THERMAL DECOMPOSITION OF COBALT AND NICKEL DOUBLE HYDROXY-CHLORIDES

L RASINES * and P. GARCÍA CASADO

Facultad de Farmacia, Universidad de Navarra, Pamplona (Spain)

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ABSTRACT

A combination of thermal analysis and X-ray diffraction is used to study the decomposition of eight samples of mixed cobalt and nickel hydroxy-chlorides at temperatures up to 900°C. The phases identified after the thermal treatments enable the processes involved and the equilibrium diagram of the oxides of the metals to be established.

INTRODUCTION

Many of the simple hydroxy-salts have layer structures which are closely related to the CdI_2-type hydroxides, $M(OH)_2$ [1]: for instance, $Co_2(OH)_3Cl$ and the hydroxy-salt of average composition $Ni_{15}(OH)_{26}Cl_4$, which Feitknecht and co-workers [2,3] termed cobalt β-hydroxy-chloride II and nickel hydroxy-chloride V. A double hydroxy-salt results when some fraction of the metal of the simple salt is replaced by another cation and usually these compounds retain their original structure.

Thermal decomposition of double hydroxy-salts yields intimate mixtures of the two oxides [4] and, for the double hydroxy-chlorides of cobalt and nickel, enables the equilibrium diagram of the two metal oxides to be determined.

This work extends that of Robin [5], who studied mixtures of nickel and cobalt nitrates in various proportions at 600, 800 and 1,000°C. Robin showed that at high temperatures CoO and NiO in any proportions are able to form solid solutions of the NaCl type. He also showed that at intermediate temperatures the solid solutions can be oxidized to two phases: a face-centered cubic, with composition different from that of the initial solid solution, and the spinel, formed by Co_3O_4. Robin [5] concluded that the mixed spinel which results from substitution of some Co^{2+} ions of Co_3O_4 by Ni^{2+} can be prepared at low temperatures in the metastable form.

EXPERIMENTAL

A series of eight samples of cobalt and nickel double hydroxy-chlorides was prepared by incomplete precipitation of binary mixtures, in various

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* Present address: Instituto Elhuyar de Química Inorgánica, Facultad de Ciencias Químicas, Madrid-3, Spain.

proportions, of 0.2 M solutions of $CoCl_2 \cdot 6\ H_2O$ and $NiCl_2 \cdot 6\ H_2O$ with 1.0 M NaOH, followed by ageing at 70°C for three days. An amount of NaOH equivalent to 25% of the cations present was used in the precipitation. All reagents were of analytical reagent grade.

After drying the samples in vacuo the amount of water remaining was determined by TGA. The cobalt present, after the samples had been dissolved, was established by spectrophotometric analysis at 565 nm of the complex formed at pH 5.5 with nitroso-R salt, after adding KF. Nickel and chloride concentrations were gravimetrically determined with dimethylglyoxime and $AgNO_3$ solutions, respectively. Finally, the amount of hydroxide was calculated.

The phases present in the samples were identified by X-ray diffraction at room temperature using Co $K\alpha$ radiation, and their thermal decomposition was studied by DTA, TGA and X-ray diffraction analysis of the products of the thermal treatments for several hours at various temperatures from 300°C to 900°C. A Philips PW 1310 diffractometer was used for X-ray diffraction and a Deltatherm D2000R (Technical Equipment Corporation) for thermal analysis. With DTA, α-Al_2O_3 previously heated at 1,000°C was used as the inert substance, the N_2 flow was constant and the heating rate was 10°C min^{-1}.

RESULTS

Table 1 shows data on preparation, chemical analysis, X-ray identification and DTA of the samples: the volume concentrations of the initial solutions of the two chlorides, the composition of the samples, the structural type of the phases they contained and the temperatures at which DTA peaks appeared. All the peaks were endothermic.

The phases present in the samples were found to be isomorphic with cobalt β-hydroxy-chloride II, nickel hydroxy-chloride V or nickel hydroxide, depending on the cobalt concentration of the initial solution. In the first three samples only one phase, isomorphic with cobalt hydroxy-chloride, was present. These phases had the compositions $Ni_{0.11}Co_{1.89}(OH)_3Cl$, $Ni_{0.17}$-$Co_{1.83}(OH)_3Cl$, and $Ni_{0.32}Co_{1.68}(OH)_3Cl$, which can de derived from $Co_2(OH)_3Cl$ by substitution of 5.5%, 8.5%, and 16.0% of cobalt by nickel, respectively. Samples 4—8 contained a mixture of the phases indicated in Table 1.

The thermograms for the first three samples were almost identical; Fig. 1 shows the TGA results compared with those of DTA for sample 3. The thermograms of samples 4—7 were similar to those of Fig. 2, which corresponds to sample 6, and Fig. 3 shows the same curves for the final sample, number 8.

The first six samples, containing one double hydroxy-chloride isomorphic with cobalt β-hydroxy-chloride II, showed three DTA peaks: the first, at about 458°C (for sample 5, this peak is superimposed on that appearing at 350°C); the second, at temperatures from 686°C for the first sample to

TABLE 1

Data on preparation, chemical analysis, identification and DTA peaks of the samples [a]

No.	v_0		Composition				r	s_p	DTA peaks					
	Co	Ni	Co	Ni	Cl	OH								
1	90	10	54.5	3.20	17.3	25.0	94	II				446 vs	686 s	876 s
2	80	20	52.8	4.89	17.3	24.9	92	II				462 vs	695 s	861 m
3	70	30	48.4	9.20	17.2	24.9	84	II				457 vs	698 s	838 m
4	60	40	42.6	15.8	13.7	27.2	73	II + V	215 vw	295 vw	350 vw	446 vs	672 m	825 m
5	50	50	30.7	28.6	11.5	28.8	52	II + V	222 w	286 w		415 vs	667 vw	752 w
6	40	60	30.2	28.6	12.0	28.3	51	II + V	220 vw	302 vw	354 w	448 s	645 vw	752 w
7	30	70	17.4	42.6	9.2	30.3	29	V + I	226 w	289 w	348 m			
8	20	80	10.6	52.0	2.6	35.0	17	I + V (t)		305 vs				

[a] v_0, Volume% of 0.2 M metal chlorides in the initial solution; r, molar ratio 100 Co/(Co + Ni); s_p, solid phases present (the most abundant first): $Ni_2Co_{2-x}(OH)_3Cl$ (II), $Co_xNi_{15-x}(OH)_{26}Cl_4$ (V), $Co_xNi_{1-x}(OH)_2$ (I); (t) traces.
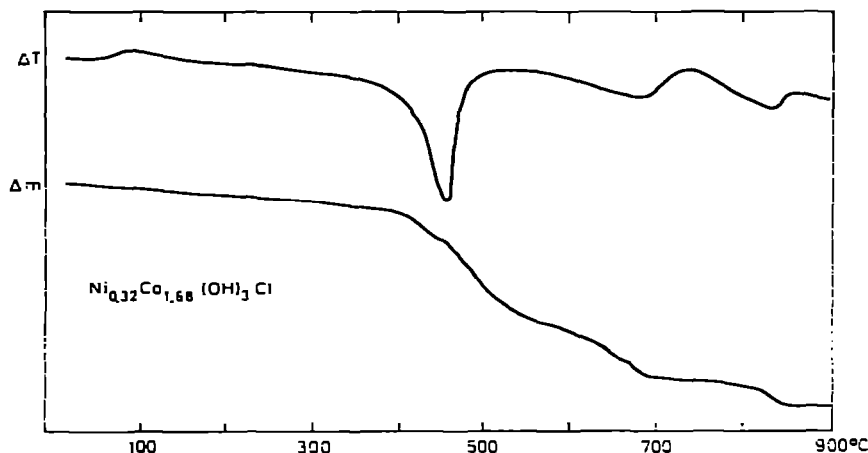
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Fig. 1. DTA (ΔT) and TGA (Δm) curves for sample 3.

645°C for the sixth; and the third, at temperatures decreasing from 876°C to 752°C.

At the same time, samples 4—7 inclusive, containing a double hydroxy-chloride isomorphous with nickel hydroxy-chloride V, showed three peaks at about 220°C, 290°C and 350°C. Sample number 8, containing almost exclusively the double hydroxide, showed only one very strong peak at 305°C.

Figure 4 shows the phases identified after various thermal treatments for at least one day: that is the face-centered cubic solid solution, $Ni_xCo_{1-x}O$, the spinel, Co_3O_4, and the mixed spinel, $(Ni_xCo_{1-x})Co_2O_4$, resulting from Co_3O_4 by substitution of some of the cobalt ions by nickel. Figure 4 is the equilibrium diagram for both oxides and three regions can be distinguished: (1) where the spinel phase is present, (2) where the face-centered cubic phase appears, and (3) where both phases coexist.
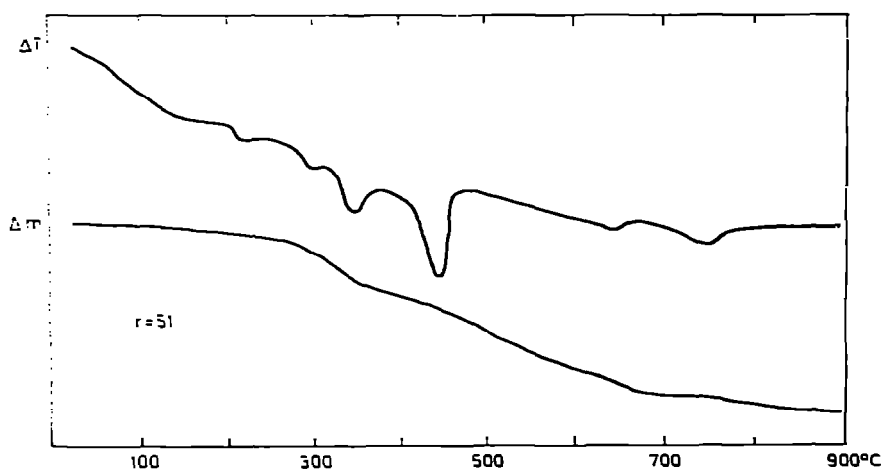

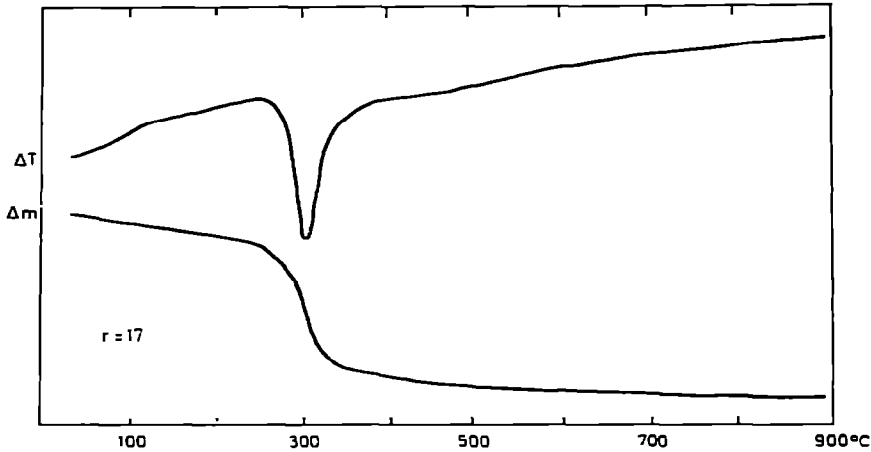Fig. 2. DTA (ΔT) and TGA (Δm) curves for sample 6.

Fig. 3. DTA (ΔT) and TGA (Δm) curves for sample 8.

It is evident that the cubic solid solution appears almost exclusively at high temperatures, whatever the cobalt concentration. However, this solid solution also appears at lower temperatures, and even at the lowest examined when the cobalt concentration is low. In contrast, the mixed spinel is the product of thermal treatment at 450°C of samples rich in cobalt. In all other cases, a mixture of both phases is obtained.
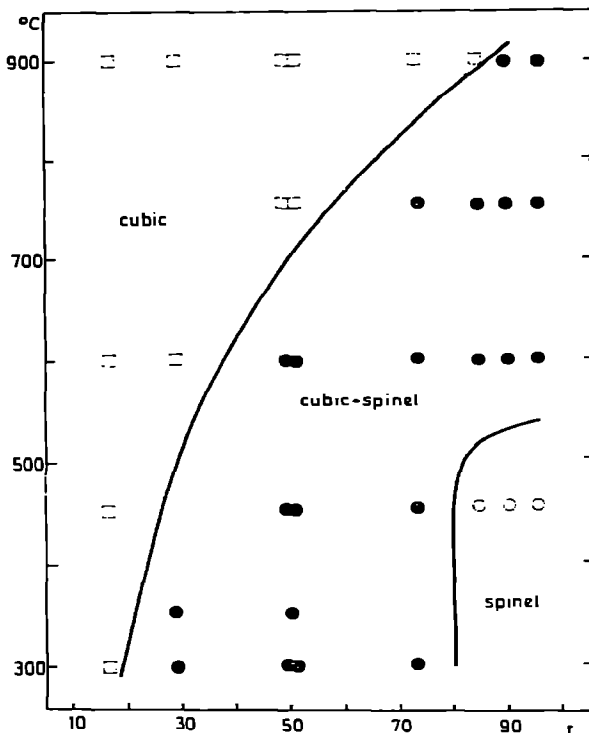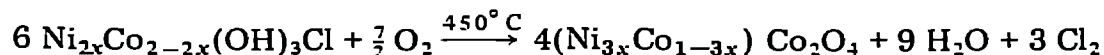

Fig. 4. Phases identified after the following thermal treatments: 300°C for 72 h, 350°C for 72 h, 450°C for 72 h, 600°C for 36 h, 750°C for 24 h, and 900°C for 24 h.

DISCUSSION

For samples 1—3, the first DTA peak, appearing at about 450°C, can be attributed to thermal decomposition of the double hydroxy-chloride

$$6\ Ni_{2x}Co_{2-2x}(OH)_3Cl + \tfrac{7}{2}O_2 \xrightarrow{450°C} 4(Ni_{3x}Co_{1-3x})\ Co_2O_4 + 9\ H_2O + 3\ Cl_2$$

because treatment at 450°C for 72 h yields the mixed spinel and the average percentage weight loss calculated for these samples is 21.4, in good agreement with the measured value of 21.6.

The products after heating at 600°C for 36 h, however, are Co_3O_4 and traces or small amounts of the face-centered cubic phase. Therefore, the second peak, appearing at about 690°C, has to be attributed to the decomposition reaction of the mixed spinel into two products

$$6(Ni_xCo_{1-x})\ Co_2O_4 \xrightarrow{690°C} 4\ Co_3O_4 + 6\ Ni_xCo_{1-x}O + O_2$$
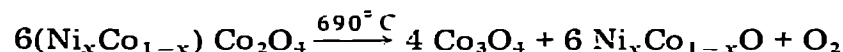
Finally, the products of the thermal treatments at 900°C for one day suggest that the third peak, which appears at temperatures of 876°C for the first sample decreasing to 838°C for the third sample, corresponds to the conversion

$$2\ Co_3O_4 \rightarrow 6\ CoO + O_2$$
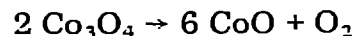
and the simultaneous homogenization of the face-centered cubic phase. From results of the thermal treatment at 900°C, this reaction is incomplete for samples 1 and 2 but proceeds to completion for sample 3.

Samples 4—7, which contained a hydroxy-chloride mixture isomorphous with cobalt β-hydroxy-chloride II and nickel hydroxy-chloride V, showed the same peaks pictured in Fig. 2 for sample 6. Those peaks appearing for sample 4 at 446°C, 672°C and 825°C, for sample 5 at 415°C, 667°C and 752°C, and for sample 6 at 448°C, 645°C and 752°C, are due to the three reactions shown above. Peaks appearing at about 220°C, 290°C and 350°C are due to thermal decomposition of the mixed hydroxy-salt isomorphous with nickel hydroxy-chloride V.

In Fig. 3, which shows DTA and TGA curves for sample 8, there is only one endothermic peak at about 305°C with a parallel loss of weight. Both effects are attributed to dehydration of the double hydroxide
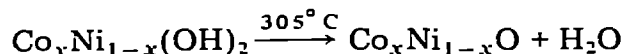
$$Co_xNi_{1-x}(OH)_2 \xrightarrow{305°C} Co_xNi_{1-x}O + H_2O$$

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