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Ceramics International 26 (2000) 25–28

CERAMICS INTERNATIONAL

Calcination effect on magnesium hydroxide and aluminium hydroxide for the development of magnesium aluminate spinel

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Received 5 May 1998; received in revised form 18 June 1998; accepted 4 December 1998

Abstract

Spinellisation and densification of magnesium aluminate spinel was studied. Magnesium hydroxide and aluminium hydroxide were calcined separately between 900 and 1600°C. Stoichiometric mixtures of the uncalcined and calcined materials were sintered between 1550°C to 1750°C. Spinellisation was found to be reduced with increasing calcination temperature but sintering at 1750°C produces similar spinellisation for different batches due to higher diffusivities of the diffusing species. Above 99% spinellisation was obtained for the uncalcined batch sintered at 1750°C. Densification was also found to be greatly dependent on calcination temperature. Control of reactivity by calcination and slower rate of sintering have reduced the negative effects of the single stage sintering and a maximum of 91% densification has been found for the batch with materials calcined at 1400°C.

Keywords: A. Calcination; Spinellisation and densification

1. Introduction

Magnesium aluminate spinel posseses a unique combination of high temperature thermomechanical, chemical properties and low electrical losses. Fabrication methods for producing quality spinel bodies has been known for a long time [1] but economic criteria have prevented its commercialisation. Reaction between magnesia and alumina is a counter diffusion process of Mg^{+2} and Al^{+3} ions [2] and the reaction is associated with a volume expansion of 5% [3]. This expansion hinders the densification process in the same firing and so the general practice is to complete the spinellisation in a separate firing prior to sintering [3].

Different workers have suggested different conditions and methods for obtaining maximum spinellisation and densification. Mansour [4] suggested eta (η) form of alumina, a metastable one (formed between 500 and 800°C during heating of aluminium hydroxide), is the best for spinellisation due to the similarity in crystal structure. He also suggested that the amount of spinel increases with the increase in crystal size of the starting raw materials. Jano et al. [5] found spinellisation is more effective with finer grain size of alumina but higher shrinkage for better densification has resulted in cracking and peeling of the bodies. They suggested an optimum grain size of 4 μm for alumina in magnesia alumina castables. Bakker and Lindsay [6] obtained a maximum densification of 3.46 g cm^{-3} in spinel from $Mg(OH)_2$ and $Al(OH)_3$ by completing spinellisation at 1400°C and then sintering above 1600°C. Bailey and Russel [7] introduced a new method of partial reaction technique where they obtained high density by completing partial (55–70%) spinellisation reaction first and then sintering in a separate firing. Slower rate of firing with reduced particle size of the starting materials [8] was able to produce very high densified spinel in a single stage firing process. Improved mechanical properties were also found for a purer variety of materials.

Here an attempt has been made to study both the spinellisation and densification of magnesium aluminate in the same firing. Effects of calcination temperatures on the characteristics of alumina and magnesia were examined, and how these calcined materials, with different characteristics, affect the spinellisation and densification process was also studied.

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0272-8842/99/$20.00
PII: S0272-8842(99)00014-0

2. Experimental

Magnesium hydroxide and aluminium hydroxide, the starting materials, were characterized in terms of chemical analysis, specific gravity, specific surface area (S.S.A.) and powder X-ray diffraction (XRD). Hydroxides were then separately calcined at 900, 1200, 1400 and 1600°C with 1 h soaking at the peak temperatures. Calcination was done as loose powders in inert high alumina crucibles with a heating rate of 4°C per min. Calcined materials were again characterized by powder XRD, specific surface area and specific gravity. Uncalcined and calcined (at each temperature) materials, taken for stoichiometric composition, were wet mixed in an alumina ball mill for 1 h. Mixed materials were dried and then pressed to briquettes (25×10 mm) in an isostatic press (made by Autoclave Engineers) at 175 MPa with polyvinyl alcohol as binder. Briquettes were dried and sintered between 1550 and 1750°C for 2 h soaking with a heating rate of 1°C per min. Sintered briquettes were tested for spinellisation and densification.

Specific surface area was determined by using BET method with nitrogen as the absorbed gas at liquid nitrogen temperature. Powder XRD was done using Cu-K_α radiation with Ni filter, in the diffraction range of 10–65°. Densification study of the sintered briquettes was carried out by using the liquid displacement method in xylene under vacuum. Spinellisation study was evaluated by using powder X-ray diffraction of all the samples and comparing them against a standard spinel sample.

3. Results and discussion

Chemical and physical properties of the starting hydroxides are provided in Table 1. Effect of calcination on the specific gravity and specific surface area of the hydroxides are shown in Figs. 1 and 2 respectively. XRD patterns show only periclase phase at and above 900°C for Mg-hydroxide. For Al-hydroxide both alpha (α) and gamma (γ) Al_2O_3 phases are present at 900°C and only alpha (α) Al_2O_3 at and above 1200°C.

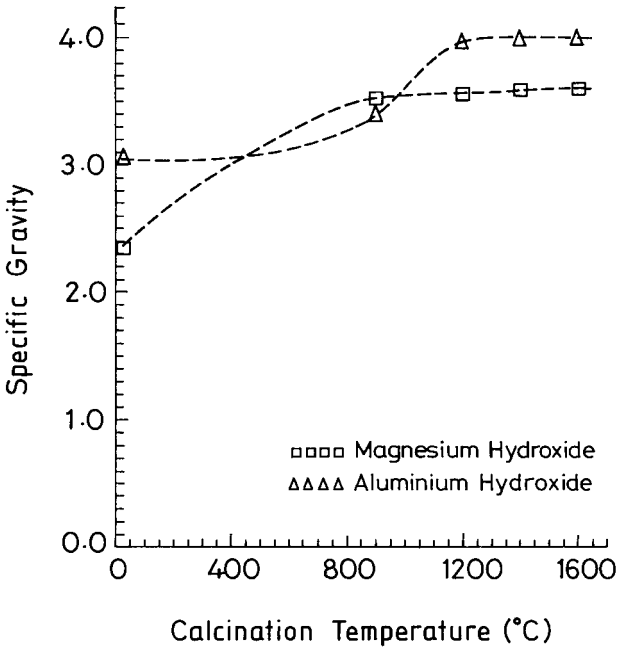

Fig. 1. Effect of calcination temperature on the specific gravity of the raw materials.

Calcination of the starting materials causes inertness and this reduced the spinel content (Fig. 3) in the sintered bodies. But higher diffusivities of the diffusing Mg^{+2} and Al^{+3} ions at 1750°C has resulted in similar spinellisation for all the different temperature calcined batches. Again calcination has a great influence on the densification behaviour (Fig. 4). Reactive (uncalcined and low calcined) materials showed poor density and densification was found to increase with calcination. But most inert, 1600°C calcined materials showed a sharp fall in density due to the greater coarsening of the starting materials on calcination. Increase in green density with increasing calcination temperature (Fig. 5)

Table 1
Physico-chemical properties of the raw materials

Chemical analysis									
	SiO_2	Al_2O_3	TiO_2	FC_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I.
Mg-hydroxides	0.35	0.207	Tr.	0.034	1.13	67.75	0.066	0.02	30.3
AI-hydroxides	0.53	83.01	Tr.	0.16	1.07	Tr.	0.18	0.02	14.6

Physical properties				
	Sp.Gr.	S.S.A. ($m^2\ g^{-1}$)	Phase analysis	
			Major	Minor
Mg-hydroxide	2.35	45.6	Brucite	
Al-hydroxide	3.06	141.1	Boehmite	Bayerite

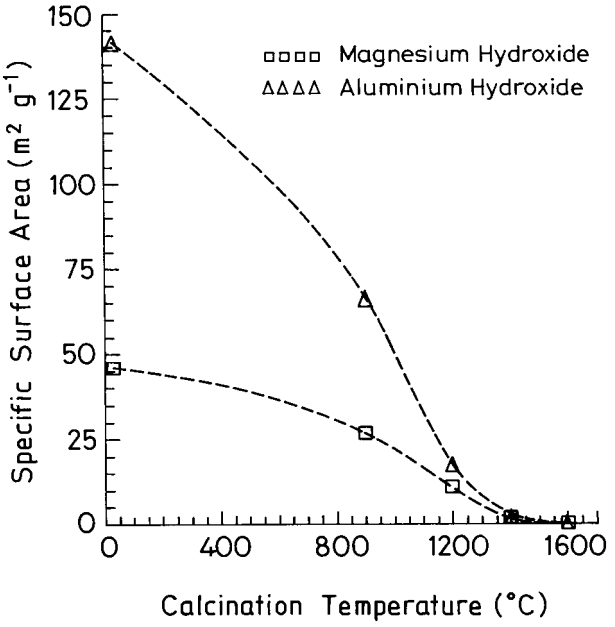

Fig. 2. Effect of calcination temperature on the specific surface area of the raw materials.

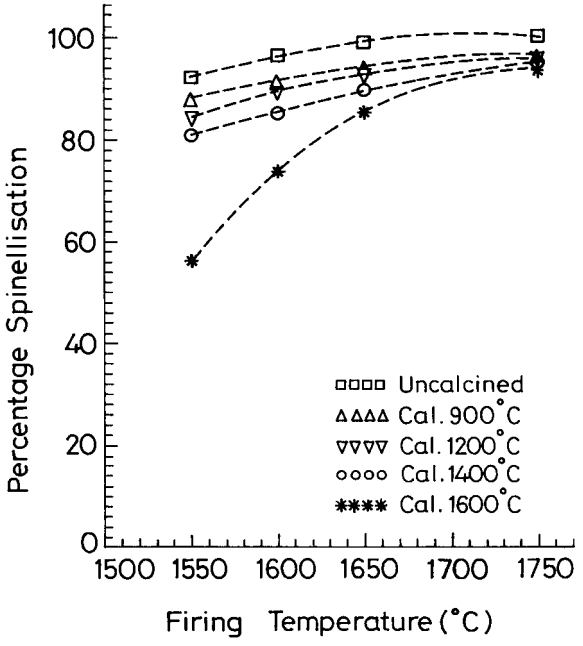

Fig. 3. Spinellisation study of the uncalcined and calcined batches.

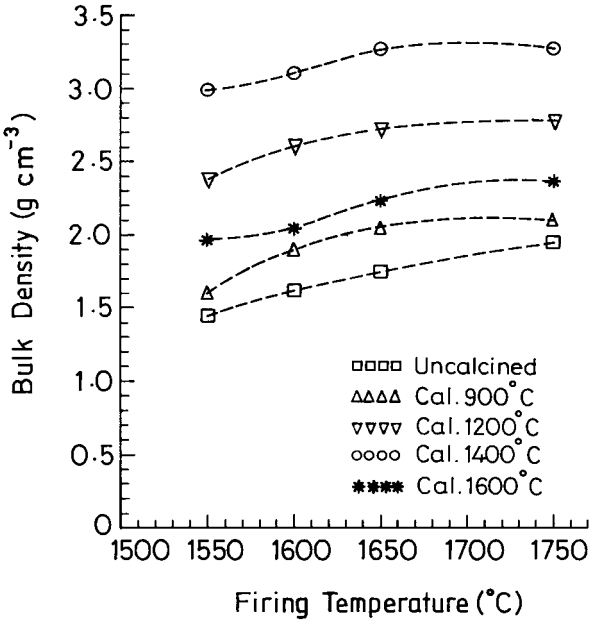

Fig. 4. Densification study of the uncalcined and calcined batches.

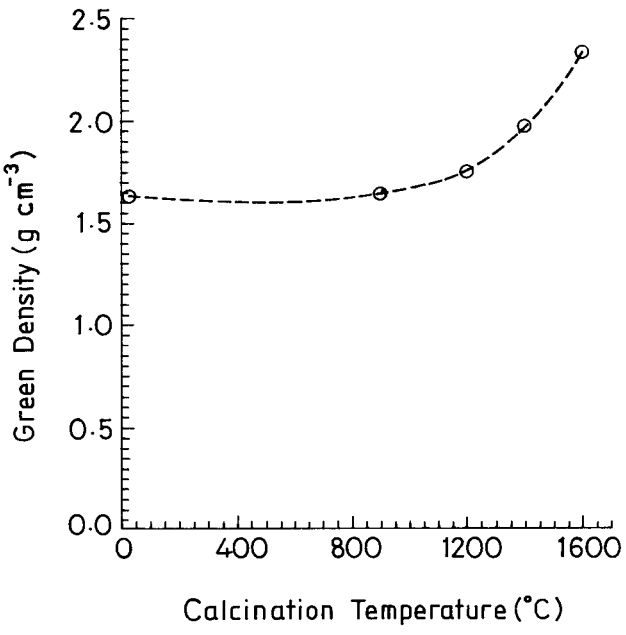

Fig. 5. Variation of green density with calcination temperature.

might have some beneficial effect even after sintering (except for the 1600°C calcined batch).

Uncalcined and low calcined (900°C) materials had higher reactivity, resulting in more intense reaction, and produced more spinel with poorer density. Densification increases with decreasing reactivity by calcination. Here, comparatively coarser particles densify intensely and this supports the findings of Petkovic and Ristic [9] who concluded that particle size much finer to a certain critical value is of no benefit for densification. Slower heating rate again reduces the intensity of the reaction and associated expansion. These (lesser reactivity and slower heating) have helped the spinel to densify in a single stage. Very coarse (< 1 m^2 g^{-1}) 1600°C calcined materials showed poor density which has obeyed the general conditions of sintering.

4. Conclusion

An attempt has been made to complete both the spinellisation and densification process of magnesium aluminate spinel in a single stage firing. Spinellisation reduces with increasing calcination temperature but very high temperature of sintering overcomes the problem for higher diffusion processes. Above 99% spinellisation was obtained for the hydroxide batch fired at 1750°C. Densification was found to be greatly influenced by the calcination process. A slower rate of sintering with reduced reactivity of the reactants has influenced the spinel to densify in a single stage process. The hydroxide batch showed the minimum densification, and a maximum density of 3.26 g cm^{-3} (91% of true density) was found for the batch with magnesia and alumina calcined at 1400°C.

Acknowledgements

The authors are highly obliged to the Director, CG & CRI, Calcutta, for his keen interest and kind permission to publish the paper. The authors are also obliged to Dr. A. K. Chakraborty, Dr. B. Mukherjee, Mr A. Ghosh, Dr. K Das and Mr J. R. Biswas for their kind help in carrying out different experiments regarding the paper.

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