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# Effect of titania on the microstructure evolution of sintered magnesite in correlation with its properties

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## Abstract

Natural Indian magnesite contains large amount of impurities like CaO, $SiO_2$ and $Fe_2O_3$. On heat treatment, these impurities chemically react and form low melting phases like monticellite (CMS), merwinite ($C_3MS_2$) and vitreous phases, which degrade the refractory properties of magnesite like hot modulus of rupture, corrosion resistance etc. In the present investigation, $TiO_2$ was used to reduce the formation of low melting phases. Compacted green pellets and bars of magnesite containing 0−5 wt% $TiO_2$ were sintered in the temperature range of 1500−1600 °C with 2 h soaking at peak temperature. It was observed that $TiO_2$ slightly increased the apparent porosity and decreased the bulk density by reducing the formation of low melting phases. High temperature flexural strength increases with $TiO_2$ content upto 3 wt% followed by slight decrease in strength after further increase in the amount of additive.



*Keywords:* A. Sintering; Magnesite; Microstructure; Hot MOR; Refractory

## 1. Introduction

Magnesia refractory has achieved widespread applications in both ferrous and non-ferrous industries due to its various advantageous properties like high melting point, excellent chemical stability under basic environment and lesser susceptibility towards hydration compare to its rivals lime and dolomite [1–4]. Natural magnesite, sea water and inland brines are the major sources of magnesia [5]. India has vast availability of natural magnesite, but their high temperature applications have been very limited due to the presence of detrimental impurities like CaO, $Fe_2O_3$ and $SiO_2$. These impurities lead to the formation of low melting phases like monticellite (CMS), merwinite ($C_3MS_2$), di-calcium ferrite ($C_2F$) etc. at elevated temperatures. These low melting phases have adverse effects on the high temperature properties of the magnesia refractories. Good quality magnesia bricks can be developed by using purer quality raw materials [6]. But, the seldom availability and relatively higher costs are the main factors, which render them unviable for commercial exploitation.

Alternatively, natural magnesite can be utilized as an economically viable substitute by carefully engineering the microstructure, bond system and the phase assemblage [7–9]. Addition of appropriate additives can effectively minimizes the low melting phase formation by reacting with the impurities present and generate high melting phases.

Lee et al. reported that upto 0.3 wt% addition of $TiO_2$ enhanced the densification by creating cation vacancies and excess titania (> 0.3 wt%) reacted with MgO and formed $Mg_2TiO_4$ as secondary phase [10]. Small quantity of titania addition favored the densification of magnesia derived from sea water at a temperature of 1300 °C [11]. It was reported that 0.2 wt% titania (anatase phase) has beneficial effect on densification and microstructure of natural magnesite [12,13]. Effect of addition of titania, zirconia and ilmenite in natural magnesite was also studied and it was observed

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that all these minerals promoted the grain growth and densification [14]. Amin et al. studied the microstructure of magnesia–zirconia refractories [15]. Monoclinic zirconia as additive was also used and found that $ZrO_2$ changed the grain morphology and increased periclase grain to grain contact [16]. Effect of kaolin on the sintering of magnesia was also reported and it was found that 10−20 wt% kaolin provided high sinterability and good thermo-mechanical properties [17].

In earlier investigation, most of the researchers have studied the densification and microstructural changes in the presence of various additives. But, the effects of additives on thermo-mechanical properties are not reported systematically. So, the objective of the present investigation has to study the effect of titania as additive on the sintering, phase assemblage, microstructural characteristics and hot strength of Indian magnesite. Physical and thermo-mechanical properties have been co-related with the microstructure of the sintered product.

## 2. Experimental

The main raw material used in this investigation was natural Indian magnesite from Almora region of Uttaranchal (India). Analytical grade titania obtained from S.D.Fine-Chem Ltd. was used as additive. The raw magnesite was characterized in terms of various physico-chemical properties. Chemical analysis was done by standard wet chemical method. Thermal analysis (TG–DTA) of raw magnesite was done by Netzsch STA 449 C analyzer. Raw magnesite was first crushed and passes through 30 mesh BS sieve. Four batch compositions (Table 1) were prepared by varying the amount of titania from 0 to 5 wt%. All the batches were individually attrition milled using zirconia pot with partially stabilized zirconia (PSZ) grinding media in ethanol medium for 1 h and 30 min. Slurry thus obtained was kept overnight for natural

Table 1
Batch composition with sample code.

| Sample code | wt% | |
|---|---|---|
| | Magnesite | $TiO_2$ |
| AM0 | 100 | 0 |
| AMT1 | 99 | 1 |
| AMT3 | 97 | 3 |
| AMT5 | 95 | 5 |

Table 2
Physico-chemical properties of raw magnesite.

| Properties | Raw magnesite |
|---|---|
| Chemical constituent, wt% (on loss free basis) | |
| MgO | 85.50 |
| CaO | 6.84 |
| $Fe_2O_3$ | 4.01 |
| $SiO_2$ | 2.65 |
| $Al_2O_3$ | 0.86 |
| $TiO_2$ | 0.02 |
| $Na_2O$ | 0.08 |
| $K_2O$ | 0.04 |
| Crystalline phases present | Magnesite (major), dolomite (minor) |
| DTA peaks | 645 °C, 725 °C |
| True density (g/cc) | 3.01 |

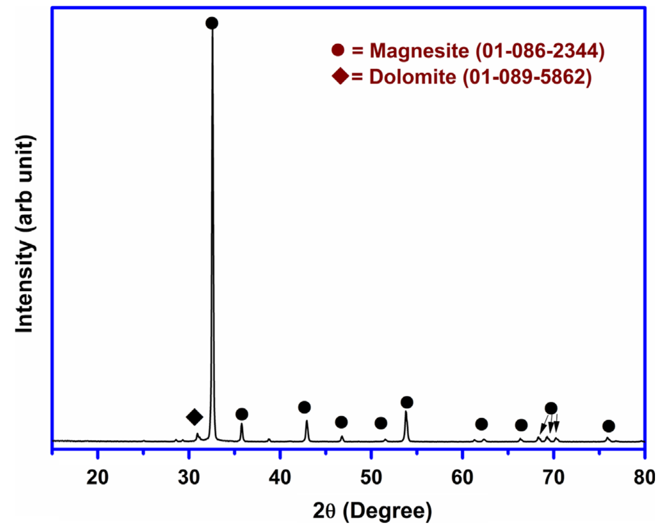


Fig. 1. x-ray diffraction pattern of raw magnesite.

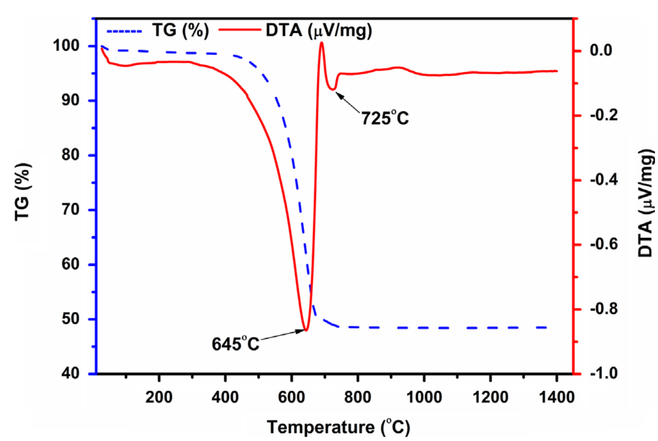


Fig. 2. TG–DTA thermogram of raw magnesite.

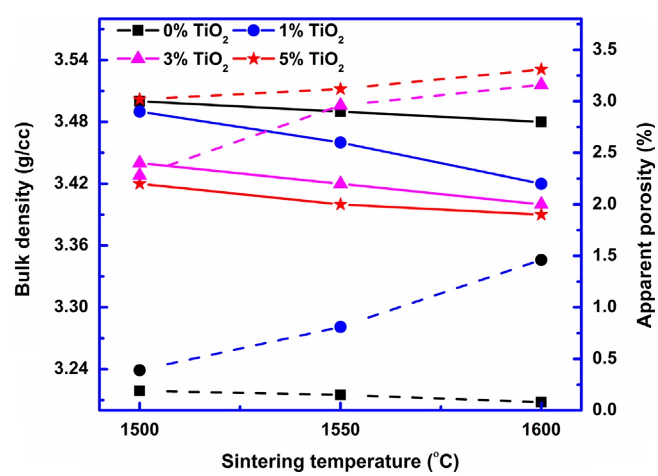


Fig. 3. Variation of bulk density (solid line) and apparent porosity (dotted line) of the sintered samples with sintering temperature and $TiO_2$ content.

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