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Effect of attritor milling on the densification of magnesium aluminate spinel

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Abstract

Densification of magnesium aluminate spinel was studied with both the single stage and double stage sintering processes using attritor mill for the reduction of particle size. Presynthesized spinel and a stoichiometric mixture of calcined magnesia and alumina were used for the study. Presynthesization of spinel and calcination of raw materials were done at 1400 and 1600°C. Milling was done for 2, 4 and 6 h. Extent of milling was characterised by measuring the specific surface area of the milled powders. Densification was found to be greatly influenced by milling. A maximum 99.5% densification was obtained. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

Keywords: D. Alumina; D. Spinel; Magnesia; Attritor milling; Single stage and double stage sintering

1. Introduction

Spinel bodies are known to offer desirable combination of properties—mechanical, chemical and thermal—both at normal and elevated temperatures. But they have not been commercially successful primarily due to the difficulty in sintering. Synthesis of spinel and fabrication as refractories are rather known since long [1]. But the volume expansion of 5% [2] during the formation of spinel from magnesia and alumina does not allow the material to densify in a single stage firing. Hence the general practice is to complete the spinellisation process first and then crushing, milling, reshaping and sintering the spinel to achieve desired properties in the second firing. Therefore two stage sintering process and a number of relevant processing parameters have greatly influenced the cost of production. Magnesium chromite refractories having similar combination of properties became the substitute of magnesium aluminate. But as people becomes more aware about the hazardous character of chrome bearing materials [3], the study on magnesium aluminate spinel again gets the momentum. The major application areas of spinel refractories are transition and burning zones of cement rotary kilns, side walls and bottoms of steel teeming ladles, checker work of glass furnace regenerators, etc.

Methods of preparing dense spinel products have improved considerably with time. In all the sintering studies reduction in particle size was a necessary criteria to obtain dense spinel product from presynthesized spinel batch. Kriegel et al. [4] suggested a method of calcining the stoichiometric mixture of MgO and Al_2O_3 at 1450 to 1470°C to complete the spinellisation part and then breaking the friable lumps below 2 μ for sintering. Bakker and Lindsay [5] obtained a maximum density of 3.46 g cm^{-3} in spinel bodies by preparing spinel from $Mg(OH)_2$ and $Al(OH)_3$ at 1400°C and then reground the material in a high alumina pot mill for 3 h to break up the aggregates of small spinel crystallites and then sintering. Bailey and Russell [6] produced a spinel of 95% theoretical density. They calcined a milled mixture of $MgCO_3$ and Al_2O_3 between 1125 and 1140°C to complete about 55 to 70% of spinellisation, then milled the calcined material, pressed and sintered. They suggested a partial reaction technique is important to obtain a dense spinel product. Amount of presynthesized spinel in the starting batch also affects the densification behaviour of spinel. Kostic and Momcilovic [7] working with spinel batches, having specific surface area of 1.5 to 2.2 m^2g^{-1}, obtained a maximum density of 3.3 g cm^{-3} at 1800°C with a batch containing 90% presynthesized spinel. K. Itatani and others [8]

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observed a maximum 96% densification at 1700°C from a magnesium aluminate powder of 0.2 μ size, produced by vapour-phase oxidation route. Hence particle size reduction is important for getting a densified spinel. Reduction of particle size below a certain critical size is important as it decreases the distance between vacancy sites (or that of grain boundaries) and enhances the vacancy diffusion to external surface thus helps in densification. But reduction of particle size much finer to that of critical one is of little negative importance [9].

In this investigation a systematic study on the densification of magnesium aluminate spinel is described. Hydroxides are chosen as the raw materials. Calcination of the hydroxides is done on the basis of an earlier work [10]. Attritor mill is used for the reduction of particle size. Densification is studied for:

1. presynthesized spinel, and
2. stoichiometric mixture of MgO and Al_2O_3,

after milling for different hours. Extent of milling is correlated with the obtained densification. Slower rate of sintering is applied as it is more effective [11] for better densification of magnesium aluminate spinel.

2. Experimental

Magnesium hydroxide and aluminium hydroxide were taken as the starting materials. Both the hydroxides were characterised by means of chemical analysis, specific gravity, specific surface area, powder X-ray diffraction, differential thermal analysis, and thermogravimetric analysis. Chemical analysis was done using the conventional acid dissolution method. Specific surface area was measured according to the BET technique using nitrogen as the gas for adsorption by the dried and de-aired sample placed in a liquid nitrogen bath. X-ray diffraction was carried out in the range of 10 to 65° using a Cu K_α radiation. Differential thermal analysis and thermogravimetric analysis were done up to 1000°C at a heating rate of 10°C per min. Hydroxides were calcined as separately and as a mixture of hydroxides (for presynthesization of spinel), with 1:1 molar ratio for MgO to Al_2O_3, (batch termed 'R'), at 1400 and 1600°C. Calcination was done as loose powders in high alumina crucible with a heating rate of 4°C per min and a soaking period of 1 h at the peak temperatures. Obtained calcined products were nearly loose powders and not hard agglomerates. All the calcined materials were again characterised by X-ray diffraction, specific surface area and specific gravity. Separately calcined hydroxides were mixed to 1:1 molar ratio of oxides (batch termed 'C'). Calcined powders, both 'R' and 'C' batches were attritor milled for 2, 4 and 6 h. An attritor mill (Union Process Inc., Model 01HD), with zirconia pot, stirrer rod and balls, was used for the purpose. Milled powders were dried and surface areas were determined. Milled and without milled powders were then isostatically pressed to briquettes. Isostatic pressing (Autoclave Engineers, Model CIP 6-23-30) was done at 175 MPa. Briquettes were dried and then sintered in electrically heated furnace at 1550, 1600 and 1650°C with 2 h soaking period. Heating rate used for sintering was 1°C per min. The sintered briquettes were tested for densification studies. All sintered 'C' batch briquettes were also tested by powder X-ray diffraction studies. Microstructure of polished and thermally etched sample was studied under scanning electron microscope (Leica model S440) at a magnification of 5000×. Chemical composition of the sintered body was also analysed by conventional methods to check any zirconia contamination or magnesia vaporization in the sintered sample.

3. Results and discussion

Chemical analysis of the starting hydroxides and the physical properties of the uncalcined and calcined materials are given in Table 1. Differential thermal

Table 1
Physico-chemical properties of the raw materials

Chemical analysis of the hydroxides

	Mg-hydroxides	Al-hydroxides
SiO_2	0.35	0.53
Al_2O_3	0.21	83.01
TiO_2	Trace	Trace
Fe_2O_3	0.03	0.16
CaO	1.13	1.07
MgO	67.75	Trace
K_2O	0.02	0.02
Na_2O	0.07	0.18
L.O.I.	30.30	14.60

Physical properties of calcined and uncalcined materials

	Sp. gravity	Sp. surface area	Phase analysis	
		($m^2 g^{-1}$)	Major	Minor
Magnesium hydroxide				
Uncalcined	2.35	45.6	Brucite	–
Calcined 1400°C	3.59	1.8	Periclase	–
Calcined 1600°C	3.60	0.3	Periclase	–
Aluminium hydroxide				
Uncalcined	3.06	140.9	Boehmite	Bayerite
Calcined 1400°C	3.99	2.9	Corundum	–
Calcined 1600°C	4.00	0.8	Corundum	–
R Batch				
Calcined 1400°C	3.57	2.8	Spinel	–
Calcined 1600°C	3.58	0.6	Spinel	–

analysis and thermogravimetric analysis studies (Fig. 1) show the conversion temperatures of the hydroxides to the respective oxides. X-ray diffraction patterns reflect the expected corundum and periclase phases in the calcined Al-hydroxide and Mg-hydroxide respectively. For calcined 'R' batch, it is only spinel phase and there are no free peaks of MgO and Al_2O_3. Coarsening at high temperature produces lower specific surface area of the calcined materials and conversion to oxides results in the rise of the specific gravity on calcination.

Milling sharply increased the specific surface area but prolong milling had lesser effect for all the different materials, [Fig. 2(A) and Fig. 3(A) for R batch and C batch, respectively]. Coarse hard agglomerates of 1600°C calcined materials were milled to a lesser extent. Formation of spinel in the R batch made it more softer (due to the associated expansion) compared to that of the C batch, resulting a higher surface area for the materials.

Hydroxide materials were first tried to density, but only 55% densification was achieved at 1650°C. Calcined materials were also found to be poorly densified in the whole sintering range of 1550 to 1650°C. Incorporation of milling had greatly improved the densification for both the R and C batches, [Fig. 2(B) and Fig. 3(B), respectively]. Similar type of densification patterns were observed for both the batches. Prolonged milling (more than 4 h) had lesser incremental effect on densification. A maximum 99.5% density was obtained for the C batch calcined at 1600°C, milled for 6 h and then sintered at 1650°C. Very little variation in sintered density was observed for the R batch with increasing sintering temperature. X-ray diffraction patterns of the sintered C batch materials confirmed only spinel phase in the body.

Milling beyond 4 h had lesser beneficial effect on the densification for all the materials. Increased surface area of the powders, by prolong milling may be of no benefit for densification as suggested by Petkovic and Ristic [9]. For C batch, the harmful effect of spinellization on densification in a single stage firing is avoided, may be due to the reaction between more inert fine particles

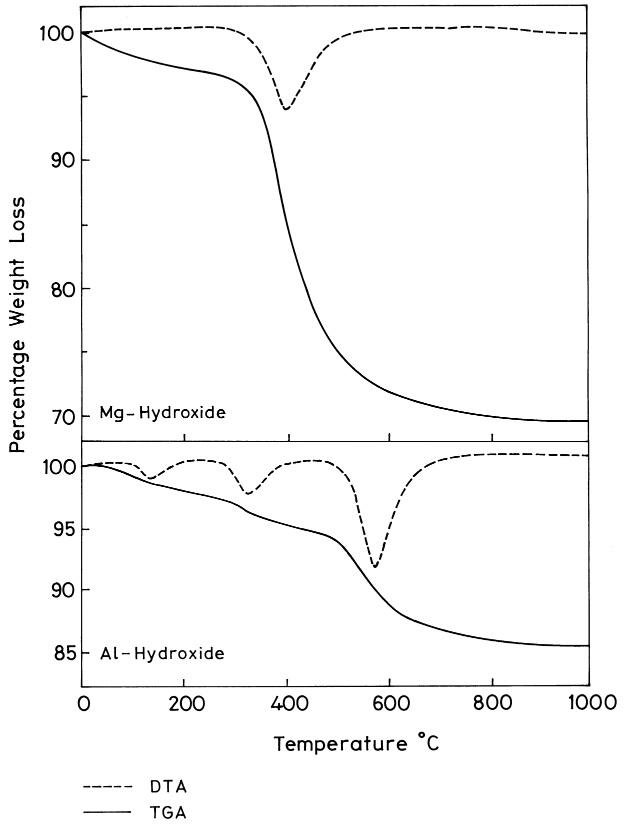

Fig. 1. Differential thermal analysis and thermogravimetric analysis of the starting hydroxides.

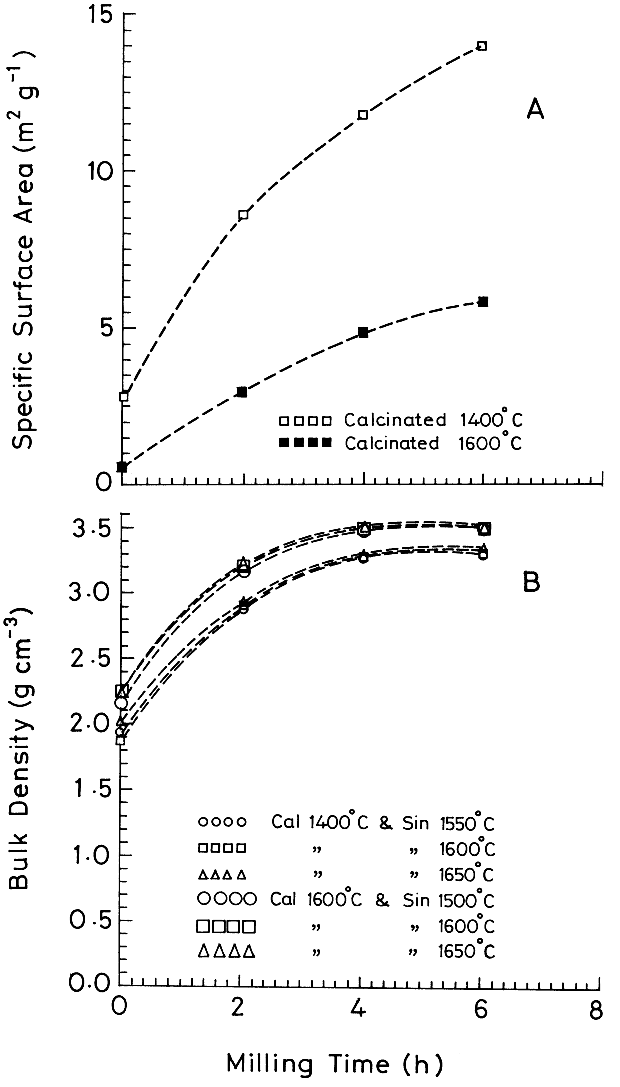

Fig. 2. Effect of milling on the R batch: (A) variation of the specific surface area with milling time; (B) variation of sintered density with milling time.

with slower rate of sintering [11]. These might have smoothened the spinellization reaction and the associated expansion. 1600°C calcined materials were more inert and hard, resulted in lesser surface area on milling, but reduction in particle size and introduction of mechanical flaws by milling were more effective that resulted higher densification in these inert materials. So, more inert and finer materials show greater densification. Again much higher green density of these materials (Fig. 4) might have helped to retain higher density even after sintering.

Microstructural and compositional study was done for the C batch material calcined at 1400°C, milled for 4 h and then sintered at 1600°C. Scanning electron photomicrograph shows (Fig. 5) close compacted grain structure, supporting very good densification. Again sharp angularity is also observed which may suggest about good mechanical characteristics. Intragranular pores in the sintered body gives the idea about grain growth, which is may be due to the slower rate of sintering. Chemical analysis of the sintered body was done to check any zirconia (ZrO_2) contamination during milling. It shows (Table 2) that the sintered body is very close to the ideal stoichiometric composition with undetectable amount of ZrO_2. Soft character of the materials, due to low temperature calcination, may be the reason for not abrading the zirconia balls. Hence chances of ZrO_2 contamination is eliminated. Again the ratio of magnesia to alumina remains very close to that of the stoichiometric one which signifies no magnesia vaporization has occurred during sintering.

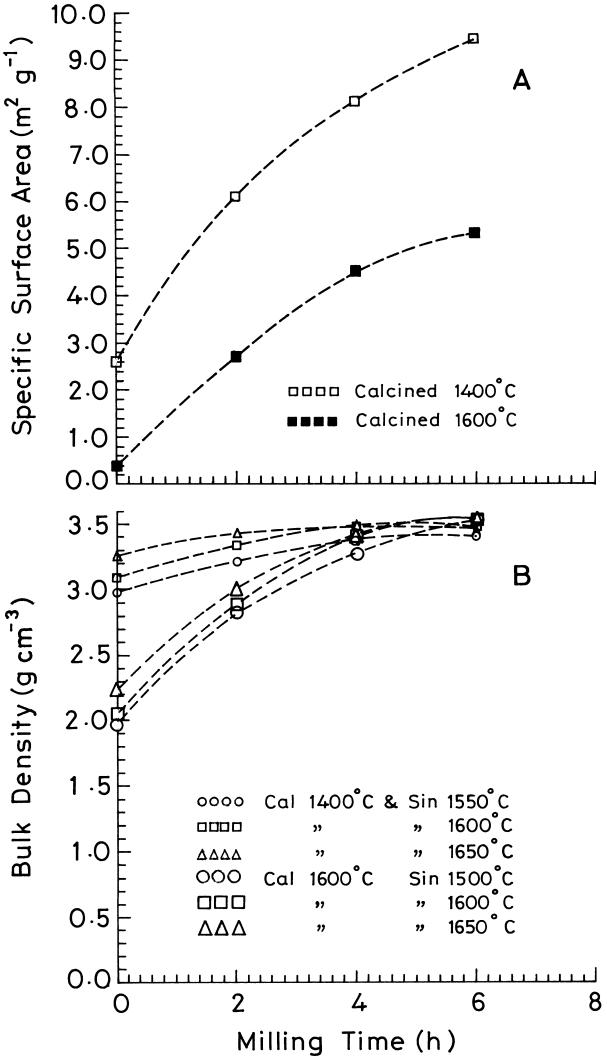

Fig. 3. Effect of milling on the C batch: (A) variation of the specific surface area with milling time; (B) variation of sintered density with milling time.

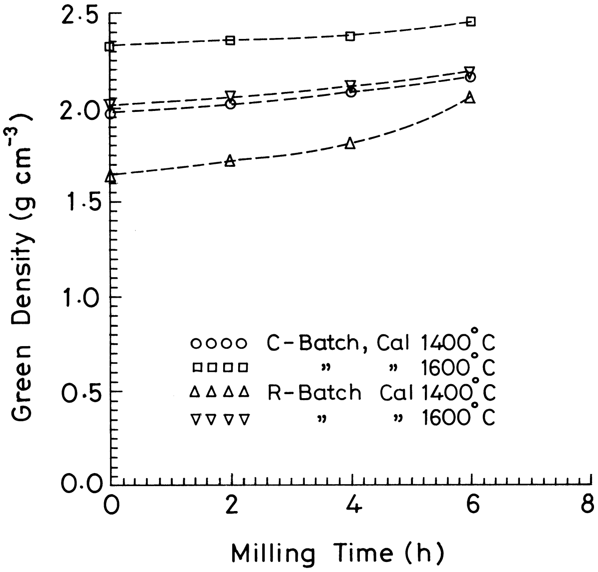

Fig. 4. Green density study of the pressed briquettes.

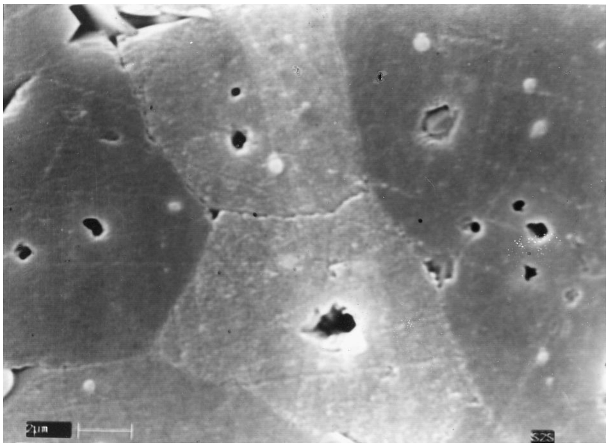

Fig. 5. Scanning electron photomicrograph of the 1400°C calcined C batch material milled for 4 h and then sintered at 1600°C (bar represents a length of 2 μ).

Table 2
Chemical analysis of the sintered body

(C batch, calcined at 1400°C, milled for 4 h, sintered at 1600°C)	
SiO_2	0.56
Al_2O_3	69.40
TiO_2	Trace
Fe_2O_3	0.16
ZrO_2	Trace
CaO	1.32
MgO	27.90
K_2O	0.03
Na_2O	0.21
L.O.I.	0.07

4. Conclusions

1. Attritor milling produces a very high density in spinel bodies.
2. A maximum of 99.5% densification was obtained in 6 h milling without carrying any presynthesization of spinel.
3. Higher calcination temperature with longer milling produces better densification.
4. Deleterious effect of spinellisation (due to the expansion) on densification in a single stage firing has been avoided in the process.

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