

## Effect of zirconia on densification and properties of natural Indian magnesite



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### ARTICLE INFO

#### Article history:

Received 10 September 2014

Received in revised form 12 June 2015

Accepted 9 September 2015

Available online 12 September 2015

#### Keywords:

Magnesite

Sintering

Microstructure

High temperature strength

### ABSTRACT

Indian magnesite mineral has substantial amount of impurities like CaO, SiO<sub>2</sub> & Fe<sub>2</sub>O<sub>3</sub>. During sintering at elevated temperature these impurities react to form low melting phases like monticellite (CMS), which can degrade the high temperature properties of magnesite. In the present study, ZrO<sub>2</sub> was added to reduce the formation of low melting phase in order to improve the hot strength. Amount of additive was varied between 2 and 6 wt.% with respect to raw magnesite. It was observed that addition of ZrO<sub>2</sub> reduces the formation of low melting CMS at higher temperature and improves the flexural strength at 1200 °C. Periclase grain shape also changed from rounded to subrounded in the presence of zirconia.

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### 1. Introduction

Magnesite refractory exhibits various advantageous high temperature properties like high softening point, excellent chemical durability in basic condition (Serry et al., 1997; Spencer, 1978) and thus the demand for this material has been significantly increased for high temperature applications over the years. Magnesite refractory are widely used in ferrous, non-ferrous and cement industries (Mcdowell and Howe, 1920; Ryder, 1993). It has extensively used in the steel converter, electric arc furnace and ladle lining in steel making processes. The primary source for magnesia is natural magnesite along with sea water and inland brine (Bhatti et al., 1984; Frith et al., 1998).

Several efforts have been made by various researchers to improve the high temperature properties of magnesite by engineering the microstructure like modification of the grain morphology, amount and distribution of low melting phases and also by changing the chemical and physical nature of bonds (Alper, 1970; Goto and Lee, 1995; Lee and Rainforth, 1994). Direct bonding amongst periclase grains can also significantly improve the high temperature mechanical and chemical properties of magnesia refractories (Lampropoulou et al., 2005). Addition of different oxides of titanium, zirconium, silicon, lithium, zinc, iron etc. promotes densification of magnesia by forming solid-solution and thereby creating cation or anion vacancies (Nelson and Cutler, 1958).

India has large reserve of natural magnesite in Salem, Almora, and Jammu regions. These magnesites, due to the presence of various

deleterious impurities like SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO are not widely used for high temperature applications. These impurities can react at elevated temperature and form various low melting phases like monticellite (CMS), merwinite (C<sub>3</sub>MS<sub>2</sub>), and di-calcium ferrite (C<sub>2</sub>F), which have pernicious effect on the thermo-mechanical properties and on the chemical stability of the magnesite bearing refractory. Hence, Indian refractory industries largely depend on the imported magnesite. Incorporate some suitable additives, which can react with the impurities present in the magnesite; convert these impurities into some other high melting phases and thus minimize the amount of low melting phases and increase the grain to grain contact can be one of the most techno-economical and industrial feasible alternative to improve thermo-mechanical properties of such low grade magnesite. It was reported that TiO<sub>2</sub> addition in natural Indian magnesite changed the secondary phase distribution by reacting with the lime present in magnesite and forms a crystalline high melting calcium titanate phase (Amin et al., 2002; Chaudhary et al., 1990, 1992, 1999; Krick et al., 1959; Petric et al., 1994). The microstructure of magnesia–zirconia refractories has been studied by different researchers (Amin et al., 2002). Monoclinic zirconia as additive was also used and found that ZrO<sub>2</sub> changed the grain morphology with increased periclase grain to grain contact (Das et al., 2010). Though the effect of these additives on the densification and microstructure of magnesite has been studied by various researchers, however, their role on thermo-mechanical behavior of magnesite refractory has not been reported earlier.

In the present paper, the effect of monoclinic zirconia addition on densification behavior, phase developments, and microstructure vis-à-vis thermo-mechanical properties of Indian natural magnesite was reported.

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**Table 1**  
Batch composition with sample code.

Sample codes	Magnesite (wt.%)	ZrO <sub>2</sub> (wt.%)
AM0	100	0
AMZ2	98	2
AMZ4	96	4
AMZ6	94	6

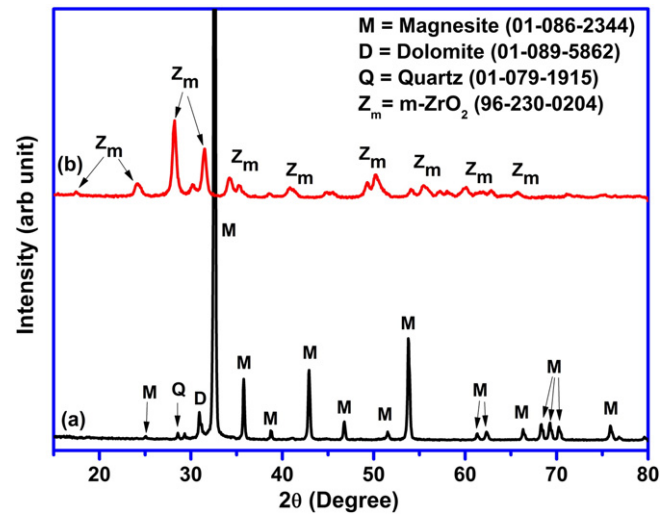
## 2. Materials & methods

The starting raw material used in this study was natural magnesite from Almora region of India. Monoclinic zirconia (obtained from Indian Rare Earth Limited) was used as additive. The raw magnesite was characterized for different physico-chemical properties. Chemical analysis was done by standard wet chemical method. Simultaneous TG-DTA analysis of the raw magnesite was performed by a Netzsch STA 449C thermal analyser. Raw magnesite was initially crushed and ground to pass through a 30 mesh BS sieve. Four batch compositions (Table 1) were prepared without and with 2, 4 and 6 wt.% of ZrO<sub>2</sub>. All the batches were individually milled in attrition mill (Model 01HD, Union Process, USA) for one and a half hour by using zirconia pot with partially stabilized zirconia (PSZ) grinding media in ethanol medium. This was then dried overnight at room temperature followed by oven drying for 24 h at 100 ± 5 °C, crushed and passed through a 100 mesh BS sieve to get the desired powder. The powder was uniformly mixed with 5 wt.% poly vinyl alcohol (PVA) solution as green binder and uniaxially pressed into bars and pellets under the specific pressure of 100 MPa. The green bars and pellets were first dried at 110 ± 5 °C and then sintered in the temperature range 1500–1600 °C with 2 h soaking at peak temperature. Sintering was done in a program controlled electric furnace in normal atmosphere. Heating rate was maintained at 5 °C/min from room temperature to 1000 °C and then 3 °C/min up to the final sintering temperature.

The sintered samples were characterized in terms of bulk density (BD), apparent porosity (AP), flexural strength, microstructure and phase assemblage. BD and AP were measured by standard liquid displacement method using Archimedes principle in kerosene medium. The identification of crystalline phases was done by X-ray diffraction technique. The X-ray diffraction patterns of the finely powdered samples were obtained in a Philips X-ray diffractometer (Model PW 1730) using nickel filtered Cu-K<sub>α</sub> radiation with a scanning rate 2° (2θ) per minute and diffraction patterns were recorded over a Bragg's angle (2θ) range of 15° to 80°. Crystalline phase quantification was performed by Rietveld refinement (Young, 1993) of XRD patterns of the samples using X'Pert High Score Plus software. The microstructural study of the thermally etched carbon coated polished surface were performed

**Table 2**  
Physico-chemical properties of raw Almora magnesite.

Properties	Almora magnesite (on loss free basis)
Chemical constituents, wt.%	
MgO	85.42
CaO	6.83
Fe <sub>2</sub> O <sub>3</sub>	4.01
SiO <sub>2</sub>	2.65
Al <sub>2</sub> O <sub>3</sub>	0.85
TiO <sub>2</sub>	0.02
Na <sub>2</sub> O	0.08
K <sub>2</sub> O	0.04
Undetermined	0.10
Crystalline phases	Magnesite (major), dolomite (minor), quartz (minor)
DTA peaks:	
Deep endothermic	657 °C
Small endothermic	726 °C
True density (g/cc)	3.01



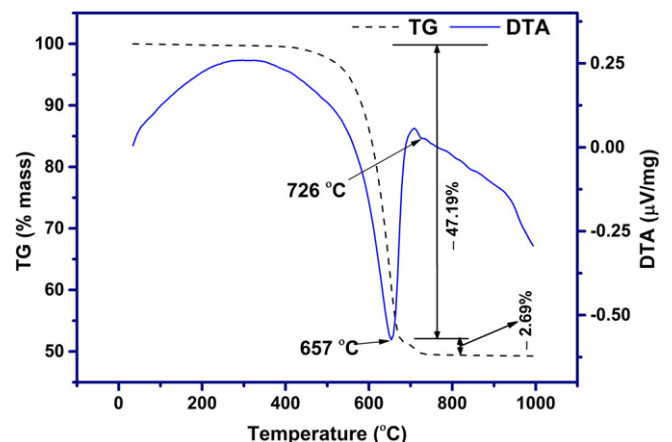
**Fig. 1.** Powder X-ray diffraction pattern of raw materials: (a) magnesite and (b) monoclinic zirconia.

by scanning electron microscopy (Supra 35VP Zeiss) and elemental analysis was done by energy dispersive X-ray. Grain sizes of the samples were measured from SEM photomicrographs using ImageJ software. High temperature flexural strength of the sintered bars was determined by 3 point bending method at 1200 °C.

## 3. Results and discussion

### 3.1. Raw materials characterizations

Chemical composition, particle size and specific surface area of the raw material have profound effect on the sintering behavior of the final products which ultimately governs the end properties of the material (Nath et al., 2015). The physico-chemical properties of the raw magnesite are shown in Table 2. The chemical analysis of the magnesite indicates that MgO content in the magnesite is 85.42% (on loss free basis) and the major impurities present are CaO, SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, which constitute about 13.49% (on loss free basis). This clearly indicates that the raw magnesite is impure in nature. The true density of raw magnesite is found to be 3.01 g/cc. Chemical reactivity of a material has a direct co-relation with the fineness of the powder particles. After one and a half hour wet milling, the average particle size (d<sub>50</sub>) and specific surface area of the powders are found to be 3.78 μm and 6.201 m<sup>2</sup>/g respectively, which indicates that the powders obtained after wet milling are quite fine. Lime to silica ratio (C/S) is another parameter,



**Fig. 2.** TG-DTA thermogram of raw magnesite.

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