

Effect of TiO₂ in Spinel Formation and Reactive Sintering of Magnesia-rich Ceramics

S. Ghanbarnezhad, A. Nemati, M. Bavand-Vandchali, R. Naghizadeh

Abstract— The solid solubility of magnesia in magnesium-aluminate spinel and magnesium-aluminate spinel in magnesia does not change with temperature thus not creating bonds over periclase grains in single stage sintering process. In the present study, magnesia and alumina powders along with tetravalent oxide (TiO₂) additive was analyzed for its role in reactive densification of spinel in single stage firing process in order to achieve a better binding system for magnesia-based refractories. This tetravalent oxide on reaction with magnesia from spinel solid solution with MgAl₂O₄ as they have similar crystal structure. The spinel solid solution formed using oxide additive is expected to higher solubility in magnesia than magnesium-aluminate spinel, resulting in improvement of the bonding during sintering through increased in solid solubility at elevated temperatures, similar to the complex spinel in magnesia-chrome refractories. The formation of spinel during firing remains as a second phase that retards the grain growth of periclase.

Index Terms— Densification, Periclase, Reaction sintering, Spinel Solid solution, tetravalent oxide.

I. INTRODUCTION

In recent years magnesium-aluminate spinels (MgAl₂O₄) are used by reason of good refractory performance in many technological application such as cement and concrete, glass, iron and steel industries. Magnesium-aluminate spinels are very much desirable phases in many refractories where improved hot strength, creep resistance, good thermal stability and slag penetration resistance are required [1-2]. The reaction of magnesia and alumina to form spinel [3] is diffusion controlled and accompanied by volume expansion, making it difficult to synthesis in a single stage process. Hence, magnesium-aluminate spinel [4] or its precursors [5] have been prepared by different techniques for use as a sintering and binding agent for alumina based refractory compositions, mainly in the preparation of castables [6]. The magnesia-rich refractories need a bonding matrix that is provided by chrome ore forming a direct bonded spinel type compositions. This direct bonding [7] is caused by chrome ore dissolving into periclase at high temperatures forming spinel that precipitates out on cooling and bonding with the precipitated spinel. The spinel that precipitates out from solid

solution adheres to the grains and the precipitate surrounding it, resulting in bonding of the particles. However, solubility to chrome ore at high temperature and thus does not bond periclase grains on cooling. The spinel formed by the reaction of magnesia with chrome ore has two bivalent cations (Mg²⁺, Fe²⁺) and three trivalent cations (Cr³⁺, Al³⁺, Fe³⁺) have individual site preferences and thus from normal, inverse or complex (mix of normal and inverse) spinel [8] depending on the cations present and their characteristics. In order to achieve a complex spinel using alumina as the base material, some tetravalent oxide additives that from spinel with magnesia may be used. This may result in lower amount of periclase and from complex spinel. The cation size, charge and electronic configuration of the cations in additives result in there occupancy in different sites within spinel structure. It is observed that ZnO improves densification [9], TiO₂ decreases the synthesis temperature [10], SnO₂ increases the thermodynamic stability of spinel solid solution containing magnesia and alumina [11] and ZrO₂ improves the mechanical properties of stoichiometric spinel, although it remains as a separate phase and does not form a solid solution with magnesium aluminate spinel [12].

II. EXPERIMENTAL PROCEDURE

The magnesia-spinel experimental compositions were designed such that the sintered magnesia (China and Czech Industries), Al₂O₃ (Alcoa company) and TiO₂ (Merck company) which are shown in "Table.1".

Table 1. Experimental compositions

Batch	Weight% MgO	Weight% Al ₂ O ₃	Weight% TiO ₂
B.S ₀	80	20	-
B.S ₂	78	20	2
B.S ₄	76	20	4
B.S ₆	74	20	6

These compositions were mixed in a laboratory blender for 15 min for homogenisation using MgCl₂ as the binder. Then, the mixes pressed to form pellets (20 mm in diameter, 10 mm thick) preessed at 0.3 T/cm², dried at 110 °C for 6 h in laboratory drier before firing at 1400 °C to 1600 °C for 6 h in a lab kiln. The samples are allowed to cool in the kiln before characterization in terms of their physical properties (bulk density, apparent porosity and apparent specific gravity by Archimedes principle) and X-ray diffraction technique for phase analysis and SEM for microstructure analysis.

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III. RESULTS AND DISCUSSIONS

A. Sintering study without additive

Sintering of magnesia-spinel without any tetravalent cation shows the presence of only MgO and just a small amount of spinel phases. Reason of low solubility of magnesia and alumina in spinel and low solubility of MgAl₂O₄ spinel in magnesia make it difficult to create a high reaction rate and the volume increase during spinel formation renders it difficult to reaction sinter without any additives. So, the higher temperature (~1600°C) denotes complete reaction, resulting in solid-state sintering.

“Fig.1” depicts the decrease in apparent porosity and apparent specific gravity as the firing temperature is increased. The increase in firing temperature results in better consolidation of particles and entrapment of pore within the grains indicating that magnesia-spinel formed with low apparent porosity needs high temperature in single step firing process. The decrease in apparent specific gravity indicates that more pores are entrapped within the grains as the firing temperature is increased with decrease in volume of open pores.

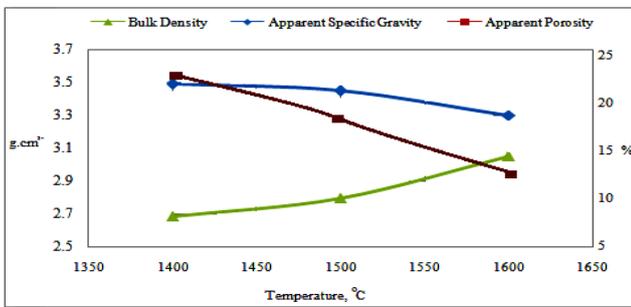


Fig. 1 Physical properties vs. firing temperature for magnesia-alumina system without additive

B. Phase analysis of compositions containing TiO₂

The unit cell length of spinel solid solution increases with TiO₂ content. Compositions containing TiO₂ had one lattice parameter for spinel solid solution. The unit cell size increased (from 8.08 Å to 8.11 Å) for all compositions with increase in temperature from 1400 °C to 1600 °C. “Fig.2” shows the X-ray diffraction patterns of sample B.S4 after sintering at 1400 °C to 1600 °C. The formation of perovskite at low temperatures in the initial stage may increase the reactivity Mg²⁺ ions into the system resulting in the formation of bonding during reaction sintering to form spinel. The increased lattice parameter of spinel solid solution as compared to MgAl₂O₄ [13] may be a result of defect structure caused by the Ti⁴⁺ ion that forms Mg₂TiO₄, with a larger unit cell.

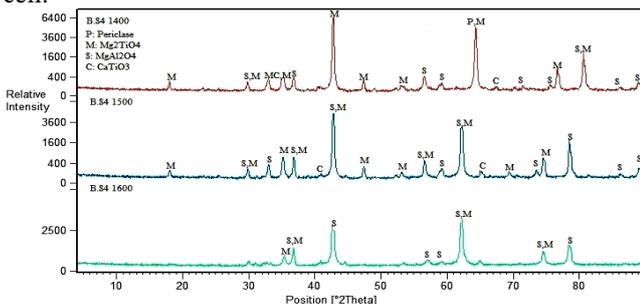


Fig 2. X-ray diffraction patterns from sample B.S4 after sintering at 1400 °C to 1600 °C ; P: Periclase; M: Mg₂TiO₄; S: Spinel (MA) and C: CaTiO₃

C. Densification Behavior

“Fig.3 (a) and (b)” shows the increase in bulk density and decrease in open porosity with increasing TiO₂ content to 4 Wt.% and by firing temperature. Further TiO₂ addition increases the open porosity. “Fig.3 (c)” shows decrease in apparent specific gravity with increasing TiO₂ content to 4 Wt.% and by firing temperature. Further TiO₂ addition increases the apparent specific gravity. The decrease in apparent specific gravity may be related to the true density of Mg₂TiO₄ (3.54 g/cm³) [14] and the creation of closed pores within the grain.

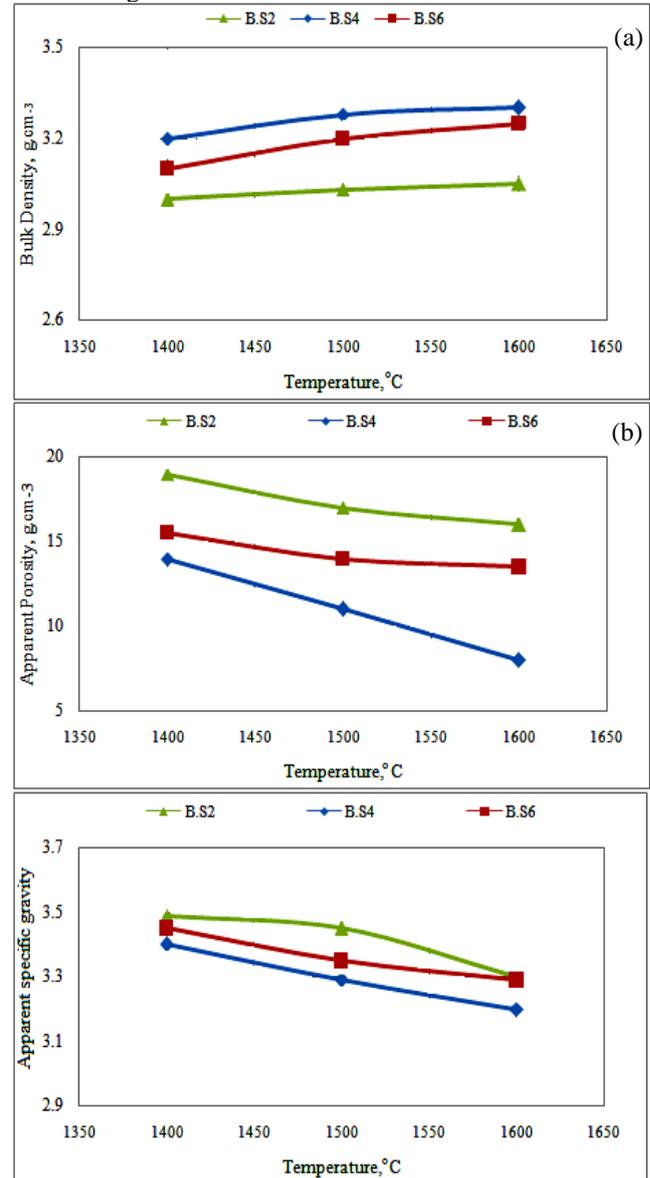


Fig 3. Physical properties vs. firing temperature, (a) Bulk Density, (b) Apparent Porosity and (c) Apparent specific gravity

“Fig.4 (a), (b), (c) and (d)” shows the microstructure of B.S₀, B.S₂, B.S₄ and B.S₆ that shows that B.S₄ has a dense structure with lowest pores and indicates that titania has created better bonding similar in bonding to magnesia-chrome bricks.



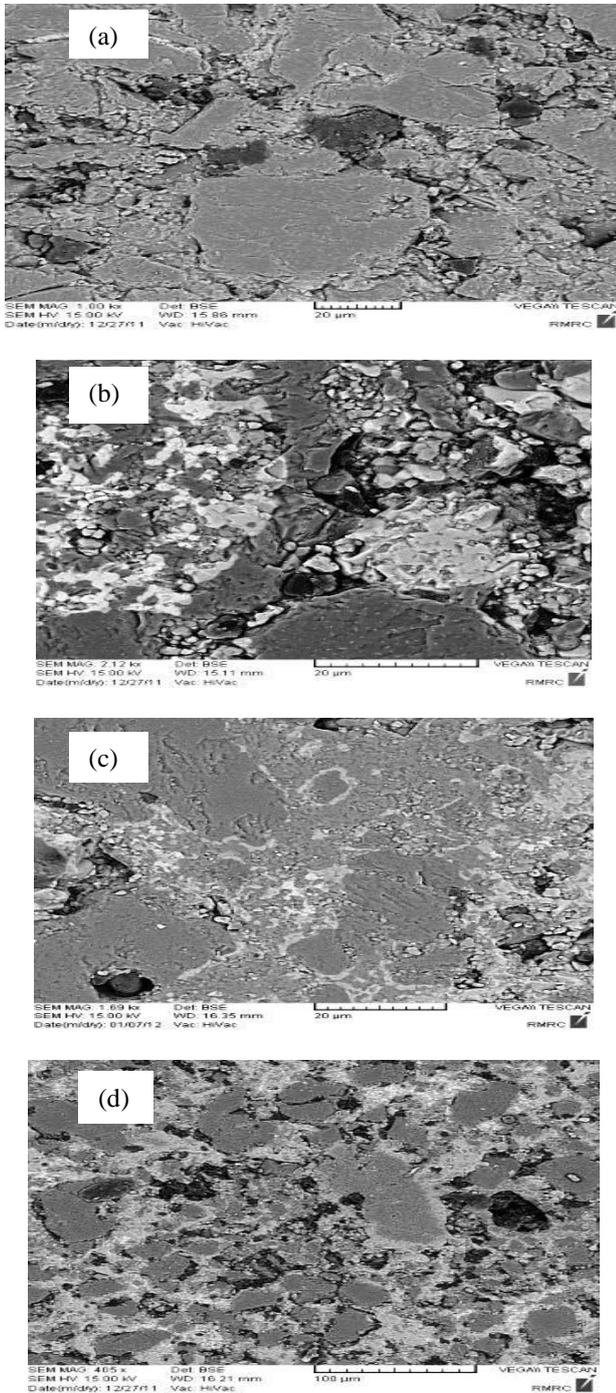


Fig 4. Scanning electron micrographs of (a) B.S₀, (b) B.S₂, (c) B.S₄, (d) B.S₆

IV. CONCLUSIONS

Due to TiO₂ creating more interstitial and substitution defects in solid solution formed in solid solution and the ability of TiO₂ to take more ions in to the structure, making it a better sintering aid, so this conclusions has achieved:

- (1) Titanium dioxide is one of the most investigated additives for the formation of in-situ spinel phases.
- (2) TiO₂ has been improved sintering, and single stage synthesis of magnesium- aluminate spinel.
- (3) Spinel containing 4 wt.% TiO₂ as solid solution has the maximum density and minimum open porosity indicating that it is the optimum concentration.

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