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# Synthesis and densification of magnesium aluminate spinel: effect of MgO reactivity

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## Abstract

Stoichiometric magnesium aluminate spinel was synthesized by reaction sintering of alumina with caustic and sintered magnesia. The volume expansion of 5–7% during $MgAl_2O_4$ formation was utilized to identify the starting temperature of spinel formation and densification by high temperature dilatometry. The magnesia reactivity was determined by measurement of crystallite size and specific surface area. Caustic magnesia and sintered magnesia behave differently vis-à-vis phase formation and densification of spinel. Densification of stoichiometric Mag-Al spinel was carried out between 1650 and 1750 °C. Attempts were made to correlate the MgO reactivity with microstructure and densification of spinel.

*Keywords:* A. Grain growth; C. Thermal expansion; D. Spinels; E. Refractories

## 1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is the only compound in the $MgO–Al_2O_3$ system. It is known for its high refractoriness, low thermal expansion, chemical stability, thermal shock resistance and corrosion resistance [1,2]. All these unique properties make magnesium aluminate spinel an attractive refractory material for the steel and cement industries. However, the spinel formation is accompanied by 5–7% volume expansion [3,4] which makes it difficult to develop a dense reaction sintered body. Therefore, a two step process is usually followed for sintering of spinel; the first step for spinel formation (900–1200 °C) and the second step for densification (1600–1800 °C). There are several other processes such as coprecipitation [5], spray drying [6] freeze drying [7] spray pyrolysis [8] by which spinel can be synthesized at low temperature. However, none of these processes is suitable for manufacturing of spinel in bulk quantity. Thus solid oxide reaction sintering is still feasible route for manufacturing of spinel aggregates for refractory application.

Workers have studied the effect of fineness of magnesia and alumina on the formation and densification of spinel. There are numerous studies of the raw material characteristics on the sintering of spinel. Petkovic et al. reported [9] the sinterability of spinel partially synthesized at low temperature. Densification intensifies with higher spinel content of powders processed at low temperature. Mansour reported [10] the effect of MgO characteristics on the formation of spinel. $MgCO_3$ calcined between 500 and 1000 °C showed that with the increase of calcination temperature, the crystal size increases which ultimately enhances spinel formation.

In the present study, the goal has been to evaluate the MgO reactivity on the reaction sintering of spinel. A lightly calcined (1100 °C) reactive MgO (caustic) and an inert MgO (sintered) were selected for the study. The volumetric expansion during spinellisation was utilized to identify the initial spinel formation temperature by dilatometry.

## 2. Experimental

The starting materials used in this investigation were Chinese magnesia and Indian alumina. One of the Chinese

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magnesia powders was lightly calcined around 1100 °C (caustic) and the other was sintered. The Indian alumina was obtained from Indian Aluminium Company Ltd. The caustic magnesia was used directly in the as received condition whereas the sintered magnesia pellets were crushed and vibro milled before processing. The chemical analysis of the raw materials was determined by wet chemical methods. The physical properties were measured in terms of surface area and crystallite size. Specific surface area of powders was measured by standard single point BET method using $N_2$ gas (Make: Carlo Erba, Model: SORPTY 1750). The crystallite size was determined by X-ray diffraction (Make: Philips, Model: PW 1710) utilizing x-ray line broadening [11]. Quartz was used as an internal standard. The instrument was run at a scanning speed of 1/4° (2θ)/min. The crystallite size was determined from the equation $D = 0.9\lambda/\beta \, \mathrm{Cos}\theta$, where $\lambda$ = wave length of characteristic beam, $\beta$ = half peak width and $\theta$ = Braggs angle.

Batches were prepared from caustic magnesia and alumina (CMA) and vibromilled sintered magnesia and alumina (SMA). The composition of the batches was in the stoichiometric spinel ratio. Pellets were fabricated by uniaxial pressing at 140 MPa using 5% polyvinyl alcohol solution as a binder. Discs of dimensions 12 mm ($\phi$) × 12 mm ($h$) were fabricated for densification study and cylinders of 10 mm ($\phi$) × 25 mm ($h$) were pressed for dilatometry. Samples were dried at 110 °C for 24 h and sintered between 1650 and 1750 °C with 2 h soaking in an electric furnace at a heating rate of 3 °C/min.

Dilatometric study of the green compacts was performed in a horizontal type 'ORTON' make dilatometer with the same heating rate of 3 °C/min. The structure-sensitive quantitative analysis of spinel was done by X-ray diffraction method with the help of Rietveld analysis [12]. Spinel content was calculated step by step after a lot of refinement in the raw scan data. Some well known software like 'Profit' based on various mathematical and statistical method was used in this connection. It is a refinement programme to refine the raw scan data, where background (by refinement of polynomial in $2\theta$), peak position [$2\theta = 2\theta/R$, where $R$ = radius of diffractometer (173 mm)], peak width (FWHM) and peak shape were refined [13]. The refinement of structural parameter and intensity was done by 'Ito and Treor' method [14]. Bulk density and apparent porosity of the sintered samples were measured by liquid displacement method using Archimedes Principle in xylene medium. Microstructural analysis was done by scanning electron microscopy on a polished surface of sintered samples. The samples before SEM analysis were thermally etched at a temperature 50 °C less than the sintering temperature.

## 3. Results and discussion

The physico-chemical analysis of the starting materials is shown in Table 1. The MgO content of magnesia is 97%. The high LOI of lightly calcined (caustic) magnesia is caused by the thermal decomposition of some $Mg(OH)_2$. DTA analysis (Fig. 1) of the caustic magnesia confirms this by showing a small peak at ~360 °C. However, as the amount is small it is not detected by X-ray analysis. The alumina used is highly pure in nature and the phase present is $\alpha$-$Al_2O_3$.

The crystallite size, specific surface area and calculated equivalent spherical diameter (ESD) of both the magnesia sources are shown in Table 2. The caustic magnesia consists of smaller crystallite size (780 Å) and has high specific surface area. On the other hand the crystallite size of vibro milled sintered magnesia is high and it has low surface area showing its inertness. The particles of powder generally consist of more than one crystal. Unlike caustic magnesia powders the sintered magnesia produced at higher temperature (1800 °C) is in agglomerated granular form. By vibro milling (8 h)

Table 1
Chemical analysis of raw materials

| Raw materials | Chemical constituent (loss free basis), wt% | | | | | | L.O.I, wt.% |
|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | |
| Magnesia | 1.0 | 0.2 | 0.3 | 1.5 | 96.9 | – | Caustic—5.8<br>Sintered—0.8 |
| Alumina | – | 99.69 | – | – | – | 0.31 | 0.4 |

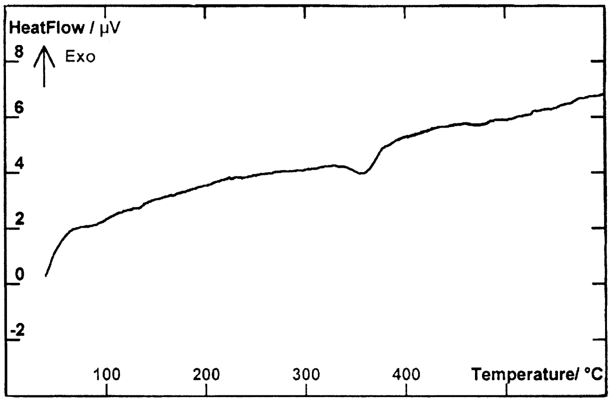

Fig. 1. DTA thermogram of caustic magnesia.

Table 2
Crystallite size and surface area of caustic and sintered magnesia

| Magnesia | Crystallite size, Å | Sp. surface area, $m^2/g$ | Equivalent spherical diameter, Å (calculated) |
|---|---|---|---|
| Caustic | 780 | 13.2 | 1300 |
| Sintered | 1780 | 1.0 | 16 800 |

though its ESD is reduced to 16 800 Å but still it is much above its crystal size (1780Å).

Dilatometric curves of the green compacts derived from caustic magnesia–alumina (CMA) and sintered magnesia–alumina (SMA) batches are shown in Fig. 2. An increase in linear expansion above 1200 °C for both the batches indicates the starting temperature of spinel formation. The percentage linear change beyond 1200 °C is the combined effect of spinel phase formation (expansion) and densification (shrinkage). The lower densification of SMA compact after 1200 °C increases the spinel formation densification ratio (slope change) compared to that of CMA. The thermal expansion of the SMA compact increases up to 1400 °C. The slope of the curve in this compact is reversed after 1475 °C, where the densification rate exceeds the rate of spinel formation. The maximum increase in length for the CMA compact is obtained up to 1460 °C and it remains constant up to 1500 °C.

The amount of spinel produced as a function of temperature is shown in Fig. 3. The spinel phase is the major phase in all the samples. They also contain unreacted periclase and corundum as minor phase. The result shows that the spinel formation of CMA compacts at different temperature is higher than that for SMA. This is because CMA compacts contain caustic magnesia which has a higher surface area and lower crystallite size compared to sintered magnesia of SMA compact and thus a higher reactivity. Considering both Figs. 2 and 3, it can be concluded that the higher slope of SMA in the temperature range of 1300 °C to 1400 °C is the result of its lower rate of densification in this temperature range. However, after 1475 °C the SMA batch tends to densify more, because the expansion due to spinellisation is drastically reduced.

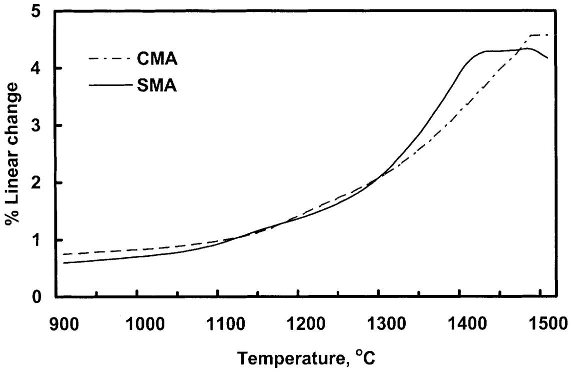

Fig. 2. Dilatometric curves of the green compacts made from CMA and SMA.

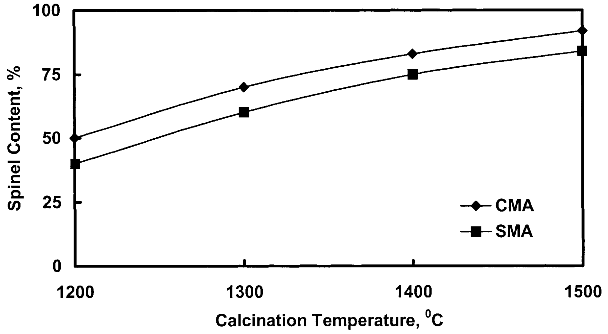

Fig. 3. Spinel content with the increase of calcination temperature.

Fig. 4 shows the result of sintering at different temperatures. It reveals that in spite of higher surface area of caustic magnesia in the CMA batch, the sintered density is low compared to SMA at any sintering temperature. The sintered density and porosity of the CMA compact at 1750 °C are 2.80 g/cc and 21% respectively.

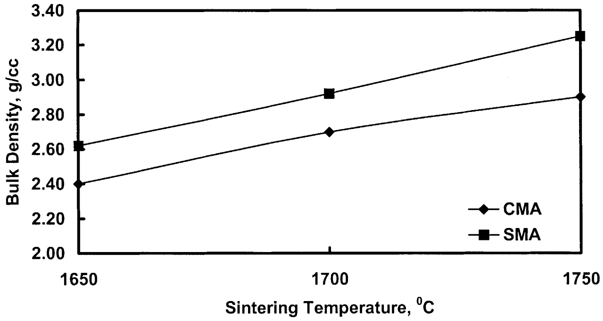

Fig. 4. Bulk density of stoichiometric spinel from CMA and SMA.

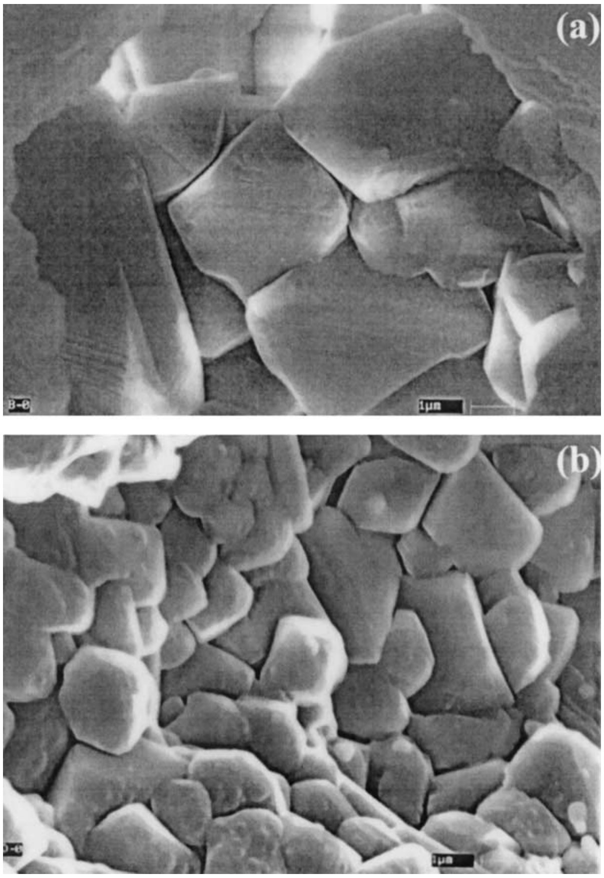

Fig. 5. SEM photomicrographs of sintered stoichiometric spinel: (a) CMA and (b) SMA.

The same for the SMA compact are 3.25 g/cc and 1.0% respectively. The higher surface area of caustic magnesia in CMA compact favours the spinel formation than densification. Higher spinel formation (Fig. 3) accompanied by volume expansion (Fig. 2) is responsible for lower densification of CMA compacts. The result corroborates a study of low temperature synthesized spinel, wherein although the starting material had smaller crystallite size it finally showed poor sintered density [15]. It is reported that the powder calcined at low temperature possessed a relatively larger amount of rod like particles which hinders uniform compaction and are responsible for decreased final density.

The SEM photomicrographs of spinel compacts (CMA and SMA) sintered at 1750 °C are shown in Fig. 5 (a) and (b). The grain size of sintered CMA [Fig. 5(a)] is significantly higher than that of sintered SMA. The photomicrograph of sintered SMA shows uniform distribution of spinel grains with smaller size and homogeneous microstructure. The high surface area of caustic magnesia in CMA compacts increases the rate of spinellisation and enhances grain growth. Therefore exaggerated grain growth and higher porosity is the reason of poor sintered density of CMA compacts. However, the pore removal of SMA is easier due to comparatively slower rate of spinellisation and uniform grain growth.

## 4. Conclusions

1. Solid oxide reaction-sintering of spinel developed from sintered magnesia–alumina (SMA) shows better densification than caustic magnesia–alumina (CMA) composition.
2. The spinel phase formation: densification ratio of CMA compact is higher than SMA due to higher surface area and lower crystallite size of the former.
3. Higher expansion due to spinel phase formation and exaggerated grain growth of CMA compacts retards the densification process.

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## References

[1] J.L. Huang, Y.C. Ko, Investigation on high alumina spinel: effect of LiF and $CaCO_3$ addition, J. Am. Ceram. Soc. 80 (1997) 3237–3241.

[2] T. Yamamura, T. Hamazaki, H. Kato, Alumina spinel castable refractories in steel teeming ladles, Taikabutsu Overseas 12 (1992) 21–27.

[3] H.C. Park, Y.B. Lee, K.D. Oh, F.L. Riley, Grain growth in sintered $MgAl_2O_4$ spinel, J. Mater. Sci. Lett. 16 (22) (1997) 1841–1844.

[4] D.O. McCreight, R.E. Birch, US patent no. 2,805,167 (1952).

[5] R.J. Bratton, Co precipitates yielding $MgAl_2O_4$ spinel powders, Am. Ceram. Soc. Bull 48 (8) (1969) 759–762.

[6] J.G.M. deLau, Preparation of ceramic powders from sulphate solutions by spray drying, Am. Ceram. Soc. Bull. 48 (6) (1970) 572–574.

[7] C.T. Wang, L.S. Lin, S.J. Yang, Preparation of $MgAl_2O_4$ spinel powder freeze drying of alkoxide, J. Am. Ceram. Soc. 75 (8) (1992) 2240–2243.

[8] Y. Suyama, A. Kato, Characterisation and sintering of Mag–Al spinel prepared by spray pyrolysis technique, Ceram. Int. 8 (1) (1982) 17–21.

[9] J. Petkovic, E. Kostic, S. Malcic, The effect of MgO powder activity on the synthesis and sintering of $MgAl_2O_4$, Ceramurgia 4 (1975) 175–178.

[10] N.A.L. Mansour, Effect of magnesia and alumina characteristics on the formation of spinel, Interceram 27 (1) (1978) 49–51.

[11] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures, Wiley-Interscience, New York, 1974.

[12] L.B. McCusker, R.B. Von Dreele, R.B. Cox, D.E. Louer, P. Scardi, Rietveld refinement guidelines, J. Appl. Cryst. 32 (1999) 36–50.

[13] R.J. Hill, I.C. Madsen, The effect of profit step width on the determination of crystal structure parameters and estimated standard deviations by X-ray Rietveld analysis, J. Appl. Cryst. 19 (1986) 10–18.

[14] G. Roy, X-ray study of second hydrated phase of copper ammonium sulphate hexahydrate, Ind. J. Phys. 7 (1965) 307–312.

[15] J.G. Li, T. Ikegami, J.H. Lee, T. Mon, Y. Yajima, A wet chemical process yielding reactive magnesium aluminate spinel ($MgAl_2O_4$) powder, Ceram. Int. 27 (4) (2001) 481–489.