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Ceramics International 35 (2009) 2541–2544
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Synthesis and densification behaviour of magnesium aluminate spinel: Effect of Dy_2O_3

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Received 2 January 2009; received in revised form 19 January 2009; accepted 14 February 2009
Available online 11 March 2009

Abstract

Magnesium aluminate spinels have been developed by reaction sintering of calcined alumina and calcined magnesia and its densification behaviour was studied in presence of Dy_2O_3. Green bar made from stoichiometric spinel composition with and without Dy_2O_3 were subjected to dilatometric study, densification study and microstructural evaluation by SEM. It was found that Dy_2O_3 additive does not have significant effect on the spinelisation but favours the densification of the spinel. Microstructure of sintered spinel without any additive is non-uniform with some exaggerated grain growth. Dy_2O_3 prevents the exaggerated grain growth and thereby helps in the densification process.

Keywords: A. Sintering; C. Thermal expansion; D. Spinels

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is an excellent structural ceramic material of immense technological importance. It possesses useful mechanical, chemical, and thermal properties, both at normal and at elevated temperatures [1]. On account of these properties, magnesium aluminate spinel has been used for various applications, such as refractories, humidity sensors, transparent ceramic materials and as an anode material in aluminum electrolytic cells [2–6]. The global experience has clearly shown that both the cost and the consumption of conventional refractories being used currently in steel, cement, and all other allied industries can be significantly reduced by using Mg–Al spinel-based refractories.

Synthesis of spinel and fabrication of spinel refractories are known since a century. In spite of its many advantages, a major disadvantage associated with magnesium aluminate spinel is its high cost. The commercial production of Mg–Al spinel refractory involves a double-stage firing process. The volume expansion of 5% [7] during spinel formation from the constituent oxides, magnesia and alumina, does not allow the material to densify in the same firing. Hence two-stage firing process was employed, first one to complete the spinel formation at a relatively lower temperature and second one to densify the formed spinel. This double-stage firing is quiet expensive, which may become unviable process commercially.

Magnesium chromite compositions from chromite ore having similar type of properties were in demand due to cheapness and have been used extensively in steelmaking, glass-tank regenerators, cement rotary kilns and copper industry. However, concern about the potential environmental hazards of Cr^{+6} species from these traditional chromite-based, or chromite-containing, refractories has recently intensified [8]. Within the past decade, interest has developed in magnesium aluminate spinel to replace the chromite spinels in refractories. As a consequence, synthetic Mg–Al spinel refractory aggregates for both monolithic and fired refractories have become increasingly common worldwide [9,10].

Using single-stage reaction-sintering technique, magnesium aluminates can be sintered to a very high density [11–13]. Effects of different additives on the development of spinel are well studied since long. Fluorine ion was found to enhance the spinel formation by replacing oxygen in the lattice [14,15]. Cr_2O_3 was reported to improve the thermal shock resistance and slag resistance of the periclase spinel bodies [16]. It was

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0272-8842/$34.00
doi:10.1016/j.ceramint.2009.02.011

observed that, addition of TiO_2 to spinel causes a continuous improvement in densification due to exsolution of alumina and dissolution of TiO_2 in spinel [17,18]. Ghosh et al. obtained 99% densification in magnesium aluminate spinel using ZnO as additive and suggested the formation of anion vacancy in the presence of ZnO, which results improved density and mechanical properties [19].

The role of Dy_2O_3 on the spinel formation and densification is very limited [20]. The present work was undertaken to study in detail the effect of Dy_2O_3 on the formation and densification of stoichiometric magnesium aluminate spinels ($MgO–Al_2O_3$ molar ratio 1:1).

2. Experimental

The starting raw materials used in this investigation were calcined magnesia obtained from NedMag Industries, The Netherlands, and calcined alumina obtained from Hindalco Industries Ltd., India. Both the raw materials were characterized in terms of chemical analysis, specific gravity and mineralogical analysis by XRD. Batch composition was made from the raw materials in such a way that $MgO:Al_2O_3$ molar ratio was 1:1. Dy_2O_3 (supplied by Indian Rare Earths Ltd.) was added to the above compositions at 0, 1, 2 and 4 wt.%. The batches are termed as MD0, MD1, MD2 and MD4. All the batches were individually attrition milled for 2 h by using a zirconia pot and zirconia grinding media in isopropanol medium (Union Process, USA, model 01HD). Slurry thus obtained were initially air dried and subsequently oven dried at 110 ± 5 °C, crushed to break the agglomerate and passed through 100 mesh sieve to get the desired powder. Milled powders were then mixed with 5% PVA solution as binder and uniaxially pressed at 100 MPa on hydraulic press into bars and blocks.

Dilatometric study of the green pressed cylindrical bars (10 mm diameter × 25 mm height) of MD0 and MD4 was performed in a horizontal type dilatometer (Orton, USA, model 1600D) at the heating rate of 5 °C/min up to 1500 °C. Briquettes (25 mm dia × 10 mm height) were dried at 110 ± 5 °C and sintered at 1550–1650 °C in a programme controlled electric furnace. Heating rate was maintained at 5 °C/min up to 1000 °C followed by 3 °C/min up to the final temperature with a holding time of 2 h at the peak temperatures.

The sintered magnesium aluminate spinels were characterized in terms of bulk density, apparent porosity, true density, phase assemblage and microstructure. Bulk density and apparent porosity were determined by the conventional liquid displacement method using Archimedes' principle. Phase analysis was done by X-ray diffraction technique. The diffraction patterns of the finely divided powdered samples were obtained in a Philips X-ray diffractometer (Model PW 1730) using nickel filtered Cu Kα radiation and the diffraction patterns were recorded over a Braggs' angle (2θ) range of 10–70°. Microstructure evaluation of the sintered compacts was done by scanning electron microscope (LEO, model 430i) using sputtered gold coating on the polished surface after thermal etching. Elemental analysis of selected grain and grain boundary was done by EDX technique using carbon coated sintered polished samples.

Table 1
Physico-chemical properties of raw materials.

Properties	Calcined magnesia	Calcined alumina
Chemical constituents (wt.%)		
SiO_2	0.06	–
Al_2O_3	0.23	99.3
Fe_2O_3	0.05	
TiO_2	–	
CaO	0.76	
MgO	98.56	
Alkali	–	0.3
Sp. surface area (m^2/g)	13.5	2.3
Sp. gravity	3.57	3.98
Crystalline phase	Periclase	Corundum

3. Results and discussion

3.1. Raw materials

The physico-chemical properties of the starting raw materials, i.e. magnesia and alumina are given in Table 1. The calcined magnesia used in this investigation contains 98.56% MgO. Minor amount of impurities like SiO_2, Fe_2O_3, CaO is also present as shown in Table 1. Calcined alumina contains 99.3 wt.% Al_2O_3 with 0.3% alkali as impurity. XRD study revealed that the mineralogical phases present in magnesia and alumina were periclase and α-Al_2O_3, respectively. No other crystalline phases were detected in any of these raw materials. The calcined magnesia and alumina were extremely fine, which had been revealed from their specific surface area.

3.2. Dilatometric study

Dilatometric behaviour of the green compacts with and without Dy_2O_3 is shown in Fig. 1. Dilatometric study of the green compacts shows a general trend of increasing linear

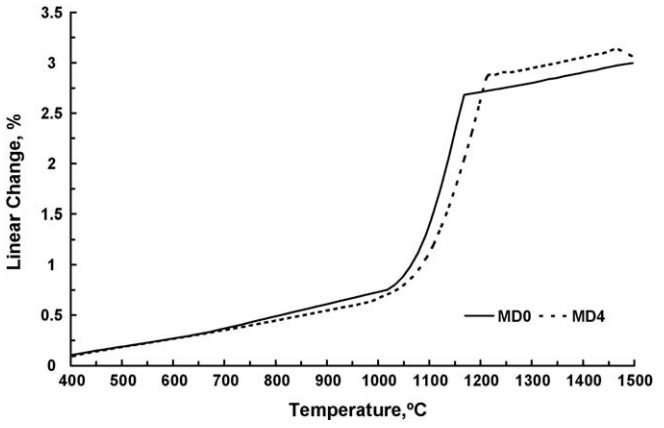

Fig. 1. Dilatometric behaviour of spinel composition without additive (MD0) and with 4 wt.% Dy_2O_3 (MD4).

change with increasing temperature. Above 1000 °C, there is sharp increase in expansion behaviour for both the samples with and without Dy_2O_3 due to the expansion resulting from spinel formation from its constituent oxides [7]. However in case of MD4 with 4 wt.% Dy_2O_3 the slope of the expansion part of the curve is less and above 1460 °C there is a negative expansion. In case of MD0 the flattening of curve starts from 1168 °C compared to that of MD4 is 1215 °C. Shrinkage from sintering begins to be little higher than the expansion from spinel formation reaction, which results in the flattening of the curve. Above 1460 °C there is a little negative expansion for MD4 samples, which may be due to much higher densification rate compared to spinelisation rate. Thus Dy_2O_3 promotes densification of stoichiometric spinel but it does not affect the spinel formation reaction significantly.

3.3. Densification

Densification is an important part of any ceramic forming process. Variation of bulk density of the spinel samples with sintering temperature and Dy_2O_3 content is shown in Fig. 2. There is an increase in the sintered density with the increase in the sintering temperature and amount of additive. Composition without additive results in a very poor density on sintering at 1550 °C, but this increases sharply with the increase in the sintering temperature. Addition of Dy_2O_3 greatly improves the densification at 1600 °C. At 1650 °C, the bulk density of 2 and 4 wt.% Dy_2O_3 containing samples is almost same and the open porosity level is almost zero. Addition of higher amount of Dy_2O_3 enhances the densification between 1550 and 1600 °C, for higher temperature the scope of further increase in sintered density is limited.

3.4. Microstructure

Scanning electron photomicrographs of the magnesium aluminate spinel developed at 1600 °C is shown in Fig. 3(a) and (b). Microstructure of sintered spinel without Dy_2O_3 is not uniform. The average grain size is 10 μm and no free MgO and Al_2O_3 grains are present. However, the grain size varies between 1 and 15 μm. The spinel grain shape is angular and

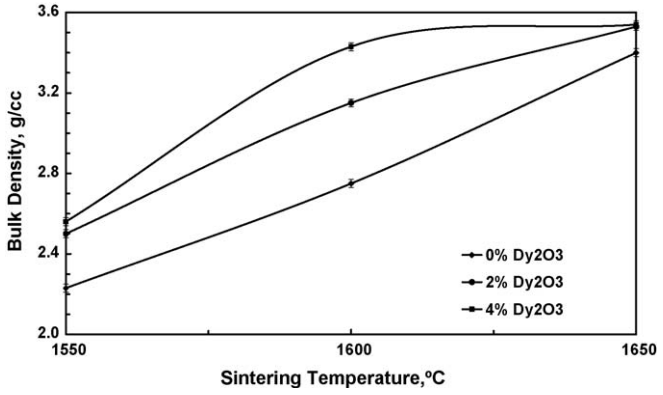

Fig. 2. Variation of bulk density of the spinel sample having different Dy_2O_3 content with sintering temperature.

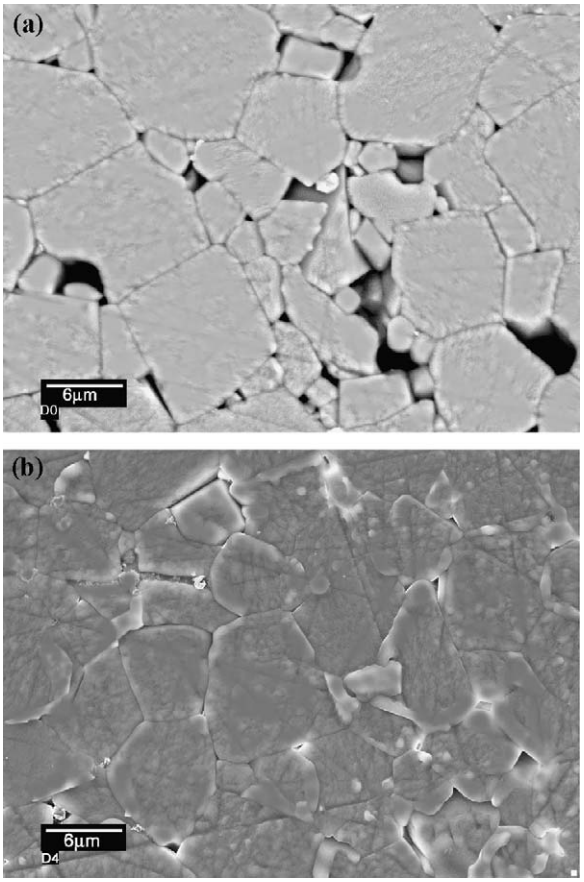

Fig. 3. Scanning electron photomicrographs of the spinel samples sintered at 1600 °C (a) without Dy_2O_3 and (b) with 4 wt.% Dy_2O_3.

pores are mainly present in the intergranular space. Fig. 3(b) is the photomicrograph of the spinel with 4 wt.% Dy_2O_3 sintered at 1600 °C. The microstructure is more uniform and compact with very small amount of intergranular pores. The very low amount of intergranular pores is responsible for the higher densification of Dy_2O_3 containing samples. Average grain size of this sintered spinel is 8.5 μm. EDX analysis of the spinel grain does not indicate solid solution of Dy_2O_3 in the spinel structure. To some extent they occupy the grain boundary position and thereby inhibit the grain growth and improve the densification. XRD pattern of both the spinel samples with and without Dy_2O_3 indicates complete conversion of MgO and Al_2O_3 to spinel.

4. Conclusion

Dense magnesium aluminate spinels are prepared by reaction sintering of calcined magnesia and calcined alumina. The presence of Dy_2O_3 enhances the densification without much effect on the spinelisation. In both the cases, spinelisation starts at ~1000 °C. For Dy_2O_3 added sample above 1460 °C the initial sintering rate increases compared to rate of spinel formation. Mg–Al spinel without Dy_2O_3 shows non-uniform microstructure with higher amount of intergranular pores. In Dy_2O_3 containing sample, the microstructure is more uniform and compact with very small amount of intergranular pores.

References

[1] C. Baudin, R. Martinez, P. Pena, High-temperature mechanical behavior of stoichiometric magnesium spinel, J. Am. Ceram. Soc. 78 (1995) 1857–1862.

[2] R.D. Maschio, B. Fabbri, C. Fiori, Industrial applications of refractories containing magnesium aluminate spinel, Ind. Ceram. 8 (1988) 121–126.

[3] I. Ganesh, S. Bhattacharjee, B.P. Saha, R. Johnson, K. Rajeshwari, R. Sengupta, M.V. Ramanarao, Y.R. Mahajan, An efficient $MgAl_2O_4$ spinel additive for improved slag erosion and penetration resistance of high-Al_2O_3 and MgO–C refractories, Ceram. Int. 28 (2002) 245–253.

[4] Y. Shimizu, H. Arai, T. Seiyama, Theoretical studies on the impedance-humidity characteristics of ceramic humidity sensors, Sensors Actuators 7 (1985) 11–22.

[5] L. Ji-Guang, T. Ikegami, L. Jong-Heum, T. Mori, Fabrication of translucent magnesium aluminate spinel ceramics, J. Am. Ceram. Soc. 83 (2000) 2866–2868.

[6] S. Angappan, L.J. Berchmans, C.O. Augustin, Sintering behaviour of $MgAl_2O_4$—a prospective anode material, Mater. Lett. 58 (2004) 2283–2289.

[7] E. Ryshkewitch, Oxide Ceramics, Academic Press, New York, 1960, pp. 257–274.

[8] D.J. Bray, Toxicity of chromium compounds formed in refractories, Am. Ceram. Soc. Bull. 64 (1985) 1012–1016.

[9] M.A.L. Braulio, L.R.M. Bittencourt, V.C. Pandolfelli, Magnesia grain size effect on insitu spinel refractory castable, J. Eur. Ceram. Soc. 28 (2008) 2845–2852.

[10] K. Goto, W.E. Lee, The direct bond in magnesia chromite and magnesia spinel refractories, J. Am. Ceram. Soc. 78 (1995) 1753–1760.

[11] R. Sarkar, H.S. Tripathi, A. Ghosh, Reaction sintering of different spinel composition in the presence of Y_2O_3, Mater. Lett. 58 (2004) 2186–2191.

[12] C.J. Ting, H.Y. Lu, Defect reactions and the controlling mechanism in the sintering of magnesium aluminate spinel, J. Am. Ceram. Soc. 82 (1999) 841–848.

[13] H.S. Tripathi, B. Mukherjee, S. Das, M.K. Halder, S.K. Das, A. Ghosh, Synthesis and densification of magnesium aluminate spinel: effect of MgO reactivity, Ceram. Int. 29 (2003) 915–918.

[14] E. Kostic, S. Boskovic, S. Kis, Influence of fluorine ion on the spinel synthesis, J. Mater. Sci. Lett. 1 (1982) 507–510.

[15] S.K. Chen, M.Y. Cheng, S.J. Lin., Reducing the sintering temperature for MgO–Al_2O_3 mixtures by addition of cryolite (Na_3AlF_6), J. Am. Ceram. Soc. 85 (2002) 540–544.

[16] D.S. Ju, G.F. Fang, C. Xi-ping, Effect of Cr_2O_3 on slag resistance of magnesia spinel refractory, Naihuo Cailiao 28 (1994) 189–192.

[17] J. Yu, K. Hiragushi, Sintering behaviour of spinel with added TiO_2, Taikabutsu Overseas 16 (1996) 61.

[18] J. Yu, K. Hiragushi, Sintering of spinel added with titania, Taikabutsu Overseas 19 (1999) 10–14.

[19] A. Ghosh, S.K. Das, J.R. Biswas, H.S. Tripathi, G. Banerjee, The effect of ZnO addition on the densification and properties of magnesium aluminate spinel, Ceram. Int. 26 (2000) 605–608.

[20] L.A. Skomorovskaya, Magnesia spinel ceramics alloyed with rare earth oxides, Glass Ceramics 50 (1993) 165–168.