduction of thermal shock results in a drastic fall in strength value for the without spinel containing A batch. Thermal shock imparts cracking in the sintered body that causes failure at a lower stress value. Impu-

Table 4
Coefficient of linear thermal expansion (α) values of the batches

α/Batch	A	B	C	D
Room temperature to 1000 °C ($\times 10^{-6}$ °C^{-1})	11.58	10.83	10.05	9.48
Room temperature to 1400 °C ($\times 10^{-6}$ °C^{-1})	12.20	11.37	11.01	10.26

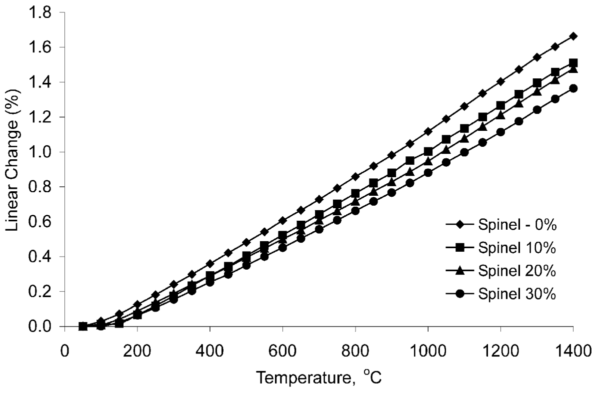

Fig. 5. Percentage of linear thermal expansion of the batches of the magnesia–spinel composites.

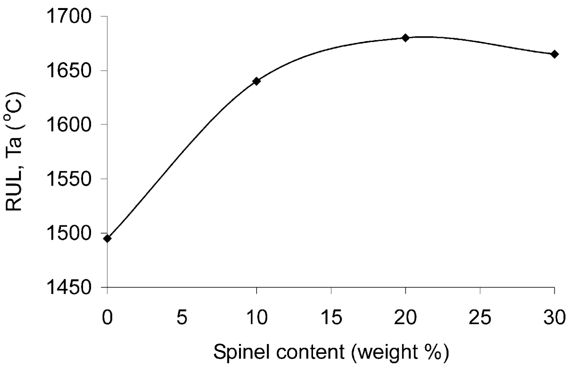

Fig. 6. RUL plot against spinel content of the magnesia-spinel composites.

rities in the only periclase composition might have resulted in the formation of viscous phase during sintering at high temperature that cracks on thermal shock, resulting in poor retained strength capacity. Introduction of spinel greatly improves the retained strength value. Microcracks present in the spinel containing batches prevents the propagation of crack generated during thermal shock, thus strengthening the body and increasing the retained strength. The effect is more significant at a higher number of thermal cycles. But a fall in retained strength is also observed in D batch containing 30 wt.% spinel. A large population of microcracks might have extended and propagated during thermal shock, causing a lower retained strength value.

3.6. Hot strength

Different batches show (Fig. 8) similar hot strength characteristics at different test temperatures. Sharp increase in the strength value is obtained on introduction of spinel in the periclase composition. Increase in spinel content from 20 to 30 wt.% results in a lowering in the hot strength, but the strength is much superior than the no spinel containing A batch. Effect of microcraking and tensile hoop stress around the spinel grains is the reason for this improvement in hot strength valiues. But the large extent of these might have reduced the strengthening at 30 wt.% spinel. Increase in the test temperature results in a significant reduction in strength values for all the batches, which may be associated with the faster and aggravated failure mechanism due to higher temperature.

3.7. Microstructure

In-homogeneity in the grain size is observed (Fig. 9 a) for the without spinel containing A batch. Compact and angular grains of periclase are observed with porosities as inter-granular type. Average grain size of the periclase grains are 6 μm. Addition of spinel to magnesia composition changes the microstructural features. Spinel grains are mainly observed in small sizes and mostly present in the intergranular spaces between the periclase grains (Fig. 9b). Intragranular porosities are also observed in addition to intergranular one, which also indicated the growth of the grains. Periclase grains are also featured with exsolved spinel phase (observed as white spots on the grains). Spinel at high temperature becomes soluble to periclase,[6] but on cooling spinel comes out of the periclase grains as exsolved phase. Average grain size of the periclase grains of 20 wt.% spinel containing C batch (shown as representative one in Fig. 9b) is 18 μm.

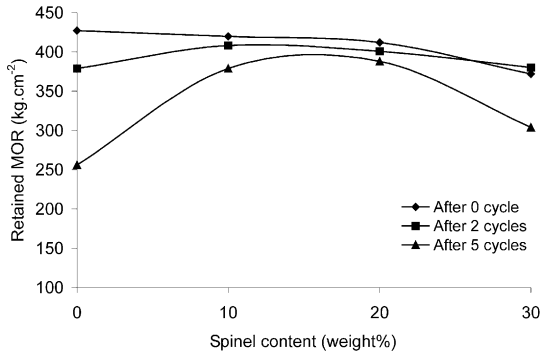

Fig. 7. Retained strength after thermal shock against spinel content of the magnesia–spinel omposites.

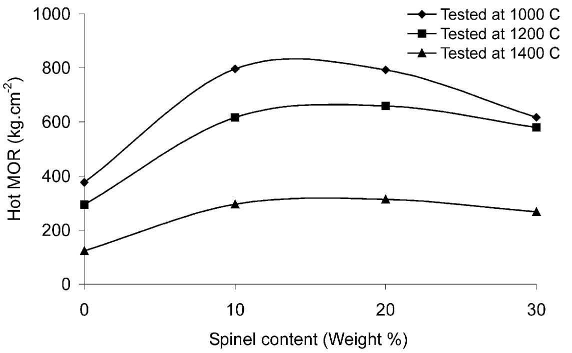

Fig. 8. Variation of hot strength against spinel content of the magnesia–spinel composites.

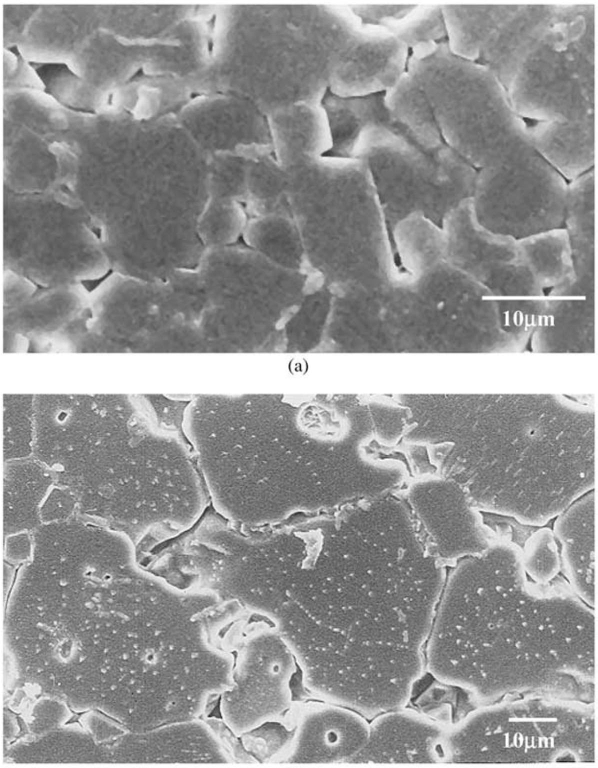

Fig. 9. a. Scanning electron photomicrograph of the 0% spinel containing A batch. b. Scanning electron photomicrograph of the 20% spinel containing C batch.

4. Conclusion

1. Stoichiometric magnesium aluminate spinel was prepared at 1400 °C.
2. Sintering at 1650 °C was found to be optimum for the magnesia–spinel composite refractory.
3. Gradual decrease in the thermal expansion is obtained with increasing spinel content.
4. Incorporation of spinel greatly improves the refractoriness under load, retained strength after thermal shock and hot modulus of rupture characteristics for the periclase body.
5. Microstructure shows spinel as intergranular particles in between the periclase grains as well as the exsolved phase on the periclase grains. Spinel also causes significant growth for the periclase grains.
6. Spinel (20 wt.%) containing body showed superior properties. Thermal expansion mismatch between the periclase and spinel phases causes micro-cracking and tensile hoop stresses around the spinel grains that strengthens the composite body by interlinking of microcracks. But the very large extent of microcracking causes extension/propagation of existing microcrack in the body at a lower stress level resulting in relatively lower mechanical/thermo-mechanical properties.

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References

1. Carter, R. E., Mechanism of solid state reaction between MgO–Al_2O_3 and MgO–Fe_2O_3. *J. Am. Ceram. Soc.*, 1965, **44**(3), 116–120.
2. Karisheff, A. D., Refractory products and method of fabrication, France Patent No. 350016, dated 24 August 1905.
3. Ryshkewitch, E., *Oxide Ceramics*. Academic Press, New York, 1960.
4. Bray, D. J., Toxicity of chromium compounds formed in refractories. *Am. Ceram. Soc. Bull.*, 1985, **64**(7), 1012–1016.
5. Maschio, R. D., Fabbri, B. and Fiori, C., Industrial applications of refractories containing magnesium aluminate spinel. *Inds. Ceram.*, 1988, **8**(2), 121–126.
6. Alper, A. M., McNally, R. N., Ribbe, P. M. and Doman, R. C., The system MgO–$MgAl_2O_4$. *J. Am. Ceram. Soc.*, 1962, **45**(6), 263–268.
7. Bailey, J. T. and Russel, R., Magnesia rich $MgAl_2O_4$ spinel. *Am. Ceram. Soc. Bull.*, 1971, **50**(5), 493–496.
8. Cooper, S. C. and Hudson, T. A., Magnesia magnesium–aluminate spinel as a refractory. *Trans.& J. Br. Ceram. Soc.*, 1982, **81**(4), 121–128.
9. Gonsalves, G. E., Duarte, A. K. and Brant, P. O. R. C., Magnesia spinel brick for cement rotary kiln. *Am. Ceram. Soc. Bull.*, 1993, **72**(2), 49–54.
10. Eusner, G. R. and Hubble, D. H., Technology of spinel bonded periclase brick. *J. Am. Ceram. Soc.*, 1960, **43**(6), 292–296.
11. Wilson, D. R., Evans, R. M., Wodsworth, I. and Cawley, J., Properties and applications of sintered magnesia alumina spinels. *Proceedings of UNITECR-93*, 1993, 749–760.
12. Kimura, M., Uasuda, Y. and Nishio, H., Development of magnesia spinel bricks for rotary cement kilns in Japan. *Interceram Special Issue*, 1984, **33**, 344–376.
13. Aksel, C., Davidge, R. W., Warren, P. D. and Riley, F. L., Investigation of thermal shock resistance in model magnesia–spinel refractory materials, in IV. Ceramic Congress, Proceedings Book, Part 1, 1998, pp. 193–199, Turkey.
14. Aksel, C. and Warren, P. D., Thermal shock parameters (R, R''' and R'''') of magnesia–spinel composites. *J. Eur. Ceram. Soc.*, 2003, **23**(2), 301–308.
15. Aksel, C., Rand, B., Riley, F. L. and Warren, P. D., Mechanical properties of magnesia-spinel composites. *J. Eur. Ceram. Soc.*, 2002, **22**, 745–754.