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# Dynamic thermal study to rationalise the role of titania in reaction sintering of magnesia-alumina system

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**Abstract**

Magnesia-rich sintered spinel (66% $Al_2O_3$ & 34% MgO) was prepared in the temperature range of 1600–1700 °C by reaction sintering of caustic magnesia and calcined alumina with and without $TiO_2$ additive in $N_2$ atmosphere. Sintered products were characterised in terms of densification, phase assemblage, and microstructure. The role of $TiO_2$ on spinelisation and densification was analysed using both dynamic and static heating regime. Although a static firing at 1700 °C with 2 h dwelling results in similar densification of spinel in presence and absence of titania, the specific role of titania was discerned only by critically analysing the dimensional change in dynamic heating regime. It was revealed that titania significantly increases only the densification rate of magnesia-alumina system with marginal effect on spinelisation. Better densification of titania-containing spinel, even at a relatively lower temperature, can be attributed to the incorporation of titania into the spinel structure and formation of magnesium aluminium titanate phase.


*Keywords:* Spinel; Reaction sintering; Dilatometry; Titania

## 1. Introduction

Spinel has been extensively used for refractory application in metallurgical and other high temperature process industries [1]. Primary experience was with chrome-based spinels, which have been widely used as refractory lining for steel-making vessels and cement rotary kilns [2]. However, in the last decade magnesium aluminate spinel ($MgAl_2O_4$) is gaining importance because of growing concern with the potential environmental hazards of $Cr^{6+}$ species from chrome-containing refractories [3,4]. Magnesium aluminate spinel (Mag-Al spinel) due to its various superior properties like its high refractoriness (melting point 2135 °C), moderate thermal expansion, excellent thermal shock resistance and corrosion resistance, and high mechanical strength at room temperature as well as at elevated temperatures is being increasingly used in monolithic and shaped refractories [5–13]. Non-stoichiometric compositions of Mag-Al spinels are generally used on the basis of the prevailing condition of the application areas. Spinel with higher bulk density is preferable for better performance in the application areas [14]. Formation of spinel phase from its constituent oxides is a diffusion controlled process and accompanied by 5–7% volume expansion owing to density difference between the constituents and the final phase which makes it difficult to develop a dense, reaction sintered spinel body in single step [15–17]. Dense spinel in solid state can be produced by reaction of magnesia and alumina primarily in a two-stage process, with completion of spinel formation below 1400 °C and densification at around 1700 °C [18,19]. Different researchers have studied various aspects of development of spinel refractories [18,20–25]. Mansour has studied the effect of characteristics of magnesia and alumina precursor on the formation and densification of spinel and it has been reported that $MgCO_3$ after calcination at 900 °C along with $Al(OH)_3$ calcined at 1100 °C maximises the spinel formation [21]. Petkovic et al. studied the sinterability of spinel partially synthesised at low temperature [24]. Additives such as $TiO_2$, $SnO_2$, ZnO and $CaF_2$ favour both the spinel formation and densification [25–29]. Decrease in grain size and increase in roundness of spinel grains are the effect of $TiO_2$ in

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spinel [27,28]. Improvement in densification of spinel ceramics by rare-earth oxides like $Y_2O_3$, $Yb_2O_3$ and $Dy_2O_3$ was also studied [28,30,31]. $Y_2O_3$ addition increases the tensile strength but reduces the thermal shock resistance. Ytterbium and dysprosium oxides have positive effect on spinel properties [30].Yu and Hiragushi [32,33] reported that $TiO_2$ reacted to form a $Mg_xAl2_{(1-x)}Ti_{(1+x)}O_5$ solid solution from which $Al_2O_3$ and $TiO_2$ were segregated at high temperature in reaction sintering of spinel, which contributed to improved sinterability of spinel. However, the specific role of $TiO_2$ on spinelisation and subsequent densification is not reported on any of the works. In addition, the beneficial effect of $TiO_2$ on densification of magnesia-alumina system is mostly reported in air and reducing atmosphere. Recently, Alumina–Magnesia–Carbon refractory has become of great interest in steel industry where in situ spinel formation and densification occurs at different gaseous atmosphere. Thermal analysis is a powerful technique to analyse the solid-state reactions in a ceramic system and has been applied for determining kinetics of crystallisation and sintering in glass and ceramic systems [34,35]. In the present work, we have studied the effect of $TiO_2$ on reaction sintering of magnesia-alumina system in $N_2$ atmosphere using both dynamic and static heat treatment separately to discern its effect on spinelisation and densification.

## 2. Experimental

The starting materials used in this investigation were caustic magnesia (NedMag Industries, Netherlands) and calcined alumina (Hindalco, Belgaum, India). Specific surface area of powders was measured by standard single point BET method using $N_2$ gas adsorption (Model: SORPTY 1750, Carlo Erba, Italy). Batches for reaction sintering were prepared from caustic magnesia and alumina in such a way that MgO-rich spinel with 66 wt % $Al_2O_3$ and 34 wt % MgO is obtained on firing. Batches were prepared without and with 3% $TiO_2$ and these are designated as 66 and 66 T, respectively. The batches were individually milled in an attrition mill (Model 01HD, Union Process, USA) for 1 h by using a zirconia pot and zirconia grinding media in isopropanol medium. Slurry thus obtained were initially air dried and subsequently oven dried at $110 \pm 5$ °C, crushed to break the agglomerate and passed through 100 mesh sieve to get the desired powder. Milled powders were mixed with 5% polyvinyl alcohol solution as a binder and shaped into bars and blocks by uniaxial pressing at 100 MPa followed by isostatic pressing at 140 MPa.

In order to identify the physicochemical processes which transform the compacted MgO-$Al_2O_3$ oxide mixture to a sintered magnesia-rich spinel body and the effect of $TiO_2$ additive, thermo-mechanical analysis (TMA) was performed up to 1500 °C at 2.5 °C/min heating rate under nominal load of 100 mN in nitrogen atmosphere. This study was performed in green pressed cylindrical bars (6 mm diameter x 10 mm height) in a vertical thermo-mechanical analyser (Model TMA 402 F3, Netzsch, Germany). Conventional horizontal dilatometer was avoided as the dilation of the sample is hindered both by the friction with base and the restraining force. In order to minimise this effect of external force on dimensional change due to reaction sintering, in TMA study the sample was vertically restrained with very nominal compressive force (100 mN). The densification study was carried out using green briquettes (12 mm diameter x 10 mm height) in the temperature range of 1500–1700 °C in a programme-controlled electric furnace in $N_2$ atmosphere. Heating rate was maintained at 5° C/min up to 1000 °C followed by 3 °C/min up to the final temperature with a 2 h dwelling time at the peak temperatures. The sintered magnesium aluminate spinel samples were characterised in terms of bulk density, apparent porosity, phase assemblage and microstructure. Bulk density and apparent porosity were determined by the conventional liquid displacement method using Archimedes' principle. Phase analysis was done by X-ray diffraction technique. The diffraction patterns of the finely divided powdered samples were obtained in a Philips X-ray diffractometer (Model X'Pert Pro PW1730, PANalytical, the Netherlands) using nickel filtered CuKα radiation and the diffraction patterns were recorded over a Braggs' angle ($2\theta$) range of 10–70°. Quantitative phase analysis was done by Rietveld Refinement using X'pert Highscore Plus software. Microstructure evaluation of the sintered compacts was done by field emission scanning electron microscope (Model Supra 35 VP, Zeiss, Germany) using carbon coated polished surface after thermal etching. Elemental analysis of selected grain and grain boundary was done by EDS technique.

## 3. Results and discussion

The physicochemical properties of the starting materials are shown in Table 1. The MgO content of caustic magnesia is 98.6%. This lightly calcined (caustic) magnesia is having a specific surface area (SSA) of 13 $m^2/g$ and highly reactive in nature. The calcined alumina used is pure in nature with SSA of 4 $m^2/g$. XRD analysis indicates that the major crystalline phases present in caustic magnesia and calcined alumina are periclase and α-$Al_2O_3$, respectively.

The reaction sintering behaviour of the green compacts of MgO-rich spinel composition performed through thermo-mechanical analysis (TMA) is given in Fig. 1. Since TMA is a dynamic process and all solid-state reactions are kinetically controlled, a lower heating rate (2.5 °C/min) was chosen to facilitate the establishment of a realistic near-equilibrium

Table 1
Physicochemical properties of the starting materials.

| Properties | Magnesia (*caustic*) | Alumina (*calcined*) |
|---|---|---|
| Chemical constituents (wt %) | | |
| $SiO_2$ | 0.06 | – |
| $Al_2O_3$ | 0.23 | 99.3 |
| $Fe_2O_3$ | 0.05 | – |
| CaO | 0.80 | – |
| MgO | 98.6 | – |
| $Na_2O$ | – | 0.3 |
| Specific gravity | 3.57 | 3.90 |
| Crystalline phase | Periclase | Corundum |
| Specific surface area, ($m^2/g$) | 13 | 4 |