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A comparative study on the effect of different additives on the formation and densification of magnesium aluminate spinel

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ABSTRACT

Commercially available fused magnesia and sintered alumina sources were used to form reaction sintered spinel by solid oxide reaction route in a single firing. The effect of the addition of four different additives, namely $MgCl_2$, LiF, $AlCl_3$, and MnO_2, at 2 wt% level was studied. Mixed oxide compositions were compacted under a uniaxial pressure of 150 MPa and then sintered between 1200 and 1600 °C. The dilatometric study and phase analysis was done to observe the spinel formation reaction. Densification study of the sintered product was done to understand the effect of additives. Cold Crushing strength and thermal shock resistance of 1600° sintered pellets were studied. Microstructural study using field emission scattered electron microscopy (FESEM) was also done to understand the grain development on sintering in the compositions and the effect of different additives on sintering. LiF and $MgCl_2$ were found to strongly enhance the spinel formation reaction. Bulk density values were found to be lower for the additive containing batches at 1200 °C due to enhanced spinel formation but higher at 1600 °C due to greater sintering. Strength values were strongly enhanced by LiF and MnO_2 due to the development of dense, compact microstructure. Also, additives containing compositions showed much higher strength retainment even after 6 cycles of thermal shock.

1. Introduction

Magnesium aluminate spinel is an important material for material scientists due to its wide range of properties. Properties like high melting point, excellent high temperature mechanical, thermal, chemical and spalling properties have made it essential refractory lining material in steel teeming ladles transition and burning zone of cement rotary kilns, checker work of glass tank furnace regenerators etc [1–3]. Along with these $MgAl_2O_4$ spinel has good combination of optical, dielectric and physio mechanical properties which make it a suitable material for use in the visible, near infrared and microwave frequency ranges [4]. The global practice shows that cost and consumption of conventional refractories have reduced in current steel, cement and all other allied industries due to the application of Mg–Al spinel based refractories [5]. The commercially acceptable process for the synthesis of magnesium aluminate spinel is a solid state reaction. This process constitutes a counter diffusion process of Al^{3+} and Mg^{2+} ions and is associated with a 5% volume expansion [6,7]. This does not allow the formed spinel to densify in a single firing process, and a separate firing is required to densify it. This double stage firing enhances the cost of production.

Magnesia chrome refractories which have similar properties were in demand due to cheapness and were being widely used. But the use of these refractories always had the risk of contamination of ground water by hexavalent chromium ions leached from waste material. The Cr^{6+} ion is associated with skin ulceration and carcinomas in human. It also bears the risk of diffusing from refractory into the cement clinker which enhances the toxic reactions during processing of the cement [8]. These disadvantages of magnesium chrome containing refractories escalated the interest on the Magnesium aluminate spinel refractories which is environment friendly [9].

Many researchers tried to produce dense spinel using several techniques like sol-gel, co-precipitation, molten salt synthesis, flame spray pyrolysis, etc [10–13]. But unfortunately all these chemical synthesis techniques are not appropriate or less industrialized for mass production [14]. The conventional solid state oxide mixing process is still the major process of synthesis because of its easeness and economic advantage. To obtain dense spinel in a single stage firing, many researchers used additives. Application of additives enhances both formation and densification of spinel. The addition of additives like TiO_2, B_2O_3, LiF, ZnF_2, BaF_2 reduces the sintering temperature [15]. It was reported that addition of LiF enhances the densification process by liquid phase sintering [16].

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Kostic et al. reported an increase in solid state reaction of $MgAl_2O_4$ by increasing cation vacancy [17]. Sarkar et al. studied the effect of 2 wt% B_2O_3,V_2O_5, Cr_2O_3. TiO_2 and 5 wt% spinel. They found TiO_2 as the best additive for densification among these additives. The addition of V_2O_5 and B_2O_3 was found to have detrimental effects [4]. TiO_2 was also reported to be beneficial for low temperature densification but at higher temperatures and the higher amount, it was reported to be deleterious on densification, strength, and hot properties [18]. The addition of Cr_2O_3 also reported to improve densification of stoichiometric spinel at lower temperatures and thermal shock resistances at 1 wt% level but at higher sintering temperatures and higher amounts were reported to deteriorate the properties [19]. Addition of Y_2O_3 was reported to enhance the densification, strength and hot strength properties of spinel [20].

Kim et al. studied the effect of 1–4 wt% $CaCO_3$, SiO_2, and TiO_2 and found to be beneficial for densification of spinel. They also reported that TiO_2 contained sample possessed the highest density [21]. Ganesh et al. compared the application of $AlCl_3$ as additive with AlF_3 in a double stage sintering process. They found $AlCl_3$ as an effective additive for both spinel formation and sintering. The addition of $AlCl_3$ was also found beneficial for removal of impurities like soda [22]. Addition of additives like AlF_3, $MgSO_4$, ZrO_2 was also studied by various researchers [23–26]. Mohan et al. used ZrO_2 as an additive for producing spinel from commercial grade reactants. The incorporation was found to improve thermal shock resistance, density, and flexural strength [27]. The addition of $MgCl_2$ in the sintering behavior of $MgAl_2O_4$ was studied by Mohammadi et al. by using an intermediate calcination stage before sintering. They reported an increase in bulk density with the addition of $MgCl_2$. The addition of $MgCl_2$ also leads to a decrease in average grain size [28].

However, limited literature is available on a comparative study of different additives on single stage sintering of $MgAl_2O_4$. In the present work, such comparative study has been undertaken by addition of 2 wt% $MgCl_2$, LiF, $AlCl_3$ and MnO_2 in stoichiometric spinel, prepared by single stage sintering method from commercially available ingredients. Dilatometry study was also done to observe the effect of additives on the spinel formation and densification process. The microstructural study was done to study the effects of additives on the development of microstructure with sintering temperature. Densification, strength, and thermal shock resistance studies were done to compare the effects of additives on properties development of spinel.

2. Experimental

Four different additives, namely, aluminium chloride, lithium fluoride, magnesium chloride and manganese dioxide were used as an additive at 2 wt% level. Fused magnesia (Chinese source) and reactive alumina fines (Almatis, India) were used as raw materials for spinel. Tables 1 and 2 represents the detail chemical

Table 1
Physio-chemical properties of the starting material.

Constituent	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	
Specific surface area, m^2/gm	8.9	
Particle size D_{50}, μ	0.5	28
True density (g/cc)	3.98	3.58

Table 2
Purity of additives used.

Additive	Purity (%)	
$AlCl_3$	99%	
$MgCl_2$	98%	
LiF	98%	
MnO_2	> 80%	
	Impurities	MnO, Mn_2O_3

composition of raw materials and additives [29–31]. Stoichiometric spinel composition (71.7 wt% Al_2O_3 and 28.3 wt% MgO) was prepared by mixing the appropriate amount of the raw materials in an alcoholic medium(isopropyl alcohol, purity ≥ 99.8%) for 6 h using a magnetic stirrer. The stirred mixture was then dried at 80 °C for 24 h. The dried mixture was divided into 5 equal batches (by weight), 2 wt% of each additive $AlCl_3$, LiF, $MgCl_2$ and MnO_2 was added in each of these equal batches respectively, and one batch was kept as without additive batch. After addition of the additives, the mixture was again stirred using a magnetic stirrer for better mixing of the additive. The mixed powder was then dried at 80 °C for another 24 h. Pellets (15 mm diameter × 15 mm height) were prepared from the dried powders in a stainless steel mould at 150 MPa pressure using 4% PVA (polyvinyl alcohol) solution (6% PVA concentration) as a green binder in an automatic hydraulic press (Model 3887, Carver Inc. US make). Pressed pellets were then dried at 110 °C for 24 h and sintered at 1200, 1400, 1600 °C in an electric resistance furnace (Kanthal, India make) with 4 h soaking at peak the temperatures. The sintering schedule is shown in Fig. 1.

Linear shrinkage of all the samples after sintering at 1200, 1400, 1600 °C was measured by measuring the change in the diameter before and after sintering. Bulk density and apparent porosity of sintered samples were measured by Archimedes principle using boiling water method. Dilatometry study of the dried samples of each batch was done in an argon atmosphere at a heating rate of 5 °C/min up to 1450 °C (peak temperature of the machine) in a high temperature dilatometer (model DIL 402 C, Netzsch, Germany make). Rectangular bar samples of dimension 25 mm × 6 mm × 6 mm pressed at 150 MPa were used for the dilatometric study. Microstructural study of the fractured sintered surfaces was done by using a field emission scanning electron microscope (model Nova Nano SEM, FEI, US make) after 240 s of gold coating in a sputter coater. Energy dispersive analysis of x-ray (EDAX) study has been done on specific spot for confirmation of elements present in the microstructural photograph using

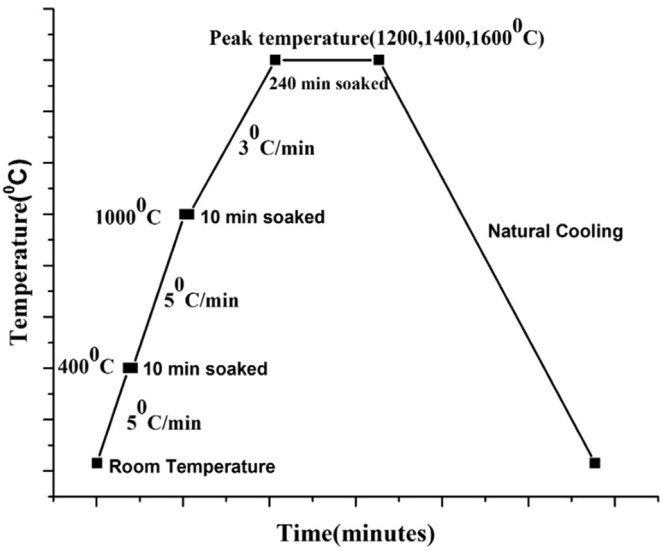

Fig. 1. Schematic of the sintering schedule.