

Microstructural and densification study of natural Indian magnesite in presence of zirconia additive

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Abstract. The sintering and microstructural evaluation of Indian magnesite was carried out in presence of zirconia. Zirconia in monoclinic form was added in the range 3–6 wt% with respect to raw magnesite and the sintering temperature selected were 1500–1600°C for 2 h. The main impurities present in the magnesite were Fe₂O₃, CaO, SiO₂. The natural crystalline magnesite could be sintered with bulk density of 3.38 g/cc (A.P. 1.54%) at 1550°C/2 h. But the higher bulk density (3.50 g/cc) and minimum apparent porosity (A.P. 0.25%) was attained at 1550°C/2 h with the 3 wt% zirconia additive. On firing magnesite with zirconia as additive, a crystalline phase, magnesio-zirconate, was identified at the triple point regions of the direct bonded periclase grains. The morphology of the periclase grains were changed from subrounded/rounded to angular shaped in presence of zirconia as additive.

Keywords. Magnesite; zirconia; sintering; direct bonded periclase; magnesio zirconate.

1. Introduction

Magnesia is an important material to the refractory industries. The importance of this basic oxide based refractories have increased considerably over the years due to the rapid expansion and technology changes of iron and steel, cement and glass industries. The main reasons of its success are high melting point (~2800°C) and its excellent resistance to attack by iron oxide, alkalis and high lime containing fluxes at working temperature of steel melting furnaces (1700°C) (Serry *et al* 1997). Unlike its rivals (e.g. lime and dolomite), it does not suffer from hydration and is not toxic. Its principal limitation is its high thermal expansion coefficient, which makes it difficult though not impossible the production of bricks having a high thermal shock resistance (Chester 1973). Today, magnesia for refractory production is coming from three basic sources (Frith *et al* 1998): (a) natural magnesite, (b) extraction from sea water and (c) extraction from inland brine.

Magnesia refractories are prepared in India mainly from naturally occurring magnesite. Though India has vast reserves of natural magnesite, the refractory industries (Indian) are mostly dependent on the imported dead burnt magnesia. This is due to the fact that Indian magnesite are rich in impurities, mainly SiO₂, Fe₂O₃, CaO, which form low melting phases at elevated temperature

causing poor refractory properties, e.g. high temperature strength, corrosion resistance.

The properties of refractories are a function of the grain material (aggregate or filler), the nature of the bond (matrix) and the distribution and shape of grains and pores. Over recent decades, property improvements have been made by using higher purity raw materials. However, there is a cost effective limit to the purity levels achievable. An alternative method of refractory properties improvement is to carefully design the phase assemblage or microstructure e.g. distribution of low melting phases and chemical and physical nature of the bond strongly affect the thermal, chemical and mechanical properties (Alper 1970; Goto and Lee 1995).

The effect of different additives on the sintering of magnesite had been studied. It was observed that direct bonded periclase grains containing 96wt% MgO with BD of 3.40 g/cc and a minimum porosity could be achieved by firing precipitated brucite doped with 0.1wt% ZrO₂ or 1wt% ilmenite (Serry *et al* 1997). This is due to the stimulation of its bulk diffusion and wetting by liquid phase in the presence of limited amounts of calcium oxide, zirconium dioxide, alumina, ferric oxide and silica. It was observed that the addition of titania altered the secondary phase distribution and formed a crystalline reaction product, calcium titanate, with calcium oxide impurity present in the natural magnesite at the intergranular space (Kriek *et al* 1959; Nath *et al* 1992). The effect of titania on the properties of sintered magnesia obtained from sea water was also studied (Petric *et al*

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1994). The addition of titania reduces boron oxide content in the sintered samples as it competes for the CaO by forming calcium titanate. The final content of boron oxide in the sintered samples, therefore, depends both on the CaO and TiO₂ contents. Doping brucite with 0.50 mol% P₂O₅ has contributed in densification of magnesia ceramics in the presence of magnesia rich calcium silicate, ferrite and phosphate liquid phase (Zawrah 2001).

The presence or absence of certain components in dead burnt magnesia used in refractory play an important role in the product properties and its suitability for various applications. High temperature flexural strength and corrosion resistance property are markedly improved with the increase in direct bonding of magnesia crystals (Lampropoulou *et al* 2005).

The objective of the present investigation is to study the effect of additive, zirconium oxide as monoclinic form, on the sintering and microstructural characteristics of Indian magnesite.

2. Experimental

Indian magnesite (Almora district of Uttaranchal supplied by TRL, Belpahar, Orissa) was selected for the present study. The physicochemical properties of the said raw material is described in table 1. The as received magnesite powder was ground in a rubber lined pot for 4 h using alumina ball as grinding media. Zirconium dioxide in monoclinic form, supplied by LOBA Chemie, Mumbai, was selected as the additive. The additive concentration was varied between 3 and 6 wt% with respect to the raw magnesite. The batch composition and the sample code used for the experiment are shown in table 2. The requisite amount of additive and magnesite was mixed thoroughly by repeated sieving and mixing. To a batch of

4% wt/v PVA solution was added and granulated through BS 30 mesh. Discs of 25 mm diameter were pressed at 1000 kg/cm² specific pressure using a hydraulic press. The pressed items were dried at 110°C for overnight followed by sintering at 1500°, 1550° and 1600°C for 2 h at highest temperature. The sintered body was characterized by measuring bulk density, apparent porosity by standard liquid displacement method using Archimedes principle. The crystalline phases developed during sintering were identified by X-ray diffraction using a Ni-filtered Cu K α radiation with a scanning speed of 2° (2 θ) per min. The true specific gravity was measured by pycnometer. The microstructural study was performed on the thermally etched polished surface. The distribution of the additive was detected by energy dispersive X-ray analysis in a scanning electron microscope (Hitachi, Japan, S-3400N).

3. Results and discussion

Table 1 shows chemical and physical properties of Almora magnesite. The impurities are mainly SiO₂, Fe₂O₃, CaO and Al₂O₃ which constituted about 11.4% (on loss free basis). The powder X-ray diffraction of magnesite shows the presence of magnesite as major phase. Calcite and dolomite are minor phases. The differential thermal analyses of the dried sample showed two endothermic peaks; one deep endotherm at 641°C due to the decarboxylation of magnesium carbonate and second small endotherm at 780°C might be due to the decomposition of dolomite, as small amount present in the magnesite as impurity. But the second peak of dolomite at 810°C was not observed. The results are very similar to the findings of Rao *et al* (1964). From the DTA analysis it could be inferred that CaO was present as dolomite. The true density of the magnesite is 3.04 g/cc which is very close to the value reported (2.96 g/cc) (Grimshaw 1971). The surface area of the milled powder was 2.2 m²/g.

Figure 1 shows the effect of additive content on the shrinkage of the sintered magnesia samples. Maximum shrinkage was attained with all the samples sintered at 1550°C for 2 h and minimum was obtained with 1600°C for 2 h.

Figure 2 is the plot of effect of sintering temperature on the bulk density (BD) of the sintered magnesia

Table 1. Chemical and physical properties of Almora magnesite.

Constituent oxide	Magnesite
SiO ₂ (%)	1.60
Al ₂ O ₃ (%)	0.92
Fe ₂ O ₃ (%)	1.62
CaO (%)	1.30
MgO (%)	46.15
K ₂ O (%)	Trace
Na ₂ O (%)	0.40
LOI (%)	48.00
Crystalline phases present	
Major	Magnesite
Minor	Calcite, dolomite
DTA peaks:	
Deep endothermic	641°C
Small endothermic	780°C
True density (g/cc)	3.04

Table 2. Batch composition and codes used.

Batch no	Sample code	Magnesite (wt%)	Zirconia (m) (wt%)
1.	MZ0	100.0	Nil
2.	MZ3	97.0	3.0
3.	MZ4.5	95.5	4.5
4.	MZ6	94.0	6.0

samples. MZ0 sample shows increase in the bulk density with increasing sintering temperature. The maximum bulk density (3.38 g/cc) was obtained with MZ0 sample at 1550°C/2 h. Minimum apparent porosity (AP 0.69%) was attained at 1600°C/2 h with lower bulk density (3.34 g/cc). The lower AP with lower bulk density corroborates the formation of higher amount of low-density glassy phase that was also observed in the SEM pictures. But zirconia containing samples showed the highest BD at 1550°C/2 h and then decreased at 1600°C for 2 h. Maximum BD was obtained with 3.54 g/cc with MZ6 samples but their apparent porosity was high with respect to MZ3 and MZ4-5. The high density with high porosity (apparent porosity) might be due to the formation of higher

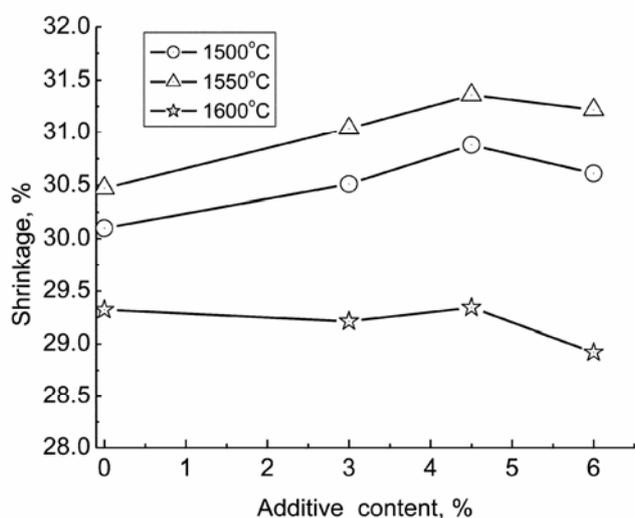


Figure 1. Linear shrinkage as a function of zirconia additive content. For sample code please see table 2.

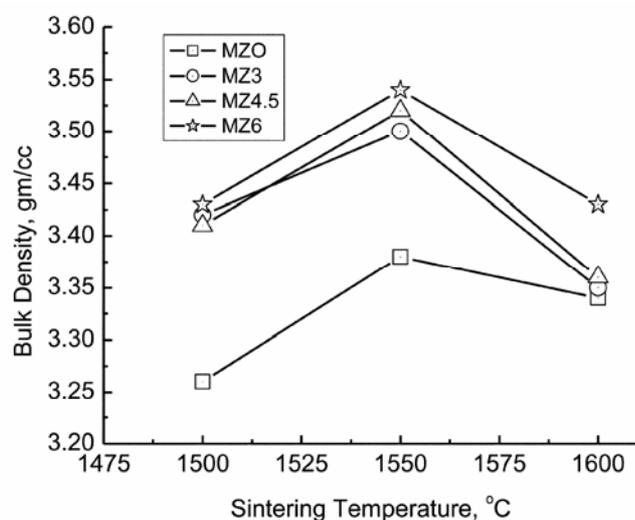


Figure 2. Bulk density as a function of sintering temperature. For sample code please see table 2.

amount of high density magnesium zirconate at the grain boundaries. The apparent porosity as a function of additive content is shown in figure 3. Minimum apparent porosity was observed with the sample MZ3 at 1550°C with 0.25%.

The powder X-ray diffraction pattern of MZ0, MZ3 and MZ6 are shown in figure 4. In all the samples the main crystalline phase is periclase. In MZ0 sample, tiny peaks of monticellite (CMS) and magnesio ferrite were detected. It was observed that when C/S ratio was <2, all Fe₂O₃ occurred in combination with MgO as spinel mag-

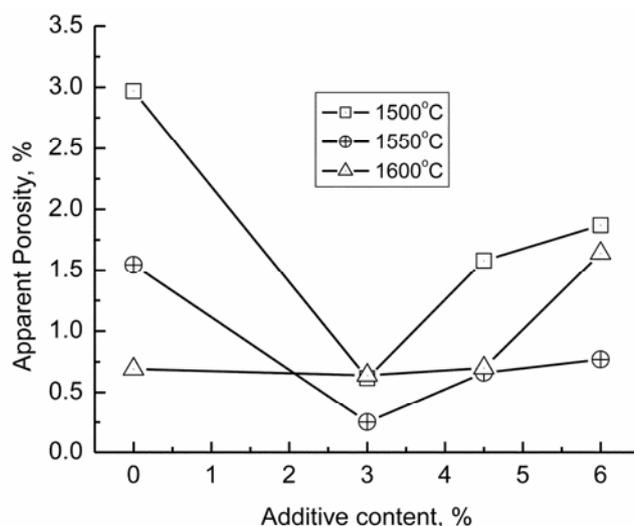


Figure 3. Effect of additive (zirconia) content on apparent porosity. For sample code please see table 2.

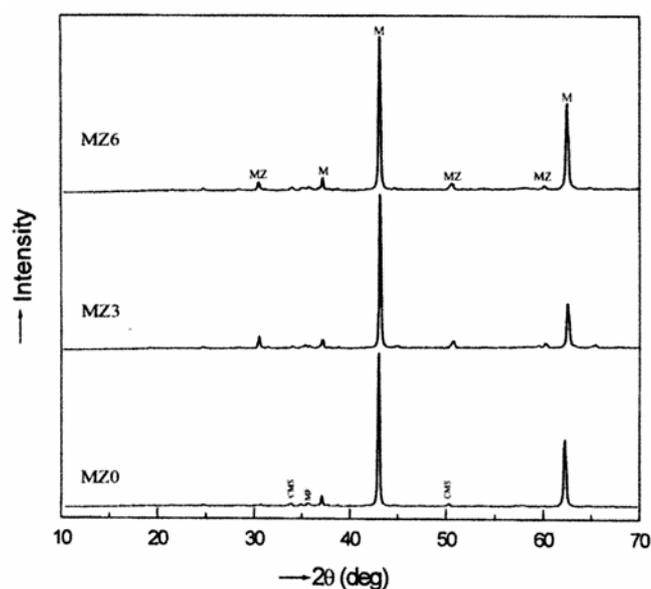


Figure 4. Powder X-ray diffraction pattern of MZ0, MZ3 and MZ6 sintered at 1600°C/2 h. (M, Periclase; MZ, magnesio-zirconate, CMS, monticellite; MF, magnesio-ferrite). For sample code see table 2.

nesio ferrite (MF). When C/S was within 1.0 the main phases are MgO, MF, forsterite (M_2S), CMS (Alper 1970). In the present study with the C/S molar ratio of 0.86, the MF and CMS phases were identified in the X-ray pattern though in very small amount.

With the addition of zirconia to the crystalline variety of magnesite, magnesio-zirconate phases in addition to periclase were identified in the powder X-ray diffraction pattern. Ghose and White (1980) investigated the compatibility relationship of periclase in the system $CaO-MgO-ZrO_2-SiO_2$ and showed that in this system, in the solid state, CZ coexists with periclase only when C/S > 1.5 (molar). At lower values of C/S, ZrO_2 is stable and coexists in turn with M_2S , CMS and C_3MS_2 (merwinite), in addition to periclase. With increasing C/S above 1.5, in

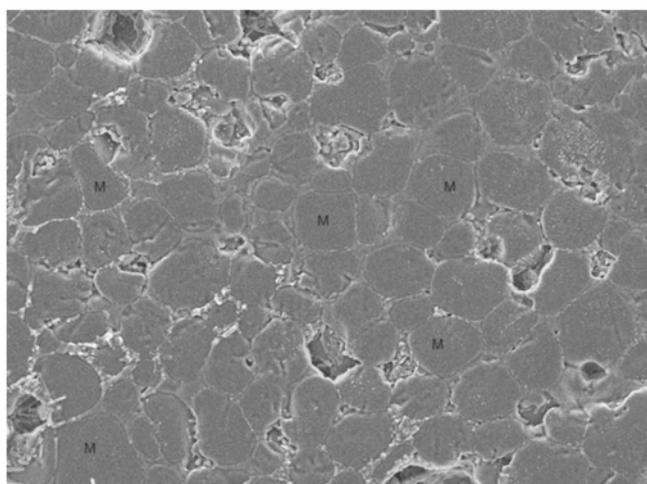


Figure 5. Secondary electron image of magnesite without any additive (MZ0) sintered at 1550°C/2 h after thermal etching. The main crystalline periclase phase (M) is rounded/subrounded in shape.

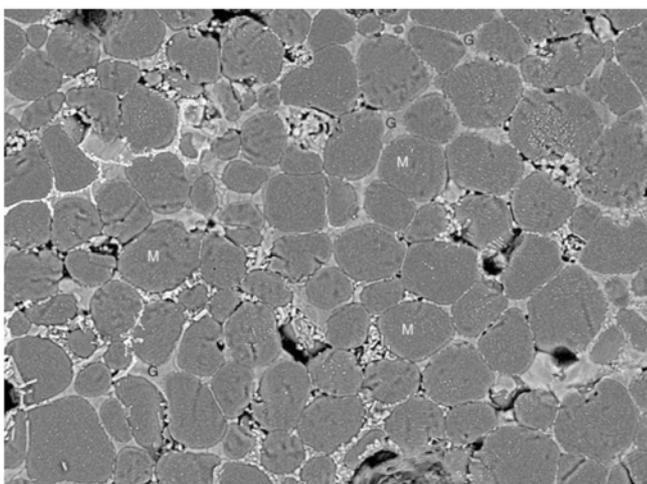


Figure 6. Back scattered electron image of MZ0 sample shows the dark periclase (M) grains are surrounded by interconnected white coloured glassy (G) phase.

the presence of periclase, CZ replaces zirconia progressively and then C_3MS_2 replaced in turn by C_2S and C_3S . In the present work, the C/S molar ratio of 0.86, < 1.5, but zirconia was not present as ZrO_2 but was seen in the combined form as magnesio-zirconate. This phase was also confirmed by EDS analyses of the zirconia containing magnesia samples. The addition of 0.5wt% zirconia to crypto crystalline natural magnesite formed isolated bright rounded zirconia by exsolution which was stated by Chaudhuri *et al* (1999).

Figure 5 shows the secondary electron image of the thermally etched polished surface of the MZ0 sample sintered at 1600°C for 2 h. The microstructure consists of mainly subrounded to rounded periclase grains (M) with the bonding material in between the grains (Chaudhuri *et al* 1990). Figure 6 is the back scattered electron image of the same sample. The dark grains are periclase (M) and are sometimes separated by thin films of liquid phase (light coloured) (G), which are interconnected within the matrix. Most of periclase grains are surrounded by liquid phase and a very few grains are direct bonded (D). The presence of isolated or interconnected liquid phase depends on the interfacial energy of solid–solid or solid–liquid interface. If the interfacial energy between solid–solid is greater than solid liquid interface, the liquid tends to be continuous and in the reverse case it tends to be isolated (Nath Choudhury *et al* 1992; Kingery *et al* 2004).

The morphology of the magnesia grains changed in presence of zirconia as additive. In the presence of zirconia the periclase grains are angular in shape. The secondary electron image of the MZ6 is shown in figure 7. The angular periclase grains (M) are mostly direct bonded (D). The presence of zirconia assisted to form direct bonded periclase and to clean the grain boundaries. A

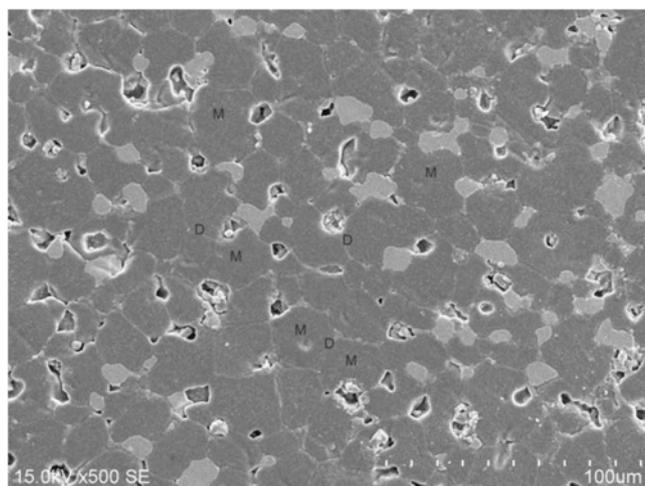


Figure 7. Secondary electron image of MZ6 sample sintered at 1550°C for 2 h after thermal etching. Most of the periclase (M) grains are direct bonded.

Table 3. Elemental distribution of phases in sintered Almora magnesite.

Phases	Wt% of elements assuming oxides						
	Mg	Fe	Ca	Si	Al	Zr	O
Intergranular space (I)	36.92	1.89	10.77	9.10	0.01	9.91	Rest
Magnesia grain (M)	56.21	2.73	0.06	–	–	9.72	Rest
White bright phase (Z)	10.02	1.15	4.8	–	0.25	62.39	Rest

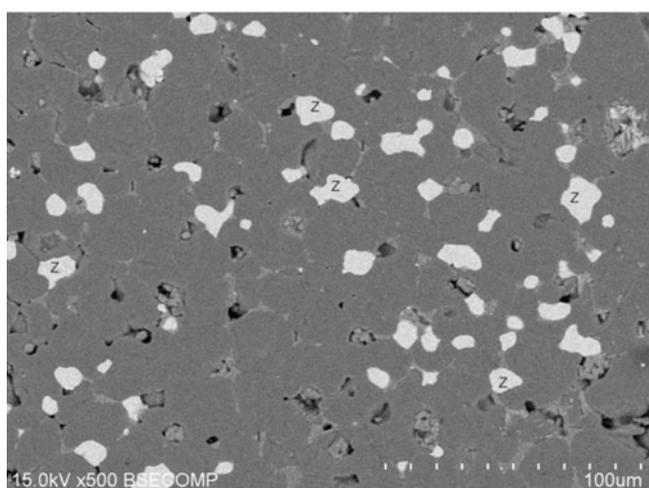


Figure 8. Back-scattered electron image of MZ6 sample sintered at 1550°C for 2 h. The white bright grains are magnesian-zirconate (Z). The isolated liquid phases (I) are identified at the triple point junction.

bright crystalline phase is also present at the triple grain junctions. The powder X-ray diffraction study identified the bright white phase as magnesian zirconate (Z). Figure 8 is the back scattered electron image of zirconia containing magnesite sample sintered at 1550°C for 2 h. The microstructure shows the bright white magnesian-zirconate phase (Z). Most of the periclase grains are direct bonded (D); few isolated liquid phases (I) are also observed.

The EDS analyses of the magnesia grains (M), intergranular region (I) and white bright grains (magnesian-zirconate) (Z) of zirconia containing magnesite sample sintered at 1550°C for 2 h is given in table 3. It was assumed that all the elements were present as oxide. Magnesium was the major constituent of the grains (M), iron, present in the raw magnesite was detected in the magnesia grains. The presence of zirconium in the magnesia grains was also detected. Small amount of calcium was identified in the magnesia grains corroborates the findings of Ghose and White (1980). The molar ratio of the MgO to ZrO₂ in magnesian zirconate (Z) is 1 : 1.62 (theoretical 1 : 2.5). In the magnesian-zirconate (Z) phase a large amount of calcium and a small percent of iron were also detected. The intergranular space (I) consisted of mainly silicon, calcium, magnesium, zirconium and a small percent of iron. As calcium and iron were identified in magnesian-zirconate phase, the amounts of glassy phase

along grain boundary was abruptly reduced and direct bonded periclase grains replaced the grain boundary glassy phase. The presence of zirconia in the intergranular glassy phase (though very little in amount) also modified the nature of the glassy phase. The zirconia would likely increase the viscosity of the intergranular glassy phase (Vargin 1967). Further work on the high temperature mechanical properties will confirm the mechanism.

4. Conclusions

The present investigation demonstrated that the natural magnesite with iron oxide, silica and calcia impurities could be sintered with BD of 3.38 g/cc fired at 1550°C/2 h. The rounded/subrounded periclase grains were surrounded by a interconnected liquid phase. But the presence of zirconia (monoclinic) additive changed the densification and microstructural characteristics of the same magnesite. The magnesite could be sintered at lower temperature, 1550°C/2 h, with the addition of 3wt% zirconia with respect to the raw magnesite content (BD 3.50 g/cc; apparent porosity, 0.25%). The presence of zirconia changed the morphology of the periclase grains from subrounded/rounded to angular shaped. Most of the periclase grains were direct bonded. The zirconia formed a compound magnesian-zirconate at the triple point region. Zirconia not only formed magnesian-zirconate, it was also identified in the magnesia grains and intergranular spaces. Silica was present exclusively in the intergranular isolated glassy phase.

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