Journal of the European Ceramic Society 7 (1991) 31–39

The Mechanism of $MgAl_2O_4$ Spinel Formation from the Thermal Decomposition of Coprecipitated Hydroxides

G. Gusmano, P. Nunziante, E. Traversa

Dip. Scienze e Tecnologie Chimiche, II Universita' di Roma 'Tor Vergata', Via O. Raimondo, 00173 Roma, Italy

&

G. Chiozzini

Ist. Teoria e Struttura Elettronica, C.N.R., Area della Ricerca di Roma, Via Salaria Km 28.500, 00016
Monterotondo Stazione (ROMA), Italy

(Received 6 July 1990; accepted 25 July 1990)

Abstract

The thermal behaviour of coprecipitated hydroxide mixtures leading to the synthesis of $MgAl_2O_4$ *spinel powders has been investigated. The mixtures of hydroxides have been prepared by coprecipitation reaction from nitrate solutions with a molar ratio for Mg/Al of 1:2. The results have been related to the thermal behaviour of separately precipitated components of the hydroxide mixtures. The different steps in the thermal decomposition have been characterized via X-ray diffractometry (XRD). A mechanism for the spinel formation from the thermal decomposition of the hydroxide mixtures has been hypothesized.*

Die Kalzinierung von Hydroxidmischungen, die durch Co-Fällung aus der Lösung hergestellt wurden und zur Synthese von $MgAl_2O_4$ *Spinell-Pulvern dienen sollen, wurde untersucht. Die Hydroxidmischungen wurden aus Nitratlösungen mit einem molaren Mg/Al-Verhältnis von 1:2 durch Co-Fällung hergestellt. Die Ergebnisse werden mit der Kalzinierung der durch getrennte Fällung hergestellten Einzelkomponenten dieser Hydroxidmischungen verglichen. Die einzelnen Stufen der thermischen Zersetzung wurden mit Hilfe der Röntgenbeugung (XRD) verfolgt. Ein möglicher Reaktionsmechanismus der Spinellbildung aus der thermischen Zersetzung der Hydroxidmischungen wird vorgeschlagen.*

On a étudié le comportement thermique de mélanges d'hydroxydes coprécipités destinés à la synthèse de poudres de spinelles $MgAl_2O_4$*. Les mélanges d'hydroxydes avaient été préparés par réaction de coprécipitation à partir de solutions nitrates de rapport molaire Mg/Al = 1:2. Les résultats ont été reliés au comportement thermique des composants des mélanges hydroxydes précipités séparément. Les différentes étapes de la décomposition thermique ont été caractérisées par diffractométrie X (XRD). On avance ici l'hypothèse d'un mécanisme de formation des spinelles par décomposition thermique des mélanges d'hydroxydes.*

1 Introduction

The use of spinel porous compacts as a sensing element for humidity-measurement devices[1] needs the microstructural design of the sintered bodies. It can be achieved by the production of ultrafine particles with a very narrow size distribution. The traditional preparation process of magnesium aluminate spinel ($MgAl_2O_4$) powders, consisting in a solid-state reaction between the corresponding oxides at a temperature not lower than 1400°C,[2–5] does not allow this target to be attained.

The addition of mineralizers, which reduce the spinel-formation temperature, can promote the attainment of a reactive spinel.[6,7] Very sinteractive Mg–Al spinel precursors were obtained by hydrothermal treatment of commercially available $Mg(OH)_2$ and $Al(OH)_3$ mixtures.[8]

The preparation of $MgAl_2O_4$ spinel at lower temperatures can be achieved by the thermal decomposition of precursors prepared by precipitation processes;[9-16] in particular, the thermal decomposition of coprecipitated mixtures of hydroxides was found to be a promising method to obtain particles with homogeneous and small average dimensions and to reduce the spinel-formation temperature to values as low as 400°C.[17,18]

In a previous paper,[19] some of the authors have investigated the chemical composition and the microstructure of Mg–Al coprecipitated hydroxides as a function of the precipitation parameters. Preliminary results[20] of the thermal behaviour of coprecipitated hydroxide mixtures were related to those of different mechanical mixtures of hydroxides.

This work aims to go deeply into investigations of the thermal behaviour of the coprecipitated hydroxide mixtures in order to state a decomposition mechanism. For this purpose, the thermal behaviour of separately precipitated hydroxides, under the same conditions as the coprecipitated mixtures, was also thoroughly studied.

2 Experimental

2.1 Materials

The Mg–Al hydroxide powders were obtained by coprecipitation from Mg and Al nitrates by following the procedure described in a previous paper,[19] briefly outlined in Fig. 1.

The following samples were examined:

- —coprecipitate from solutions with Mg/Al molar ratio 1:2, at pH = 10 and 60°C;
- —separately precipitated hydroxides, prepared from Mg nitrate and Al nitrate under the same conditions as the coprecipitate;
- —coprecipitate from solutions with a Mg/Al molar ratio of 2:1.

In order to obtain a better understanding of the thermal behaviour of hydroxide mixtures, the different samples were heated at temperatures corresponding to the completion of the main DTA effects; this was made possible by performing the heating with the equipment used for the thermal analysis, with a heating rate of 10°C/min.

Finally, all powders were calcined at 1100°C for 4 hours.

2.2 Characterization

The powders were characterized by the following techniques:

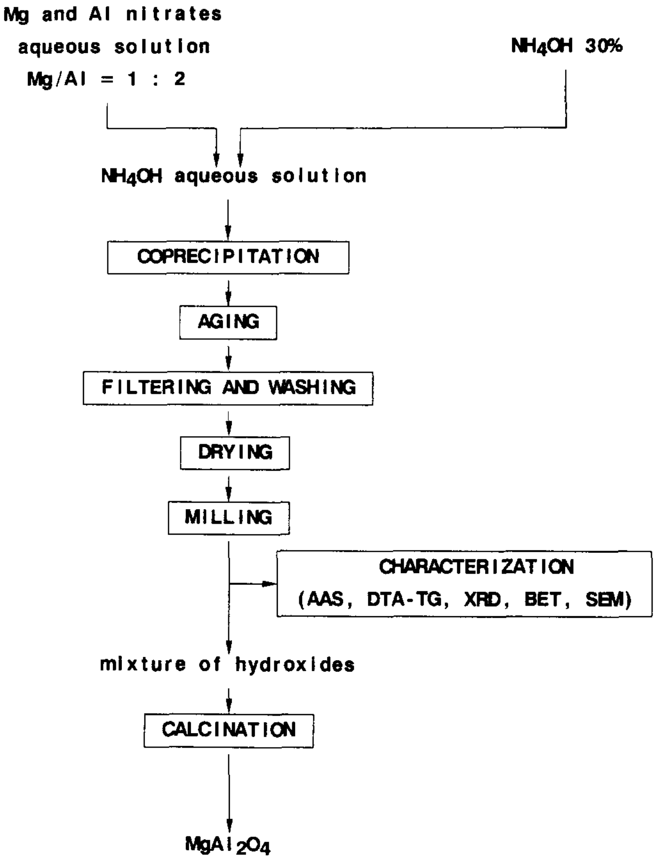


Fig. 1. Flowsheet of the spinel-preparation process.

- —simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) (Stanton model 781) under the following conditions: static air, heating rate 10°C/min, sample mass about 20 mg, reference sample Al_2O_3, sensitivity 40 μV;
- —X-ray-diffraction analysis (XRD), performed by means of Siemens model D500 equipment by using CuKα radiation ($\lambda = 0{\cdot}1542$ nm);
- —elemental chemical analysis: Mg and Al were determined by atomic-absorption spectrophotometry (Philips model PU 2500), and C, H, and N by using an elemental analyzer (Carlo Erba Strumentazione model 1106).

3. Results

3.1 Coprecipitation with Mg/Al molar ratio of 1:2

The chemical analysis gave the following results:

	Mg	Al	H	C	N
%wt	10·62	23·30	3·83	1·20	—

XRD pattern (Fig. 2(a)) showed the presence of three different crystalline phases: a mixed Mg–Al hydroxide with a molar ratio of 2:1,[21] α-$Al(OH)_3$ (gibbsite) and β-$Al(OH)_3$ (bayerite). According to the literature, the mixed hydroxide has a layered structure,

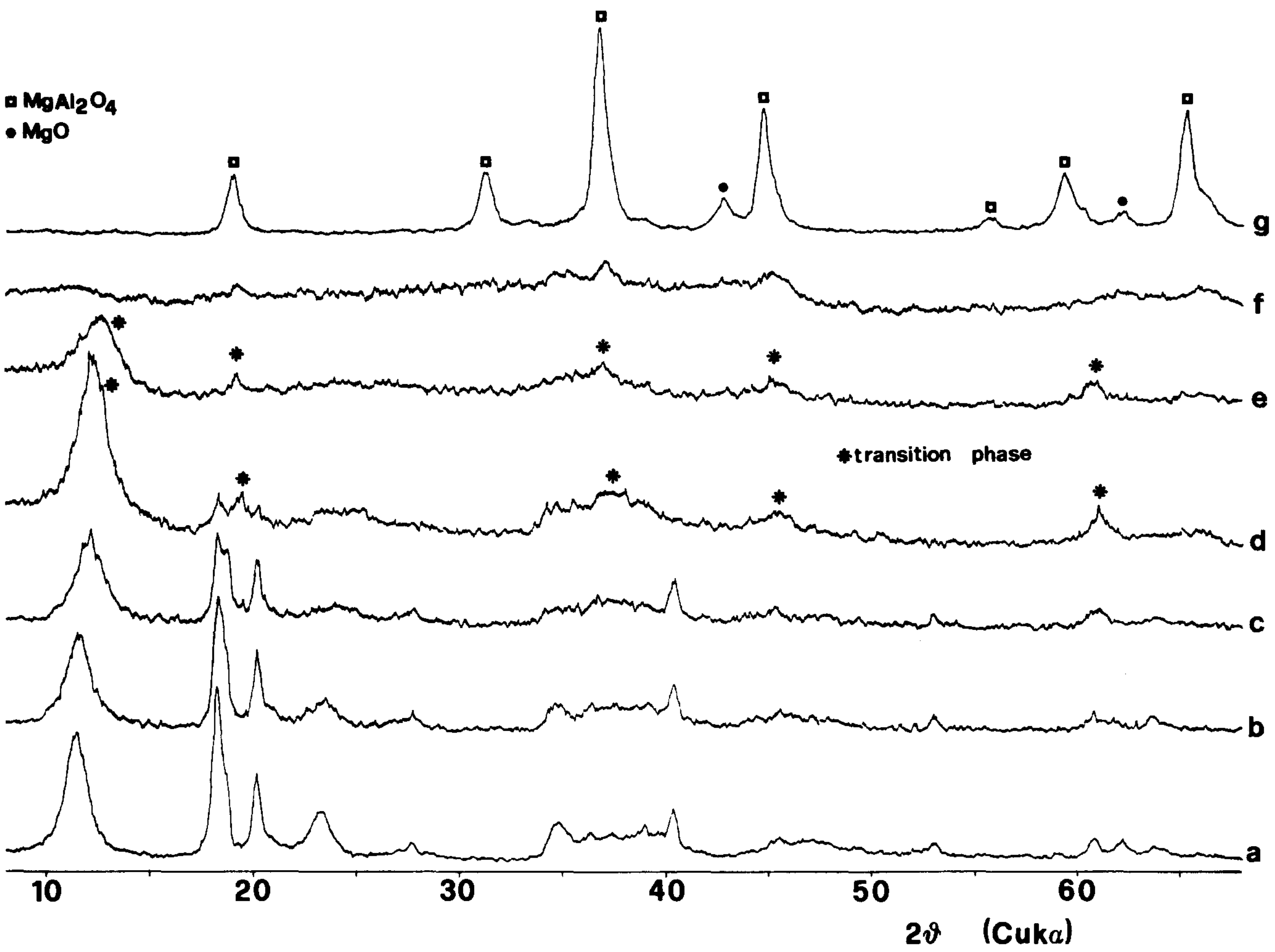


Fig. 2. XRD patterns of the coprecipitate with Mg/Al ratio of 1:2, heated at different temperatures: 100°C (a); 220°C (b); 230°C (c); 240°C (d); 280°C (e); 400°C (f); 1100°C (g).

consisting of positively charged brucite-like layers, intercalated by layers of anions and water molecules.[22,23]

The DTA and TG curves are shown in Fig. 3. The DTA curve showed two endothermic peaks, with maxima at 220 and 265°C, and two endothermic effects at about 340 and 380°C. The TG curve showed that, after the loss of free water, the thermal decomposition can be divided into three steps. The first one, until about 250°C, is the result of the overlapping of more effects; from 250°C, the weight loss occurs at constant rate up to about 400°C. The last step, characterized by decreasing weight-loss rate, is nearly completed at 650°C.

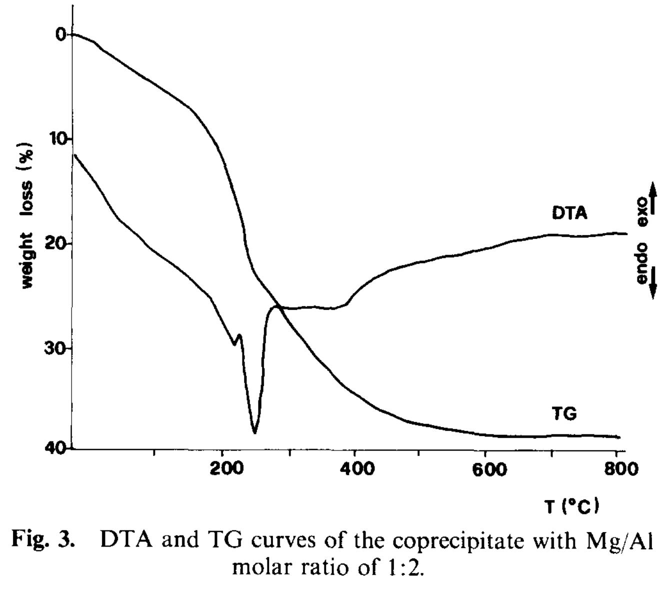


Fig. 3. DTA and TG curves of the coprecipitate with Mg/Al molar ratio of 1:2.

The precipitate was heated at temperatures corresponding to the completion of each DTA effect and analysed via XRD (Fig. 2). The following results were obtained: at a temperature corresponding to the completion of the first endothermic peak (Fig. 2(b)), the only difference from the XRD pattern of unheated powder consists of a broadening of the mixed hydroxide peaks; at 230°C (Fig. 2(c)), a first variation of the XRD pattern is noticeable: the peaks of the mixed hydroxide disappeared, and those of the Al hydroxides, mainly gibbsite, decreased in intensity; moreover, three unidentified broad reflections at about 12·1°, 19·5°, and 61·0° in 2θ, corresponding, respectively, to d = 0·732, 0·455, and 0·152 nm, were detected. On again slightly increasing the temperature, at about 240°C (Fig. 2(d)), the peaks of the Al hydroxides nearly disappeared, apart from the two main ones; the three unknown peaks detected at 230°C increased their intensity, and two other unidentified broad peaks at about 37·5° and 45·3° in 2θ were noticed; at 280°C (Fig. 2(e)), that is, at the completion of the second endothermic DTA peak, the Al hydroxide peaks are completely missing, but the unidentified peaks are still present, although decreased in intensity and slightly shifted. At 400°C, the XRD pattern (Fig. 2(f)) shows only very small and broad $MgAl_2O_4$ reflections. The XRD pattern (Fig. 2(g)) of the calcined powder shows the presence of MgO, besides that of the spinel, according to the chemical analysis, which shows an atomic ratio of $Mg/Al = 0{\cdot}513$.

3.2 Separately precipitated hydroxides

(a) Precipitate from Mg nitrate

The XRD analysis of the precipitate showed only the presence of brucite, $Mg(OH)_2$. The DTA and TG curves are reported in Fig. 4; the DTA curve shows one endothermic peak with a maximum at 400°C; the decomposition begins at 330°C and ends at about 750°C, as evidenced by the TG curve; likely results were obtained by other authors for brucite produced in similar conditions.[24]

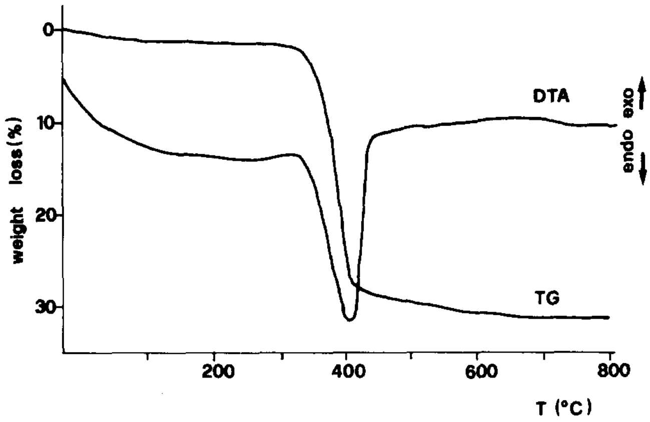


Fig. 4. DTA and TG curves of the precipitate from Mg nitrate.

(b) Precipitate from Al nitrate

The precipitation from Al nitrate yielded a mixture of α-$Al(OH)_3$ (gibbsite), β-$Al(OH)_3$ (bayerite), and pseudoboehmite, a weakly crystalline gel with a boehmite (AlOOH) structure,[25,26] as evidenced by the XRD pattern (Fig. 5(a)).

The TG and DTA curves of Al hydroxides are reported in Fig. 6; the DTA curve shows one endothermic peak with a maximum at 260°C. The loss of free water is very small. The TG curve shows that the decomposition of $Al(OH)_3$ occurs through a two-step weight loss. The first one, up to 260°C, corresponds to a weight loss of 22·8% of the

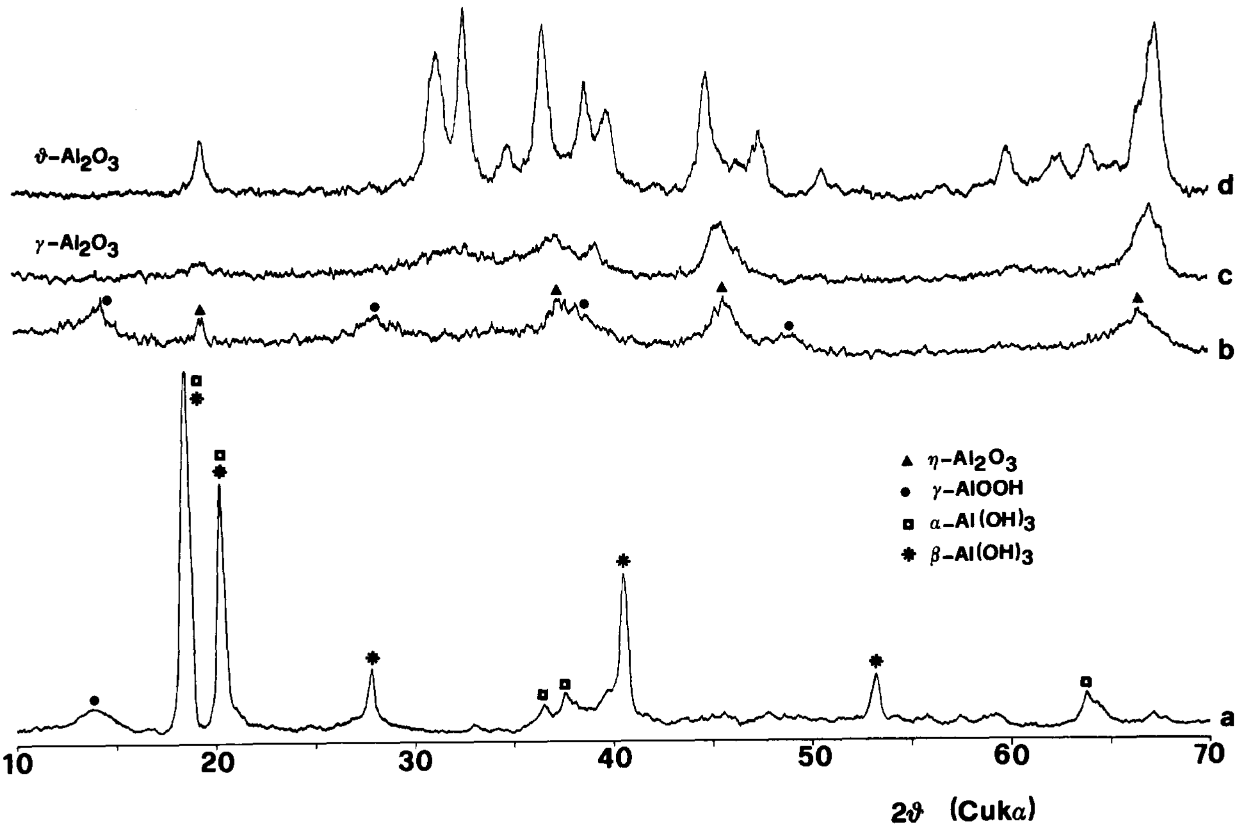


Fig. 5. XRD patterns of the precipitate from Al nitrate, heated at different temperatures: 100°C (a); 300°C (b); 950°C (c); 1100°C (d).

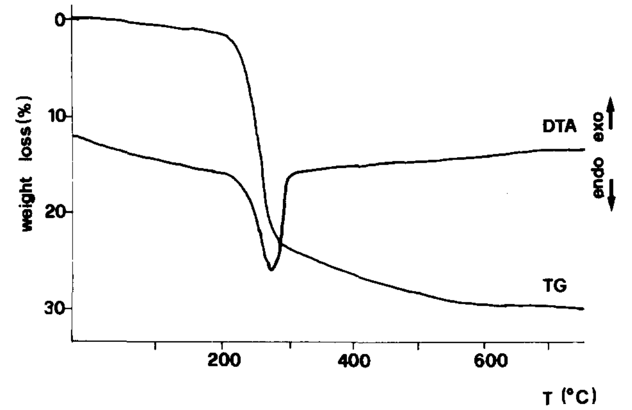


Fig. 6. DTA and TG curves of the precipitate from Al nitrate.

anhydrous weight, while the second corresponds to a 7·2% weight loss.

The XRD pattern of the precipitate heated at 300°C (Fig. 5(b)) shows the presence of boehmite and η-Al_2O_3. On increasing the temperature up to 1100°C (Figs 5(c) and 5(d)), Al_2O_3 changed its crystalline structure from eta- to gamma- to theta-, thus conserving the transition spinel structure, as evidenced by XRD analysis. Corundum formation can occur only at temperatures above 1100°C.

3.3 Coprecipitation with Mg/Al molar ratio of 2:1

In order to investigate the nature of the mixed hydroxide found in the coprecipitate with a Mg/Al ratio of 1:2, keeping in mind the results obtained by other authors,[23,27–34] coprecipitations were performed from Mg and Al nitrate solutions with a Mg/Al molar ratio of 2:1; XRD analysis (Fig. 7(a)) showed the presence of only one crystalline phase, similar to those already synthesized by other authors.[23,27–30]

The elemental chemical analysis gave the following results:

	Mg	Al	C	H	N
%wt	20·25	11·43	2·62	3·88	—

The thermal analysis is reported in Fig. 8; in the DTA curve, two endothermic peaks are noticeable with their maxima at temperatures of 240 and 400°C, the second peak having a shoulder at lower temperature.

After the loss of free water, the TG curve can be divided into three steps: the first one ends at about 230°C; when this step is completed, a sharp decrease in the weight-loss rate is noticeable. The second step, until about 400°C, starts slowly and then becomes faster. The last step, characterised by a decreasing weight-loss rate, is nearly completed at 650°C.

XRD analysis of the precipitates heated at various temperatures showed the following results: the pattern of the powder heated at the completion of the first endothermic peak (Fig. 7(b)) still showed the mixed-hydroxide peaks but less crystalline; at 310°C

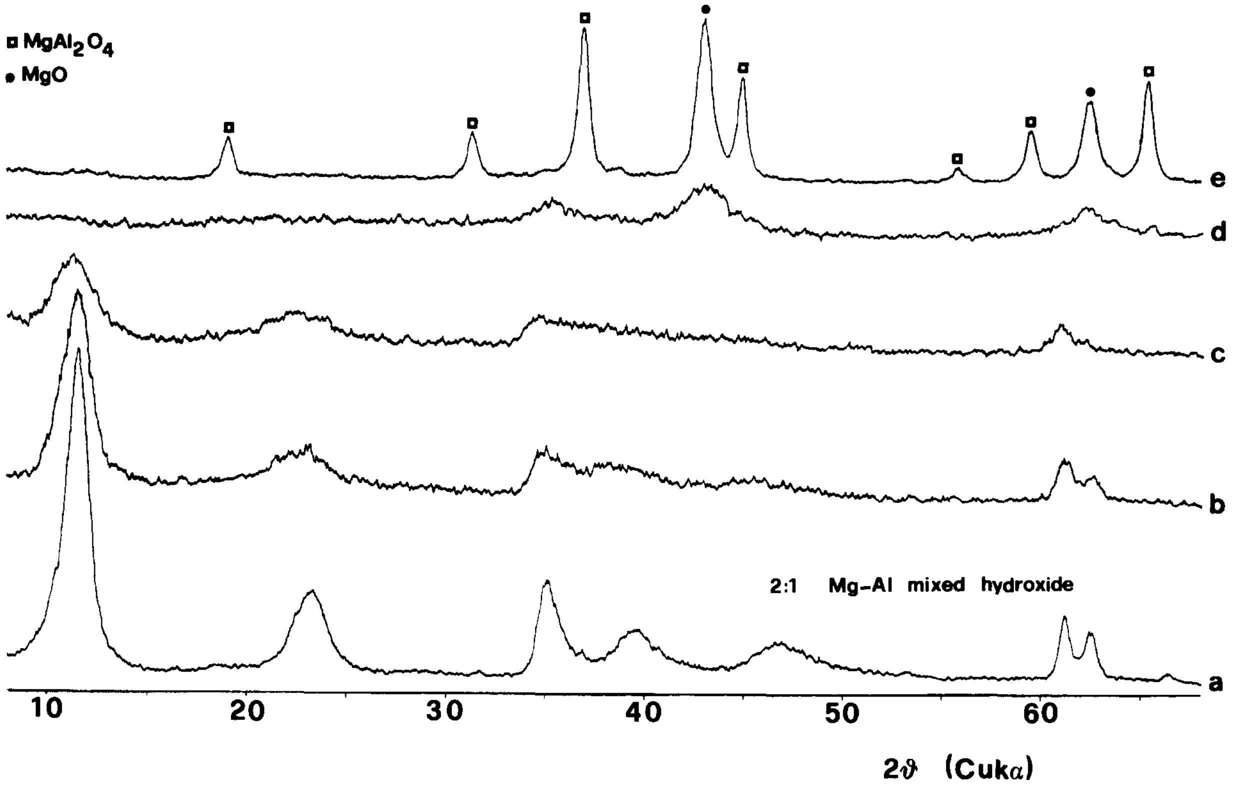


Fig. 7. XRD patterns of the coprecipitate with Mg/Al ratio of 2:1, heated at different temperatures: 100°C (a); 250°C (b); 310°C (c); 410°C (d); 1100°C (3).

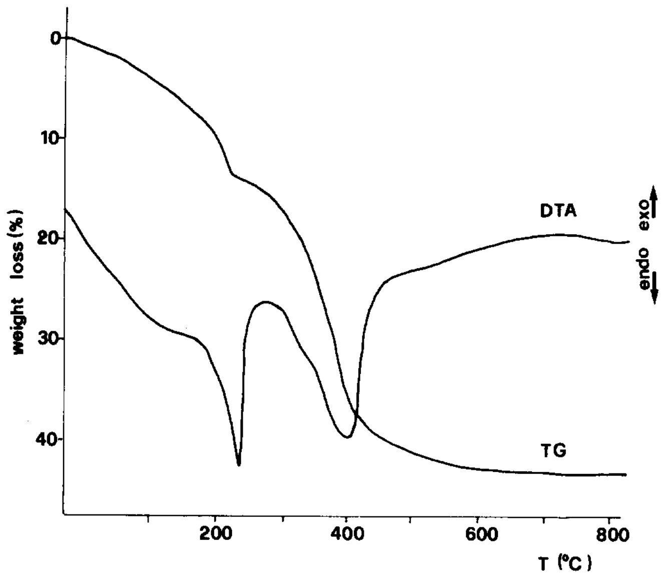


Fig. 8. DTA and TG curves of the coprecipitate with Mg/Al molar ratio of 2:1.

(Fig. 7(c)), only four broadened peaks of mixed hydroxide were detectable. At the completion of the second endothermic peak, that is, at about 410°C (Fig. 7(d)), the peaks of the mixed hydroxide were completely missing, while broad reflections of MgO and $MgAl_2O_4$ were detectable. On increasing the temperature, MgO and $MgAl_2O_4$ crystallized, and the XRD pattern showed that the higher the temperature, the sharper were the peaks (Fig. 7(e)).

4 Discussion

4.1 Separate components of the hydroxide mixtures

The mechanism of the $Mg(OH)_2$ thermal decomposition to MgO has been deeply investigated in the literature,[35,36] and our results agree with it.

For the thermal decomposition of Al hydroxides, many possible mechanisms have been proposed in the literature;[25,26,35,37] in particular, a strong relationship between the water-vapour pressure above the sample and its decomposition mechanism was pointed out.[38] Results previously reported by the authors showed that, in the experimental conditions described, a mixture of $Al(OH)_3$ and AlOOH is obtained; the thermal decomposition in static air of a moist sample with this composition occurs through a two-step dehydration process: the first step, to 270°C, is the $Al(OH)_3$ decomposition to AlOOH, while the second one is the final decomposition to alumina.[20]

On the other hand, if an anhydrous sample is taken into consideration, as in the present case, $Al(OH)_3$ is directly transformed almost completely into alumina at 270°C.

Considering the precipitate with a Mg/Al ratio of 2:1, it must be pointed out that the mixed hydroxides and the corresponding hydroxycarbonates have very similar XRD patterns, which do not allow one to distinguish between the hydroxide and the corresponding carbonated forms.[32] The presence of C in our precipitate confirmed that the synthesized product was not merely mixed hydroxide.[28,29] In fact, the strong ability of Mg–Al mixed-hydroxide layered structure[22,39,40] to exchange anions[41-44] can explain the presence of C, owing to the substitution of the hydroxyl ions of the interlayer sheet with carbonate ions,[45] coming from atmospheric CO_2 dissolved into the starting solutions and the washing water.

Studies of the thermal decomposition of synthesized Mg–Al mixed hydroxides with various Mg/Al molar ratios[23,28,46] and of natural[47,48] and synthesized corresponding carbonated forms[29,31,32,49,50] are reported in the literature. At temperatures lower than 300°C, DTA curves of mixed hydroxides are always characterized by the presence of two endothermic peaks, whereas, in the same temperature range, the corresponding carbonated forms show only one peak.[32] According to these data, the DTA curve of our precipitate (Fig. 8) gives further confirmation to the fact that a carbonated form was obtained.

As reported in the literature,[31,32] the first endothermic peak, at 240°C, is due to the loss of interlayer water.

The peak at 400°C is at nearly the same temperature as the brucite-decomposition peak (Fig. 4) and corresponds to the final decomposition step of the mixed hydroxide, according to the fact that XRD analysis showed the presence of MgO only in samples heated at the completion temperature of the second peak.

On the hypothesis that $1\,MgAl_2O_4 + 3\,MgO$ are produced by the mixed-hydroxide decomposition, the weight losses corresponding to the different TG steps were calculated to be equivalent, respectively, to $2{\cdot}5\,H_2O$, $5{\cdot}5\,H_2O$, and about 1 CO_2 for one molecule of spinel produced. According to the results of chemical and thermal analyses, the composition of the mixed hydroxide can be assumed as the following: $Mg_4Al_2CO_3(OH)_{12}\,.\,2H_2O$, whose theoretical weight loss (41·8%) fits with the experimental one on the anhydrous weight (41·2%). This composition is in accordance with the one reported in the literature.[32]

Keeping in mind these results, the following decomposition mechanism can be suggested: after the loss of free water, the mixed-hydroxide dehydration starts from the interlayer water and continues at a slower rate with the loss of the hydroxyl ions from the brucite-like layer, as shown by the sharp slope variation of the TG curve. It seems probable that the loss of the hydroxyl ions starts at the Al sites: in fact, the interlayer-water loss ends at 240°C, the temperature at which the Al hydroxides are partially decomposed.

A confirmation of this mechanism was given by tests performed on Mg–Al mixed hydroxides with atomic ratios of 3:1 and 4:1. Morever, in these cases, DTA curves showed two endothermic peaks at slightly decreasing temperatures, increasing the Mg/Al ratio, in agreement with the results of other authors;[23,28,31] it was observed that the higher the Mg/Al ratio, the larger was the area of the second DTA peak, thus confirming that this effect is due to the decomposition of $Mg(OH)_2$ in excess with respect to the spinel composition.

During the thermal decomposition, the layered structure is maintained up to about 400°C, when only the MgO in excess and $MgAl_2O_4$ are detectable by XRD.

4.2 Coprecipitation with Mg/Al ratio of 1:2

Coming back again to the thermal analysis of the coprecipitate in an atomic ratio stoichiometric to the spinel formation (Fig. 3), it must be pointed out that the second peak of the mixed-hydroxide DTA curve (Fig. 8) nearly disappeared.

This result is in agreement with the one obtained by Bratton[17] for likely mixtures; Yamaguchi *et al.*, who synthesized similar compounds by a different method, also detected the disappearance in the DTA curve of the second peak of the mixed hydroxide.[16,46]

The total anhydrous weight loss was 36·4%, showing that, according to the results of chemical analyses and those previously reported,[20] the composition of the mixture can be assumed as the following:

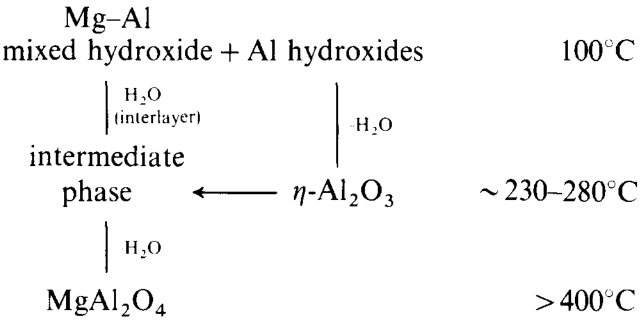
$$Mg_4Al_2CO_3(OH)_{12}.2H_2O + 4{\cdot}3Al(OH)_3 + 1{\cdot}7AlOOH$$

Considering that this mixture leads to the formation of $4\,MgAl_2O_4$, the different TG steps can be attributed to the following: after the loss of about four molecules of free water, the first step corresponds to the loss of $9{\cdot}5\,H_2O$, which is in agreement with the loss of the mixed-hydroxide interlayer water and to the Al hydroxide dehydration to Al_2O_3; during the following steps, $6\,H_2O$ and $1\,CO_2$, respectively, were lost. All weight losses are referred to four molecules of spinel.

Bratton[17] proposed a possible reaction sequence leading to the spinel formation, based on the formation of an intermediate Mg oxide in a spinel-type crystal structure, reported in the past by other authors.[51] The existence of this form of MgO has been definitely rejected,[35,36] weakening the above-mentioned mechanism; moreover, the results of XRD and thermal analyses induced us to suggest a different spinel-formation mechanism. Whereas the XRD pattern of $Al(OH)_3$ heated at 230°C already showed the presence of η-Al_2O_3 peaks, the one of the coprecipitate heated at the same temperature did not show any trace of η-Al_2O_3 but showed the peaks of a phase not yet reported in the literature and the contemporary reduction of the peaks corresponding to $Al(OH)_3$ and to the mixed hydroxide. This trend is confirmed by the XRD patterns of the powder heated to higher temperatures.

The peaks of the transition phase were not detected when the separately precipitated mixed hydroxide was heated.

According to these results, the following mechanism can be proposed:



After the loss of interlayer water of the mixed hydroxide, the first reaction stage, which starts at about 230°C, is the decomposition of the free $Al(OH)_3$ to η-alumina; according to the results obtained for the $Al(OH)_3$ precipitation, under the experimental conditions, the Al hydroxides directly decompose to Al_2O_3; the freshly formed η-alumina, with a spinel-type crystal structure, immediately reacts with the mixed hydroxide to form an intermediate phase, evidenced by the XRD analysis (Fig. 2d); this transition phase, between 230 and 400°C, is gradually transformed into $MgAl_2O_4$, with the loss of $6\,H_2O$ and $1\,CO_2$.

The nature of the intermediate phase is not clear; however, since the weight loss in this temperature range is continuous and occurs at a constant rate, it could be suggested that it is a hydrated form of the spinel ($MgAl_2O_4.1{\cdot}5\,H_2O$).

Considering that the mixed hydroxide (hexagonal) reacts with η-alumina (cubic) to give spinel (cubic), through this intermediate phase, it seems reasonable that the transition phase can be cubic. A tentative indexing of the XRD reflections of this transition phase gave the result that this phase could be indexed as cubic, even if with scattered results; the scattering of the unit-cell dimensions obtained for the transition phase can be attributed to the presence of some regions with stacking faults, which cause shifts in the position of the XRD peaks, as evidenced for the peaks in the experimental patterns with increasing temperature.

5 Conclusions

The thermal decomposition of coprecipitated hydroxide mixtures, made of mixed Mg–Al hydroxycarbonate with a molar ratio of 2:1, $Al(OH)_3$, and AlOOH, precursors to the $MgAl_2O_4$ synthesis, can be summarized as the following: the decomposition starts with the loss of the mixed-hydroxide interlayer water, completed at about 220°C; in the same temperature range, the Al hydroxides begin to transform into η-alumina up to about 280°C. The η-alumina reacts with the mixed hydroxide to give a transition phase, probably constituted by a hydrated spinel. This form is in turn decomposed to $MgAl_2O_4$ at about 400°C.

The spinel formation at a temperature as low as 400°C is therefore allowed by the reaction between η-Al_2O_3 and the mixed phase, through the formation of this transition phase, which contains in itself Mg and Al in an atomic ratio stoichiometric to the spinel formation.

Acknowledgments

This work was supported by the National Research Council of Italy (C.N.R.), in the frame of the Targeted Project 'Special Materials for Advanced Technologies'.

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