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Effect of in situ generated nascent magnesia and alumina from nitrate precursor on reaction sintered magnesium aluminate spinel

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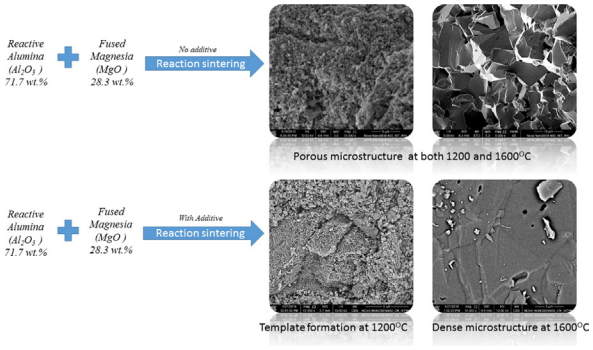
HIGHLIGHTS

- Dense magnesium aluminate spinel was synthesized using reaction sintering method.
- Aluminium nitrate nonahydrate and magnesium nitrate hexahydrate was used to produce insitu nascent alumina and magnesia.
- Spinel formation and density increased in presence of nascent alumina and magnesia.
- Template formation was observed in microstructure.
- Thermal shock resistance and strength increased.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of dense magnesium aluminate spinel using a single stage solid oxide reaction is difficult owing to volume expansion associated with spinel formation. In the present work, reaction sintered magnesium aluminate spinel was prepared using commercial grade oxide in a single stage solid oxide reaction reactants. The effect of incorporation of nascent MgO and Al_2O_3 from nitrate precursor additives was studied. Aluminium nitrate nonahydrate and magnesium hexahydrate were used up to 2 wt.% as a source of nascent Al_2O_3 and MgO respectively. Sintering of the mixed oxide compositions was done in the temperature range 1200–1600 °C after compaction under a uniaxial pressure of 150 MPa. The dilatometry study was used as a tool to observe the spinel formation reaction. Sintered products were characterised by densification study, flexural strength, thermal shock resistance measurement, phase analysis and microstructural development. The presence of excess MgO and Al_2O_3 enhanced the spinel formation reaction and densification of spinel at a higher temperature. The template mechanism of spinel formation was observed in the microstructures. The addition of excess alumina and magnesia was found to increase strength values. Also, much higher strength retainment even after 6–8 cycles of thermal shock was observed in additive contained batches.

1. Introduction

Magnesium aluminate spinel is a technologically important material owing to its excellent thermo-mechanical and chemical properties. It has a congruent melting point of 2135 °C, shows high resistance to both acid and alkali. Beside these, it has high hardness, high strength both room and elevated temperature, relatively low density, excellence transmittance, high thermal shock resistance, etc. [1–3]. Owing to these properties, $MgAl_2O_4$ spinel has applications in optical windows of the pressure vessel, as an anode material in aluminium electrolytic cells, cement rotary kilns and steel ladles as a refractory material, humidity sensors, etc. But the major application of magnesium aluminate spinel

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is in refractory industry. It is used as refractory material in the transition zone of cement rotary kiln, the lining of steel teeming ladles, checker bricks of glass furnace regenerators, etc. [4,5]. Magnesium aluminate spinel is also a suitable replacement for magnesium chrome refractories as the former have an environment-friendly advantage with similar properties. The chrome contain refractories possess the risk of environment pollution due to the presence of toxic Cr^{6+} ions, which is carcinogenic in nature [6–8].

Despite these applications and advantages, magnesium aluminate has not received wide commercial success till date. The main reason for this is the volume expansion associated with its formation from oxide reactants due to the difference in specific gravity of alumina and spinel [9]. The volume expansion associated with spinel formation (~5%) makes it difficult to produce dense spinel in a single stage sintering process. So, in the conventional process, a double stage firing technique is used in which spinel is synthesised in the first firing stage. The formed spinel is crushed, ground, pressed and sintered during second stage firing to produce dense spinel. This process increases the cost of production of spinel [10,11].

So in order to produce dense spinel, many researchers used different non-conventional techniques such as sol-gel, co-precipitation, hydrothermal synthesis, etc. to produce pure, dense spinel at low temperature [12–16]. Reduction in particle size increases the surface area, which in turn increases the reactivity of material. Many researchers tried to implement this logic to produce dense spinel by using intermediate mechanical milling processes [2,17,18]. Kong et al. used high energy ball milling of 12 h. with 200 rpm to produce magnesium aluminate spinel from MgO and Al_2O_3.·They reported the formation of spinel to start from 900 °C.·They achieved 96% theoretical density sintering at 1550 °C with 2 h. soaking for milled composition [19]. Domanski et al. synthesised $MgAl_2O_4$ using mechano-chemical synthesis at room temperature and air atmosphere. They produced 99% spinel using γ-alumina, boehmite, and magnesia as starting material. They milled maximum up to 140 h. The ball to powder ratio used was 44:1 [20]. Many researchers studied the effect of additives on reaction sintered magnesium aluminate spinel [21,22]. Addition of LiF was studied by Rozenburg and Reimanis et al. They reported LiF to increase sintering due to the formation of a liquid phase at high temperature [23,24]. But literature does not provide much knowledge about the addition of additives that can affect the stoichiometry of the spinel composition. Sarkar et al. [25] studied the effect of the addition of $MgSO_4$ on reaction sintered spinel. They added 0.5–2 wt.% of $MgSO_4$ in stoichiometric, Mg-rich and Al-rich composition. They reported an increase in strength with the addition of $MgSO_4$ in all compositions. They found the addition of $MgSO_4$ increase solubility of corundum phase in low sintering temperature leading to grain growth. However, the addition of $MgSO_4$ was reported to deteriorate thermal shock for all compositions. They also studied [26] effect of addition of 1–3 wt.% AlF_3 in spinel formation. The spinel formation temperature was reported to decrease with AlF_3 addition. They also reported shrinkage and a low specific surface area in additive containing compositions. Ganesh et al. studied [27] the effect of $AlCl_3$ on spinel formation and sintering using double stage firing process. They added 0.01–0.03 mol% of $AlCl_3$.·The addition of $AlCl_3$ was reported to enhance spinel formation during calcination and aid in sintering in the later stage. They reported achieving a bulk density of 3.40 g/cm^3. Mohammadi et al. [28] used $MgCl_2$ as a sintering aid in $MgAl_2O_4$ prepared via solid-state reaction. They used 0.5–6 wt.% of $MgCl_2$ as an additive. The addition of $MgCl_2$ was reported to increase spinel formation. Formation of nano spinel was reported on the surface of larger grains as a result of the reaction between MgO and Al_2O_3.

In the present work, the effect of the addition of magnesium nitrate hexahydrate and aluminium nitrate nonahydrate on reaction sintered spinel was investigated. Stoichiometric spinel composition was chosen for the study. The spinel formation and sintering were investigated using a dilatometry and X-ray diffraction technique. The effect of the addition of these additives on bulk density, microstructure, strength and thermal shock resistance was also investigated.

Table 1
Chemical properties of the starting material.

Constituent oxide content (%)	Alumina fines	Fused magnesia
SiO_2	0.05	0.47
Al_2O_3	99.8	0.12
Fe_2O_3	0.03	0.063
CaO	0.05	1.46
MgO	0.06	97.14
$Na_2O + K_2O$	0.10	–

Table 2
Physical properties of the starting material.

Properties	Alumina Fines	Fused magnesia
Specific surface area, m^2/g	8.9	–
Particle size D_{50}, μ	0.5	~28
True density (g/cm^3)	3.98	3.58

2. Experimental

Commercial grade raw materials, namely, fused magnesia fines (Chinese source) and reactive alumina (Almatis, India) were mixed in the stoichiometric ratio (71.7 wt.% Al_2O_3 and 28.3 wt.% MgO) in an alcoholic medium (Isopropyl alcohol, purity >99%). The chemical and properties of the raw materials are mentioned in Tables 1 and 2 respectively [27,29]. The mixing was done using a magnetic stirrer for 6 h. The mixture was then dried at 80 °C for 24 h. 0.5–2 wt.% each of $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ (both Himedia Labs., India make >98% purity) was added in the stoichiometric composition respectively and then was again mixed and dried. All the different batches after mixing and drying were pressed into cylindrical pellet (15 mm dia. × 15 mm height) and rectangular bar (60 mm × 6 mm × 6 mm) shapes at 150 MPa pressure in an automatic hydraulic press (Model 3887, Carver Inc., US make) in high carbon steel molds. 4 wt.% PVA (6 wt.% concentration) was used as a binder to provide the green strength to the pressed samples. The pressed shapes were then oven dried at 110 °C for 24 h and sintered at 1200,1300,1400,1500 and 1600 °C with 4 h soaking at the peak temperatures. Sintering was done in a programmable electric furnace (Kanthal, India make). The schematic of sintering process is given in Fig. 1 for better understanding. The linear shrinkage of the pellets was calculated by measuring the diameter before and after sintering. The bulk density and apparent porosity were evaluated by Archimedes principle using boiling water method. The spinel formation and sintering

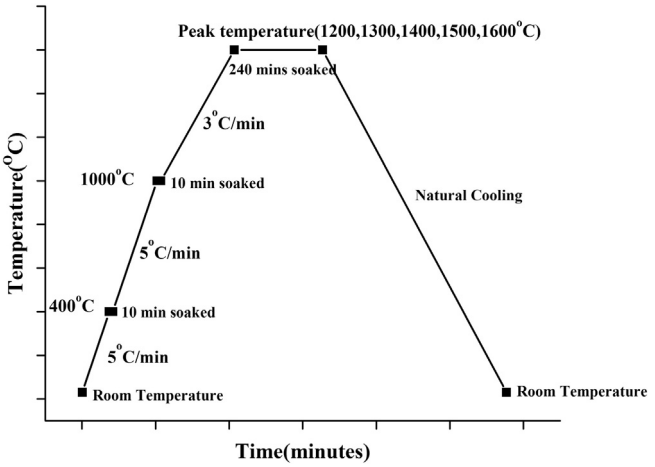

Fig. 1. Schematic of the sintering schedule.