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Enhancement of reaction-sintering of alumina-excess magnesium aluminate spinel in presence of titania

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ABSTRACT

Alumina-excess magnesium aluminate spinel finds use in different high temperature applications including steel ladles. Alumina-excess spinel was prepared by solid oxide reaction using magnesia (MgO = 10 wt%) and calcined alumina (Al_2O_3 = 90 wt%), in the sintering temperature range of 1500–1700 °C. The role of titania on the densification, spinelisation, evolution of microstructure and phase assemblage was investigated in this MgO-Al_2O_3 system. Titania addition increased the rate of densification 20x compared to undoped composition at 1500 °C under dynamic heating condition. However, under static firing, the beneficial effect of titania on densification could only be discerned at lower temperatures. The microstructure of titania doped sintered alumina-excess spinel compacts contain magnesium aluminium titanate phase in the grain boundary of corundum and spinel grains. The beneficial effect of titania on densification is attributed to magnesium aluminium titanate phase ($Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$) development and also by incorporation of Ti^{4+} into the spinel structure.

1. Introduction

Magnesium aluminate (MA) spinel is used for wide gamut of functional and high temperature structural applications. Its optical transparency behavior is exploited in the protective windows of the sensor operating in mid infrared range, armor window, barcode reader, optical microlithography, tunable laser hosts, humidity sensors and in many more applications [1–10]. Owing to its higher melting point and other advantageous thermal properties it is used as an excellent refractory material (melting point 2135 °C). It exhibits superior mechanical, thermal and chemical properties both at room and at elevated temperatures [11–20]. Due to excellent corrosion resistance to basic slag it has been used in the side wall of steel teeming ladle [21,22]. The high temperature applications of MA spinel have been increased due to its various superior properties like excellent thermal shock resistance as well as its less non-hazardous nature compared to mag-chrome materials [23]. The application area of magnesium aluminate spinel is largely governed by the alumina content in the composition. The magnesia excess spinel (< 28% of MgO) is widely used in clinkering zone of cement rotary kiln. The alumina excess spinels are used in different areas of steel teeming ladle [21,22]. Best performance in the application area is achieved with the highly dense material with minimum porosity. So, the challenge lies with densification of magnesium aluminate spinel.

Magnesium aluminate spinel exhibits a volume expansion of 8.1% when formed from MgO and Al_2O_3 due to the higher average density of the starting oxides than that of the spinel formed [24]. This intrinsic volume expansion at relatively higher temperatures (> 1000 °C) acts as a restraining force for single stage densification and hence, the dense spinel aggregates are prepared in a two-stage process. i.e. spinelisation at lower temperature followed by densification at higher temperature. Enormous efforts have been concentrated to achieve the densification in single stage process. The nature of the starting materials plays a significant role on the densification in a single stage process and was investigated by many researchers [25–30]. Mechanical activation of alumina precursor improves the densification, spinel content and the grain size of MA spinel by significantly enhancing the reaction sintering of magnesia and alumina [25]. The beneficial effect of additives such as TiO_2, Y_2O_3, ZnO and Dy_2O_3 on spinelisation as well as densification was reported by different researchers [20,31–38]. Yu and Hiragushi suggested the formation of a titania containing solid solution which promotes the densification of spinel [36,37]. It has been reported that TiO_2 enhances the densification process of magnesia-excess magnesium aluminate spinel with a negligible role on spinelisation reaction [38]. The solid state reactions during reaction sintering of magnesium aluminate spinel are governed by defect reactions, which vary for MgO:Al_2O_3 [39,40]. For MgO excess hypostoichiometric (with respect to alumina content) composition the dominant defect reactions [39] are

$$4MgO \rightarrow 2Mg'_{Al} + Mg^{X}_{Mg} + 4O^{X}_{O} + Mg^{\cdot\cdot}_{i}$$

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or

$$4MgO + Al_{Al}^{X} \rightarrow 3Mg'_{Al} + Mg_{Mg}^{X} + 4O_{O}^{X} + Al_{i}^{\cdots}$$

or

$$3MgO \rightarrow 2Mg'_{Al} + Mg_{Mg}^{X} + 3O_{O}^{X} + V_{O}^{\bullet\bullet}$$

While, in alumina excess hyperstoichiometric system (with respect to alumina content) the defect reactions are different.

$$4Al_2O_3 \rightarrow 5Al_{Al}^{X} + 12O_{O}^{X} + 3Al_{Mg}^{\bullet} + V''_{Al}$$

or,

$$4Al_2O_3 \rightarrow 6Al_{Al}^{X} + 12O_{O}^{X} + 2Al_{Mg}^{\bullet} + V''_{Mg}$$

For this reason, the effect of TiO_2 on MgO excess spinel should not be extrapolated to alumina-excess spinel system. Accordingly it is imperative to analyse the role of titania in alumina excess MgO-Al_2O_3 system separately. In the present work, the effect of TiO_2 on reaction sintering of alumina-excess spinel (with starting composition of Al_2O_3 = 90%, MgO = 10%) composition has been studied under static and dynamic heating regimes to discern the role of TiO_2 on densification and spinelisation.

2. Experimental

Caustic magnesia (NedMag Industries, Netherlands) and calcined alumina (Hindalco, India) were used as source of magnesia and alumina respectively. The batch was prepared with a starting composition having 90wt% Al_2O_3 and 10wt% MgO to obtain an alumina excess spinel after sintering (designated as MA90). In another batch, TiO_2 (3 wt%) was added to the same composition and designated as MA90T. These two batches were separately processed in an attrition mill (Union Process, USA, model 01HD) for 1 h in a zirconia pot using zirconia grinding media and isopropyl alcohol as medium with 200 rpm. The homogenised slurry was dried in air followed by oven drying at 110 ± 10 °C. The dried and de-agglomerated powder was compacted into bar (80mmx8mmx6mm) in a hydraulic press (uniaxial) at a specific pressure of 100 MPa using 5% PVA solution as green binder and subsequently subjected to iso-static pressing at 140 MPa. Thermo mechanical analysis was performed in unfired pressed bar of 6 mm diameter x 10 mm height cut from the bars prepared earlier to understand the physicochemical changes that can take place during the formation of alumina-excess spinel from its starting precursors and to study the effect of TiO_2 as additive in this oxide system. The test was carried out in a vertical thermomechanical analyser (Model TMA 402 F3, Netzsch, Germany) up to 1500 °C with a heating rate of 2.5 °C min^{-1} and at a nominal load of 100 mN in nitrogen atmosphere. This vertical analyser has an edge over the conventional horizontal dilatometer to examine the dimensional changes due to reaction sintering as it minimizes the hindering effect of the frictional force with the base and the restraining force of that of a conventional horizontal dilatometer. In this study a very nominal compressive load (100 mN) was applied in order to restrain the sample in its position. The densification behavior of the samples was studied in static condition using green pellets of 12 mm ø and 10 mm height in the temperature range of 1500–1700 °C in an electric furnace in nitrogen atmosphere. Uniform heating of 5 °C up to 1000 °C and 3 °C up to the final firing temperature with a soaking time of 2 h was maintained for all the samples. Sintered pellets were characterized in terms of apparent porosity, bulk density, microstructure and phase abundance. Bulk density was determined by liquid displacement method using Archimedes principle in kerosene medium. The phase evolution of the sintered pellets was studied through powder XRD data and the quantification of the crystalline phases was done by Rietveld refinement technique using X'Pert HighScore Plus (PANalytical) software.

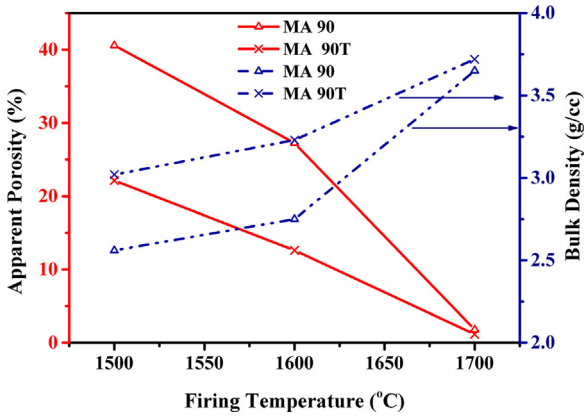

Fig. 1. Apparent porosity and bulk density of the samples sintered at different temperature (in N_2 atmosphere).

3. Results and discussion

The calcined caustic magnesia employed in this study is highly reactive in nature (specific surface area ~13 m^2/g) and the MgO content is 98.6% (remaining is LOI). The complete chemical analysis of the raw materials had already been documented earlier [38]. The other raw material is calcined alumina having a specific surface area of 4 m^2/g and the alumina content is more than 99%. Periclase and corundum are the major phases present in the caustic magnesia and calcined alumina respectively as revealed by X-ray analysis.

3.1. Reaction sintering under static heat treatment

Reaction-sintering of spinel is a combination of different interrelated processes of phase formation, pore annihilation, consolidation and growth of particles. Densification process requires high temperature to activate the necessary diffusion mechanisms. Study of densification behavior in terms of apparent porosity and bulk density of the samples sintered at different temperatures is shown in Fig. 1. During heat treatment at suitably high temperature, the porosity of a ceramic compact gradually decreases. This is attributed to formation of grain to grain neck formation and subsequent densification process where a net material transport occurs from grain boundary to the neck region. This results in removal of porosity and shrinkage of the ceramic compact. Both the undoped (MA90) and TiO_2 doped spinel (MA90T) compact show gradual decrease in open porosity and consequent increase in bulk density (Fig. 1). In the entire experimental sintering temperature range (1500 −1700 °C), titania doped sample show greater densification (lower porosity and higher BD). Titania addition decreases the apparent porosity from 27.3% to 12.6% and increases the bulk density of the sample from 2.75 g/cc to 3.25 g/cc at 1600 °C. At 1700 °C the beneficial effect of titania is less apparent as both MA90 and MA90T achieve similar densification. As both the samples attain their near-theoretical density at high temperature, the beneficial effect of TiO_2 is not much evident. Several possibilities can account for this enhanced densification in presence of titania viz., formation of a secondary phase and/or formation of defects in spinel lattice. Proper assignment of the underlying process can only be justified by XRD studies to detect formation of new phases and/or incorporation of titania in spinel lattice to create defect sites.

The crystalline phases formed in the sintered samples were studied using XRD technique to correlate with the reaction sintering process undergone by the experimental batches. XRD patterns of the MA 90 samples fired at three different temperatures and the corresponding reflection of (004) plane of spinel are shown in Fig. 2. The analysis of diffraction data is presented under following three sub sections-