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NOTE

Effect of MgO : Al_2O_3 mole ratio on the densification of magnesia-alumina precursor leading to spinel formation

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Magnesia-alumina precursor with different non-stoichiometric mole ratios of Al_2O_3 : MgO spinel system, were synthesized using semi-colloidal route. Sintering of the compacted powders was carried out at different temperatures (1400–1550°). Magnitude of densification of the sintered compacts was measured by various physicomechanical methods. The degree of non-stoichiometry in the spinel composition strongly affected the sintering process.

Carole *et al.*[1] produced magnesium aluminate by sol-gel technique. Kadokawa and Suzuki[2] studied the effect of alkali chlorides on spinel formation by sol-gel route. Posquier *et al.*[3] studied the spinel formation and seeding effect on it by preparing spinel by four different methods using different solutions. Molten cast magnesia-alumina refractory was studied by Provlovski *et al.*[4]. Synthesis of magnesium aluminate precursor was studied by various workers[5]. Magnesium aluminate whiskers were prepared by Hashimoto and Yamaguchi[6].

In the present investigation, a series of MgO-Al_2O_3 system was considered starting from stoichiometric spinel to both higher and lower MgO and Al_2O_3 content in composition. After mixing the starting salts, the mixed hydroxide was precipitated in the form of a gel. The precursor powder was characterized and subjected to sintering in compact forms.

Results and Discussion

During dispersion of caustic magnesia, a part of it went into $Al(NO_3)_3$ solution. The method adopted for the preparation of precursor powder has the advantage of the mixing of the ingredients in the molecular level and the process can be controlled as per the requirement. Compositional effect was not so much prominent in the gel formation reactions. The chemical analysis of the dehydrated gel (Table 1) reveals that there is a wide variation in the molar ratio of MgO : Al_2O_3 from 0.5 to 4, as desired in the batch composition.

Thermogram of the samples consists of three major endothermic peaks at 100, 272 and 348°. The initial peak was due to the removal of the loosely bound gel water, second and the third ones were related to the dehydroxylation of hydroxides of $Al(OH)_3$ and $Mg(OH)_2$, respectively. A small exothermic peak at about 1500° indicated the commencement of spinellization reaction. IR spectra of the precursor powder of 1 : 4 Al_2O_3 : MgO sample reveal bands at 3455 (OH), 1385 (OH bending), 447–1000 cm^{-1} (Al-O and Mg-O) and 673 cm^{-1} (six-coordinated Al-O and Mg-O). The calcined precursor powder gave strong bands at 694 and 594 cm^{-1}, assigned to the stretching of Al-O and Mg-O of MgO-Al_2O_3 spinel formed. X-Ray diffraction analysis of the hydrogel powder indicated complete amorphous nature with no distinct peak.

Table 1. Properties of precursor gel powder

Gel sample	Al_2O_3/MgO mole ratio	Analysis, wt% MgO	Al_2O_3
A	0.50	43.95	56.01
B	0.66	37.27	67.70
C	1.0	28.17	71.80
D	2.0	16.40	83.60
E	4.0	8.90	91.10

Volume shrinkage of the hydrogel after sintering followed a direct relationship with the MgO content in the mixed hydrogel (Fig. 1a,b). Shrinkage also increased with the increase in sintering temperature. In MgO-rich composition, the formation of more liquid phase is probably responsible for higher shrinkage.

The composition having mole ratio of Al_2O_3 : MgO = 0.5 exhibited significantly low porosity which is an indication of its higher degree of densification. This is also in good agreement with the shrinkage values. The overall results indicated that within the temperature zone of sinter-

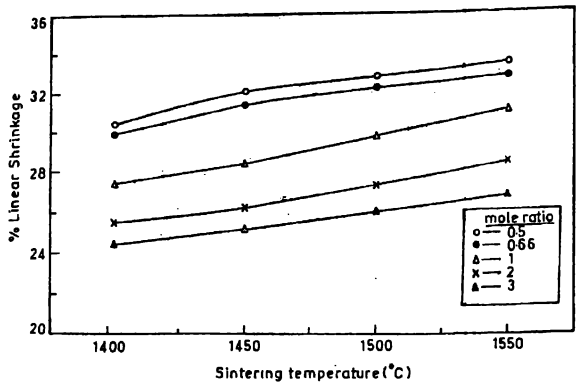

Fig. 1a. Relationship between linear shrinkage with sintering temperature at different (Al_2O_3/MgO) mole ratios.

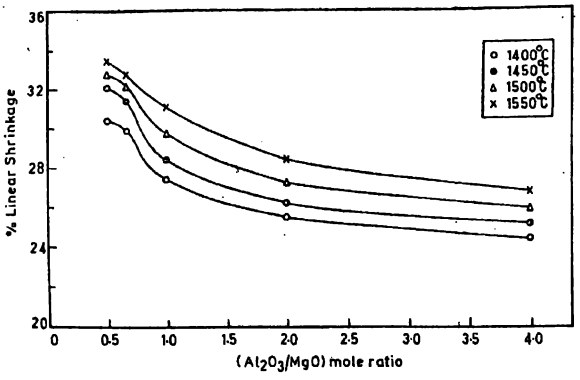

Fig. 1b. Relationship between linear shrinkage with (Al_2O_3/MgO) mole ratio at different sintering temperatures.

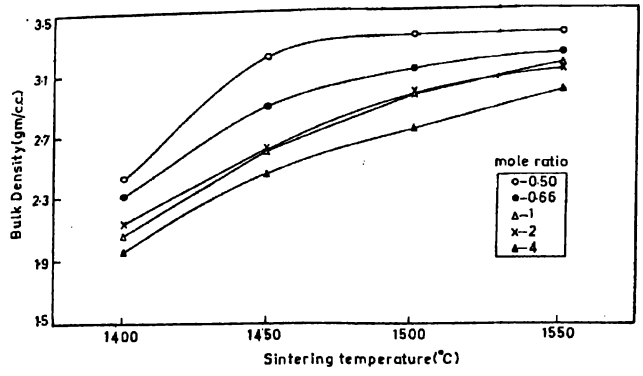

Fig. 2a. Relationship between bulk density with different sintering temperatures for different (Al_2O_3/MgO) mole ratios.

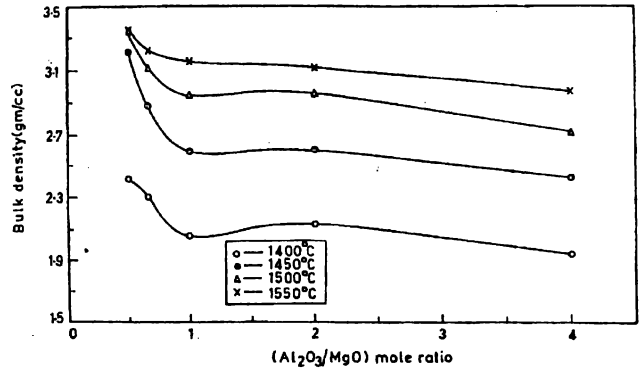

Fig. 2b. Relationship between bulk density with (Al_2O_3/MgO) mole ratios at different temperatures.

ing, densification was hindered in the alumina-rich zones as exhibited by relatively high porosity. Maximum porosity was observed with Al_2O_3 : MgO mole ratio of 4.0

Maximum value of the bulk density of sintered samples (Figs. 2a,b) was observed at sintering temperature of 1550°. MgO-rich compositions exhibited higher bulk density which was in good agreement with the porosity value. With the increase in Al_2O_3 content the bulk density of the samples decreased. At 1550° minimum value was observed with Al_2O_3 : MgO mole ratio of 4.0. Initial increase in bulk density of the samples was sharp up to the sintering temperature of 1500°. The course of densification followed parabolic relationship and the individual curve differed in its magnitude and the temperature coefficient was more or less uniform. At the stoichiometric composition the extent of densification was about 91%.

True specific gravity values of the sintered samples were found to be a positive function of temperature at all compositions. For sample with Al_2O_3/MgO mole ratio 4.0, it increased steadily with the increase in sintering temperature. But for Al_2O_3/MgO mole ratios of 0.5 and 0.66, the maximum value was attained at 1450°. For Al_2O_3/MgO mole ratio of 1.0, it slightly decreased up to 1500°. Formation of more corundum bearing phases at batches with higher proportion of Al_2O_3 is probably a reason for this.

From the XRD patterns of the sintered samples the major phase observed in all the samples was spinel. In the MgO-rich portion, periclase was the associated phase and in the Al_2O_3 rich zone it was corundum. Microstructural variation with composition of the sintered samples at 1450° was studied by SEM. Spinel phase of large grain size was observed in the MgO-rich composition up to the stoichiometric ratio. In the alumina-rich zone the grain size was smaller. In both the cases the grain boundary was sharp. Existence of sub-rounded pores was observed in the microstructure. The residual pores were observed as entrapped intra-granular which appears to be responsible for the abnormal grain growth of the spinel phase. The MgO-rich compositions evolved inter-granular periclase of smaller sub-rounded dimensions. With the increase of Al_2O_3 up to the mole ratio of 1.0, the grain size increased due to the forma-

tion of more spinel phase.

Conclusions : Mole ratio of MgO : Al_2O_3 in the precursor influences the densification of $MgAl_2O_4$ spinel synthesized via non-conventional semi-colloidal route. With the increase in sintering temperature, the apparent porosity value of the sintered compacts decreased and the density increased. With the increase in Al_2O_3 content also, the densification was found to increase in the sintered compacts as evident through apparent porosity and density values. The major phases identified in the sintered compacts were spinel, periclase and corundum. In the alumina-rich zone smaller grain size in the micro-structure was observed.

Experimental

$MgCO_3$ and $Al(NO_3)_3$ (AnalaR) were used as the starting material for the synthesis of the hydrogel. $MgCO_3$ was first calcined at 90° in an $Al(NO_3)_3$ solution. The required amount of MgO powder was dispersed properly with thorough stirring. The mole ratios of Al_2O_3 : MgO are shown in Table 1. A 1 : 1 ammonia solution was added to the suspension slowly with constant stirring till pH of the suspension reached 9 and this caused gelation of the suspension. The gel was allowed to age, washed and dried in an air-oven. Chemical analysis of the gel was carried out following conventional procedures. DTA analysis was carried out with a Netzsch STA-409 instrument. IR spectra (KBr) were recorded on a Nicolet FTIR spectrophotometer (Magna IR series II). Pellets of the samples were fabricated at a pressure of $2T/cm^2$ with a hydraulic press. The pellets were sintered at 1400, 1450, 1500 and 1550° in a muffle furnace with 2 h of soaking period. Apparent porosity and true density were measured following standard procedures. XRD analysis was carried out with a Siemens diffractometer. Scanning electron microscopic analysis were carried out in Hitachi S-530 microscope.

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