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Mechanochemical synthesis and sintering behaviour of magnesium aluminate spinel

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X-ray amorphous precursor phases for the synthesis of spinel ($MgAl_2O_4$) have been prepared by grinding mixtures of gibbsite ($Al(OH)_3$) with brucite ($Mg(OH)_2$) or hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$). The mechanochemical treatment does not remove any water or carbonate, but converts some of the gibbsite octahedral Al sites into tetrahedral sites and other sites with a ^{27}Al MAS NMR resonance at about 38 ppm. The brucite-derived precursor forms spinel on heating at ≤850°C, by contrast with unground mixtures which show little spinel formation even at 1250°C. The hydromagnesite-derived precursor transforms at about 850°C into a mixture of spinel and hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), the latter decomposing to spinel and MgO by 1050°C. Spinel derived from the hydromagnesite-containing precursor shows superior pressureless sintering properties at 1400–1600°C, producing a body of 97% theoretical bulk density at 1600°C. Under the same conditions, the brucite-derived spinel sintered to 72% theoretical density and showed a morphology consisting of widely disparate grain sizes.

1. Introduction

Magnesium aluminate spinel, Mg_2AlO_4 is commonly used as a refractory material in heavy industries because of its excellent mechanical and thermal properties at elevated temperatures [1]. Its solid state synthesis from magnesia and alumina occurs by interdiffusion ($3Mg^{2+} \leftrightarrow 2Al^{3+}$) of cations through the product layer between the oxide particles [2], necessitating the use of high processing temperatures (>1400–1500°C) [2, 3]. The formation of Mg-Al spinel from a mixture of magnesia and alumina is accompanied by a large volume expansion (theoretically 8% [3]) which makes it difficult to obtain dense spinel ceramics by single stage firing. However, Sarkar *et al.* [4] obtained high density spinel ceramics in a single firing by using aluminium and magnesium oxides derived from their parent hydroxides in a preliminary heating at 1400–1600°C, followed by attrition milling of the mixtures to reduce their particle size. Their results suggested that finer and more inert materials show greater densification and avoid the harmful effect of spinelization. Similarly Itatani *et al.* [5] obtained 96% densified spinel ceramics at 1700°C by using 0.2 μm magnesium aluminate powder produced by vapour-phase oxidation.

Tomilov and Devyatkina [6] have synthesised spinel at 800–1000°C from poorly crystalline layer-structure magnesium aluminate hydroxides. Spinel powder synthesised at 1000°C by their route had a specific surface area (SSA) of 80 m^2/g and a particle size <0.1 μm [6]. Tarasov and Isupov [7] synthesised magnesium aluminate of similar structure by "soft" mechanochemical methods from mixtures of crystalline hydrates of soluble Mg and Al salts with excess alkali or ammonium carbonate (or hydrogen carbonate).

"Soft" mechanochemical reactions require at least one component to contain water or hydroxyl groups [8–10]. Normally only short grinding times are necessary, although Mazerollos *et al.* [11] milled of equimolar Al_2O_3-MgO mixtures for 4 days to form the spinel phase. Such prolonged grinding in tempered steel sealed containers with steel balls caused iron contamination which necessitated an acid washing step.

It would therefore be beneficial to be able to obtain the magnesium aluminate precursor by mechanochemical processing; this could then be converted at about 1000–1050°C to spinel with a high surface area and low particle size [6] to achieve good sintering behaviour.

In the present work we have synthesised magnesium aluminate precursors from mechanochemically treated mixtures of aluminium hydroxide with both magnesium hydroxide and basic magnesium carbonate and compared the spinel formation and sintering behaviour of the products derived from the two precursors. Spinel synthesis from mechanochemically activated precursors was compared with the process in unground mixtures heated under similar conditions.

2. Experimental procedure

The starting materials were aluminium hydroxide (gibbsite), basic magnesium carbonate (hydromagnesite), both of analytical reagent grade (Reachim, Russia) and magnesium hydroxide (brucite). The latter was prepared by dissolving 1 mole $MgCl_2 \cdot 2H_2O$ in deionized water, precipitating with ammonia solution and washing well with distilled water to eliminate traces of chloride. 1 : 1 $MgO : Al_2O_3$ mixtures were prepared by batching $Al(OH)_3$ with both $(Mg(OH)_2$ and $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ and ground for 4 h in a Fritsch planetary mill (Pulverisette 5) at a rotation speed of 300 rpm. These samples are designated MH and MC respectively. Both the pot and milling media were of corundum and the weight ratio of balls to powder was 15 : 1. During grinding, the mill was stopped every hour for 10 min. After grinding, the samples were examined by DTA-TG (Rigaku Thermoplus TG8120), XRD (Siemens D-5000 diffractometer with Cu K_α radiation) and solid state ^{27}Al MAS NMR at 14.1T, using a Chemagnetics Infinity 600 MHz spectrometer with a 3.2 mm. MAS probe in which the sample was spun at 18 kHz. The spectra were acquired at 156.374 MHz using a 15° pulse of 0.5 μs and a recycle time of 1 s and were referenced by using the secondary standard of the AlO_6 resonance of $Y_3Al_5O_{12}$ at 0.7 ppm.

The ground precursors, and a comparison set of unground mixtures, were then fired in air for 1 h. at various temperatures chosen with reference to the thermal analysis curves. Crystalline spinel powders were synthesised by firing the precursors at 1000°C for 1 h. then densified as follows:

The powder was ball milled in isopropanol for 1 h. using corundum milling media, the mass ratio of balls to powder being 2 : 1. The slurry was then dried at 100°C, uniaxially pressed into pellets at 100 MPa and sintered in air at 1400, 1500 and 1600°C with a 2 h. holding time. The sintering heating rate was 4°C min^{-1}. The densities of the synthesised powders were determined using a Micromeritics AccuPys 1330 instrument, and the bulk densities of the sintered samples were determined by the Archimedes principle. The microstructure of the fractured pellet surfaces was observed using a CamScan 3 scanning electron microscope.

3. Results and discussion

Fig. 1 shows the XRD powder patterns of the ground and unground samples.

Grinding caused both mixtures to become amorphous, although MH (Fig. 1B) shows broad reflections between $2\theta = 17° - 21°$ and $36° - 41°$, these regions corresponding to several of the spinel reflections, suggesting the incipient formation of the cubic phase in the still-hydrated sample. The highly reactive nature of this system is similar to that of magnesium hydroxide-silicic acid systems [12] in which a layer structure of low crystallinity has been shown to be formed by mechanochemical treatment. The ease with which the crystalline structure of aluminium hydroxide is distorted by milling has previously been reported [8, 10]; this may account for the ease with which spinel precursors are mechanochemically formed by grinding gibbsite with magnesium hydroxide [12, 13]. After grinding, sample MC shows very weak residual reflections of basic magnesium carbonate superimposed on a broad amorphous background feature (Fig. 1D).

Differences in grinding behaviour may occur with components of greatly differing hardness or rheological properties. In the present experiments, the hardness of brucite and gibbsite is similar (2.5) while that of hydromagnesite is not very much greater (3.5). Thus, any disparities in the grinding behaviour of the two mixtures would not be expected to arise for this reason.

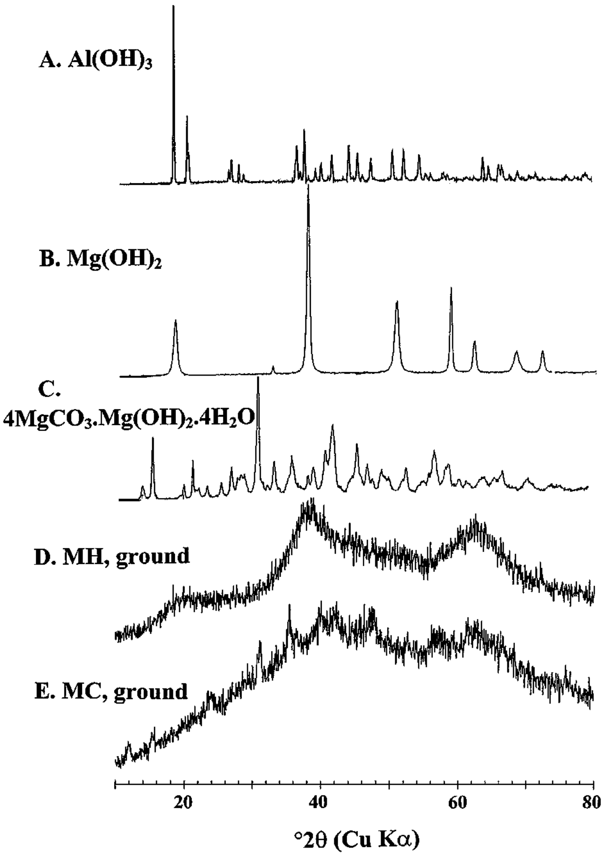


Figure 1 Powder X-ray diffractograms of the starting materials and ground mixtures MH ($Al(OH)_3$ + $Mg(OH)_2$) and MC ($Al(OH)_3$ + $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$).

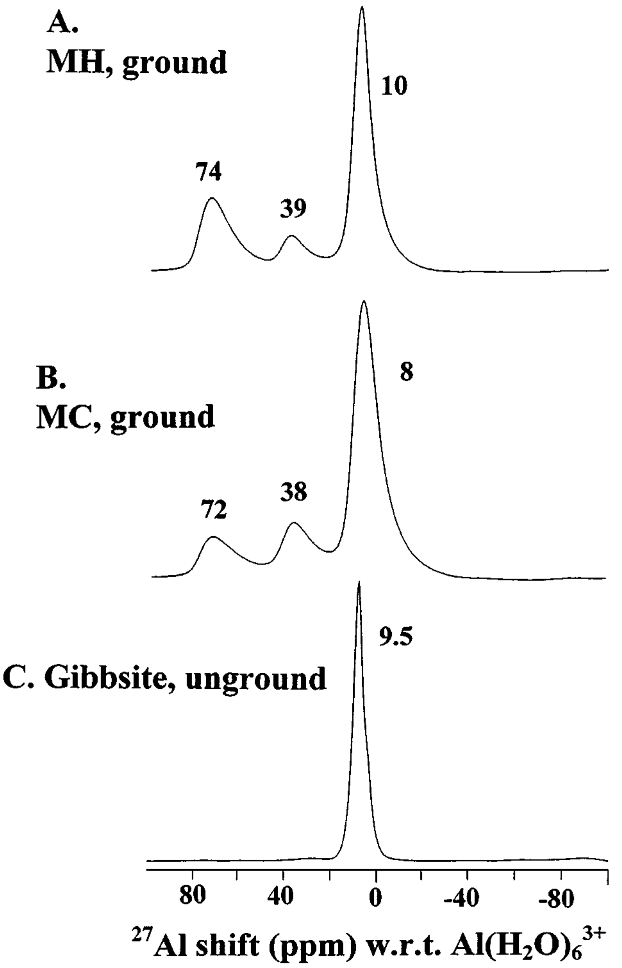


Figure 2 14.T ^{27}Al MAS NMR spectra of gibbsite and the mixtures MH and MC ground for 4 hr.

Fig. 2 shows the ^{27}Al MAS NMR spectra of the gibbsite and the ground mixtures MH and MC. In both MH (Fig. 2A) and MC (Fig. 2B), grinding causes some of the octahedral Al of gibbsite, (characterised by the resonance at 9.5 ppm) to be converted to tetrahedral (resonance at 72–74 ppm and to a third type of site, characterised by a resonance at 38–39 ppm. The latter has been identified as arising from Al in either penta-coordinated sites [14] or in distorted tetrahdral triclusters associated with a charge-balancing oxygen vacancy [15]. Such an NMR resonance is common in amorphous aluminates or aluminosilicates where its presence is taken as indicating a degree of homogeneity. Accurate simulation of such spectra requires a detailed determination of the mean interactions and their distributions [16]. However, semi-quantitative estimates of the relative intensities of these peaks were made by direct spectral integration. These results show the more highly reactive present mixture (MH) contains a higher porportion of tetrahedral intensity than MC (25.4% and 12.5% respectively), and relatively less of the 39 ppm resonance (9.8% and 15.5% in MH and MC respectively). Since the final product (spinel) contains only tetrahedral and octahedral Al, the early formation of a precursor phase containing tetrahedral Al sites is more beneficial. This is confirmed by the appearance of broad spinel reflections in ground MH even prior to thermal dehydration.

3.1. Thermal reactions of the spinel precursors

Fig. 3 shows the thermal analysis traces of the ground and unground mixtures heated in air to 1300°C.

The DTA trace of the unground sample MH (Fig. 3A) shows several endotherms associated with the dehydroxylation of the gibbsite (299°C) and brucite (392°C) [17]. The two smaller endotherms at 250 and 530°C are also associated with the gibbsite decomposition, the latter being attributed to the decomposition of a small amount of boehmite formed in the primary gibbsite decomposition reaction [17]. The weight losses associated with these endotherms are as expected for the overall thermal reaction:

$$2\text{Al(OH)}_3 + \text{Mg(OH)}_2 \rightarrow \text{MgAl}_2\text{O}_4 + 4\text{H}_2\text{O}\uparrow \quad (1)$$

predicting a loss of 25.2% and 8.4% from the gibbsite and brucite components respectively. The observed loss from the gibbsite (including the boehmite contribution >450°C) is 24.5%, and that from the brucite is 8.8% (Fig. 3E), both in satisfactory agreement with the theoretical values. The small exothermic feature at about 830°C may be associated with the formation of a small

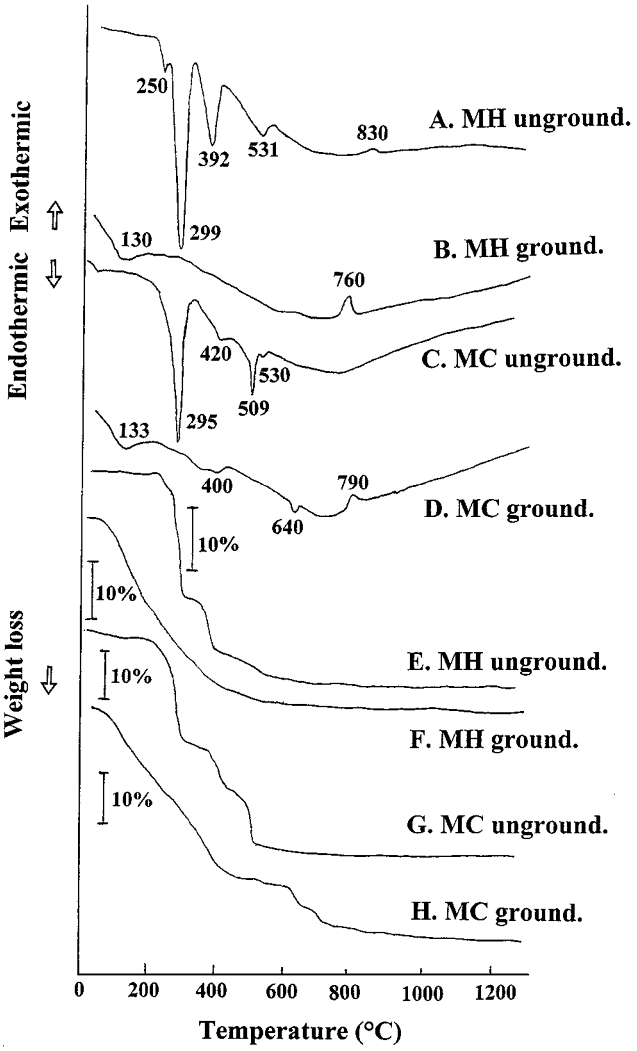


Figure 3 Thermal analysis traces of the unground and ground mixtures MH and MC. (A–D) DTA traces, (E–H) TG curves. Heating rate: 10°C·min^{-1} in air.

amount of crystalline product, but the amount is too small to be detected by XRD at that temperature (see below).

The DTA trace of ground mixture MH (Fig. 3B) shows a much broadened endotherm at about 130°C and an exotherm at 760°C. The individual weight losses of $Al(OH)_3$ and $Mg(OH)_2$ are merged by the grinding into one gradual loss of 33.3% which is complete by 600°C (Fig. 3F). This total weight loss is in good agreement with the theoretical value (33.6%) for complete dehydroxylation, indicating that the mechanochemical reaction does not involve dehydration. The exotherm at 760°C is related to spinel crystallization, which occurs shortly after the removal of the last of the water from the system.

The DTA trace of unground MC (Fig. 3C) shows several endothermic events as expected for the decomposition of the components. The major gibbsite decomposition peak at 298°C is accompanied by shoulders at 250 and 530°C, the former also incorporating the loss of the hydromagnesite hydration water which normally occurs at 270–340°C [17]. The endotherms at 420 and 509°C are due respectively to the loss of hydroxyl water and CO_2 from the hydromagnesite [15]. On the basis of the total thermal reaction:

$$\begin{aligned} &10Al(OH)_3 + 4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O \\ &\quad\rightarrow 5MgAl_2O_4 + 20H_2O\uparrow + 4CO_2\uparrow \qquad (2) \end{aligned}$$

the expected total weight loss is 43.0%, in reasonable agreement with the observed loss of 45.2%. The TG curve for this sample (Fig. 3G) shows several inflexions; the initial weight loss of 22.8% is in agreement with that expected for the gibbsite component (21.7%), while that of the highest-temperature loss (13.4%) is in reasonable agreement with the theoretical value for hydromagnesite decarboxylation (14.1%). The intermediate region of weight loss between about 350–450°C shows evidence of overlapping reactions, namely the removal of components of the hydromagnesite hydration and hydroxyl water.

The DTA of ground MC (Fig. 3D) is much simpler and broader than for the unground sample, having an endotherm at 130°C due to the removal of adsorbed water and a second endotherm at about 400°C which appears to be due to dehydroxylation of both the gibbsite and the basic carbonate. Fig. 3H shows that the weight loss associated with this temperature interval (34.3%) contains at least two inflections and is slightly greater than the theoretical value for the removal of all the hydration and hydroxyl water (28.9%). A third endotherm at 600–750°C has an associated 10.2% weight loss, occurring in at least two overlapping stages (Fig. 3H). This final weight loss is significantly less that the theoretical loss of 14.1% for hydromagnesite decarboxylation, suggesting that notwithstanding the persistence of residual hydromagnesite XRD reflections in this sample, the grinding has disrupted the carbonate structure so as to cause at least part of the carbonate to decompose contemporaneously with the alumina. Comparison of Fig. 3H with Fig. 3G also shows that grinding of this sample has caused its thermal decomposition reactions (especially decarboxylation) to be prolonged, concluding about 170°C higher than in the unground mixture. The weak exotherm at about 790°C is related to spinel formation (see below).

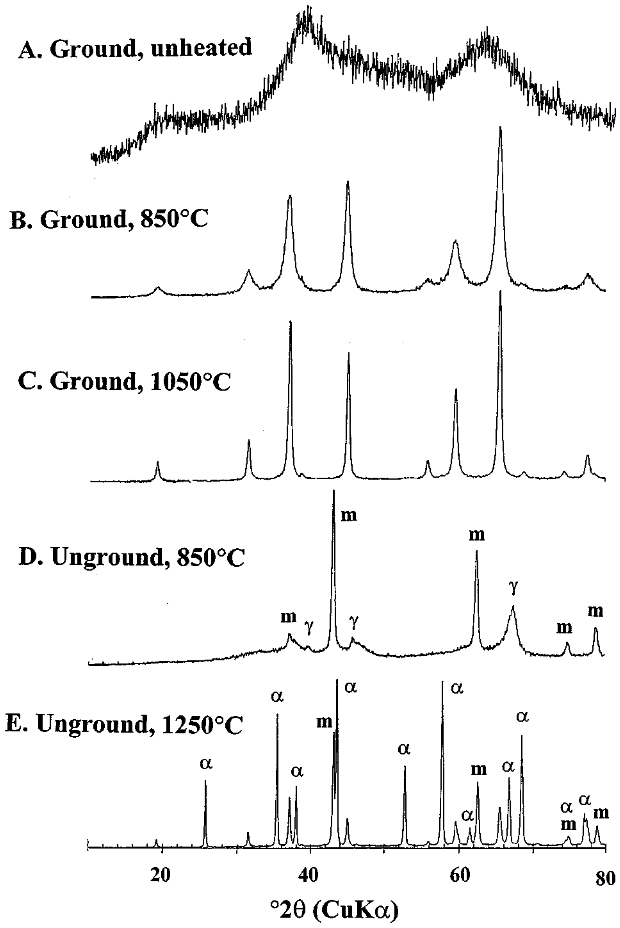


Figure 4 Powder X-ray diffractograms of ground and unground mixture MH heated as indicated for 1 hr. Key: m = MgO (PDF no. 4-829), $\gamma = \gamma$-alumina (PDF no. 10-425), $\alpha = \alpha$-alumina (PDF no. 10-173), unmarked peaks are of $MgAl_2O_4$ spinel (PDF no. 21-1152).

Fig. 4 shows the XRD powder patterns of ground and unground mixture MH heated at various temperatures.

On heating ground MH to 850°C (Fig. 4B), the broad spinel XRD peaks which were already present in the hydrated precursor (Fig. 4A) have sharpened to a crystalline $MgAl_2O_4$ pattern (PDF no. 21-1152) which becomes even sharper and more crystalline on firing at 1050°C (Fig. 4C). By contrast, unground MH heated at 850°C (Fig. 4D) contains only the reflections of the decomposition products of the components (γ-alumina, PDF no. 10-425, and MgO, PDF no. 4-829). When heated to 1250°C (Fig. 4E), the γ-alumina has transformed to α-alumina (corundum, PDF no. 10-173) and a small amount of $MgAl_2O_4$ has formed by solid state reaction. Thus, grinding lowers the formation temperature of spinel in MH by at least 400°C, promoting the formation of a crystalline monophase product by 850°C.

Fig. 5. Shows the XRD powder patterns of ground and unground mixture MC heated to various temperatures.

Heating the ground mixture MC to 850°C (Fig. 5B) results in the formation of both spinel and hydrotalcite

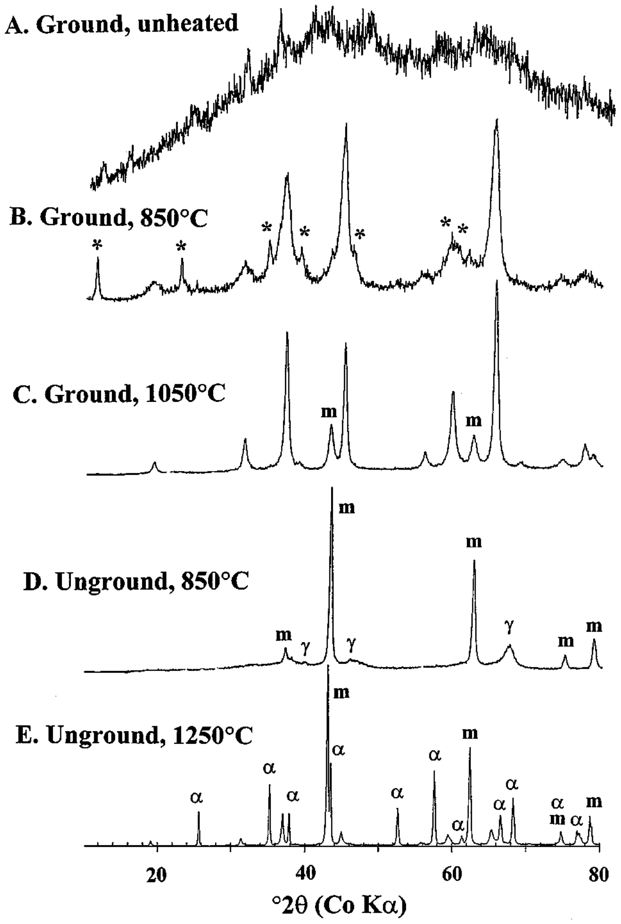


Figure 5 Powder X-ray diffractograms of ground and unground mixture MC heated as indicated for 1 hr. Key: * = hydrotalcite (PDF no. 22-700), m = MgO, $\gamma = \gamma$-alumina, $\alpha = \alpha$-alumina, unmarked peaks are of $MgAl_2O_4$ spinel.

(PDF no. 22-700), a hydrated magnesium aluminium hydroxycarbonate with the ideal formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$ but which can have a variable Mg : Al ratio. The Mg and Al atoms in this compound are distributed randomly over the octahedral sites in a brucite-like sheet, with charge compensation provided by the interlayer carbonate ions. The thermal evolution of hydrotalcite in ground MC provides evidence of mechanochemical reaction between the gibbsite and carbonate under conditions which must be hydrothermal-like, as found in the mechanochemical processing of brucite-silicic acid [12]. Heating to 1050°C improves the crystallinity of the spinel, but also produces some crystalline MgO (Fig. 5C), resulting from the decomposition of the hydrotalcite [18]. Thus, the formation of hydrotalcite as a secondary product of the mechanochemical treatment of MC militates against the formation of single-phase spinel at higher temperatures, since its thermal decomposition results in a mixture of spinel and MgO. Furthermore, the XRD patterns suggest that the spinel derived from ground MC is less crystalline than in ground MH. This result is consistent with differences found in the densities of the products formed at 1000°C from the ground precursors (3.58 and 3.43 g·cm^{-3} for MH and MC respectively). The absence of α-alumina from both the ground fired samples confirms that in each case a mechanochemical reaction has occurred between the starting materials, since any uncombined but amorphized $Al(OH)_3$ present should have transformed to α-alumina by about 800°C [19].

Heat treatment of unground mixture MC at 850°C results in similar products to those found in unground mixture MH at this temperature (γ-alumina and MgO, Fig. 5D). Heating to 1250°C (Fig. 5E) transforms the γ-alumina to α-alumina (corundum), the other phases being MgO and some spinel. This phase assemblage is similar to that found at this temperature in unground MH, but comparison of the two diffractograms suggests that MC contains relatively more spinel and corundum, and less MgO than in MH.

3.2. Sintering behaviour of the mechanochemically synthesised spinels

The bulk densities and apparent porosities of the sintered samples are shown in Fig. 6 as a function of the sintering temperature.

At 1600°C the bulk density and porosity values for the sample derived from MH (77.2% and 22.7% respectively) were significantly poorer than the corresponding values for the MC (97% and 0%), even though the synthesis of spinel occurred more readily in MH. This sintering result applies over the whole range of sintering temperatures (Fig. 6). Thus, although the use of basic magnesium carbonate as the starting material

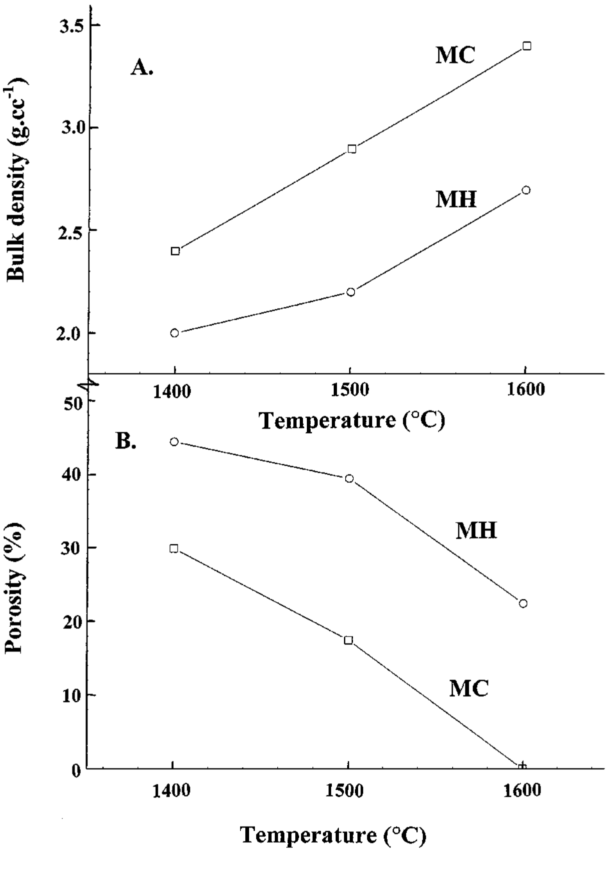
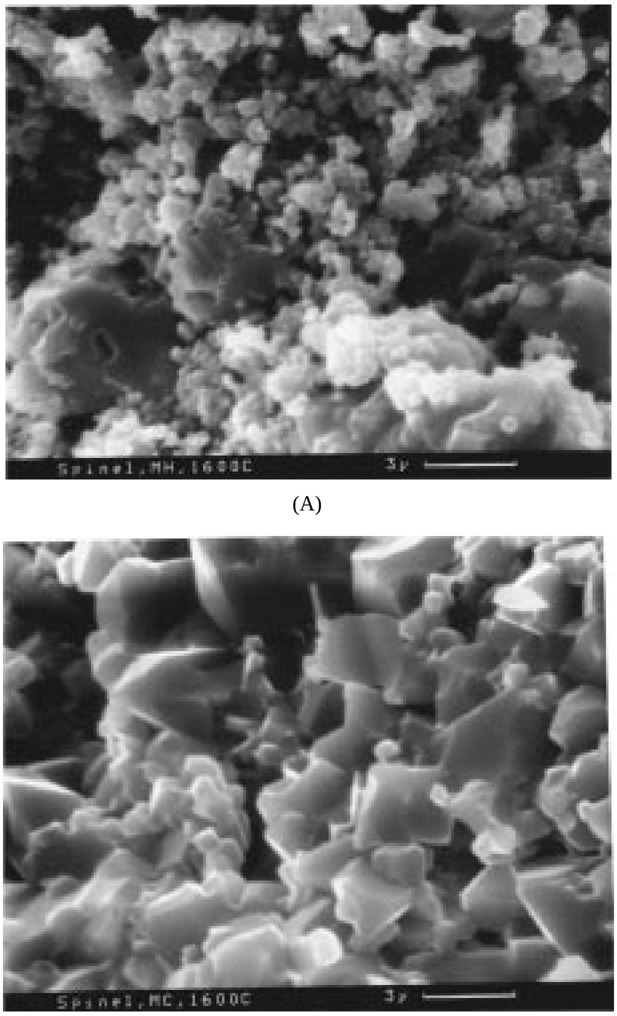


Figure 6 (A) Bulk density and (B) porosity of spinel derived from ground precursors MH and MC fired at 1050°C then sintered in air for 2 hr, as a function of sintering temperature.



(A)

(B)

Figure 7 Scanning electron micrographs of the fracture surfaces of spinels sintered in air for 2 hr at 1600°C. (A) Sample derived from ground precursor MH, (B) Sample derived from ground precursor MC.

for mechanochemical precursor synthesis leads to a slightly less reactive precursor which requires a higher temperature to thermally decompose to spinel and a little MgO, the sintering behaviour of this product is better.

Fig. 7 shows scanning electron micrographs of the fracture surfaces of samples sintered at 1600°C.

Since the composition of these samples gives no scope for the formation of a eutectic liquid, solid state sintering is expected to predominate. At 1600°C sample MC shows the typical prismatic particles resulting from normal sintering and grain growth during which the spinel becomes fully crystalline. By contrast, the sintered MH samples contain a mixture of fine 0.3–0.5 μm particles together with abnormally large particles. The abnormal grain growth of some particles may originate in regions of unreacted precursor relicts enclosed by agglomerated particles. During sintering, the fast growth of these active regions may occur at the expense of the smaller fully crystalline spinel particles of lower activity.

4. Conclusions

Mechanochemical treatment of $Al(OH)_3$ (gibbsite) with both $Mg(OH)_2$ (brucite) and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ (hydromagnesite) destroys the X-ray reflections of the starting materials and produces phases which are virtually X-ray amorphous, but retain their water and carbonate contents. When both the starting materials are hydroxides, the product contains X-ray evidence of incipient spinel formation, with broad background features in the regions of the spinel reflections. When the magnesium is introduced as the basic carbonate (hydromagnesite) the amorphous product contains small residual hydromagnesite peaks. Grinding converts some of the octahedral Al of the the initial gibbsite to tetrahedral sites, and other sites characterized by a ^{27}Al MAS NMR peak at about 38 ppm. The brucite-derived product contains relatively more tetrahedrally coordinated Al, reflecting a more developed incipient spinel character.

Thermal treatment ($<$850°C) of the brucite-derived precursor transforms it to $MgAl_2O_4$ spinel which becomes increasingly crystalline at higher tmperatures. By contrast, this unground mixture contains only the decomposition producs of its components (MgO and γ-alumina) at 850°C, and shows only slight solid-state spinel formation at 1250°C. Heating the ground precursor obtained from hydromagnesite at 850°C produces a mixture of spinel and hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), the latter decomposing to a mixture of spinel and MgO at 1050°C. Without grinding, this mixture behaves similarly to the unground hydroxide-derived mixture, but produces slightly less spinel at 1250°C.

At 1400–1600°C, the spinel produced by thermal treatment of the ground hydroxide-derived precursor sinters more pooly than the carbonate-derived precursor, and contains a mixture of fine (0.3–0.5 μm) particles together with some abnormally large particles. The mechanochemically processed precursors derived from the present gibbsite-hydromagnesite mixtures are therefore preferable for the production of a dense sintered body.

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