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HYDROTHERMAL PROCESSING OF CERAMIC POWDERS FOR ALUMINA-MAGNESIA SPINELS

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Composite powders for spinels, $MgO \cdot nAl_2O_3$ ($n = 1$ and 2), have been synthesized hydrothermally using commercially available hydroxide reactants. The synthesis was carried out in an aqueous suspension using a pilot plant installation operating at 4 MPa corresponding to a saturated steam temperature of 523 K. Powder characterisation has shown that the particle size ranges from 2 to 10 μm. Sintering of preformed green bodies without the use of additives was carried out at 1873 K in air resulting in a dense material. Structure and microstructure have been studied by X-ray diffraction and scanning electron microscopy. Compressive strength of the spinels has been determined.

1. Introduction

Magnesia–alumina spinels ($MgO \cdot nAl_2O_3$) are candidate materials for structural applications at high temperatures [1–3]. On a laboratory scale synthesis has been studied by solid state reaction using analytical grade oxides. The sintering behavior indicates that densification may lead to virtually near net shaped products [1]. With respect to the aforementioned, there is a need to produce magnesia–alumina based spinels on a large scale using commercially available hydroxide reactants. A hydrothermal process which has been developed for the production of ceramic powders [4,5] is a possible alternative to the solid state synthesis, the advantage of this method being the expected homogeneity of the reaction product.

2. Experimental

Two series of batches for the hydrothermal synthesis of magnesia–alumina composites were prepared using magnesium hydroxide, 99% type C from Dead Sea Periclase (Israel) and aluminium hydroxide, 99%, SH 100 from Sochalu (France). The reactants were weighed and mixed separately in water for 15 min at 333 K. Subsequently the two aqueous mixtures were fed into the laboratory reactor. The first batches, denoted spinel I, contained equimolar quantities of both hydroxides based on the oxides, i.e. forming $MgO \cdot Al_2O_3$. The second batches, denoted spinel II, contained a double amount of aluminium hydroxide, i.e. forming $MgO \cdot 2Al_2O_3$. The hydrothermal synthesis has been described in detail previously [6,7]. The pilot plant consists of two vessels connected to one another by means of a heat exchanger (fig. 1). One vessel is the reaction vessel. Its walls are heated electrically or with thermal oil (Santotherm 66). The contents of the reaction vessel, 50 kg water and 1 kg reactants, is stirred continuously. The reaction time is 4 h, measured from the moment the vessel reached its pressure of 4 MPa at the corresponding saturated steam temperature of 523 K. After the reaction is completed, the products are transferred through the heat exchanger into the

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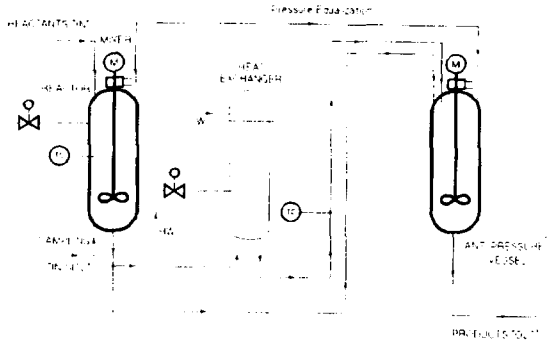

Fig. 1. Schematic set up of the laboratory hydrothermal plant.

receiving vessel under controlled laminar conditions by creating a small difference in pressure between the two vessels. Damage of the product crystals is therefore avoided. The hydrothermally treated slurries thus obtained were fed into a laboratory spray dryer. The resulting powders are virtually dry, 0.6% was the highest recorded residual moisture content.

Pellets and tablets were pressed uni-axially in a dye at a pressure of 13.5 MPa from approximately 2 g of the powders harvested from the spray dryer. Green densities of about 55% of the theoretical were achieved without the use of any binder.

The pellets were sintered under atmospheric conditions for two hours at 1873 K; both heating and cooling rates were 5 K/min. During sintering a weight loss of about 24% occurred, consistent with the formation of water from the decomposition of the hydroxide and oxide-hydroxide.

3.Results and discussion

X-ray diffraction showed that the hydrothermally treated powders consist of boehmite, AlOOH and magnesium hydroxide, $Mg(OH)_2$ (table 1). No spinel has been formed during the hydrothermal treatment, probably due to problems with the solubility of the reactants. Although the diffraction pattern shows two compounds, in the SEM micrograph of fig. 2 only one type of crystal can be observed. This indicates that during the hydrothermal treatment a coprecipitation of the two compounds occurs. The rather broad lines of boehmite in the diffraction pattern suggest, that boehmite is in the form of very fine particles.

Table 1
X-ray diffraction data for (a) the hydrothermally treated powder with starting composition $Mg(OH)_2$·$[Al(O)H)_3]_2$=spinel I; (b) spinel I after sintering; (c) spinel II after sintering.

d-value (a)	*d*-value (b)	*d*-value (c)
4.78 [a]		4.624 [c]
		3.463 [d]
3.174 [b]		2.846 [c]
	2.860 [c]	
2.725 [a]		2.544 [d]
	4.445 [c]	2.544 [d]
2.351 [a,b]		2.428 [c]
		2.375 [d]
	2.027 [c]	2.081 [d]
1.985 [b]		2.013 [c]
1.864 [b]		
1.797 [a]		
1.779 [b]		
1.667 [b]	1.653 [c]	1.737 [d]
		1.645 [c]
1.575 [a]		1.600 [d]
	1.559 [c]	
1.535 [b]		1.551 [c]
1.529 [b]		
1.496 [a]		
1.458 [b]		
1.440?	1.432 [c]	
1.400 [b]		1.426 [c]
1.388 [b]		1.404 [d]
1.377 [a]	1.369 [c]	
	1.280 [c]	1.373 [d]
	1.234 [c]	
	1.168 [c]	
	1.133 [c]	

[a] $Mg(OH)_2$ JCPDS: 7-239; [b] AlOOH JCPDS: 21-1307; [c] $MgAl_2O_4$ JCPDS: 21-1152; [d] Al_2O_3 JCPDS: 10-173.

The particle size distribution was determined by means of a laser beam operated Fraunhofer diffraction analyser, Sympatec, type Helos. More than 80% of the particles harvested from the spray dryer have sizes between 2 and 10 μm. This is an extremely narrow distribution and a relatively small grain size, which is beneficial for sintering behaviour [8]. The results of the hydrothermal treatment of spinel I are similar to those of spinel II [9].

X-ray diffraction of the sintered pellets showed, that the boehmite–magnesium hydroxide mixture was completely transformed to spinel, $MgAL_2O_4$

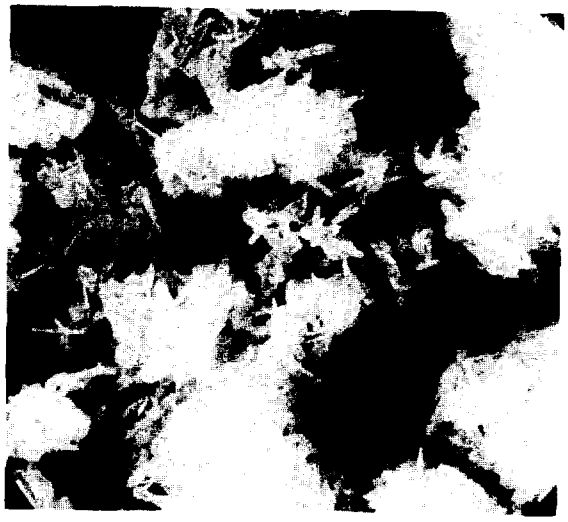

Fig. 2. Scanning electron micrograph of spinel I, showing one type of crystals with uniform size.

Fig. 3. Scanning electron micrograph of a fracture surface of spinel I, showing the absence of pores of second phase.

(table 1), and spinel plus alumina Al_2O_3 (table 1) in case of spinel II, where an excess of boehmite was present. The interplanar spacings of spinel in spinel II are somewhat smaller than in spinel I, suggesting that some alumina has dissolved in spinel.

A volume contraction of 74% results in densities greater than 94% of theoretical for spinel I, although a large amount of water has to be removed during sintering and no sinter additives have been used. The extent of densification is illustrated by the micrograph of the fractured surface of spinel I in fig. 3. Only a few pores are left. Spinel II does not show such a great densification, as illustrated in fig. 4. We clearly see a second phase present (alumina). It should be noted here, that this densification is accomplished in a single, short sinter procedure, which is very simple compared to the process necessary if other reactants are used [10]. This is probably due to the very intimate mixture existing in the hydrothermally treated powders, since a common mixture of boehmite and magnesium hydroxide does not reach such high densities in the same procedure.

The sintered pellets were exposed to destructive testing on a laboratory Instron, model 1000 with a maximum load of 5 kN. Since the shape of the pellets concerned is that of a tablet with spherical ends, loads will always be applied in the form of point or contact loads. Because of the very small area involved, contact stresses for even small loads are very high. The point load, N, upon collapse of the pellets was recorded and used in the Herz equation [11] to calculate the compressive strength. The static tests were carried out at 300 K and the results are presented in table 2. These results indicate that the pellets have reproducable properties. Furthermore, the presence of an excess of alumina in spinel II seems to weaken the samples.

Fig. 4. Scanning electron micrograph of a fracture surface of spinel II, showing pore formation and the presence of a second phase.

Table 2
Data on the destructive testing of spinel I and spinel II.

	Sample no.	Load in N	Compressive strength (MPa)
spinel I	1	86.9	609.5
	2	86.4	608.3
	3	87.4	610.6
spinel II	1	76.6	584.3
	2	76.6	584.3
	3	78.6	589.3

The values of the compressive strength of both spinel I and II are much larger than the 130 MPa given by Gray [12]. The small grain sizes in the sintered pellets might be responsible for this.

4. Conclusions

(1) The present hydrothermal treatment of commercially available hydroxides yields highly sinteractive magnesia–alumina spinel precursors.

(2) Sintering of the magnesia–alumina spinel precursors leads to the formation of spinel with a density greater than 94%, without the use of sintering aids.

(3) Compressive strength data are at least a factor 4 better than published data.

(4) Scanning electron microscopy and mechanical testing show that an excess of alumina is not desirable.

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