THERMAL STABILITY OF Ni, Al DOUBLE HYDROXIDES WITH VARIOUS INTERLAYER ANIONS

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ABSTRACT

Hydrotalcite-type compounds of formula $[Ni_{1-x}Al_x(OH)_2]^{x+} X_{x/n}^{n-} \cdot m\,H_2O$, where $0.25 \leqslant x \leqslant 0.33$ and $X^{n-} = CO_3^{2-}$ and SO_4^{2-}, have been synthesized hydrothermally. The thermal decomposition of the compounds was followed by DTA and TG and the resulting products were studied by X-ray techniques. In every case, there was a loss of interlayer H_2O in a first stage, followed by the complete decomposition of the product at around 500°C. The hydroxysulphates lost SO_3 at 850°C. NiO was identified by X-ray diffraction as the decomposition product at temperatures above 600°C, whereas the corresponding spinel, $NiAl_2O_4$, was formed by interaction between both oxides at temperatures higher than 1000°C. We suggest several decomposition schemes for the hydroxycarbonates and hydroxy-sulphates.

INTRODUCTION

Takovite, of typical composition $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, is a pyro-aurite-like mineral related to hydrotalcite, whose structure consists of positively charged brucite-like layers resulting from the replacement of a divalent ion by a trivalent one, with the interlayer space filled by CO_3^{2-} ions and water molecules [1,2].

There are several other minerals with interlayer anions other than carbonate, such as carrboydite, an Ni–Al–SO_4 mineral [3].

The synthetic procedures of analogous compounds include the preparation of magnesium and aluminium mixed hydroxides [4], as well as other double hydroxides with various di- and trivalent cations [5,6]. The chemical composition of these compounds can be expressed by the formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+} X_{x/n}^{n-} \cdot m\,H_2O$ where $M^{2+} = Mg^{2+}$, Ni^{2+}, Fe^{2+}, etc.; $M^{3+} = Al^{3+}$, Fe^{3+}, etc.; $X^{n-} = OH^-$, Cl^-, NO_3^-, CO_3^{2-}, etc.; and $0.25 \leqslant x \leqslant 0.33$ [2], and exhibit anion-exchange properties [7]. The recent synthesis of a hydrotalcite-like compound of composition $[Al_2Li(OH)_6]CO_3 \cdot nH_2O$ sug-

gests that the general formula for layered double hydroxides should be extended to include the monovalent cations in an octahedral arrangement [8].

The physicochemical properties of the above-mentioned compounds are linked to the nature of the anion and the hydration state, which is reflected in a variation of the electrostatic attraction between layers and interlayers [9].

The object of this investigation is the synthesis and thermal decomposition of Ni–Al compounds of varying cationic composition with different interlayer anions.

EXPERIMENTAL

Ni–Al double hydroxycarbonates were prepared as previously described [10] by coprecipitation from Ni^{2+} and Al^{3+} salt solutions by slowly adding an NaOH solution until a suitable pH of 11–12 and 8–8.5 is reached for the molar ratios of $3:1$ and $2:1$, compounds A and B, respectively. The resulting gel was subjected to a hydrothermal treatment for several days in order to improve the compound's crystallinity.

The hydroxy compounds with SO_4^{2-} as interlayer anion were obtained by anion exchange from their corresponding hydroxycarbonates, by dissolving 0.5 g of sample in 500 ml of a 0.01 M H_2SO_4 solution and allowing it to stand for 15–20 h at room temperature [7].

NiO and Al_2O_3 were determined after dissolution of the solids in dilute HCl by atomic absorption on a Perkin-Elmer 380 instrument. IR spectra were recorded on a Beckman AccuLab-2 in the range 4000–600 cm^{-1} using the KBr-pellet technique. X-ray powder diffraction (XRD) patterns were recorded on a Philips PW 1130 with Fe-filtered CoK_α radiation at a scanning rate of 1° 2θ min^{-1}. The DTA and TG diagrams were recorded with a Rigaku-Thermoflex TG–DTA instrument; the rate of heating was 8°C min^{-1}.

RESULTS AND DISCUSSION

The XRD patterns of the synthesized compounds show that the basal reflection appears between 7.7 and 7.9 Å for hydroxycarbonates and between 8.6 and 9.01 Å for compounds exchanged with SO_4^{2-}, which is consistent with the greater diameter of the sulphate ion since the aforementioned spacing represents the thickness of the unit layer [2]. On the other hand, the IR spectra of the hydroxysulphates show the bands corresponding to the SO_4^{2-} but not those of the CO_3^{2-} ion, which have disappeared [10].

Figure 1 shows the DTA and TG curves for the four compounds synthe-

sized. In every case, the DTA plots show a first endothermic peak below 300 °C and a second one at temperatures in the range 250–600 °C. A third peak is observed between 800 and 900 °C for compounds with SO_4^{2-} as interlayer anion.

According to the TG data, the endothermic peak appearing at the lowest temperature can be attributed to the loss of molecular H_2O from the interlayer sheet [11]. For compound A, this peak occurs at temperatures up to 250 °C, whereas the loss of water from the compound with sulphate does not disappear until reaching a temperature of 330 °C.

Compound B shows a similar behaviour, its loss of molecular water yielding a peak at 255 °C, the temperature corresponding to the hydroxy-sulphate derivative being 280 °C.

These results suggest that the greater the extent of substitution of Al^{3+} by Ni^{2+}, and hence the positive charge density in the basic layer, the stronger the attraction between layers, which could account for the fact that the loss of molecular water takes place at higher temperatures for compound B and
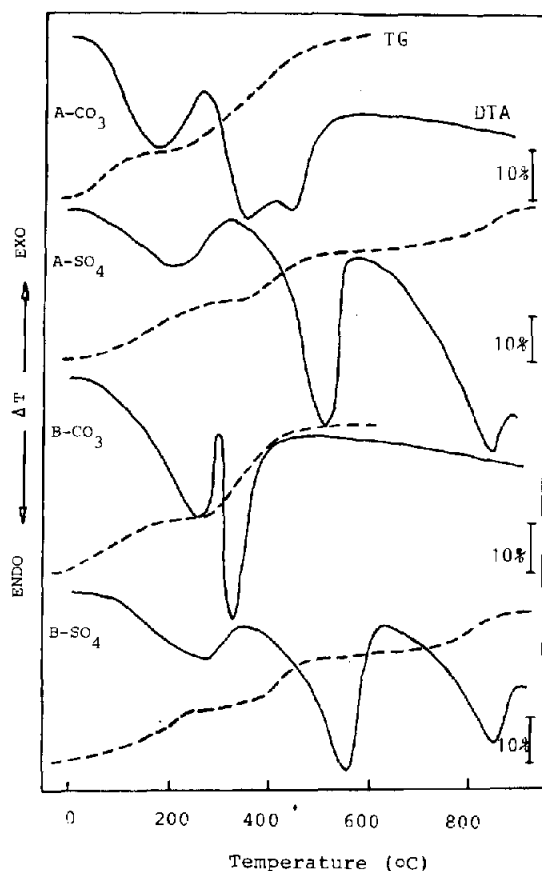

Fig. 1. DTA and TG curves for samples A-CO$_3$, A-SO$_4$, B-CO$_3$ and B-SO$_4$.

its hydroxysulphate derivative than for compound A and its corresponding sulphate compound.

The second endothermic peak is linked to the decomposition of the brucite-like layer [12]. This heat absorption occurs between 250 and 500°C for compound A, and the analysis of its corresponding TG curve is in agreement with the loss of water from the brucite layer and that of CO_2 from the interlayer sheet. This endothermic peak, which appears at 517°C for the hydroxysulphate derivative, according to the TG analysis corresponds solely to the loss of water molecules from the layer, because the loss of the interlayer anion only takes place in this case at higher temperatures. These data can be indicative of the fact that the bond strength between the anions and the basic layer is greater for sulphate than for carbonate.

The aforementioned heat absorption occurs between 275 and 500°C for compound B, whereas that of the corresponding hydroxysulphate continues up to 600°C, the peak temperature being 557°C. The analysis of the TG curves shows that the weight loss from the hydroxycarbonate corresponds to the water molecules from the hydroxyl groups in the brucite-like layer and to CO_2, whereas that of the sulphate compound can only be attributed to the water molecules.

The hydroxysulphates exhibit a third endothermic peak at 852°C in both cases, and the TG analysis is consistent with the loss of interlayer SO_3.

Table 1 shows data corresponding to the chemical analysis. The determination of H_2O and CO_2 was carried out by analyzing the TG curves. The determination of SO_3 was carried out by precipitating SO_4^{2-} as $BaSO_4$.

Figure 2 shows the XRD patterns for the hydroxysulphate of compound A, both in its original form and after calcination at temperatures between 350 and 1100°C. The diagram corresponding to the compound before heating shows all the peaks attributable to this double hydroxide, the data of which are shown in Table 2. The compound heated at 350°C exhibits the same peaks, although a decrease in the d_{001} spacings (due to the contraction brought about by the loss of interlayer water) is observed. The diagram for the compound at 550°C (immediately following the disappearance of the second endothermic peak) does not exhibit the spacings corresponding to the laminar compound, thus showing the relationship with the hydroxysulphate

TABLE 1

Chemical analysis of synthetic Ni–Al double hydroxides (wt.%)

Sample	NiO	Al_2O_3	CO_2	H_2O [a]	SO_3	X_{Ni}
A-CO_3	47.0	10.7	5.4	9.2	—	0.75
A-SO_4	44.8	11.0	—	5.8	10.6	0.74
B-CO_3	40.5	13.9	7.6	2.9	—	0.67
B-SO_4	38.4	14.3	—	9.9	15.6	0.65

[a] Interlayer H_2O.

TABLE 2

X-ray powder data for synthetic Ni–Al double hydroxides with a ratio Ni/Al = 3:1 [a]

Hydroxycarbonate			Hydroxysulphate		
d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
7.87	100	002	8.6	100	002
3.91	38	004	4.30	28	004
2.65	10	100	2.60	15 }	100
2.59	18	006	2.58	16 }	
2.31	7 br	103	2.49	10	102
1.98	6 br	105,008	2.36	8 }	103,105,008
1.522	13	110	2.01	6 vbr }	
1.491	14	112	1.515	10	110
			1.494	10	112

[a] br = broad; vbr = very broad.

decomposition. Only characteristic lines of poorly crystalline NiO are detected, which seems to indicate that the remaining decomposition products must be amorphous solids.

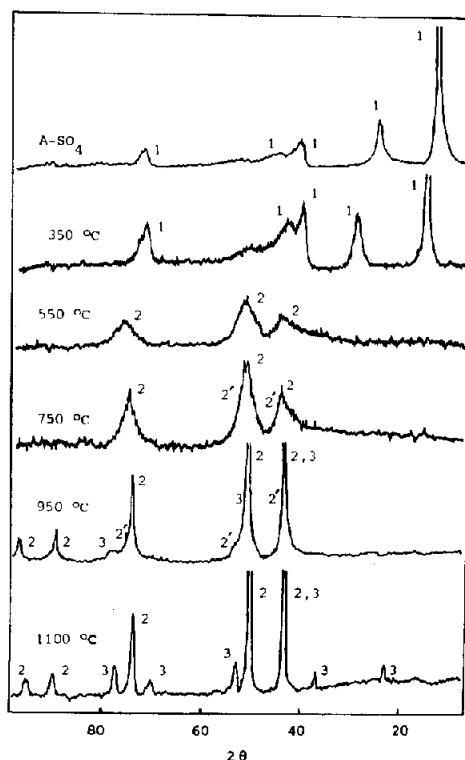The intensity of the lines corresponding to NiO increases with the

Fig. 2. XRD patterns for sample A-SO₄ and after calcination at different temperatures: (1) A-SO₄; (2) NiO; (2′) γ-Al₂O₃; (3) NiAl₂O₄.

calcination temperature between 550 and 950 °C as can be seen on comparing the diagrams obtained in this temperature range. As we stated with regard to DTA data, the detachment of SO_3 occurs at 852 °C and the XRD pattern obtained at 950 °C corresponds to the products formed after the appearance of the third endothermic peak. This pattern shows the peaks corresponding to well-crystalline NiO, but the Al_2O_3 phase, which should be present, is not clearly detected. Its presence cannot be ruled out, however, since a peak occurs at 1.423 Å (coincident with a peak of intensity 100 for ν-Al_2O_3), whereas the other two peaks of maximum intensity which should appear at 1.98 and 2.39 Å, respectively, practically coincide with others for NiO. Nevertheless, the aforementioned spacing (1.432 Å) could also be related to the formation of the spinel, $NiAl_2O_4$, since the solid–solid interaction between both oxides to yield this new compound starts at 900 °C [13]. The XRD pattern found for the hydroxysulphate at 1100 °C clearly shows the spacings corresponding to the spinel and non-reacted, well-crystalline NiO, which indicates that, as expected, the increase in the calcination temperature improves the crystallinity of these compounds.

The above reasoning allows the following scheme to be proposed for the thermal decomposition of the hydroxysulphates
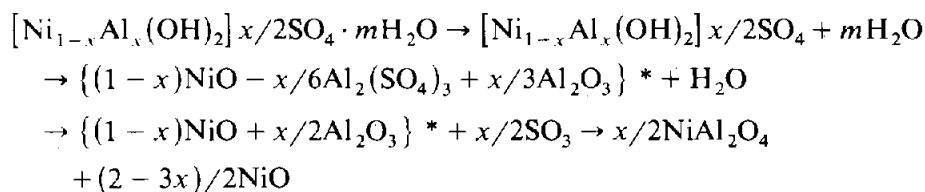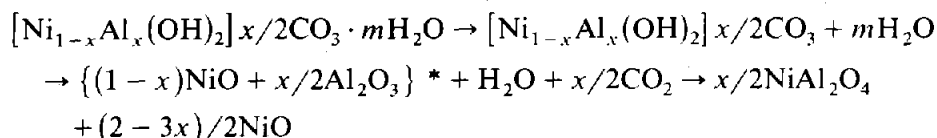
$$\left[Ni_{1-x}Al_x(OH)_2\right] x/2SO_4 \cdot mH_2O \rightarrow \left[Ni_{1-x}Al_x(OH)_2\right] x/2SO_4 + mH_2O$$

$$\rightarrow \left\{(1-x)NiO - x/6Al_2(SO_4)_3 + x/3Al_2O_3\right\} * + H_2O$$

$$\rightarrow \left\{(1-x)NiO + x/2Al_2O_3\right\} * + x/2SO_3 \rightarrow x/2NiAl_2O_4$$

$$+ (2-3x)/2NiO$$

Figure 3 shows the XRD patterns for the hydroxycarbonate (compound A), both at room temperature and after calcination at various temperatures. The d-spacings of the original compound are presented in Table 2. The compound calcined at 250 °C shows d-spacings corresponding to the laminar compound with a small decrease in the d_{001} spacings resulting from the loss of interlayer water. The compound decomposes after heating at 550 °C, and only the presence of NiO crystals is observed in the corresponding XRD pattern, whereas the Al_2O_3, which should be yielded, would be an amorphous solid. No increase in the crystallinity of Al_2O_3 is observed from the XRD pattern when the compound is heated at 750 °C. The presence of NiO and the calcination of the oxide mixture at 750 °C should give rise to the formation of crystalline ν-Al_2O_3, with NiO acting as a crystallization nucleus [13]. Therefore, the oxides formed exhibit a great thermal stability, at least up to 900 °C. The formation of the spinel together with non-reacted NiO can be detected in the XRD pattern for the compound heated at 1100 °C.

On the basis of the preceding argument, the following scheme can be

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* Only NiO was detected by XRD.

proposed for the thermal decomposition of the hydroxycarbonates

$$\left[Ni_{1-x}Al_x(OH)_2\right] x/2CO_3 \cdot mH_2O \rightarrow \left[Ni_{1-x}Al_x(OH)_2\right] x/2CO_3 + mH_2O$$

$$\rightarrow \left\{(1-x)NiO + x/2Al_2O_3\right\} * + H_2O + x/2CO_2 \rightarrow x/2NiAl_2O_4$$

$$+ (2-3x)/2NiO$$

An analogous study to that of compound A and its sulphate derivative was carried out for compound B and its corresponding hydroxysulphate. The results obtained suggest decomposition schemes analogous to those proposed for compound A and its hydroxysulphate.

As far as the crystallinity of the products from the thermal decomposition is concerned, the XRD patterns for the compounds heated above 550°C (once the destruction of the laminar compound has been accomplished) shows that the lower the proportion of Al_2O_3 present in the mixture with NiO, the higher the crystallinity of the latter, i.e., the diffraction lines of the NiO formed by decomposition of compound A (with a higher Ni/Al ratio)
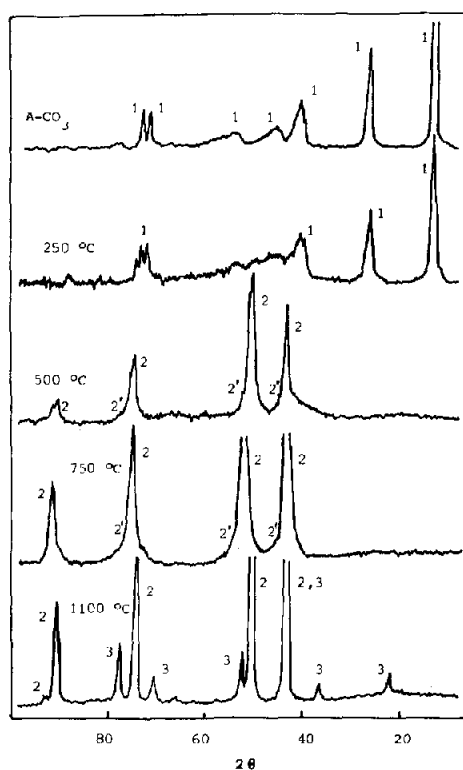

Fig. 3. XRD patterns for sample A-CO$_3$ and after calcination at different temperatures: (1) A-CO$_3$; (2) NiO; (2') γ-Al$_2$O$_3$; (3) NiAl$_2$O$_4$.

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* Only NiO was detected by XRD.

indicate that this compound is more crystalline than that resulting from the decomposition of compound B (with a lower Ni/Al ratio). An analogous variation is found on comparing the XRD patterns corresponding to the hydroxysulphates with varying Ni/Al ratios, which can be interpreted as indicative of the fact that Al_2O_3 slows down the crystallization of the NiO phase [13].

On the other hand, the crystallinity of the formed spinel, $NiAl_2O_4$, is higher from the decomposition of compound B or its hydroxysulphate than that obtained from A or its sulphate derivative, which indicates that the higher the percentage of non-reacted NiO, the smaller the crystallinity of the nickel aluminate.

REFERENCES

1 R. Allmann, Acta Crystallogr., Sect. B, 24 (1968) 972.
2 H.F.V. Taylor, Mineral. Mag., 39 (1973) 377.
3 E.H. Nickel and R.M. Clarke, Am. Mineral., 61 (1976) 366.
4 M.C. Gastuche, G. Brown and M.M. Mortland, Clay Miner., 7 (1967) 177.
5 S. Miyata, Clays Clay Miner., 23 (1975) 369.
6 S. Miyata and A. Okada, Clays Clay Miner., 25 (1977) 14.
7 D.L. Bish, Bull. Mineral., 103 (1980) 170.
8 C.J. Serna, J.L. Rendón and J.E. Iglesias, Clays Clay Miner., 30 (1982) 180.
9 G.W. Brindley and S. Kikkawa, Clays Clay Miner., 28 (1980) 87.
10 M.J. Hernandez, M.A. Ulibarri, J.L. Rendón and C.J. Serna, Phys. Chem. Miner., in press.
11 G. Mascolo and O. Marino, Mineral. Mag., 43 (1980) 619.
12 G. Mascolo and O. Marino, in D. Dollimore (Ed.), 2nd Eur. Symp. Thermal Analysis, Aberdeen, 1981, Heyden, London, 1981, p. 391.
13 G.A. El-Shobaky and N.M. Ghoneim, Thermochim. Acta, 63 (1983) 39.