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Effect of addition of Cr_2O_3 on the properties of reaction sintered MgO–Al_2O_3 spinels

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Abstract

Effect of addition of Cr_2O_3 up to 4 wt.% was studied on three different spinel compositions with MgO:Al_2O_3 molar ratios 2:1, 1:1 and 1:2. Attritor mill was used to reduce the particle size of the starting materials and a single stage sintering technique was employed in the temperature range of 1550–1650 °C for all the compositions. Final sintered products were then characterised in terms of densification and shrinkage studies, phase analysis, strength evaluation both at the ambient temperature and at 1300 °C, strength retention capacity after different cycles of thermal shock at 1000 °C, quantitative elemental analysis and microstructural studies. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Magnesium aluminate spinel is a potential refractory material with excellent high temperature mechanical, thermal and chemical properties. Development of magnesium aluminate spinel bodies and method of fabricating spinel refractories were available from about a century ago;[1] and phase diagram of MgO–Al_2O_3 system was established in 1916,[2] which has not modified essentially. But the use of such materials was limited due to higher cost of production and magnesium chromite bodies were the substitutes. But now, as the refractory practice has changed to high quality items to cope up the changing critical operating parameters and less down time than practiced earlier, magnesium aluminate spinel is gaining its ground in a hard competitive market. Again it has the additional advantage of environment friendliness that attracts the users and discards the use of magnesium chromite refractories due to toxic nature of the chrome bearing compounds.[3]

Spinel in its major applications,[4] in burning and transition zones of cement rotary kilns and bottom and sidewalls of steel teeming ladles, is used as a major component in magnesia rich or alumina rich matrix respectively. Again another important application is the checker work of the glass tank furnace regenerators where pure spinel products are important. Hence all the stoichiometric, magnesia excess and alumina excess spinel compositions are important from the application point of view.

Formation of magnesium aluminate from its constituent oxides is a counter diffusion process of Al^{+3} and Mg^{+2} ions[5] and accompanies a volume expansion of 5%.[6] The expansion does not allow the material to densify in a single firing and thus a double stage sintering process was essential for obtaining dense spinel bodies. But utilising the technique of reaction sintering by the reduction of particle size,[7,8] well-densified magnesium aluminate spinels are obtained in a single stage sintering process from oxide reactants[9–11] through attritor milling.

Effects of different additives on the development of magnesium aluminate spinel were studied by a number of workers. Addition of salt vapours were reported[12] to increase the amount of spinel formation and that of alkali fluorides to increase the crystal growth of the formed spinel which can hinder the sintering process. Kostic and others[13] reported that fluorine ions (from AlF_3 or CaF_2) enhance the solid-state reaction synthesis of magnesium aluminate spinel by increasing the cation vacancy concentration when fluorine was incorporated in the lattice by replacing oxygen ions. Addition of LiF to make a liquid phase sintering was reported[14,15] to improve the densification characteristics of magnesium aluminates. Better sintered properties were also reported for the

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addition of different rare earth oxides like 5 wt.% of Y_2O_3,[16] 4 wt.% of Yb_2O_3[17] and 4 wt.% of Dy_2O_3.[17] Again TiO_2 was reported to be a better additive for densification of magnesium aluminate than MnO_2.[18] Yu and Hiragushi reported[19] a gradual improvement in sintered density on addition of TiO_2 up to 1.5 mass% and above which no further betterment was observed. They also concluded that exsolution of alumina and dissolution of titania was the reason for better densification.

Addition of Cr_2O_3 in spinel bodies is also available in the literature. Ju and co-workers observed[20] improved thermal shock resistance for the periclase spinel products by addition of Cr_2O_3 as chrome concentrate. They also found increased slag resistance for Cr_2O_3 containing bodies and reported that Cr_2O_3 formed solid solution with spinel phase. Behaviour of chromium in spinel was also studied by Arlett[21] for compositions $MgOx\ Al_2O_3$, where x varies between 0.5 and 7. He used 0.5 wt.% of Cr_2O_3 to all the compositions. Arlett observed an exsolved phase for $x > 2.5$ and this phase was $\gamma\ Al_2O_3$. He also found chromium to accompany the exsolved alumina phase rather than with the spinel phase.

The literature does not provide any systematic work on the effect of Cr_2O_3 on the refractory properties of various stoichiometric and nonstoichiometric spinel compositions and here such a study is undertaken. Cr_2O_3 was added at 1, 2 and 4 wt.% to three different 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. Sintered products were characterized by bulk density, linear shrinkage, phase content, cold and hot strength, thermal shock resistance, microstructure and elemental analysis.

2. Experimental

Starting oxides, magnesia and alumina, were first characterised in terms of chemical analysis (by acid dissolution method), powder X-ray diffraction (using Cu-K_α radiation), specific gravity and specific surface area (applying BET technique) measurements. Physicochemical 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 Cr_2O_3 (99% pure, supplied by S.D. Fine Chemicals Pvt. Ltd., India) was added at weight percentages of 1, 2 and 4. Spinel with stoichiometric composition is termed as S batch, with magnesia rich composition is M batch and with alumina rich composition 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). Milling of 4 h was employed as per previous works.[10,11] All the mixing and milling processes were done in the liquid medium of iso-propyl alcohol. Specific surface areas of the milled materials were measured and 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 (60×6×6 mm). Pressed shapes were dried at 110 °C and sintered at 1550, 1600 and 1650 °C with a heating rate of 1 °C per mm 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 evaluate 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 MOR 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.

Table 1
Physico-chemical properties of magnesia and alumna

Constituents	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 ($m^2\ g^{-1}$)	1.8	2.9
Phase analysis	Periclase	Corundum

Table 2
Batch composition and surface area of mixtures

	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
Al_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

3. Results and discussion

Chemical analysis of the starting oxides show that both the oxides are more than 97% pure and have impurities like lime, silica and minute amounts of iron oxide and alkalis. 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.

3.1. Bulk density

Introduction of Cr_2O_3 to all the compositions was found to improve the bulk density slightly (Fig. 1). For A batch sintered at 1550 °C the beneficial effect of addition of Cr_2O_3 was most prominent. Chromium ion having similar characteristics can substitute the aluminium ion in spinel, causing a lattice strain (due to ionic size variation) that helps in sintering. Presence of Cr^{3+} in spinel grains was confirmed from the EDAX results. Again a little fall in density was also observed at higher temperatures (1650 °C), associated with the grain growth and pore coalescence, which was prominent for higher percentages of Cr_2O_3. Open porosity for all the

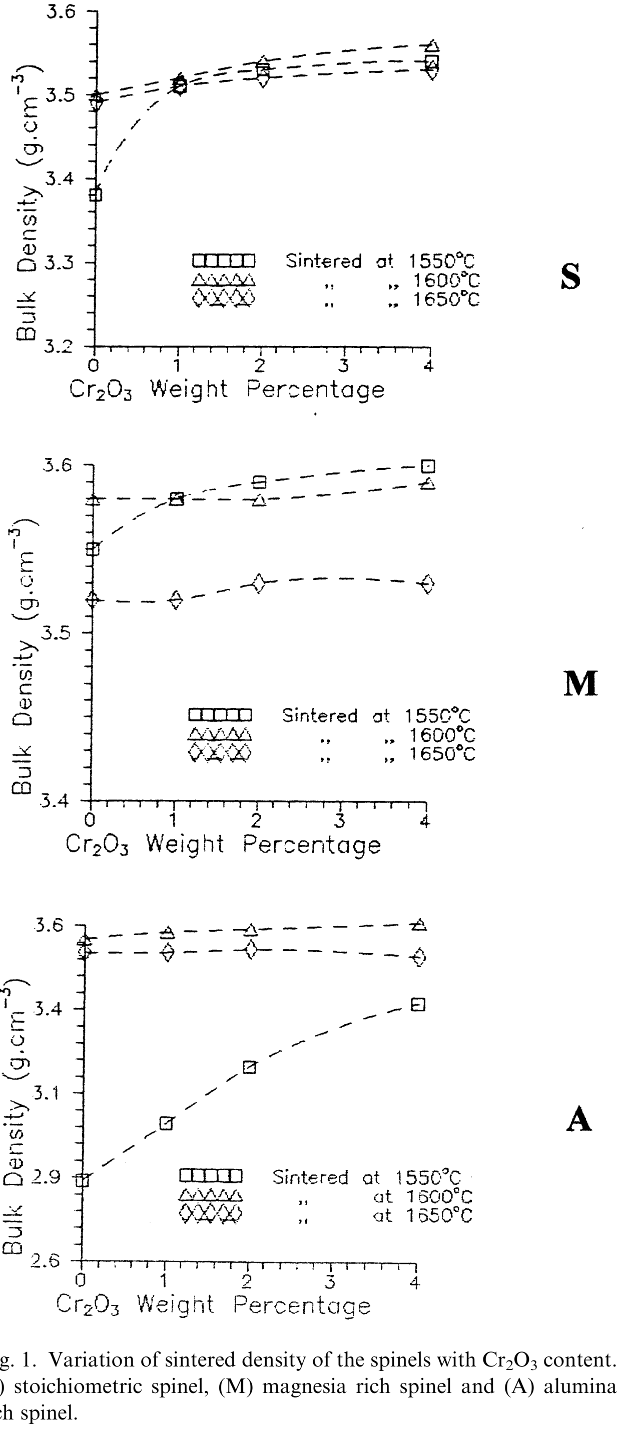

Fig. 1. Variation of sintered density of the spinels with Cr_2O_3 content. (S) stoichiometric spinel, (M) magnesia rich spinel and (A) alumina rich spinel.

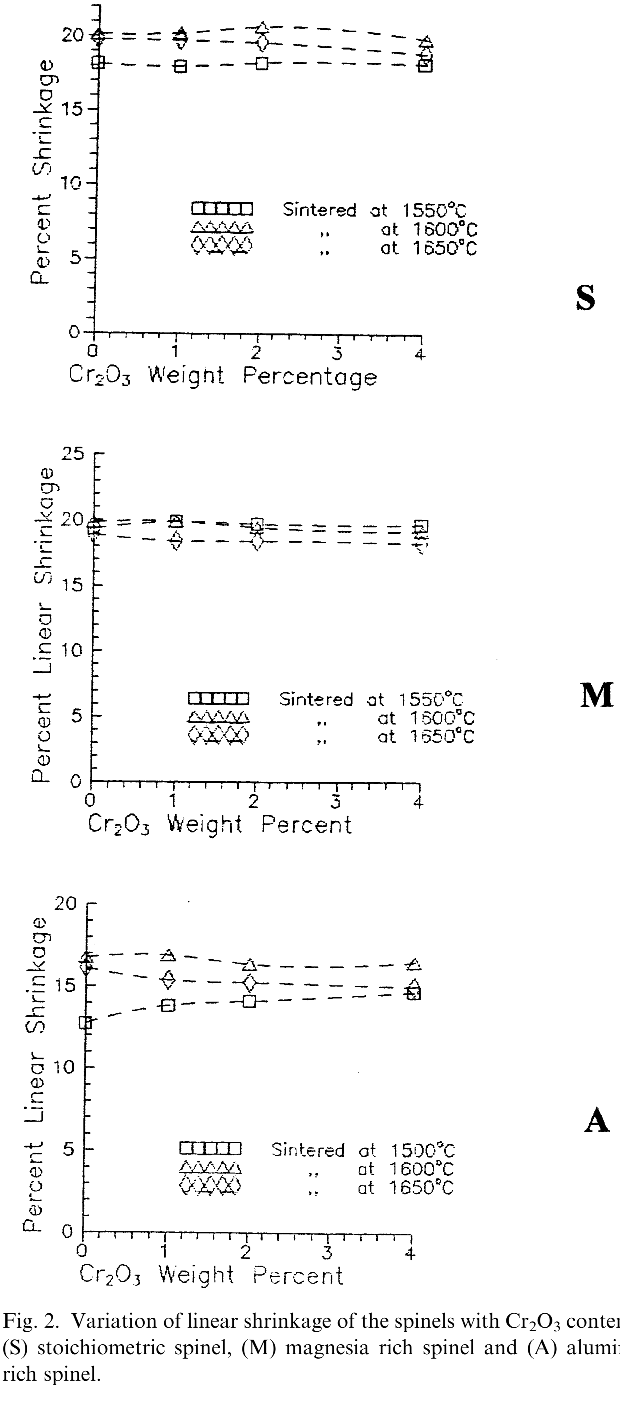

Fig. 2. Variation of linear shrinkage of the spinels with Cr_2O_3 content. (S) stoichiometric spinel, (M) magnesia rich spinel and (A) alumina rich spinel.

batches were found to be very low (except for the A batch) and so variation in open porosity was not studied thoroughly.

3.2. Linear shrinkage

Percentage of linear shrinkage also measures the extent of sintering. For S and M batch linear shrinkage varied (Fig. 2A and B) only a little with the amount of Cr_2O_3, but at 1650 °C it was found to reduce a little for all the compositions. Pore coalescence at higher temperature can be responsible for this. Again for A batch increased shrinkage was observed (Fig. 2C) with increasing Cr_2O_3 content, indicating better sintering with higher Cr_2O_3, which supports the bulk density study. For A batch it can be concluded that Cr_2O_3 is an essential additive for better sintering even at 1550 °C.

3.3. Phase analysis

Phase analysis study of all the compositions is given in Table 3. All the sintered products of S batch showed only spinel phase for all the conditions of temperature and Cr_2O_3 percentage. All the sintered products of M batch show free periclase phase along with the developed spinel phase for all the different conditions. Again A batch, without Cr_2O_3, showed spinel phase with corundum on sintering at 1550 °C, on sintering at 1600 °C the intensity of the free corundum phase was reduced and at 1650 °C only spinel phase was obtained with no

Table 3
Phase analysis of different reaction products

Batch	Cr_2O_3 (wt.%)	Sintered at		
		1550 °C	1600 °C	1650 °C
S	0	Spinel	Spinel	Spinel
S	1	Spinel	Spinel	Spinel
S	2	Spinel	Spinel	Spinel
S	4	Spinel	Spinel	Spinel
M	0	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
M	4	Spinel and periclase	Spinel and periclase	Spinel and periclase
A	0	Spinel and corundum	Spinel and corundum	Spinel
A	1	Spinel and corundum	Spinel	Spinel
A	2	Spinel and corundum	Spinel	Spinel
A	4	Spinel and corundum	Spinel	Spinel

Table 4
EDAX analysis of different reaction products

Batch	Cr_2O_3 (wt.%)	Sintered at (°C)	Analysis of	EDAX analysis as % of oxides				
				MgO	Al_2O_3	Cr_2O_3	CaO	SiO_2
S	0	1650	Grain	26.6	73.2		0.2	
S	0	1650	Grain boundary	24.3	72.9		1.2	0.4
S	4	1650	Grain	26.2	69.1	3.7	0.5	0.3
S	4	1650	Grain boundary	25.1	68.7	3.8	1.3	0.4
M	0	1650	Grain	26.4	73.3		0.2	
M	0	1650	Grain (small and rounded)	95.1	2.8		1.3	
M	0	1650	Grain boundary	48.9	47.9		2.6	0.6
M	4	1650	Grain	24.8	66.7	3.9	1.6	0.2
M	4	1650	Grain (small and rounded)	93	2.7	3.6	0.5	
M	4	1650	Grain boundary	46.6	47.8	3.7	1.8	0.3
A	0	1550	Grain	24.3	75.6			
A	0	1550	Grain	6.7	92.3			
A	0	1650	Grain	6.6	82.7		0.2	
A	0	1650	Grain boundary	16.9	79.2		2.4	1.2
A	4	1550	Grain	16.3	78.7	3.5	0.4	
A	4	1550	Grain	5.3	90.8	3.7		
A	4	1650	Grain	15.1	81.2	3.6		
A	4	1650	Grain boundary	16.9	77.8	3.8	1.2	0.2

free corundum phase; this confirms the complete solid solubility of excess alumina in spinel at 1650 °C. This observation finds similarity with the work of Bailey and Russel.[22] Again the addition of Cr_2O_3 was found to reduce the temperature of this complete solid solution as no free corundum phase was observed even at 1600 °C. Chromium ion substitutes aluminium ion in spinel and at higher temperatures oxidation state of chromium changes to higher values,[23,24] causing a defective spinel structure, which increases the diffusion in spinel. Thus solid solubility of free alumina increases. No chromium bearing phase was observed for the different spinel compositions. Cr_2O_3 makes solid solution in spinel phase. Presence of chromium in spinel grains and grain boundaries, as found in EDAX study, also supports the solid solution of Cr_2O_3 in spinel, not the formation of any compound. Again solid solution of $MgAl_2O_4$–$MgCr_2O_4$ (formed by the reaction between MgO and Cr_2O_3) may also present, specially in the M batch.

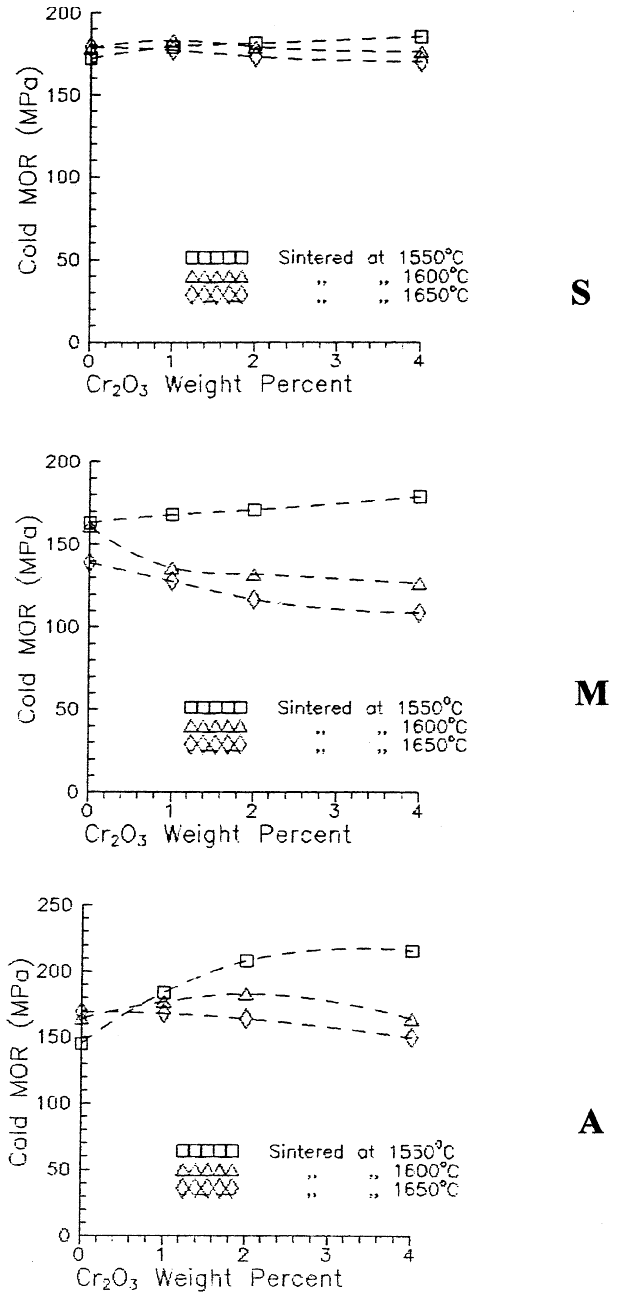

Fig. 3. Variation of cold strength (MOR) of the spinels with Cr_2O_3 content. (S) stoichiometric spinel, (M) magnesia rich spinel and (A) alumina rich spinel.

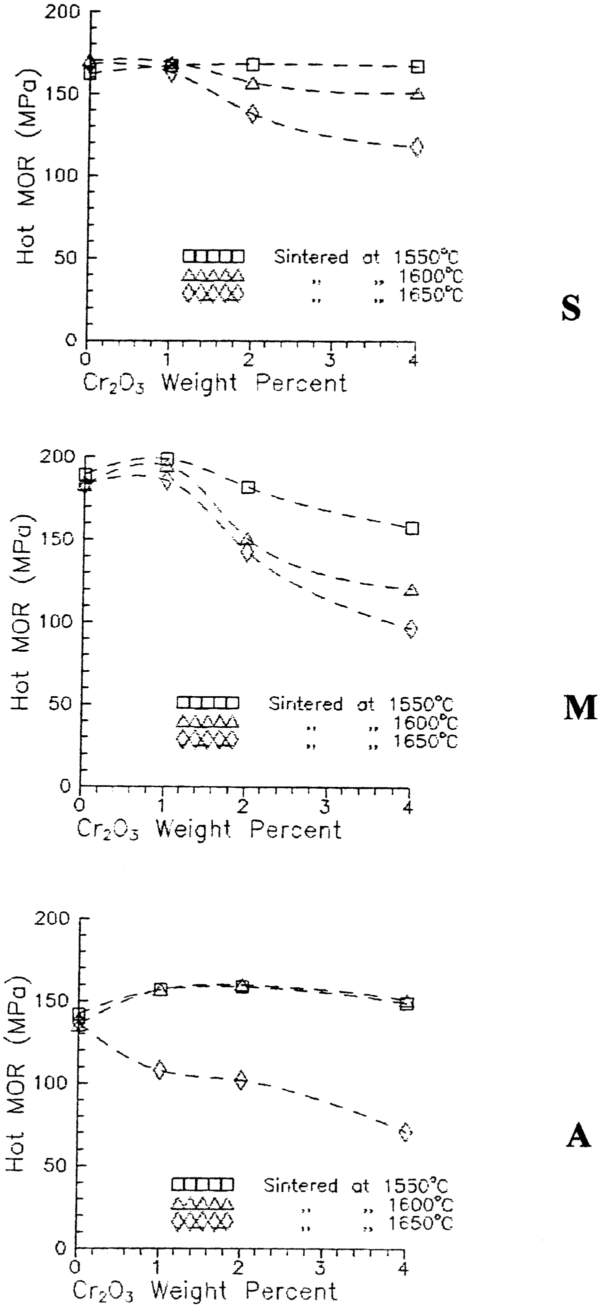

Fig. 4. Variation of hot strength (MOR) of the spinels with Cr_2O_3 content. (S) stoichiometric spinel, (M) magnesia rich spinel and (A) alumina rich spinel.

3.4. Strength

Cold strength of the S batch (Fig. 3A) was found to remain nearly unchanged with increasing the sintering temperature and amount of Cr_2O_3. But for M batch (Fig. 3B) Cr_2O_3 was found to be detrimental above a sintering temperature of 1550 °C. Again for A batch (Fig. 3C), increase in strength was observed with increasing Cr_2O_3 content at 1550 °C due to greater densification. But a little fall in strength with higher amount of Cr_2O_3 was also found on sintering at 1650 °C. Chromium ion that substitutes aluminium causes a strain in the lattice due to the difference in their ionic sizes, resulting a strengthening effect. But grain growth at higher sintering temperature and higher amount of Cr_2O_3 (Fig. 6) destroys the strengthening phenomena.

Hot strength, measured as hot MOR at 1300 °C, showed (Fig. 4) a decreasing value with increasing Cr_2O_3 content for 1650 °C sintered products. Presence of impurities namely, CaO, SiO_2, alkalis etc. in the starting materials with the additive Cr_2O_3 in the MgO–Al_2O_3 system may form a liquid phase, which is also supported by the

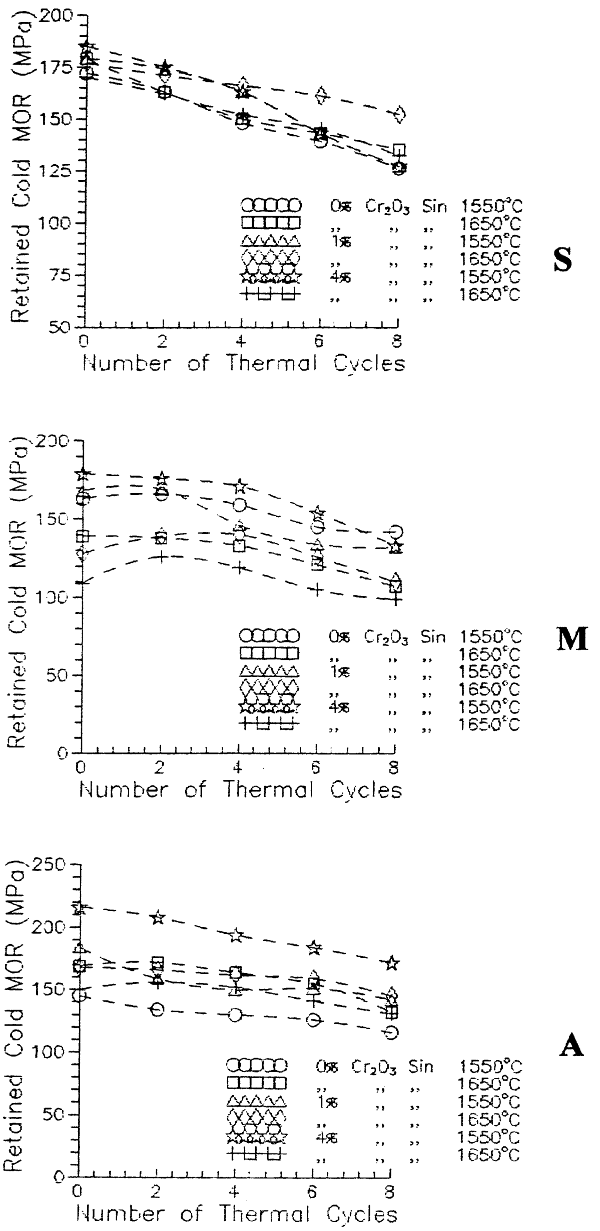

Fig. 5. Cold strength retainment study of the spinels after thermal shock. (S) stoichiometric spinel, (m) magnesia rich spinel and (a) alumina rich spinel.

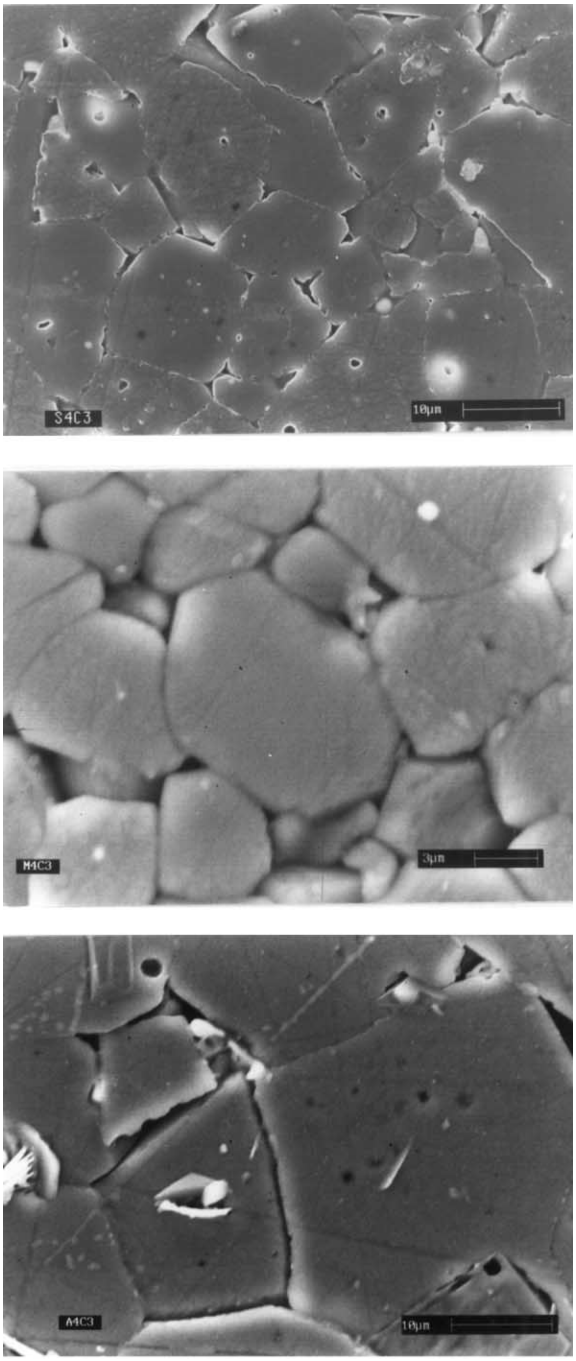

Fig. 6. Effect of Cr_2O_3 addition on the microstructure of the spinels. Cr_2O_3 content 4 wt.%. (S) stoichiometric spinel, (M) magnesia rich spinel and (A) alumina rich spinel.

presence of the impurities at the grain boundaries of the reaction products. Formation of liquid phase is increased for high sintering temperature and higher amount of Cr_2O_3. Presence of this liquid phase drastically reduces the hot strength.

3.5. Thermal shock

The extent of damage on the sintered products due to thermal shock was determined as the retainment of cold MOR after different numbers of thermal cycles. For S batch (Fig. 5A) without Cr_2O_3, there was a gradual degradation of strength with increasing number of cycles. Addition of 1 wt.% of Cr_2O_3 was found to restrict the degradation, but 4 wt.% of Cr_2O_3 showed no such improvement. For M batch (Fig. 5B) addition of Cr_2O_3 was found to have detrimental effect on strength retainment capacity and this degrading effect was severe for higher sintering temperatures and higher amounts of Cr_2O_3. Again A batch showed (Fig. 5C) increased resistance against strength degradation after thermal shock for the Cr_2O_3 containing bodies.

3.6. Elemental analysis

Quantitative elemental analysis of various samples by EDAX technique was converted to oxide percentages and shown in Table 4. It shows that S batch sintered at 1650 °C had nearly stoichiometric grain and grain boundary compositions for with and without Cr_2O_3 containing conditions. Cr_2O_3 was uniformly distributed in the grains and grain boundaries, indicating the solid solubility of Cr_2O_3 in spinel. Again for M batch, free periclase grains (small rounded ones) containing MgO about 95–97% were observed along with the nearly stoichiometric spinel grains (larger ones). Again A batch sintered at 1650 °C showed only alumina rich grain and grain boundary compositions. Cr_2O_3 was also uniformly distributed in both the grains and grain boundaries. But A batch sintered at 1550 °C showed grains of two types, one having Al_2O_3 content of about 75 wt.% and others having about 92 wt.%. Higher alumina containing grains were responsible for the free corundum phase as observed in the phase analysis. Cr_2O_3 was also found to make solid solution with corundum phase at 1550 °C, as observed in these high alumina grains.

3.7. Microstructure

Cr_2O_3 was found to be an effective additive for the grain growth of all the three different spinel compositions (Fig. 6). A maximum effect was observed for the A batch which showed an average grain size of 15.8 µm on addition of 4 wt.% of Cr_2O_3 at 1650 °C. S batch had a size of 6.9 µm and M batch had a size of 7.7 µm for similar conditions. Without Cr_2O_3 containing batches (Fig. 7) were much smaller in size, S batch was 3.9 µm, M batch was 2.2 µm and A batch was 0.6 µm. All the grain sizes were measured as per lineal intercept method.[25] Again the photomicrographs showed an inhomogeneous grain growth for all the batches on sintering at 1650 °C, which may be responsible for the fall in strength.

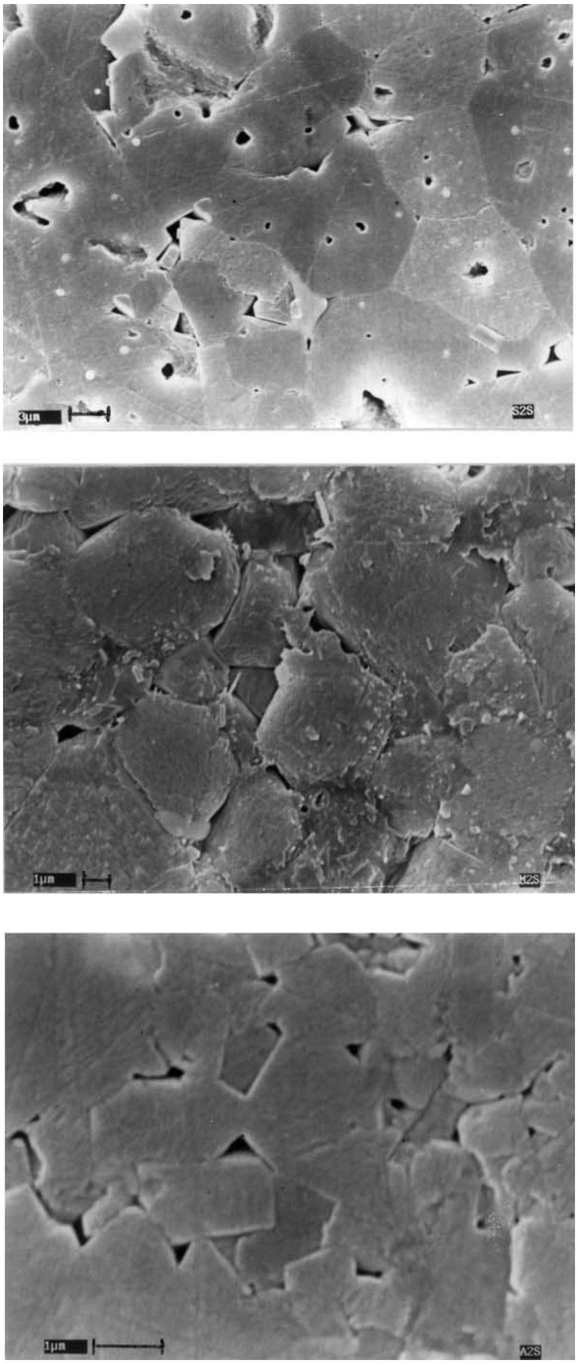

Fig. 7. Photomicrograph of the without additive containing batches. (S) stoichiometric spinel, (M) magnesia rich spinet and (A) alumina rich spinel.

4. Conclusion

1. Cr_2O_3 showed the greatest effect on densification for the alumina rich spinel at 1550 °C.

2. No Cr-bearing phase was observed in XRD for all the three spinel compositions. Cr_2O_3 was found to decrease the temperature of complete solid solubility of excess alumina in spinel for the alumina rich composition. Strength was not highly affected by the addition of lower percentages of Cr_2O_3 but 4 wt.% of additive was found to be detrimental for all the compositions on sintering at 1650 °C. Deleterious effect was much pronounced for the hot strength values and mainly for the magnesia rich composition.

3. 1 wt.% of Cr_2O_3 was found to be beneficial in restricting the strength degradation after thermal shock for the S batch, but higher percentages showed poor results. For M batch Cr_2O_3 was found to be detrimental and for A batch higher strength retention capacity was observed in presence with the addition of Cr_2O_3.

4. Quantitative elemental analysis by EDAX study shows that Cr_2O_3 was uniformly distributed throughout the grains and grain boundaries, which confirms the solid solubility of Cr_2O_3 in spinel. Cr_2O_3 was also found to be effective for the grain growth of all three different spinel compositions at high temperature. The effect was much pronounced for the alumina rich composition.

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