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THE THERMAL BEHAVIOUR OF THE HYDROXIDE MIXTURES USED FOR THE SYNTHESIS OF $MgFe_2O_4$ SPINEL

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The thermal behaviour of hydroxide mixtures, precursors to the synthesis of $MgFe_2O_4$ spinel powders, was investigated.

The mixtures of hydroxides were prepared by coprecipitation reaction from nitrate solutions with an Mg/Fe atomic ratio of 1:2. The results were related to the thermal behaviour of separately precipitated components of the hydroxide mixtures. Samples prepared by mechanically mixing the separately precipitated hydroxides were also studied.

The spinel formation temperature was identified by performing XRD analysis on powder samples heated to different temperatures. The presence of spinel from the thermal decomposition of coprecipitated mixtures was detected at a temperature as low as 380°C. The separate formation of MgO and Fe_2O_3 from the thermal decomposition of mechanical mixtures was observed; nevertheless the formation of $MgFe_2O_4$ through a solid state reaction between the oxides was noted at a temperature as low as 500°C.

Keywords: hydroxide mixtures, $MgFe_2O_4$ spinel

Introduction

The thermal decomposition of coprecipitation-derived precursors in order to obtain oxides with homogeneous and ultrafine particle dimensions, even though it is one of the oldest non-conventional powder preparation techniques, is still a widely used and a powerful method [1]. This method was applied in the past to $MgFe_2O_4$ synthesis, using Mg and Fe oxalate mixtures as precursors [2–4]. The coprecipitation of hydroxides in order to obtain precursors of $MgFe_2O_4$ preparation was recently investigated by the authors [5], following a procedure already developed for the analogous Mg–Al system [6].

In this paper the thermal behaviour of Mg–Fe hydroxide mixtures, coprecipitated from nitrate solutions with an Mg/Fe atomic ratio of 1:2, is described. The thermal behaviour of each separately precipitated component of the mixtures was also studied in order to obtain more information about the thermal decomposition of hydroxide mixtures. Moreover, the thermal analysis of mechanical mixtures of the separately precipitated $Mg(OH)_2$ and FeOOH, also stoichiometric to the spinel formation, was carried out, using the process which had previously been developed for the Mg–Al system [7].

Experimental

Materials

The Mg–Fe hydroxide mixture powders were prepared by coprecipitation from Mg and Fe nitrate solutions, using the procedure described in a previous paper [5].

The following samples were investigated:

i) coprecipitate from solutions with an Mg/Fe atomic ratio of 1:2, at $pH = 10$ and 60°C;

ii) precipitate from Fe nitrate, under the same conditions as the coprecipitate; the results for the precipitate from Mg nitrate have been reported in a previous paper [8];

iii) coprecipitate from solutions with an Mg/Fe atomic ratio of 3:1;

iv) mechanical mixture of $Mg(OH)_2$ and FeOOH, with Mg/Fe ratio 1:2, obtained by mixing the products of the precipitations from Mg nitrate and Fe nitrate in a vibratory ball mill for two hours.

Characterization

The powders were characterized using the following techniques:

a) elemental chemical analysis: Mg and Fe were determined by atomic absorption spectrophotometry (Philips mod. PU 2500); C, H and N by the use of an elemental analyzer (Carlo Erba Strumentazione mod. 1106);

b) simultaneous thermogravimetric (TG) and differential thermal analysis (DTA), under the following conditions: static air, heating rate 10 deg·min^{-1}, sample weight about 20 mg, reference sample Al_2O_3, sensitivity 40 μV (Stanton mod. 781);

c) X-ray diffraction analysis (XRD), using Zr filtered Mo$k\alpha$ radiation (λ = 0.0711 nm) (Philips mod. PW 1729).

Results and discussion

Separately precipitated hydroxides

Taking the preliminary results obtained into consideration [5], precipitations were performed from Fe nitrate and from Mg and Fe nitrate solutions with an Mg/Fe atomic ratio of 3:1. Results of the precipitation from Mg nitrate, reported in a previous paper [8], showed that the precipitation product was made up of $Mg(OH)_2$ (brucite); its thermal decomposition was characterized by an endothermic peak at about 400°C.

Precipitation from Fe nitrate

The XRD pattern of the precipitation product, even though weakly crystalline, showed the presence of α–FeOOH (goethite) reflections. DTA and TG curves (Fig. 1) confirmed that the product was hydrated Fe oxyhydrate. The less-linked water is eliminated below 100°C. The transformation of α–FeOOH into Fe_2O_3 occurs between 100° and 400°C, at which temperature the crystallization of α–Fe_2O_3 takes place.

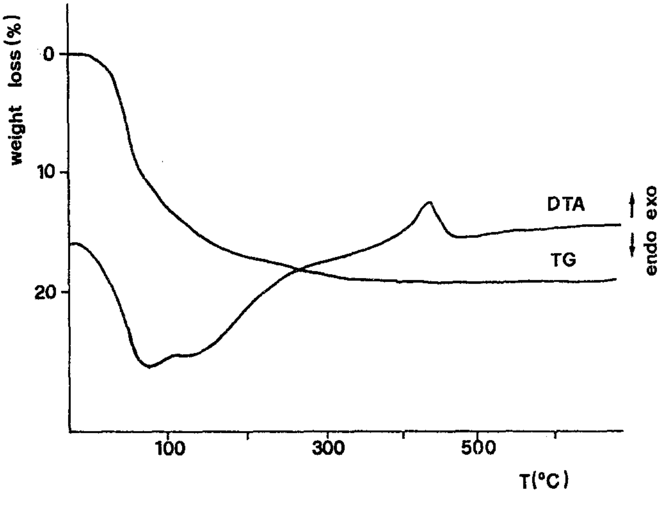

Fig. 1 DTA and TG curves of the precipitate from Fe nitrate

Coprecipitation with Mg/Fe atomic ratio 3:1

Our preliminary results [5] showed a 3:1 Mg/Fe ratio in the mixed phase obtained, and precipitations performed with an Mg/Fe atomic ratio of 2:1 showed the presence of the mixed phase with a 3:1 ratio and FeOOH in excess. Given that the results of Hashi *et al.* [9] establish that this is the minimum Mg/Fe ratio for this phase, we will deal here with the coprecipitations performed at the Mg/Fe ratio of 3:1.

The chemical analyses gave the following results:

	Mg	Fe	H	C	N
wt /%	21.2	16.8	3.6	2.3	—

The XRD pattern of the precipitate showed one crystalline phase, ascribable to the hexagonal system, which was very similar to the pattern of pyroaurite [10], as reported in Table 1. Hashi *et al.* [9], who synthesized similar compounds, obtained similar results. The crystal structure of pyroaurite has been thoroughly studied in the literature [11–15]. It consists of positively charged brucite-like layers with Fe(III) substituting a number of Mg ions. Between these layers there are intermediate, negatively charged, layers formed by carbonate ions and H_2O molecules.

Table 1 Comparison between X-Ray diffraction spacings for the coprecipitate with Mg/Fe 3:1 and for pyroaurite

Coprecipitate Mg/Fe 3:1 *d*/nm	Pyroaurite ASTM card 25 – 521 *d*/nm	*hkl*
0.780	0.777	003
0.391	0.389	006
0.262	0.262	012
0.235	0.233	015
0.199	0.197	018
0.153	0.155	1110
0.152	0.152	113
0.145	0.144	116

DTA and TG curves are shown in Fig. 2. In the relevant literature similar thermal analyses are reported for natural [16] and synthetic pyroaurite [9, 17]. From the TG curve, it may be seen that the total weight loss was 40.8%. The theoretical weight loss of the natural pyroaurite, which has 4 H_2O molecules in the interlayer sheet, is 39.4%. It may be therefore assumed that the water content of this precipitate is quite comparable with that of natural pyroaurite, since the precipitate was not conditioned in a controlled atmosphere before performing the measurements.

The DTA curve (Fig. 2) showed two endothermic reactions, in the ranges from 120° to 190°C and from 200° to 400°C.

Using the procedure already adopted for the Mg–Al system [8], in order to investigate in depth the thermal decomposition of the precipitate, samples were heated to the temperatures corresponding to the completion of the main DTA effects and were then subjected to XRD analysis. The XRD patterns of these samples were, however, practically amorphous until 950°C, at which temperature the peaks of MgO and $MgFe_2O_4$ were clearly evident.

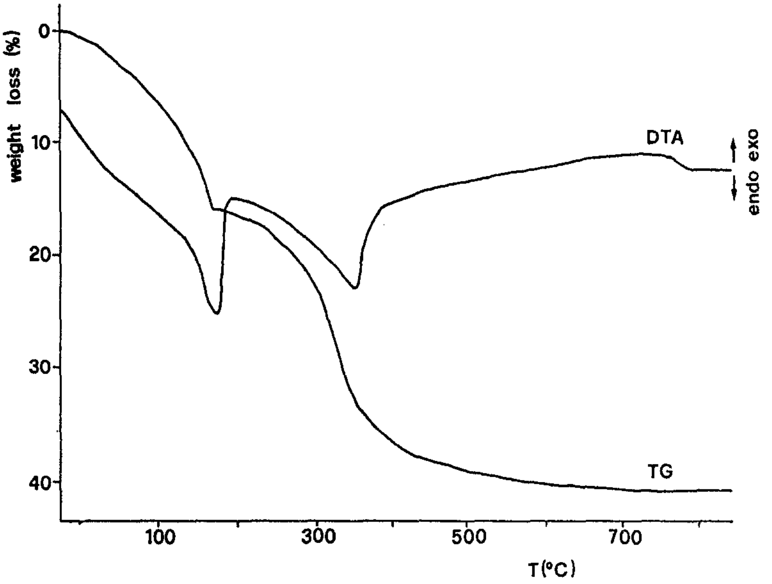

Fig. 2 DTA and TG curves of the coprecipitate with Mg/Fe atomic ratio of 3:1

The TG curve is very similar to the TG of the corresponding Mg–Al hydroxycarbonate, prepared by the authors [8]. The weight loss is continuous up to 185°C, at which temperature a sharp reduction of the weight loss rate is observed; the weight loss rate then increases up to 380°C, with a decreasing slope till about 700°C. It is given that the product of the decomposition of 1 mole of precipitate is 5 MgO and 1 $MgFe_2O_4$, as confirmed by XRD analysis, the number of moles lost in correspondence with each TG stage was evaluated for 1 mole of $MgFe_2O_4$ formed. About 2 moles of water are lost below 100°C, then between 100° and 185°C we recorded a weight loss of $4.5H_2O$; this corresponds to the loss of the 4 molecules of the interlayer water, overlapped with the beginning of the loss of hydroxyl ions present in the brucite-like layers of the pyroaurite phase. This loss starts at a slow rate, at a temperature below the completion of the rapid loss of interlayer water. Considering the results obtained for the analogous Mg–Al compound [8], it seems probable that the first stage of dehydroxylation involves the hydroxyl ions bonded to the Fe ions, since the separately precipitated FeOOH is partly decomposed at these temperatures. During the second stage the dehydroxylation is completed with a residual loss of 7 moles of H_2O; in the last stage the loss of 1 CO_2 occurs.

The second DTA peak can therefore be ascribed to the final decomposition of the mixed phase into MgO and $MgFe_2O_4$, the crystallization of which takes place very slowly up to about 900°C.

Coprecipitation with Mg/Fe *atomic ratio 1:2*

The chemical analyses gave the following results:

	Mg	Fe	H	C	N
wt/%	9.6	43.7	2.5	1.3	—

According to previous results [5], the XRD patterns of these coprecipitated mixtures are nearly amorphous. However, broad reflections of pyroaurite and of α–FeOOH (goethite) were identified.

DTA and TG curves are shown in Fig. 3. The DTA curve of this coprecipitated mixture shows two endothermic peaks, with maxima at about 105°C and 190°C respectively, and two small endothermic effects with maxima at about 310°C and 360°C. The TG curve shows a first stage up to about 190°C which involves both the loss of free water and the first hydroxide mixture dehydration stage. The second multicomponent stage is completed at about 370°C. The final weight loss occurs below about 400°C and is nearly completed at 650°C. The total experimental weight loss was 28.6%, while excluding the free water, the weight loss was 22.2%.

If we suppose, from the above, that the composition of the mixture is the following:

$$Mg_6Fe_2(OH)_{16}CO_3\cdot 4H_2O + 10FeOOH$$

the theoretical weight loss for this mixture would be 22.6%, which is in agreement with the experimental results.

After checking by XRD analysis that the powder heated to 950°C was made up of only $MgFe_2O_4$, the loss for each TG stage was determined using the procedure adopted for the coprecipitated mixture with Mg–Fe 3:1. It was found that 16 water moles were lost in the first stage for every 6 spinel moles produced, approximately 7 of free H_2O, up to 100°C, and the remaining 9 coming from the hydroxide mixture. The other two stages were found to involve the loss of $8H_2O$ and $1CO_2$ moles respectively for every 6 spinel moles produced.

Therefore, the thermal decomposition can be thus defined: after the loss of free water, the first TG stage can be attributed to the loss of the 4 molecules of the interlayer water and to $5H_2O$ from the decomposition of goethite to hematite. The other H_2O and CO_2 moles come from the decomposition of the mixed phase, which, with the hematite formed, leads to $MgFe_2O_4$ formation.

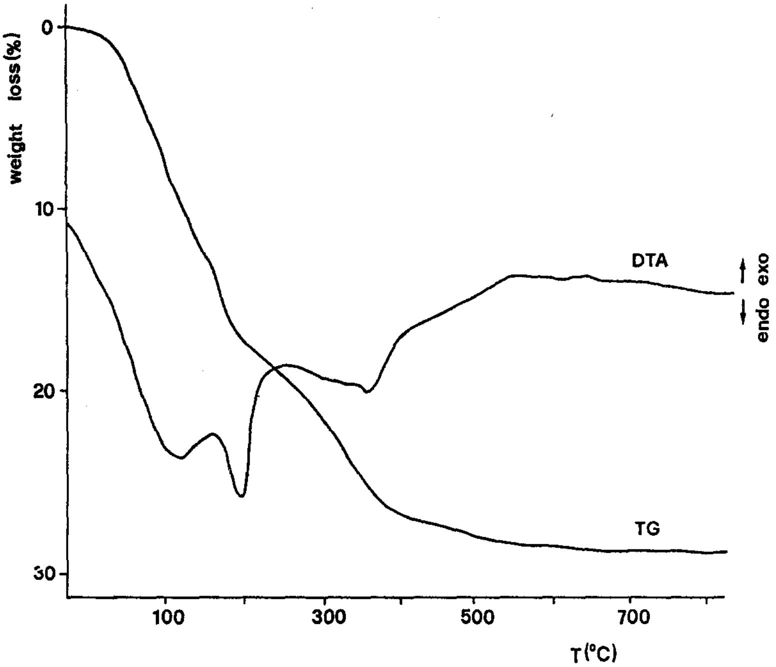

Fig. 3 DTA and TG curves of the coprecipitate with Mg/Fe atomic ratio of 1:2

The similarity between the simultaneous thermal analysis results found for $MgAl_2O_4$ synthesis from the thermal decomposition of coprecipitated hydroxide mixtures [8], and those found for $MgFe_2O_4$ synthesis, seems to indicate the possibility that the formation of $MgFe_2O_4$ occurs through a reaction step between the Fe oxide formed and the mixed phase. The occurrence of this reaction step, however, and the mechanism of spinel formation cannot be ascertained by XRD analysis, as was carried out for the Mg–Al system, because of the poor crystallinity of the Mg–Fe hydroxide mixtures and of their thermal decomposition product. Nevertheless, the XRD patterns of the powder heated to increasing temperatures [5] showed, at the completion of the DTA effect (at 200°C), the presence of three broad peaks, missing at higher temperatures, and did not show the presence of the mixed phase peaks; at this temperature goethite is decomposed to oxide, not detectable in the XRD pattern. Although these factors are not entirely conclusive, the presence of the peaks mentioned may indicate the presence of a transition phase coming from the reaction between the mixed phase and the product of goethite decomposition. Nothing can be stated, however, about the structure of this hypothetical transition phase. These considerations, together with the results of thermal analysis, may support the reaction mechanism hypothesis for the $MgFe_2O_4$ formation.

XRD analysis showed the first broad spinel reflections at a temperature as low as 380°C. Due to the poor crystallinity of the spinel at this temperature, it is rather difficult to establish whether the spinel formation is already completed at 380°C or not.

Mechanical mixture of $Mg(OH)_2 + 2FeOOH$

DTA and TG curves are shown in Fig. 4. The DTA curve shows one broad endothermic peak with a maximum at about 110°C. At higher temperatures, the beginning of an exothermic peak at about 360°C overlaps with a large endothermic peak with a maximum at 380°C. The TG curve shows that the total experimental weight loss was 19.9%. This weight loss can be divided in two distinct, non-overlapping stages, the first in the range 40° to 300°C corresponding to the loss of water from hydrated FeOOH, and the second to the loss of water from $Mg(OH)_2$.

The above results, similar to those for the equivalent Mg–Al mixture [7], clearly show the independent decomposition of the two hydroxides. The exo-thermic peak is ascribable to a crystalline phase transformation of the formed Fe_2O_3, overlapping the endothermic peak above 380°C, characteristic of $Mg(OH)_2$ dehydration [8].

The XRD pattern of the powder heated to 500°C, even though nearly amorphous, already shows weak $MgFe_2O_4$ reflections. At 950°C the peaks of the spinel, in addition to those of MgO and α-Fe_2O_3, are clearly present.

Therefore, the spinel formation occurs through a different mechanism with respect to that of the coprecipitated mixture: in this case the newly formed MgO is able to react with Fe_2O_3 to produce $MgFe_2O_4$ even at about 500°C. Therefore, in the case of the thermal decomposition of mechanical mixtures of Mg and Fe hydroxides, the spinel synthesis starts at temperatures much lower than those observed for the analogous Mg/Al system [7]. We can thus conclude that Fe_2O_3 is much more reactive than alumina.

Conclusions

$MgFe_2O_4$ spinel is formed from the thermal decomposition of coprecipitated hydroxide mixtures at temperatures as low as 380°C. The poor crystallinity of the mixtures does not permit the definition of a mechanism for the spinel synthesis by means of XRD analysis. A reaction between the mixed phase and the product of the FeOOH decomposition seems probable, however, correlating the results of XRD and thermal analyses with those obtained for the Mg–Al hydroxide mixtures. The crystalline structure of this intermediate product has not been established. The transformation into spinel begins at about 380°C. Around 500°C, the spinel is already rather crystalline.

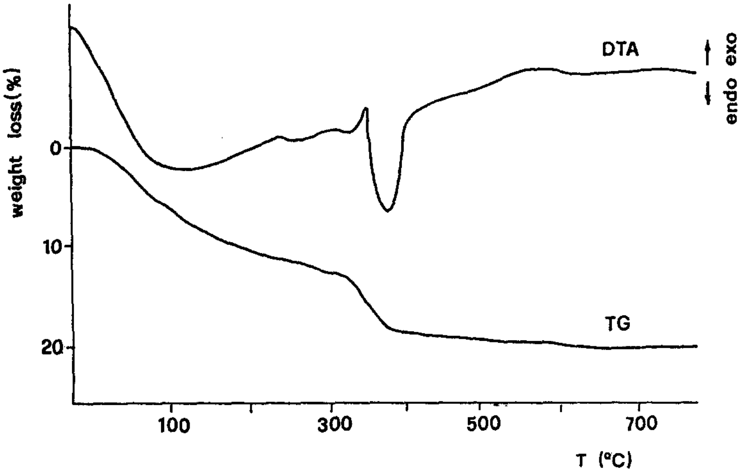

Fig. 4 DTA and TG curves of the mechanical mixture $Mg(OH)_2$ + 2FeOOH

Thermal analysis results clearly show the independent decomposition of the components of the mechanical mixture of hydroxides, with first the decomposition of FeOOH and second that of $Mg(OH)_2$. The spinel formation begins at 500°C, through a solid state reaction between the oxides, and it is completed at about 1000°C. The spinel formation can be thus achieved at low temperature in this case too, but we believe that the mechanism is different. The solid state reaction between the newly formed oxides of Fe and Mg occurs at much lower temperatures than is the case for the corresponding Mg/Al system, showing the much higher reactivity of Fe oxide with respect to alumina.

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References

1 D. W. Johnson Jr., in G. L. Messing, K. S. Mazdiyasni, J. W. McCauley and R. A. Haber (Eds), Advances in Ceramics, Vol. 21: Ceramic Powder Science, The American Ceramic Society, Westerville, Ohio 1987, p.3.

2 I. V. Granovskii, E. M. Kriger, E. A. Nazarova and F. T. Yakushevskaya, Poroshk. Metall. (Kiev), 7 (1967) 19.

3 M. Takahashi, I. R. C. Guimaraes and M. E. Fine, J. Am. Ceram. Soc., 54 (1971) 724.

4 I. Lukacs and C. Strusievici, J. Thermal Anal., 7 (1975) 359.

5 G. Gusmano, P. Nunziante, E. Traversa, R. Montanari and G. Chiozzini, in H. E. Exner and V. Schumacher (Eds), Advanced Materials and Processes, Vol. 1: Advanced Processing and High Temperature Materials, DGM Informationgesellschaft, Oberursel 1990, p. 647.

6 D. Beruto, R. Botter, M. Giordani,, G. Gusmano, E. Traversa and E. Proverbio, in G. de With, R. Terpstra and R. Metselaar (Eds), Euro-Ceramics, Vol. 1: Processing of Ceramics, Elsevier Applied Sciences, London and New York 1989, p. 82.

7 G. Gusmano, P. Nunziante, E. Traversa and G. Chiozzini, J. Thermal Anal., 37 (1991) 1967.

8 G. Gusmano, P. Nunziante, E. Traversa and G. Chiozzini, J. Eur. Ceram. Soc., 7 (1991) 31.

9 K. Hashi, S. Kikkawa and M. Koizumi, Clays Clay Min., 31 (1983) 152.

10 J.C.P.D.S., 1986, A.S.T.M., card number 25–521.

11 R Allman and H. H. Lohse, N. Jahrb. Min., Monatsh., (1966) 161.

12 L. Ingram and H. F. W. Taylor, Mineral. Mag., 36 (1967) 465.

13 R. Allman, Acta Cryst., B24 (1968) 972.

14 H. F. W. Taylor, Mineral. Mag., 37 (1969) 338.

15 R. Allman, Chimia, 24 (1970) 99.

16 P. G Rouxhet and H. F. W. Taylor, Chimia, 23 (1969) 480.

17 M. A. Ulibarri, C. Barriga and J. Cornejo, Thermochim. Acta, 135 (1988) 231.

Zusammenfassung — Es wurde das thermische Verhalten von Hydroxidgemischen, Vorstufen bei der Synthese von $MgFe_2O_4$ Spinell, untersucht.

Die Gemische der Hydroxide wurden durch Kopräzipitationsreaktionen aus Nitratlösungen mit einem Mg/Fe-Atomverhältnis von 1:2 hergestellt. Die Ergebnisse wurden mit dem thermischen Verhalten der separat gefällten Komponenten des Hydroxidgemisches verglichen. Es wurden auch Proben untersucht, die durch mechanisches Vermischen der separat gefällten Hydroxide hergestellt wurden.

Die Spinellbildungstemperatur wurde mittels Röntgendiffraktionsanalyse von Pulverproben unter Erhitzen auf verschiedene Temperaturen identifiziert. Die Gegenwart eines Spinells wurde bei der thermischen Zersetzung der kopräzipitierten Gemische bei einer niedrigen Temperatur von 380°C gefunden. Es wurde eine getrennte Bildung von MgO und Fe_2O_3 bei der thermischen Zersetzung der mechanischen Gemische beobachtet; dennoch konnte bei einer niedrigen Temperatur von 500°C die Bildung von $MgFe_2O_4$ in einer Feststoffreaktion zwischen den Oxiden beobachtet werden.