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The effect of ZnO addition on the densification and properties of magnesium aluminate spinel

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Abstract

Stoichiometric magnesium aluminate spinel can be developed by solid oxide reactions of calcined magnesia and calcined alumina. The raw materials were mixed; attrition milled, compacted under a uniaxial pressure of 100 MPa and finally fired in the temperature range of 1500 to 1650°C. Up to 2 wt% ZnO was incorporated as an additive. In this investigation the effect of ZnO on the densification and properties of the magnesium aluminate spinel has been studied. It was found that 99% of theoretical density was achieved on firing at 1550°C with the addition of 0.5 wt% ZnO. The optimum properties in terms of bulk density, hot strength and thermal shock resistance was obtained with 1 wt% ZnO. All the ZnO containing samples retained their strength up to 6–8th cycle on thermal shock. ZnO containing samples are comparatively more resistant to thermal shock than ZnO free samples.

Keywords: C. Thermal shock resistance; D. Spinells; Densification

1. Introduction

The $MgO–Al_2O_3$ system includes highly refractory materials, which have a wide range of applications in steel, cement and glass industries [1,2]. $MgO–Al_2O_3$ spinel has a high melting point, a low thermal expansion, good chemical stability, resistant to thermal spalling and corrosion [3]. Various methods can be adopted to produce Mag–Al spinel, e.g. coprecipitation, alkoxide route, spark discharge process, freeze drying, plasma discharge process, etc. But all these processes are not cost effective for commercial production. The solid state reaction of alumina and magnesia is a simple approach for spinel formation, however the densification temperatures are relatively high. The effect of various additives on the spinelisation and densification of magnesium aluminate were studied previously [4,5].

The present investigation was undertaken to develop the stoichiometric Mag–Al spinel from calcined magnesia and calcined alumina by solid oxide reaction route. Attempts have been made to study the effect of ZnO additive in the densification and properties of the magnesium aluminate spinel.

2. Experimental

The raw materials selected for the study were high pure calcined alumina and calcined magnesia. Alumina was obtained from Indian Aluminium Co., India and magnesia was obtained from M/s. Ned Mag Industries, The Netherlands. Raw materials were characterised in terms of chemical analysis, phase identification by X-ray diffraction study and surface area measurement. Chemical analysis of the raw materials was done by standard wet chemical method and surface area was measured by BET method in a BET apparatus (Sorpty 1750, Carlo Erba, Italy).

Four batch compositions were selected in such a way that they contain MgO and Al_2O_3 in the stoichiometric ratio with 0 to 2 wt% ZnO additive as shown in Table 1. All the batches were attrition-milled in isopropyl alcohol in a zirconia pot using zirconia grinding media for 3 h. Slurries thus obtained were dried at 110 ± 5°C, crushed to break the agglomerate, mixed with PVA solution as binder and discs and bars were fabricated under a uniaxial

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Table 1
Batch composition and sample codes used

Sample code	Raw materials		Additive
	Calcined magnesia (wt%)	Calcined alumina (wt%)	ZnO (wt%)
MA	30.39	69.61	–
MAZV	30.24	69.26	0.5
MAZ1	30.09	68.91	1.0
MAZ2	29.78	68.22	2.0

Table 2
Chemical analysis of raw materials

Constituent (wt%)	Calcined magnesia	Calcined alumina
SiO_2	0.15	
Al_2O_3	0.25	99.3
Fe_2O_3	0.49	
MgO	89.87	
CaO	1.64	
K_2O	0.05	
Na_2O	0.04	0.3
LOI	7.75	

pressure of 100 MPa. After drying at 110 ± 5°C these samples were fired at a temperature varying from 1500 to 1650°C at an interval of 50°C with 2 h soaking at peak temperature. Firing was done in an electric furnace and the heating rate was maintained at 5°C min^{-1} throughout the range.

The sintered products were characterised by bulk density, flexural strength at room temperature and at elevated temperature, thermal shock resistance, microstructural analysis by optical microscopy and elemental analysis of the spinel grain by energy disperssive X-ray (EDX) analysis.

Bulk density and apparent porosity of the sintered products were measured by liquid displacement method in xylene medium using Archimedes' principle. Flexural strength was measured at different temperature by three point bending method using samples having dimension $0.5 \times 0.5 \times 5.0$ cm. The samples used were polished and edges were chamfered with a diamond disc.

Thermal shock resistance of the samples was studied by measuring the retained flexural strength using multiple thermal shock quench cycle method. Each cycle comprised 10 min heating at the temperature 1000°C and 10 min cooling at ambient air. At a regular interval of two cycles the retained flexural strength of the samples were measured at room temperature. The microstructures of polished and thermally etched samples were observed under optical microscope in reflected light. EDX analysis of the spinel grains was carried out using sputtered carbon coating on polished surface after thermal etching.

3. Results and discussion

3.1. Characterisation of raw materials

The two basic raw materials used in this study, i.e. calcined magnesia and calcined alumina, were very pure in nature. Chemical analyses of the raw materials used in this investigation are given in Table 2. The magnesia which was originated from brine solution consists MgO level of 97 wt% and 1 wt% impurity (on dry basis), while the calcined alumina contain 99.3 wt% Al_2O_3. Both the raw materials were obtained in powder form. The surface area of alumina was 5.7 m^2/gm and that of magnesia was 0.7 m^2/gm. XRD study revealed that the mineralogical phases present in magnesia and alumina were MgO and α-Al_2O_3, respectively. No minor phases were detected.

3.2. Densification

The variation of bulk density (BD) with the sintering temperature is shown in Fig. 1. Sample MA (without additive) achieves a bulk density of 2.99 g/cc at 1500°C, which is 84% of the theoretical density (TD) of magnesium aluminate spinel (3.58 g/cc). Bulk density gradually increases with sintering temperature and reached 3.55 g/cc (99% of TD) at 1600°C. The nature of densification was different in case of ZnO incorporated Mag–Al spinel. All the samples containing ZnO achieves their highest bulk density at 1550°C and thereafter decrease slightly. The additive ZnO was supposed to enter into the spinel structure and create anion vacancy in Al_2O_3 and thereby favours the densification process. But when the amount of ZnO is higher (about 2 wt%) the density decreases marginally. Though the substitution of ZnO in spinel creates anion vacancy, as it is not fully soluble, the excess ZnO remained in the grain boundary. Therefore, it obstructed the boundary migration, which may

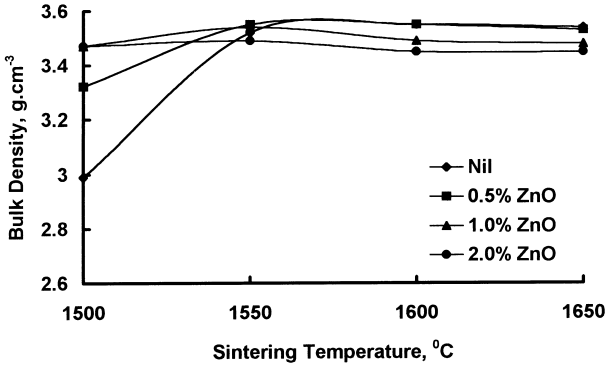
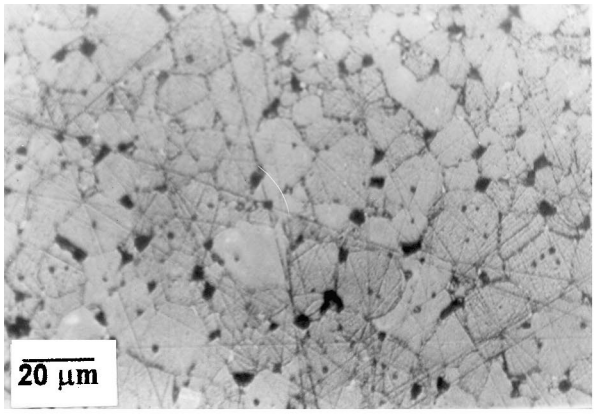


Fig. 1. Variation of bulk density with the sintering temperature.

be the cause of decrease in density. It is revealed from the above study that 0.5 to 1.0 wt% ZnO is beneficial for the densification of spinel.

3.3. Microstructure

The optical photomicrographs of polished and thermally etched samples MA and MAZ2 are shown in Fig. 2(a) and (b). All the spinel grains are rounded in shape. In case of sample MA (without additives) both intergranular and intragranular pores are present [Fig. 2(a)]. But the intragranular pores are reduced with 2 wt% ZnO addition [Fig. 2(b)]. However, the grain sizes were smaller for ZnO doped Mag–Al spinel. EDX analysis of the spinel grain of the samples MA and MAZ2 is given in Table 3. From Table 3 it is seen that in case of MAZ2 out of 2 wt% ZnO added as additive, 1.25 wt% goes into the Mag–Al grains by solid solution. Therefore it is supposed



(a)

(b)

Fig. 2. Optical photomicrograph of the samples sintered at 1600°C (thermally etched): (a) samples MA and (b) sample MAZ2.

Table 3
Composition of spinel grain by EDX analysis

Sample number	MgO (wt%)	Al_2O_3 (wt%)	ZnO (wt%)
MA	28.32	71.68	–
MAZ2	28.14	70.61	1.25

the extra ZnO remained in between the grains and acts as a barrier for boundary movements and restricted the grain growth. Mag–Al spinel formed in ZnO doped/undoped compositions is stoichiometric in nature but spinel without ZnO is slightly rich in alumina, although the batch compositions of both the samples were stoichiometric.

3.4. Strength

The variations of flexural strength with temperature of the samples sintered at 1600°C are shown in Fig. 3. There is no reduction of strength up to 500°C, above which strength of all the sample decreases. Minimum strength was noticed at 1300°C. ZnO additions from 0.5 to 1.0 wt% improve the hot strength above 500°C. In these samples the spinel grains were dense with minimum intragranular porosity, which was the reason for high strength. Above 1 wt% ZnO the strength reduced drastically, which was even below to that of spinel without ZnO. Since ZnO addition beyond 1 wt% reduces the grain growth, there is rapid drop of strength at 1300°C in the samples containing >1 wt% ZnO.

3.5. Thermal shock resistance

Samples sintered at 1600°C were selected to evaluate the thermal shock resistance. Fig. 4 represents the

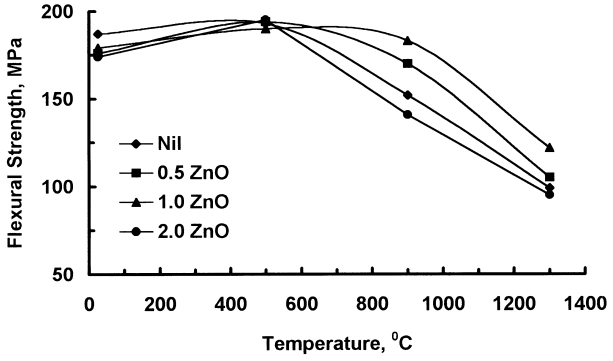


Fig. 3. Variation of flexural strength of the samples sintered at 1600°C with temperature.

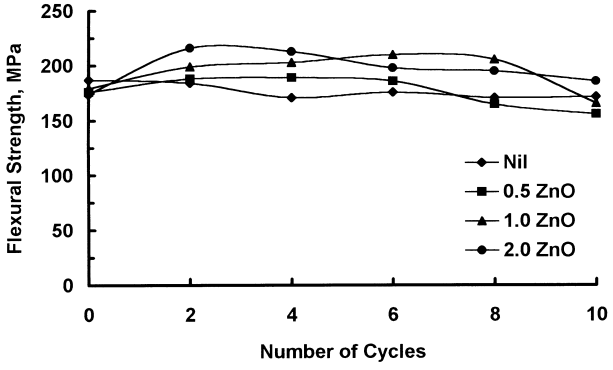


Fig. 4. Variation of flexural strength of the samples sintered at 1600°C with the number of quench cycles.

variation of retained flexural strength on air quenching from 1000°C with the number of quench cycle. From this figure it is seen that all the ZnO containing samples exhibit a slight increase in strength up to two cycles. In most of the cases strength degradation starts after 6–8 cycles. 1 wt% ZnO containing sample (MAZ1) is more resistant to thermal shock compared to the others. In case of sample MAZ2 the ZnO is in excess of the solubility limit remains in the grain boundary position, thereby weakens the structure and it shows the least resistance to thermal shock.

4. Conclusions

Magnesium aluminate spinel can be developed by solid oxide reaction of calcined alumina and calcined magnesia in the temperature range of 1550–1600°C. ZnO incorporation in magnesium aluminate spinel favours the densification and up to 99% of theoretical density can be achieved at 1550°C. Samples containing 1 wt% ZnO show highest flexural strength at all temperatures (except 500°C). ZnO goes into the spinel structure by solid solution formation and the maximum solid solubility of ZnO in Mag–Al at 1600°C is 1.25 wt%. ZnO addition in excess of the solubility limit deteriorates product quality. Spinel grain formed in all the samples is rounded in nature. Intragranular porosity reduces with the addition of ZnO. An addition of 1 wt% ZnO is optimum to achieve maximum densification, hot strength and thermal shock resistance.

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