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The role of TiO_2 in the densification of low cement Al_2O_3–MgO spinel castable

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Abstract

Fused alumina (70%) and dead burnt magnesia (30%) of different grain sizes were used to synthesize Al_2O_3–MgO spinel castable. Calcium aluminate (75% Al_2O_3) cement was used as binder of the castable. Densification behaviour of such castables in the presence of TiO_2 was assessed through the measurement of parameters like, bulk density, volume shrinkage, apparent porosity, specific gravity and microstructure evaluation by SEM and XRD studies. It was observed that TiO_2 exhibited a positive influence on the densification behaviour of these compacts.

Keywords: D. Spinel; Castable; Titania; Low cement; Densification

1. Introduction

Due to its advantages like, high resistance to thermo-mechanical stresses, low thermal expansion, high resistance to changes in the environment, etc., alumina–magnesia spinel has been widely used as a high temperature refractory material for applications in different metallurgical and non-metallurgical processes in the recent years. Many workers [1–7] have been working on the alumina–magnesia spinel system to improve its different high temperature application related properties.

De Azza et al. [1] described a new and inexpensive spinel containing refractory cement obtained by a reaction sintering process between dolomite and alumina. Korgula et al. [2] carried out micro-structural analysis of corroded alumina-spinel castable refractories and observed that MgO-rich spinel-alumina castables undergo less corrosion in the presence of liquid steel ladle slag as dissolution of MgO leads to a viscous MgO-rich slag, which is less corrosive to the Al_2O_3 components of the refractory. Sarkar and Banerjee [3] studied the effect of TiO_2 addition on reaction sintered MgO–Al_2O_3 spinel with different MgO:Al_2O_3 molar ratios. Attrition milling was used to reduce particle size and the sintered products were characterized in terms of densification and shrinkage studies, phase analysis, strength evaluation both at ambient temperature and at elevated temperature, strength retention after thermal cycling at 1000 °C, quantitative elemental analysis and micro-structural studies.

Ganesha et al. [4] prepared a stoichiometric dense $MgAl_2O_4$ spinel according to a conventional double stage firing process using $AlCl_3$ as a sintering aid. By the addition of stoichiometric $MgAl_2O_4$ spinel, the slag erosion and penetration resistance of high Al_2O_3 and MgO-C refractories was improved remarkably, and their permanent linear changes (PLCs) exhibited stable positive values after the spinel addition. Ko [5] studied the role of spinel composition in the slag resistance of Al_2O_3-spinel and Al_2O_3–MgO castables. The experimental results indicated that slag penetration decreased with increasing MgO content in spinels. The role of spinel composition in the slag resistance of Al_2O_3-spinel and Al_2O_3–MgO castables is to dissolve itself in the penetrating slag, and as a result, to lessen the penetration.

Chena et al. [6] studied the thermal characteristics of Al_2O_3–MgO and Al_2O_3-spinel castables for steel ladles. The authors found no correlation between hot strength and slag resistance for castables. The magnitude of specific surface area of pores is more important than pore size and porosity for governing the slag resistance of Al_2O_3–MgO castables, with and without micro-silica addition. Mukhopadhyay et al. [7] developed easy-to-use mullite and spinel sols as bonding agents in a high

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alumina based ultra low cement castables. The results indicated that the mullite sols improve while the spinel sol degrades the refractory castable quality.

In the present investigation, the role of TiO_2 on the densification of low cement castables prepared by using fused alumina and dead burnt magnesite with 5% calcium aluminate cement, was investigated. These castables form in situ spinels during firing at temperatures between 1400 and 1600 °C. It has been observed that an addition of MgO to aluminium titanate improves its stability by grain boundary stabilization [8]. This observation is the basis for the present investigation, whether the addition of TiO_2 leads to the stabilization of $MgO–Al_2O_3$ spinel. The densification behaviour was studied by evaluating bulk density, apparent porosity, specific gravity, phase analyses and the micro-structure of the fired castables.

2. Experimental

Fused Al_2O_3 and dead burnt magnesite (both natural and sea water) were used as the aggregates in different size fractions (as depicted in Table 1) in the weight ratio of 70:30. TiO_2 (surface area 3.4 m^2/g) in different proportions was added to the batches (the compositions are given in Table 2). The aggregates, including the fines, were thoroughly mixed in a tilting type laboratory tumbler mixer for 1 h to ensure thorough mixing of the ingredients. The mixed aggregates were then properly mixed with calcium aluminate cement (composition detailed in Table 3) with 6% moisture, followed by casting in 75 mm size cubic die. After the cast samples set, they were dried at 110 °C for 5 h in an air oven, then fired in a muffle furnace at temperatures of 1400, 1500 and 1600 °C with 2 h soaks. Parameters like volume change after firing; bulk density, specific gravity and compressive strength of the compacts were measured following specifications in BS 1902: Part 1A: 1966. XRD analysis of the fired samples was carried out with Sciefert X-ray Diffractometer (model 3000P), and scanning electron photomicrographs of the samples were taken with Leo, Cambridge, UK.

Table 1
Castable additives

Size fractions (mesh)	Al_2O_3	Dead burnt MgO	Sea water MgO
−4 + 8	24.5	10.5	–
−8 + 16	7	3	–
−16 + 30	10.5	–	4.5
−30 + 72	7	–	3
−72 + 120	10.5	–	6
−120 + 325	7.5	–	1.5
−325	3	–	1.5
Additives (added over 100% aggregate as parts per hundred)			
Fume SiO_2			3 parts
Al powder			2.5 parts
Fe_2O_3 powder			1 part
Sodium hexa meta phosphate			1 part
Calcium aluminate cement			5 parts

Table 2
Composition of different batches

B-1 ⋙	Castable + no additive
B-2 ⋙	98% castable + 2% TiO_2
B-3 ⋙	96% castable + 4% TiO_2
B-4 ⋙	94% castable + 6% TiO_2

Table 3
Chemical composition of starting materials (wt%)

Constituents	Calcium aluminate cement	Sea water magnesia	Dead burnt magnesia	Fused alumina	Titania
Al_2O_3	74.48	0.05	0.1	99.0	–
CaO	34.21	0.6	1.5	–	–
SiO_2	0.48	0.05	7.5	0.01	0.22
Fe_2O_3	0.43	0.06	0.2	0.009	0.31
B_2O_3	–	–	–	–	–
TiO_2	0.02	–	–	–	99.0
MgO	0.1	99.00	90.00	–	–
Na_2O	0.22	–	–	0.35	0.27
K_2O	0.05	–	–	–	–

3. Discussion

Although $MgO–Al_2O_3$ spinel has excellent spalling and slag corrosion resistance, its performance in service is mixed because of sintering difficulties and because of destabilization during service. The particle sizing of fused alumina and dead burnt magnesia was adjusted so that it contained about 45% coarse (−4 + 16 mesh), 25% medium (−16 + 72 mesh) and 30% fine (−72 mesh) sized grains.

Calcium aluminate cement was used as a binder and the green strengths of the castables were found to be satisfactory. In the batch without TiO_2 additive (B-1 in Fig. 1), the extent of volume shrinkage decreased sharply from the firing temperature of 1400–1500 °C, but from the firing temperature of 1500–1600 °C, it steeply increased. About 9% shrinkage was observed at a firing temperature of 1400 °C. The reason for this shrinkage might be ascribed to the formation of some lime bearing vitreous phases; like calcium aluminium silicates, calcium silicate, magnesium aluminium silicate, etc.; at this

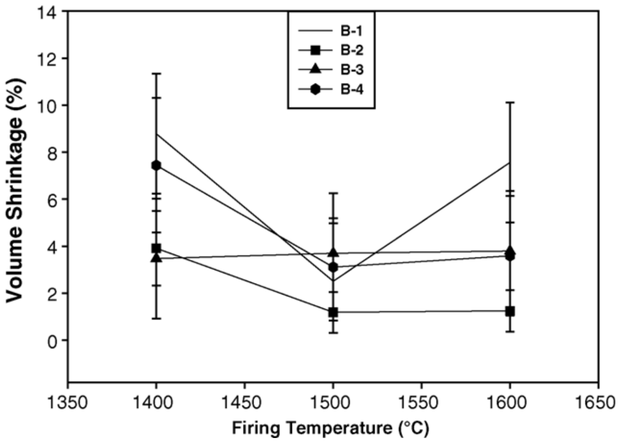

Fig. 1. Variation in volume shrinkage (%) with firing temperature.

Table 4
Physical properties of TiO_2

Properties	TiO_2
Surface area (m^2/g)	3.4
Particle size analysis (cumulative, %)—45 (μm)	99
d_{50} (μm)	1.5

elevated temperature. For two batches with TiO_2 additions (B-2 and B-4), when the firing temperature was increased, the shrinkage first decreased and then became steady (Fig. 1). However, in the B-3 sample, the volume shrinkage remained more or less steady with the increase in firing temperature.

TiO_2 can influence sintering by forming liquid phases that interact with other components present in the system, like CaO, trace alkalis, Fe_2O_3, SiO_2, etc. It can also form a solid solution with MgO and Al_2O_3, causing lattice defects with the formation of ionic vacancies, thereby promoting the formation of MgO–Al_2O_3 spinel. In addition, TiO_2 acts as a nucleating agent, recrystallizing the magnesium aluminium silicate type liquid phases, with the further formation of secondary MgO–Al_2O_3 spinel (Table 4).

From the volume shrinkage trends, it can be inferred that 2% TiO_2 most likely assisted in the formation of glassy phase. Four percent TiO_2 assisted in the formation of liquid phases and also it formed solid solutions with MgO and Al_2O_3. It also assisted in the formation of extensive spinel phases, which remained stable at all the firing temperatures under the experimental conditions [9]. With 6% TiO_2, in addition to the above functions, a portion of TiO_2 acts as nucleating agent, recrystallizing some part of the liquid phase at higher temperatures to form secondary spinel phases. The grain sizes of spinel phases were found to decrease with the increase in TiO_2 additives in the batches, as calculated using Sherrer's formula from the XRD data [10]. For the batch without additive it was 117 μm, for B-2 it was 102 μm, for B-3 it was 89 μm and for B-4 it was 73 μm. TiO_2, therefore, acted as grain boundary stabilizer for spinel grains, with the formation of reduced sized grains. In general, with the addition of TiO_2, the percent volume shrinkage decreased, and the trend was observed to be quite prominent at 1600 °C, which was the highest sintering temperature under the experimental condition. This clearly indicated a positive influence of TiO_2 on the sintering process.

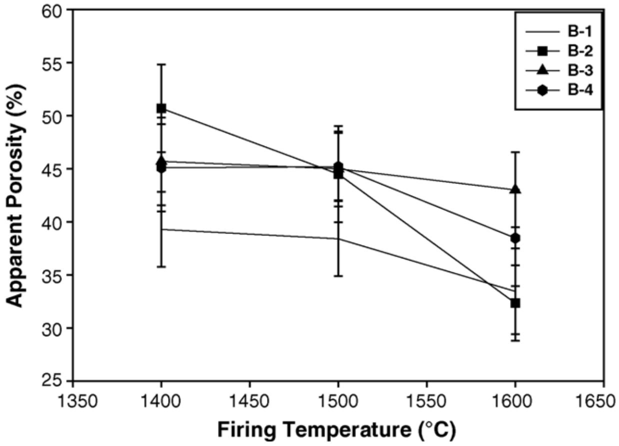

Fig. 3. Variation in apparent porosity (%) with firing temperature.

The bulk density (Fig. 2) of the fired samples without a TiO_2 additive was found to increase slightly with the increase in firing temperature then decrease significantly. This might be a consequence of the trend in volume shrinkage during firing, as indicated in Fig. 1. The apparent porosity of B-1 was found to decrease gradually with an increase in firing temperature (Fig. 3). The decrease in apparent porosity and the increase in bulk density can be related directly to the formation of more glassy phases in the batches during firing. Dissimilar trends in bulk density and apparent porosity can be related to the formation of some sealed pores at higher sintering temperatures. Batches with 2% and 6% TiO_2 showed a steady increase in bulk density with the increase in firing temperature (Fig. 2). But with 4% TiO_2, the density values held steady through 1500 °C, and then decreased through the 1600 °C firing temperature. The increase in bulk density was related to the formation of more glassy phases with the increase in firing temperature, which resulted in higher compactness in the structure. Beyond 1500 °C, the formation of more pores and voids in the structure due to the decrease in the grain sizes and

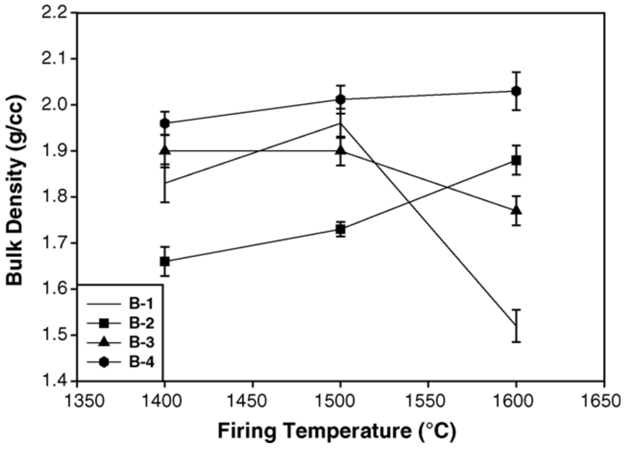

Fig. 2. Variation in bulk density (g/cm^3) with firing temperature.

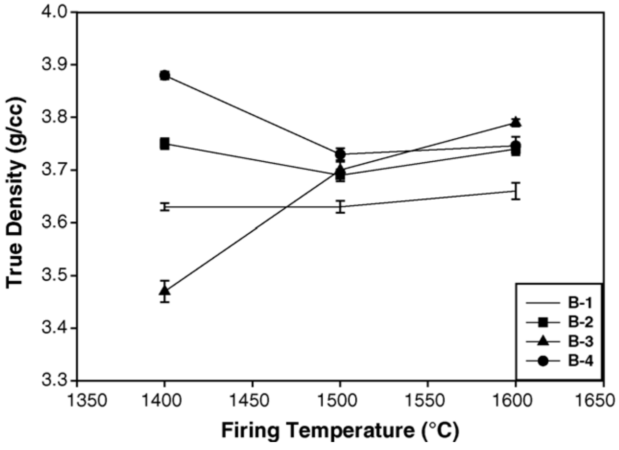

Fig. 4. Variation in true density (g/cm^3) with firing temperature.

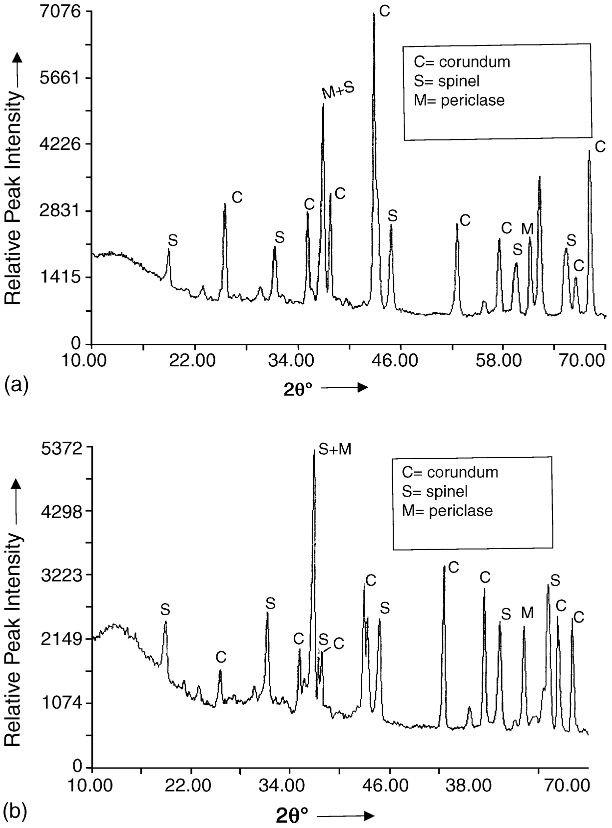

Fig. 5. XRD pattern of the fired sample (1600 °C) (a) without additive (B-1) and (b) with 4% TiO_2 additive (B-3).

subsequent increase in the interfacial tension between the solid phases and liquid phases was responsible for the reduction in bulk density values. It was more prominent for the batch containing 4% TiO_2, as it did not form much glassy phases to compensate this effect. With batch containing 6% TiO_2, due to the formation of more vitreous phases, this effects is somewhat compensated. In general the presence of TiO_2 improved the bulk density of all the batches at 1600 °C versus no additions. As a consequence of the increase in bulk density with TiO_2 additive (with some irregularities), the apparent porosity of these fired batches decreased with the increase in firing temperature.

True density values for the batches containing no TiO_2 additives were found to remain more or less constant with the increase in sintering temperature (Fig. 4), and was related to the formation of a more consistent pattern of vitreous and crystalline phases and their distribution in the fired body, as evidenced from the SEM photographs of the fired samples (Fig. 6). For the batch containing 2% TiO_2 additive, true density values also remained more or less the same with an increase in firing temperature. The batch containing 4% TiO_2 (B-3), however, had a sharp increase in true density with the increase in sintering temperature. The anomalous lower value of true density for this batch at 1400 °C can be related to the transformation of corundum, with a higher specific gravity, to spinel, with a lower specific gravity. The increase in true density values with firing temperature can be related to the decrease in the relative proportion of glassy phases in the batch. Again, for

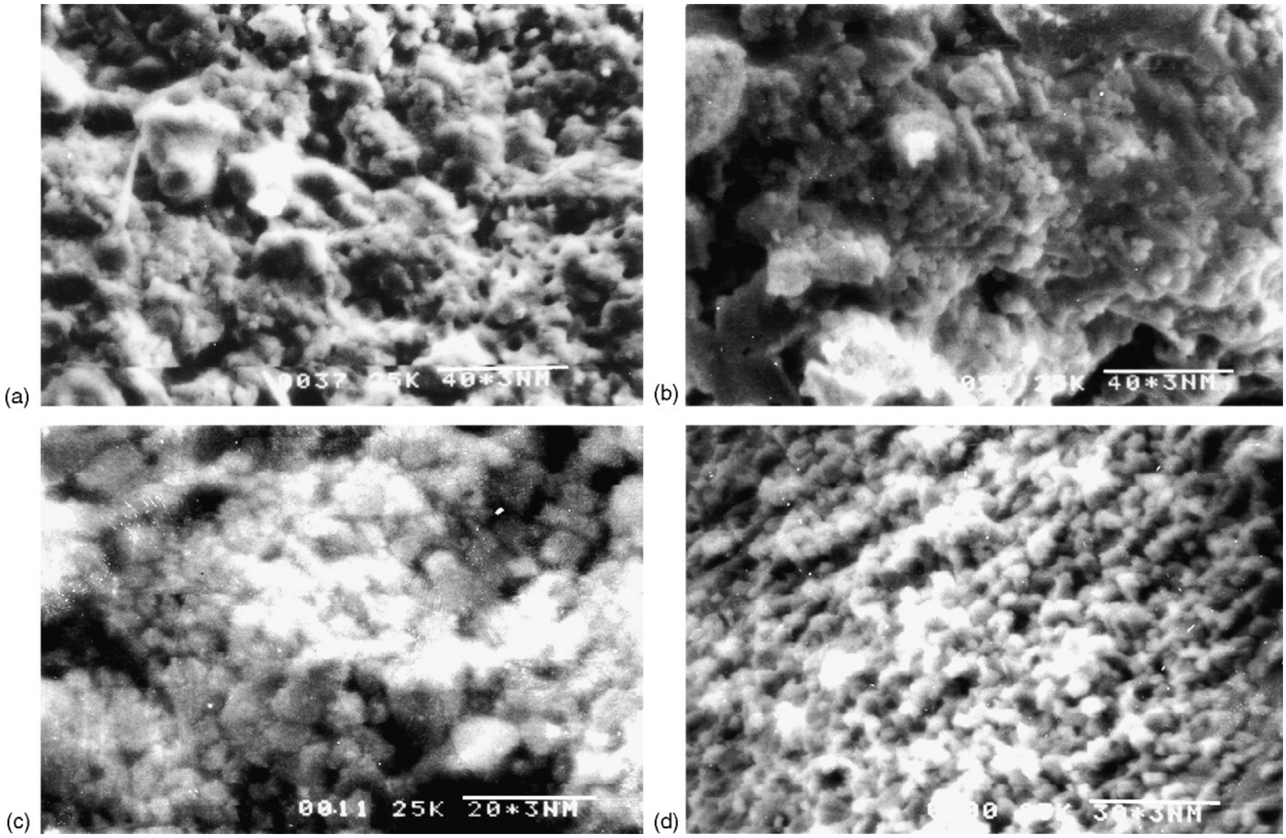

Fig. 6. SEM photograph of fired sample (1600 °C) (a) without additive (B-1); (b) with 2% TiO_2 additive (B-2); (c) with 4% TiO_2 additive (B-3) and (d) with 6% TiO_2 additive (B-4).

the batch with 6% TiO_2, a decrease in true density values with firing temperature was observed, which could be related to the formation of some TiO_2 bearing liquid phases.

XRD diffraction of the powdered fired samples revealed that TiO_2 additive increased the formation of spinel phases at elevated temperatures in the $MgO–Al_2O_3$ system (Fig. 5A and B). In batches with TiO_2 additives (Fig. 5), both the number of peaks and their intensity corresponding to the spinel phase was found to be more. Substantial amount of corundum and periclase phases were also observed in the crystalline phase analysis of the samples.

From the scanning electron micrographs of the fired samples (Fig. 6) it was observed that TiO_2 additions caused the relative proportion of crystalline phases to increase and the amorphous phases to decrease. The average grain size of the crystalline phases decreased with the increase in TiO_2 additive. Both the formation of the glassy phases and porosity development were found to be less in the batch with a higher proportion of TiO_2 additive and microstructure was more uniform.

4. Summary and conclusion

Low cement alumina–magnesia based castable was prepared by the interaction between fused alumina and calcined magnesia with 75% Al_2O_3 cement. TiO_2 as an additive exhibited a positive influence on the densification, spinel formation and the reduction of the grain sizes of the formed spinels at elevated temperatures in this system, and modified the physical properties such as firing shrinkage, bulk density, apparent porosity and true density distinctly. Microstructure of the fired bodies with TiO_2 additive became more uniform and contained less glassy phases.

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