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Ceramics International 29 (2003) 195–198

CERAMICS
INTERNATIONAL

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Effect of alumina reactivity on the densification of reaction sintered nonstoichiometric spinels

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Received 25 February 2002; received in revised form 6 March 2002; accepted 10 May 2002

Abstract

Densification of two different nonstoichiometric spinels (Al_2O_3 content 66 wt.% and 90 wt.%) was studied by using the reaction sintering technique. Sintered sea water magnesia and commercial alumina were used as starting materials. Reactivity of alumina was changed by calcinations between 800 and 1600 °C. Sintering for all the batches was carried out in the temperature range of 1600 and 1700 °C. Sintered products were characterized by bulk density, phase analysis and microstructure. Alumina calcined at 1200 °C was found to be optimum for densification of non-stoichiometric spinels.

Keywords: Alumina reactivity; Densification; Reaction sintered; Nonstoichiometric spinals

1. Introduction

Magnesium aluminate spinel is an excellent refractory material for its high melting point, superior strength at ambient and elevated temperatures, excellent resistance against chemical attack and thermal spalling. These properties make it a superior refractory material for applications in side walls and the bottom of steel teeming ladles, burning and transition zones of cement rotary kilns, etc. [1]. For such applications spinel is used as a major component in an alumina rich or magnesia rich matrix, depending upon the environmental conditions prevailing in the application zone. Hence, magnesia rich or alumina rich spinel (nonstoichiometric) compositions are important from the application point of view.

Spinel formation from its constituent oxides is associated with 5% volume expansion which hinders the densification process to take place in the same firing [2]. Various workers studied the effect of raw materials reactivity on spinel formation and densification. Spinel formation was found to be maximum when starting material $MgCO_3$ was calcined at 900 °C and Al $(OH)_3$ calcined at 1100 °C in presence of MgO vapour [3]. Spinel formation—to the extent of 82%—has been reported from the precursor material $Mg(OH)_2/Al_2O_3$ at 1043 K, but from $MgCO_3/Al_2O_3$ only 11% spinel formation takes place [4]. An increase in calcination temperature of the starting materials to increase the sintered density was adapted [5]. Maximum densification has been experienced [6] for co-precipitated spinel calcined at 860 °C, but further increase in calcination temperature reduces the density. Greater spinel formation from finer starting material was observed [7], though the advantage gradually reduced at higher temperatures and prolonged soaking. Higher spinellisation reaction in oxidizing atmosphere due to higher oxygen diffusion and greater vacancy reaction has been also reported [8], as well as the beneficial effect of high oxygen pressure on sintering. Calcination at 1400 °C for hydroxide starting materials was found to be optimum for densification [9]. Very high density of spinel was reported [10] by flux of vacancies, diffusing from the pore to surface, by changing the Al_2O_3:MgO ratio at the surface through MgO vapourisation.

Literature shows that reactivity of starting materials largely influences both spinellisation reaction and densification of the spinel. The present work describes a

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PII: S0272-8842(02)00105-0

densification study of two nonstoichometric spinels with Al_2O_3 content 66 and 90 wt.% by changing the reactivity of alumina. Starting alumina powder was calcined in the range of 800–1600 °C and then mixed with sintered sea water magnesia for desired compositions. Attrition milling was employed to reduce the particle size and different batches were reaction sintered at 1600–1700 °C. Sintered products were characterized by phase analysis, bulk density and microstructural evaluation.

2. Experimental

The starting materials, sintered sea water magnesia and commercial alumina were first characterized by chemical analysis, specific gravity and specific surface area measurements, and phase analysis. Alumina was calcined at 800, 1200 and 1600 °C with 1 h soaking. Uncalcined and calcined alumina was characterized by specific surface area measurement. Two different batches of spinel, with alumina content 66 wt.% (magnesia rich) and 90 wt.% (alumina rich) were prepared by mixing magnesia and alumina sources in a alumina lined pot mill for 30 min. This was followed by attrition milling for 3 h to reduce the particle size of the batches. All the batches were then uniaxially pressed at 1000 kg/cm^2, then dried at 110 °C for 24 h and sintered at 1600, 1650 and 1700 °C for 2 h. Sintered products were characterized by bulk density, phase analysis and scanning electron photomicrography.

Chemical analysis of the starting materials was done by the acid dissolution method. Specific gravity was measured by a standard method, using specific gravity bottles. Phase analysis was carried out by X-ray diffractometer ('Philips' Model PW 1730) at a scanning speed of 2° per min. All the calcinations and sintering processes were carried out in an electrically heated programmable furnace. Specific surface area was measured by BET method ('Carlo Erba' Model: SORPTY 1750) using nitrogen as adsorbed gas at liquid nitrogen temperature. Pressing was done uniaxially in a hydraulic press ('Fred S Carver Inc' Model 2698). The densification study of the sintered products was performed by conventional liquid displacement method using Archimedes' principle in xylene medium. Microstructure of the polished and thermally etched samples was observed under scanning electron microscope.

3. Results and discussion

Physicochemical properties of the starting materials are shown in Table 1. The raw materials have > 97% purity with the presence of minor impurities like SiO_2, Fe_2O_3, CaO and alkalis. Fig. 1 shows the effect of calcination temperature on the specific surface area of alumina. There is a drastic decrease in surface area of alumina when calcined above 800 °C, due to coarsening of the alumina particles. The coarsening effect is less prominent above 1200 °C.

All the sintered products were characterized by phase analysis (Table 2). The phase content of two different spinels does not change with the increase in calcination temperature of alumina or the sintering temperature of spinel. Magnesia rich spinel (Al_2O_3–66 wt.%) showed spinel as the major phase with a small amount of periclase phase. Alumina rich spinel (Al_2O_3–90 wt.%) showed the presence of both corundum and spinel

Table 1
Physico chemical properties of the starting materials

Chemical analysis	Magnesia	Alumina
SiO_2	0.06	
Al_2O_3	0.23	97.0
Fe_2O_3	0.05	
TiO_2	–	
CaO	0.76	
MgO	98.56	
Alkali		0.8
Physical properties		
Specific gravity	3.57	3.98
Sp. Surface area (m^2/gm)	–	35
Phase analysis	Periclase	Corundum

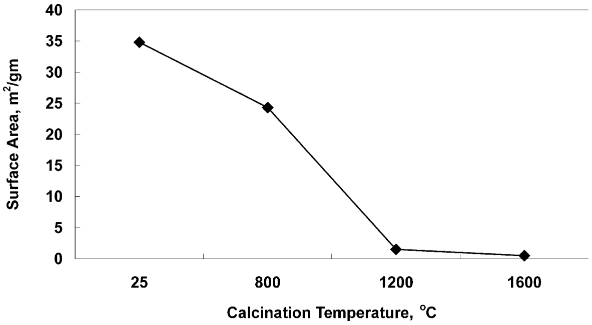

Fig. 1. Surface area of alumina after calcinations.

Table 2
Phase analysis study of nonstoichiometric spinels sintered at 1600 °C

Batch	Calcination temperature of alumina (°C)	Phase present
MgO rich	0	Spinel and periclase
	800	Spinel and periclase
	1200	Spinel and periclase
	1600	Spinel and periclase
Al_2O_3 rich	0	Spinel and corundum
	800	Spinel and corundum
	1200	Spinel and corundum
	1600	Spinel and corundum

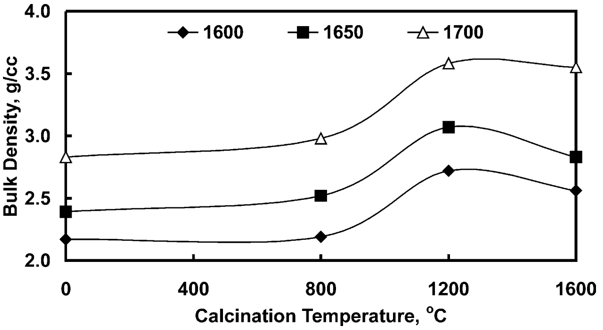

Fig. 2. Bulk density of alumina rich spinel with sintering temperature.

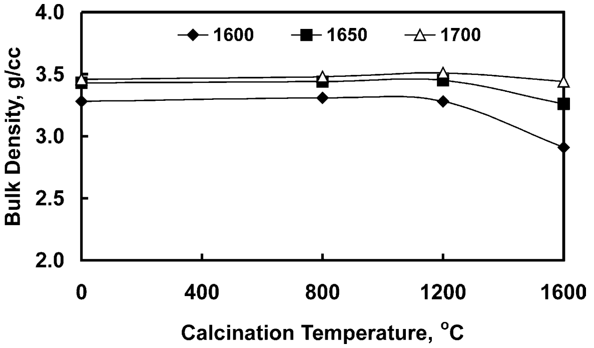

Fig. 3. Bulk density of magnesia rich spinel with sintering temperature.

phases. Calcination of alumina source does not cause changes in the phase content of the sintered products.

3.1. Densification study

The uncalcined batch shows (Fig. 2) poor densification for the alumina rich spinel. However, magnesia rich composition (Fig. 3) shows much better sinterability. The sintered density increases for both the compositions with increasing sintering temperature and the extent of increase in density is much higher for alumina rich composition. Increase in calcination temperature of alumina also greatly improves the densification of alumina rich spinel. Highest sintered density was obtained for the batch with 1200 °C calcined alumina. However, for MgO-rich spinel, high densification is observed at a lower temperature for all the batches with uncalcined and calcined alumina. Moreover, the calcination of alumina has nearly no effect on the sintered density of MgO-rich spinel. Both the magnesia rich and alumna rich compositions developed with alumina calcined at 1600 °C show a decrease in sintered density, which is associated with increased inertness at high temperature calcination.

For reaction sintering, property optimization can best be achieved if the densification of the reacting powders is completed prior to reaction [11]. Again rate of reaction depends on L^{-1} or L^{-2} and the rate of densification depends on L^{-3} or L^{-4} (where L is the mean particle size) [12,13]. Here calcination of alumina increases inertness of the system, which retards the spinel formation reaction. On the contrary, densification is being promoted by milling of the reacting powders. Hence calcination in combination with milling enhances the densification of poorly sinterable alumina rich spinel composition.

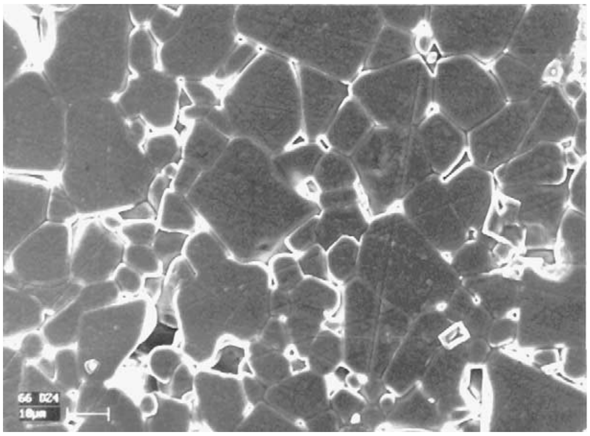

Fig. 4. SEM photomicrograph of MgO-rich spinel.

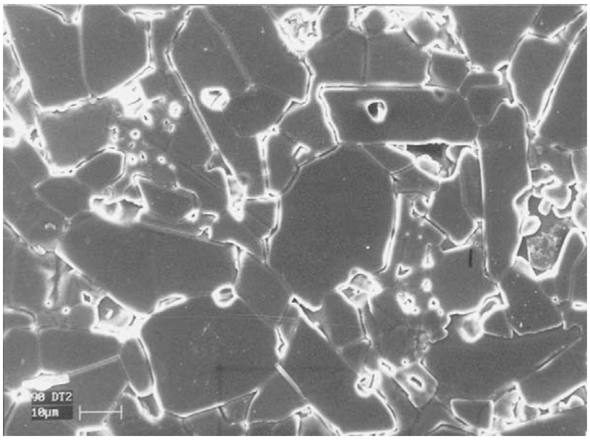

Fig. 5. SEM photomicrograph of Al_2O_3-rich spinel.

3.2. Microstructure

The SEM photomicrographs of sintered spinels are shown in Figs. 4 and 5. The grains of magnesia rich spinel (Fig. 4) are non uniform and pores are present in between the grains. The average grain size is 9.8 μm. Excess MgO is present in between the spinel grains, which suppress grain growth. The alumina rich sintered spinel (Fig. 5) consists of bigger grains with an average grain size of 13.2 μm. As excess alumina is solid soluble in spinel at the sintering temperature it facilitates grain growth. In this type of spinel some intragranular pore phase is also present along with the inter-granular one.

4. Conclusions

(1) The effect of calcination on the specific surface area of alumina powder is drastic between 800 and 1200 °C.

(2) Calcination of alumina shows no effect on the phase content of the sintered nonstoichiometric spinels.

(3) The increase in calcination temperature as well as of sintering temperature has beneficial effect on densification of alumina rich spinel. Nevertheless, 1600 °C calcined product shows slight reduction in the density, due to increased inertness (least reactivity).

(4) Increase in sintering temperature increases the sintered density of magnesia rich spinel. However, calcination of alumina source does not show any beneficial effect on its densification and calcination at 1600 °C reduces the sintered density due to increased inertness.

(5) The grain size of alumina rich spinel is higher than that of magnesia rich spinel. The presence of free MgO phase (non solid soluble in spinel) in magnesia rich spinel suppresses grain growth.

References

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

[2] E. Ryshkewitch, Oxide ceramics, Academic Press, New York, 1960.

[3] N.A.L. Mansour, Effect of magnesia and alumina characteristics on the formation of spinel, Interceram 27 (1) (1978) 49–51.

[4] D. Beruto, et al., Effect of MgO precursor microstructure on Mg–Al spinel formation from gamma alumina ultra fine particles, in: Engineering Materials, Proc. of 2nd Int. Conf., 1988, pp. 683–690.

[5] W.T. Baker, J.G. Lindsay, Reactive magnesia spinel: preparation and properties, American Ceramic Society Bulletin 46 (11) (1967) 1094–1097.

[6] R.J. Bratton, Co-precipitates yielding $MgAl_2O_4$ spinel powders, American Ceramic Society Bulletin 48 (8) (1969) 759–762.

[7] J. Petkovic, E. Kostic, S. Malcic, The effect of MgO powder activity on the synthesis and sintering of $MgAl_2O_4$, Ceramurgia 5 (40) (1975) 175–178.

[8] E. Kostic, J. Petkovic, V. Merkovic, The influence of the atmosphere on the reaction sintering in Al_2O_3–MgO system, Ceramurgia 6 (2) (1976) 81–86.

[9] R. Sarkar, S.K. Das, G. Banerjee, Calcination effect on magnesium hydroxide and aluminium hydroxide for the development of magnesium aluminate spinel, Ceramics International 26 (1) (2000) 25–28.

[10] M. Matsui, T. Takashi, I. Oda, Influence of MgO vapourisation on the final stage sintering of MgO-Al_2O_3 spinel, in: W.D. Kingery (Ed.), Advances in ceramics, vol. 10, The American Ceramic Society Inc, Columbus, OH, 1984, pp. 562–573.

[11] S. Yangyun, R.J. Brook, Preparation of zirconia toughened ceramics by reaction sintering, Science of Sintering 17 (1) (1985) 35–47.

[12] S. Yangyun, R.J. Brook, Preparation and strength of forsterite-zirconia ceramic composites, Ceramics International 9 (2) (1983) 39–45.

[13] P. Bosh, J.P. Giry, Preparation of zirconia–mullite ceramics by reaction sintering, Science of Sintering 20 (2/3) (1988) 141–148.