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Effect of additives on the densification of reaction sintered and presynthesised spinels

Ritwik Sarkar*, S.K. Das, G. Banerjee

Central Glass and Ceramic Research Institute, Refractories Division, P.O. Jadavpur University, Kolkata 700032, India

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Abstract

Densification of reaction sintered and presynthesised stoichiometric spinels were studied adding various oxides as additives. Using hydroxides as starting materials, presynthesisation of spinel was done at 1400 and 1600 °C. For reaction sintered products the hydroxides were also calcined separately at 1400 and 1600 °C for similar nature of reactivity and then mixed for spinel composition. Oxides namely, B_2O_3, V_2O_5, TiO_2, Cr_2O_3 and calcined coprecipitated spinel were used as additives on both the types of spinels. Pressure-less sintering was done in the temperature range of 1550–1650 °C and the sintered products were characterised for densification study.

Keywords: A. Sintering; D. Spinels; Densification study; Additives

1. Introduction

Magnesium aluminate spinel possesses an unusual combination of properties and is an important material for materials scientists. High melting point, excellent high temperature mechanical, thermal, chemical and spalling properties have made it an essential refractory item for many applications, namely, lining materials [1] for bottom and sidewalls of steel teeming ladles, transition and burning zones of cement rotary kilns, checker work of glass tank furnace regenerators, etc. Again a combination of optical, dielectric and physicomechanical properties makes it a desirable window and dome material for use in the visible, near infrared and microwave frequency ranges [2]. The method of making spinel shapes was known from about a century ago [3] and the system $MgO–Al_2O_3$ was established in 1916 [4], which has not essentially changed. However, the use of spinel products were limited due to its higher cost of production. But with the advancement of science and technology, people became more quality conscious and the environmental friendliness character of the materials are being demanded. Dense magnesium aluminate spinel bodies with superior properties have good prospect and are in demand.

Formation of spinel from its constituent oxides is a counter diffusion process of Al^{+3} and Mg^{+2} ions and the reaction is associated with a volume expansion of 5% [5]. Reactant alumina with higher specific gravity converts to spinel of lower density results this expansion, which again does not allow the formed spinel to densify in the same firing [6]. Hence a separate firing is required to densify the formed spinel, enhancing the cost of production.

Different workers to enhance the spinel formation and to densify the material at lower temperatures used various additives. Addition of salt vapors were found [7] to enhance the spinel formation and alkali fluorides to increase the crystal growth of formed spinel which can hinder the sintering process. Kostic and others [8] reported that fluorine ion from $A1F_3$ or CaF_2 increases the solid-state reaction synthesis of magnesium aluminate spinel by increasing the cation vacancy. Addition of LiF was reported [9] to enhance the densification characteristics of spinel products through liquid-phase sintering. Better densified spinel products were also reported on the addition of different rare earth oxides namely, 5 wt.% Y_2O_3 [10], 4 wt.% of Yb_2O_3 [11] and 4 wt.% of Dy_2O_3 [11]. Yu and Hiragushi found [12] a gradual betterment in sintered density of spinel on addition of TiO_2 up to 1.5 mass%, they concluded that dissolution of TiO_2 and exsolution of Al_2O_3 in spinel was probably the reason for this betterment. Again TiO_2 was reported [13] to be a better additive for densification of magnesium aluminate

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* Corresponding author. Tel.: +91-9(0)33-483-8084; fax: +91-(0)33-473-0957.

E-mail address: ritwiksarkar@rediffmail.com (R. Sarkar).

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than MnO_2. Ju and coworkers [14] found improved resistance in spinel bodies against thermal spalling and slag attack in presence of Cr_2O_3 and also reported that Cr_2O_3 makes solid solution with spinel phase. SrO, BeO and Y_2O_3 were reported [15] to reduce the spinel formation temperature. Yi and others [16] found that presence of SiO_2 hinders the spinellisation reaction due to the formation of some intermediate compounds. Bin and others [17] found that addition of $ZrSiO_4$ and TiO_2 to magnesium aluminate spinel resulted in better densification and hot strength due to the formation of high viscous ZrO_2 and SiO_2 containing glassy phase.

The literature does not provide any parallel study on the effect of various oxide additives on densification of both reaction sintered and presynthesised spinels. The present work describes the densification behavior of presynthesised spinel, prepared at 1400 and 1600 °C from hydroxides, and reaction sintered spinel, using oxides by calcining the hydroxides at 1400 and 1600 °C. Sintering of the samples were done in the temperature range of 1550–1650 °C and additives used were 2 wt.% B_2O_3, 2 wt.% V_2O_5, 2 wt.% Cr_2O_3, 2 wt.% TiO_2 and 5 wt.% 800 °C calcined co-precipitated (from nitrate solution) spinel.

2. Experimental

Starting hydroxides were first characterised for chemical analysis, specific gravity, specific surface area and phase analysis. Calcination of each hydroxide and presynthesisation of the mixture of the hydroxides (mixed in a pot mill for 2 h) for spinel composition were done as loose powders in high alumina crucibles at 1400 °C and 1600 °C with 1 h soaking at the peak temperatures. Calcined oxides and presynthesised spinel powders were characterised for specific gravity, specific surface area and phase analysis. Calcined oxides were mixed for spinel composition in pot mill for 2 h. Two batches of presynthesised spinel (presynthesised at 1400 and 1600 °C) and two batches of calcined oxide mixtures for reaction sintered spinels (with oxides calcined at 1400 and 1600 °C) were uni-axially pressed at 100 MPa using 7 wt.% PVA solution (5 wt.% concentration) as green binder. Pressed products were dried and then sintered at 1550, 1600 and 1650 °C with 2 h soaking at the peak temperatures. Sintered products were then characterised by densification study.

Chemical analysis was done by the acid dissolution method. Specific gravity was measured by the standard method of using specific gravity bottles. The instrument of M/S Carlo Erba Strumentazole, Italy, applying BET principle and using nitrogen as the absorbed gas at liquid nitrogen temperature was used to determine the specific surface area. Phase identification was done by X-ray diffractometer (Phillips model PW 1730) at a scanning speed of 2° per min. Calcination and sintering was done in an electrically heated programmable furnace. All mixing was done in an alumina lined pot mill using alumina balls as grinding media and alcohol as medium. Pressing was done in a hydraulic press (Fred S. Carver Inc. model 2698). Densification study was done by conventional liquid displacement method using Archimedes' principle in xylene medium.

3. Results and discussion

Physico-chemical properties of the starting hydroxides are provided in Table 1. It shows that both the hydroxides are more than 97% pure as loss free basis and contain small amounts of SiO_2 Fe_2O_3, CaO and alkalis as impurities. The X-ray diffraction study reveals that source of alumina is present as a mixture of monohydrate and tri-hydrate phases. Surface area measurement shows that both the starting materials are extremely fine. Table 2 shows some physical properties of the calcined oxides and presynthesised spinels. Great reduction in surface area of the calcined oxides indicates coarsening of the particles. Presence of very minor

Table 1
Physico-chemical properties of the raw materials

Chemical analysis (weight%)	Magnesium hydroxide	Aluminum hydroxide
SiO_2	0.35	0.53
Al_2O_3	0.207	83.01
TiO_2	Trace	Trace
Fe_2O_3	0.304	0.16
CaO	1.13	1.07
MgO	67.75	Trace
Na_2O	0.066	0.18
K_2O	0.024	0.02
L.O.I.	30.3	14.6
Physical properties		
Specific gravity	2.35	3.06
Specific surface area (m^2 g^{-1})	45.6	141
Phase analysis		
Major Phase	Brucite [$Mg(OH)_2$]	Boehniite [A100H]
Minor Phase	–	Bayerite [$Al(OH)_3$]

Table 2
Physical properties of the calcined oxides and presynthesised spinel

	Calcined at 1400 °C			Calcined at 1600 °C		
	MgO	Al_2O_3	Raw mix	MgO	Al_2O_1	Raw mix
Specific gravity	3.58	3.98	3.60	3.58	3.99	3.58
Specific surface area	1.8	2.9	2.6	0.6	0.6	0.8
Phase content						
Major	P	C	S	P	C	S
Minor			P, C			

P: perictase; C: corundum; S: spinel.

amount of unreacted corundum and periclase phases in the raw mix reveals that spinel formation reaction is not completed at 1400 °C; little higher specific gravity of the spinel presynthesised at 1400 °C than that of spinel presynthesised at 1600 °C also supports the phenomenon (due to presence of heavier free corundum phase). 1600 °C presynthesisation shows complete spinellisation.

In the phase analysis study of all the sintered products, with and without additives, sintered at different temperatures, showed only spinel phase. No free additive phase and no additive bearing compound was observed for any of the conditions.

3.1. Densification without additive

A general trend of increasing bulk density with increasing sintering temperature was observed for all different spinel batches (Fig. 1). Again spinel presynthesised at 1400 °C showed relatively lower sinterability than to that of the 1600 °C presynthesised spinel. This is probably due to the presence of free oxide phases that react during sintering and hinder the densification process. But for reaction sintered products, spinel using 1400 °C calcined oxides showed much higher sintered density due to greater reactivity than the product with 1600 °C calcined oxides. Higher temperature calcination of the individual oxides increases coarseness and reduces reactivity of the materials resulting in poor density.

3.2. Densification with additives

Different additives were found to influence the densification behavior in different ways but the trend for different spinel batches was similar (Figs. 2–5). The mechanism of influence of different additives on densification behavior of different spinel batches is the same; hence the effects of the additives do not vary with variations in spinel batches.

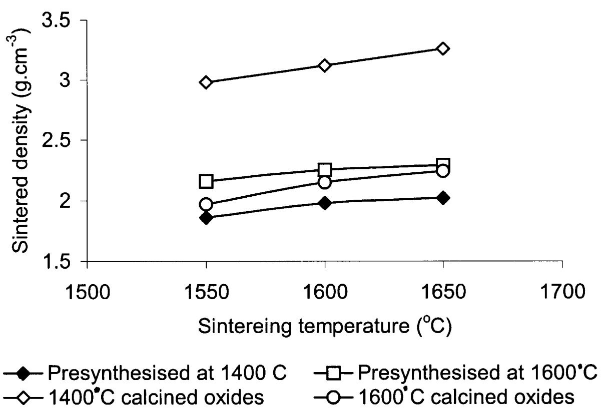

Fig. 1. Densification study of different spinel compositions without additive.

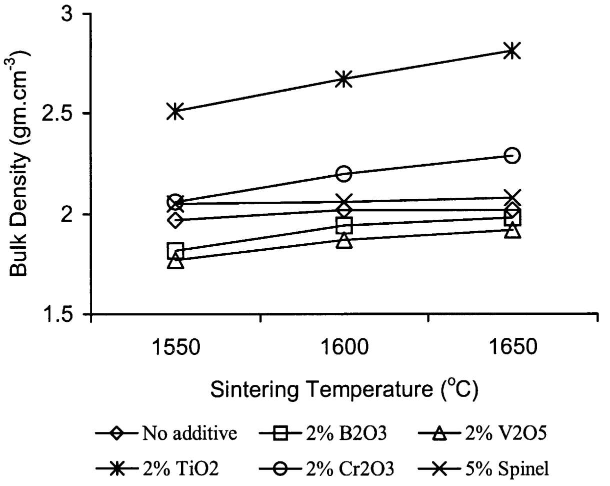

Fig. 2. Densification of 1400 °C presynthesised spinel with additives.

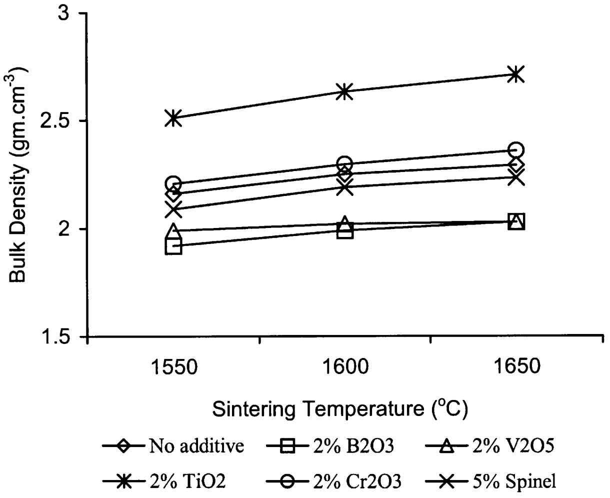

Fig. 3. Densification of 1600 °C presynthesised spinel with additives.

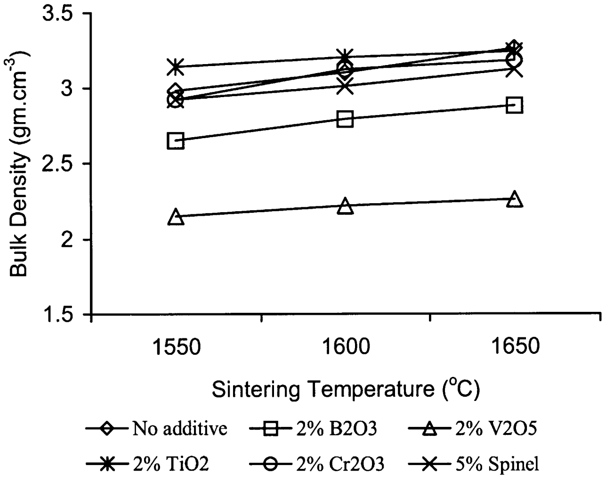

Fig. 4. Densification of reaction sintered spinel, using 1400 °C calcined oxides, with additives.

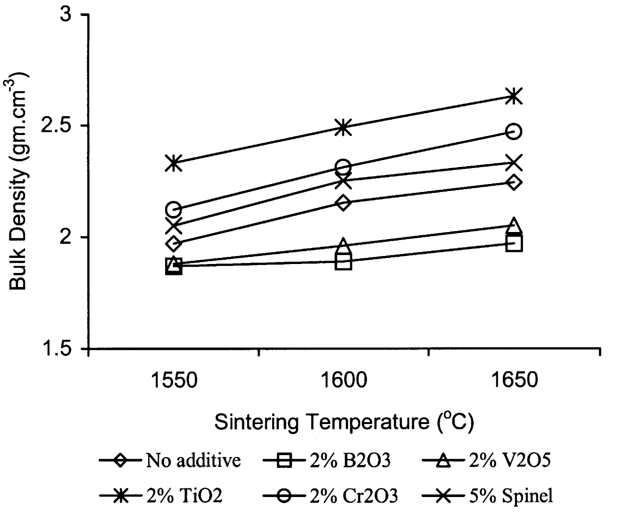

Fig. 5. Densification of reaction sintered spinel, using 1600 °C calcined oxides, with additives.

3.2.1. *Effect of TiO_2*

Addition of TiO_2 in all the different spinel batches showed (Figs. 2–5) greatest benefit than any other additives. Again increase in sintering temperature also increases the sintered density for all the batches in presence TiO_2 due to higher diffusion at higher temperatures. The literature shows that dissolution of TiO_2 and exsolution of Al_2O_3 in spinel structure [12] causes better densification in TiO_2 containing spinel bodies. Dissolution and exsolution is associated with diffusion, which enhances the mass transport for densification. Dissolution of TiO_2 in spinel structure results in cation vacancy that enhances the cation movement and mass transfer. Again titanium ion in aluminum site of spinel lattice causes lattice strain (due to higher size of the titanium, size of titanium ion is 0.68 Å and that of aluminum ion is 0.5 Å), which also enhances the mass transport process for densification.

3.2.2. *Effect of Cr_2O_3*

Cr_2O_3 also showed (Figs. 2–5) beneficial effects for all the different spinel batches and an increase in sintered density was obtained with increasing sintering temperature. Cr_2O_3 makes solid solution [14] with spinel, enters in the spinel lattice (chromium ion substitutes aluminum ion due to ionic similarities, size of chromium ion is 0.6 A and that of aluminum ion is 0.5 Å) increases diffusivity of cations and improves the mass transfer for the densification process. Again at higher temperatures the oxidation state of chromium shifts to higher values [18,19] causing a defective spinel structure, with cation vacancy, which in turn enhances the mass transfer and densification.

3.2.3. *Effect of co-precipitated spinel*

Addition of co-precipitated spinel in all the different spinel batches does not show (Figs. 2–5) much difference to that of the without additive condition. Calcined co-precipitated spinel does not provide any vacancy in spinel lattice and does not enhance the mass transfer. Hence, it has nearly no influence on the densification.

3.2.4. *Effect of V_2O_5 and B_2O_3*

Addition of V_2O_5 and B_2O_3 resulted in the poorest density, a reduction in sintered density is observed than that of the without additive ones, for all the different spinel batches (Figs. 2–5). A little increase in sintered density was also observed with the increase in the sintering temperature for all the batches. It was found from the literature that addition of V_2O_5 and B_2O_3 resulted higher crystal growth [20], which can hinder the sintering process. Again both V_2O_5 and B_2O_3 can produce low melting phases with the MgO–Al_2O_3 system that adversely affects the densification behavior.

4. Conclusion

1. Spinellisation from hydroxides was not completed at 1400 °C.
2. Reaction sintered products showed always a higher sintered density than the presynthesised spinels, both for the with additive and without additive conditions.
3. TiO_2 showed the greatest beneficial effect and Cr_2O_3 also showed some benefit on densification of all the presynthesised and reaction sintered spinels.
4. V_2O_5 and B_2O_3 showed detrimental effects on densification behavior of presynthesised and reaction sintered spinels.

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