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# Identification of solid solutions of coprecipitated Ni-Co oxalates using XRD, TG and SEM techniques

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**Abstract**

Homogeneous solid-solution oxalates of $Ni^{2+}$ and $Co^{2+}$ ions were synthesized by coprecipitation from nitrate solutions using a double-inlet technique. The identification of the solid solutions used X-ray powder diffraction (XRD), thermogravimetry (TG) and scanning electron microscopy (SEM) techniques. The experimental results showed that the coprecipitated powders have characteristics that are different from those of the mechanical mixtures with the same stoichiometry.

## INTRODUCTION

The usual preparation of various ferromagnetic materials (alloys, ferrites, and oxides) involves a solid reaction between two metals or two metal oxides. Because this requires the diffusion of the cations or metal atoms over large distances (about $10^4$ Å), high temperatures are necessary. It seemed possible to eliminate this long-range diffusion problem by starting with two metal ions in a solid solution, in which case the ions would have to diffuse only the distance of the lattice spacings or a few ångströms.

Various unconventional methods of powder preparation have been investigated and evaluated [1–3]. Wickham [4] and Robin [5] indicated that some bimetal oxalates form solid solutions. Schuele [6] successfully prepared Co-Fe, Ni-Fe, Zn-Fe, Mg-Fe and Mn-Fe oxalate solid solutions, but failed with the Cu-Fe system. He concluded that ions with nearly the same ionic radii can form solid solutions with each other. Fischer and coworkers [7, 8] prepared Ni-Fe-Zn oxalate solid solutions by similar methods, and discussed the effect of different preparations on the properties of the coprecipitates as well as on the final decomposition products. Because these oxalates can be decomposed thermally at moderate temperatures to yield the metal or metal oxides, they can be

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selected as an intermediate product containing metal ions of the required stoichiometry. Dollimore [9] discussed the possibility of producing metal and alloy powders with a very high surface area by decomposition of the corresponding oxysalts.

Ni-Co alloys, and Ni and Co metals and oxides, as well as their spinel oxides, are all commonly used in industry. The finely powdered forms of these materials are required to meet some specific purposes. The aim of the research described in this paper was to develop a method of preparing and identifying Ni-Co solid solution in a very finely powdered form, so that powder of either Ni-Co alloy, metals or spinel oxide with a required surface area might be produced by decomposing the corresponding solid solution of the oxalates.

## PREPARATION

### *Materials*

$Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were obtained from J.T. Baker Chemical Co.; the former is a blue crystalline powder, the latter a pink crystalline powder. Oxalic acid was purchased from Fisher Scientific, and is a fine white powder. All three compounds were chemically pure, and were used without further treatment.

### *Methods*

The general composition of the coprecipitated Ni-Co oxalates is $Ni_xCo_{1-x}C_2O_4 \cdot 2H_2O$. They were prepared as follows Distilled water (500 ml) and 0.125 M oxalic acid solution (50 ml) were mixed together in a reactor. (We have found that crystals of the corresponding oxalate precipitates grow with a uniform shape when the solution is acidic.) A 0.125 M solution of nitrate ion (1000 ml), made by mixing nickel nitrate and cobalt nitrate in the required mole ratio of $Ni^{2+}$ and $Co^{2+}$, was added simultaneously with a 0.125 M oxalic acid solution (950 ml) to the solution already present in the reactor, using a double-inlet technique employing dosing pumps at 50°C with stirring. The dosing was completed in 24 h, and was followed by another 24 h of stirring. Then, the reacted solution was left until all the precipitate had settled, the remaining clear solution was decanted off, and the precipitate was washed twice with distilled water. The precipitate was then filtered, and during filtering, it was washed sequentially with ethyl alcohol and acetone. After filtering, the precipitate was dried at 60°C. When these conditions are strictly observed, a precipitate of composition $Ni_xCo_{1-x}C_2O_4 \cdot 2H_2O$ in about 98% yield is obtained. The nickel oxalate and cobalt oxalate are slightly soluble in acidic solution: this may be why we cannot get an even higher yield. In this study, five different compositions of the precipitate were prepared: $CoC_2O_4 \cdot 2H_2O$, $Ni_{0.3}Co_{0.7}C_2O_4 \cdot 2H_2O$, $Ni_{0.5}Co_{0.5}C_2O_4 \cdot 2H_2O$, $Ni_{0.7}Co_{0.3}C_2O_4 \cdot 2H_2O$ and $NiC_2O_4 \cdot 2H_2O$. For convenience, these five precipitates are called sample Nos. 1, 2, 3, 4 and 5, respectively.

## EXPERIMENTAL

The X-ray powder diffraction analysis was performed on a Scintag XDS2000 powder diffractometer with Cu K$\alpha$ radiation, $\lambda = 1.540598$, using a solid-state Ge detector cooled by liquid nitrogen. The experimental conditions, for all patterns taken, were: working voltage, 45 kV; working current, 40 mA; $10° < 2\theta < 70°$; continuous scan with a speed of 3.0° $min^{-1}$ and a 0.03° step for intensity integration. The measurements were taken at room temperature in air under normal pressure. The data were processed using Scintag software DMS version 2.0 on a Micro VAX 3100 with a Tektronix terminal.

The TG (thermogravimetry) analysis was performed on a Du Pont 1091 thermal analysis unit, the experiment was carried out at a heating rate of 10°C $min^{-1}$ in a dynamic nitrogen flow of 25 $cm^3$ $min^{-1}$. Sample weights were $6.63 \pm 0.1$ mg.

The scanning electron microscopic studies were performed on a JEOL JSM-6100 scanning electron microscope. The surface of the sample was coated with a thin, uniform, electrically conductive gold film. The excitation voltage used was 20 kV.

## RESULTS AND DISCUSSIONS

Samples No. 1 and No. 5 are single oxalates. Figure 1, a and b, shows the X-ray patterns of these two compound; both were identified as $\alpha$-type crystals by comparing our results with those obtained by Deyrieux [10]. Figure 1, c, d, e, f, g, h and i are X-ray patterns for mechanical mixtures of nickel oxalate and cobalt oxalate in different mole ratios, namely, cobalt oxalate: nickel oxalate = 8:2, 7:3, 6:4, 5:5, 4:6, 3:7 and 2:8. All these patterns are similar, but are differentiated by the relative heights of the two peaks at about $2\theta = 22.5°$ and 30.2°, respectively. From Fig. 1, it can be seen that nickel oxalate has a peak at $2\theta = 30.4272°$, and cobalt oxalate has a peak at $2\theta = 30.1969°$. Therefore, when these two compounds are mixed together, the shape of the peak at about $2\theta = 30.2°$ could be the result of the overlap of their respective peaks. Figure 2 gives detailed structures of the peak at about $2\theta = 30.2°$ for the same compositions as in Fig. 1. A systematic change in the peak shape can be seen in Fig. 2, and it was found by profile analysis that the peak is an overlap of the cobalt oxalate and nickel oxalate peaks. As an example, Fig. 3 is the separation of the overlap peak for the mechanical mixture of cobalt oxalate and nickel oxalate in the

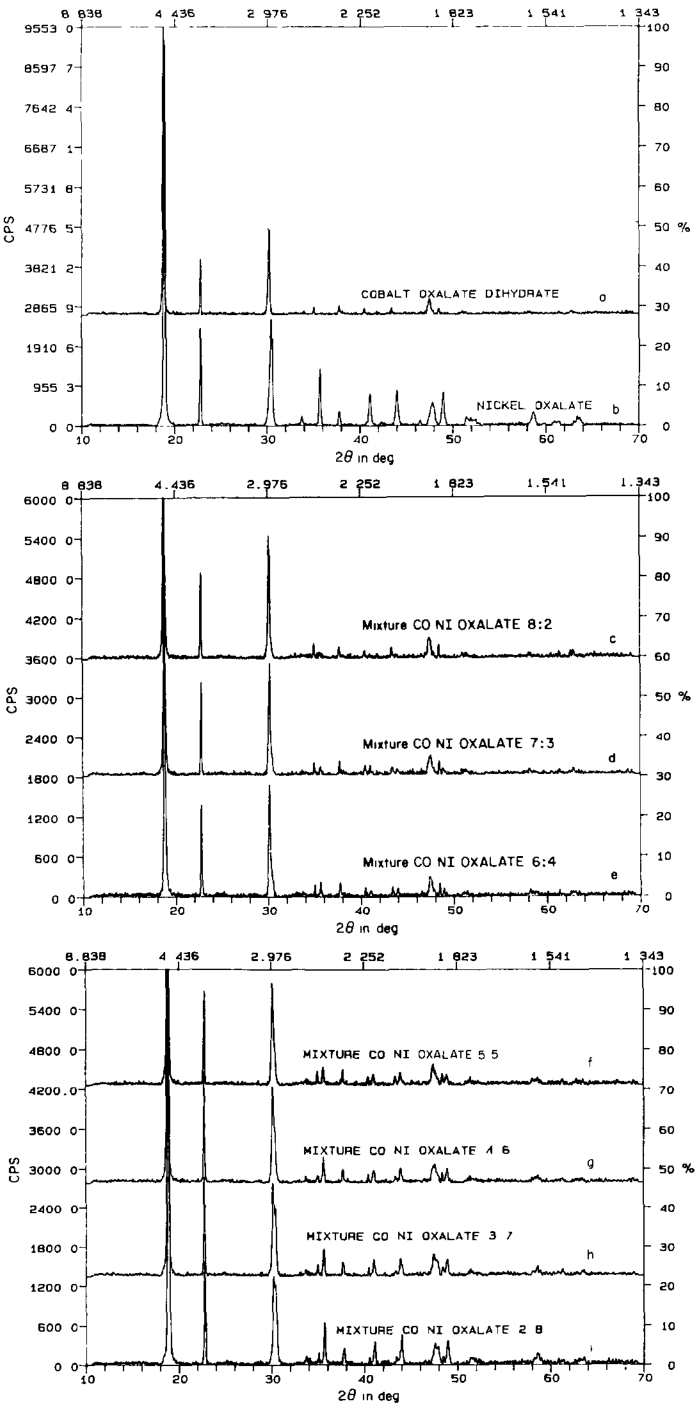


Fig. 1. The X-ray diffraction patterns: a, cobalt oxalate dihydrate; b, nickel oxalate dihydrate; c, d, e, f, g, h, i, mechanical mixtures of cobalt oxalate dihydrate and nickel oxalate dihydrate in mole ratios 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, respectively.

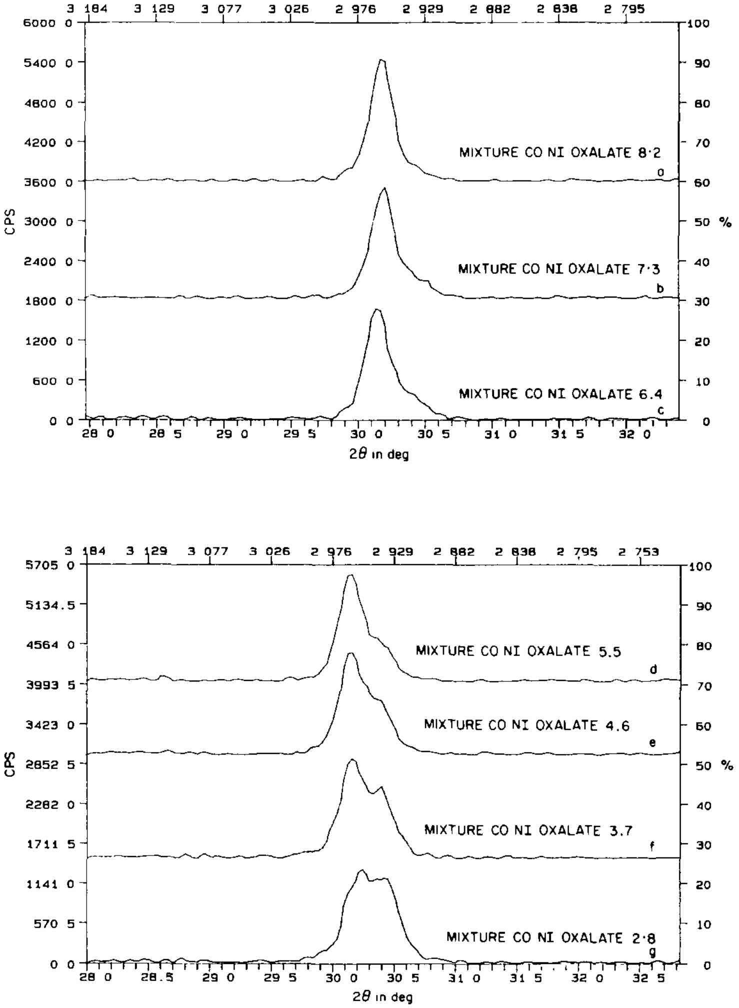
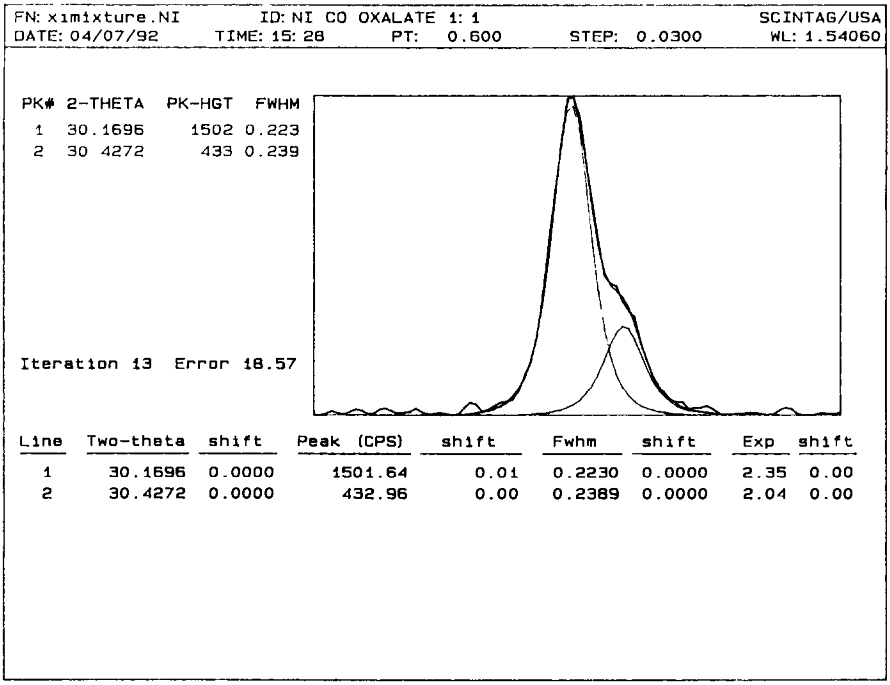


Fig. 2. The detailed structure of the X-ray peaks at about $2\theta = 30.2°$ for the same compositions as in Fig. 1: a, b, c, d, e, f, g, mechanical mixtures of cobalt oxalate dihydrate and nickel oxalate dihydrate in mole ratios 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, respectively.

mole ratio 7:3. From Fig. 3, it can be seen that the $2\theta$ values of the two separated peaks fit perfectly with the $2\theta$ values of the peaks of cobalt oxalate and nickel oxalate. Therefore, it can be concluded that the mechanical mixing of the two single oxalates does not cause any changes in their crystal structure, i.e. their original structures are preserved.

Figure 4 shows the SEM photos of samples No. 1 and No. 5. These indicate that nickel oxalate has rounded particles with a radius of about 2.5 μm. Cobalt oxalate, however, is in the form of rods, about 2 μm wide and about 25 μm long. Figure 5 shows the SEM photos of the mechanical mixtures of samples No. 1 and No. 5, in mole ratios 3:7, 5:5 and 7:3,



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FN: ximixture.NI          ID: NI CO OXALATE 1: 1                              SCINTAG/USA
DATE: 04/07/92        TIME: 15: 28        PT:    0.600        STEP:  0.0300     WL: 1.54060

PK#  2-THETA   PK-HGT  FWHM
 1   30.1696    1502  0.223
 2   30 4272     433  0.239

Iteration 13   Error 18.57

Line   Two-theta   shift    Peak (CPS)    shift     Fwhm    shift     Exp   shift
 1     30.1696    0.0000     1501.64      0.01    0.2230   0.0000    2.35   0.00
 2     30.4272    0.0000      432.96      0.00    0.2389   0.0000    2.04   0.00
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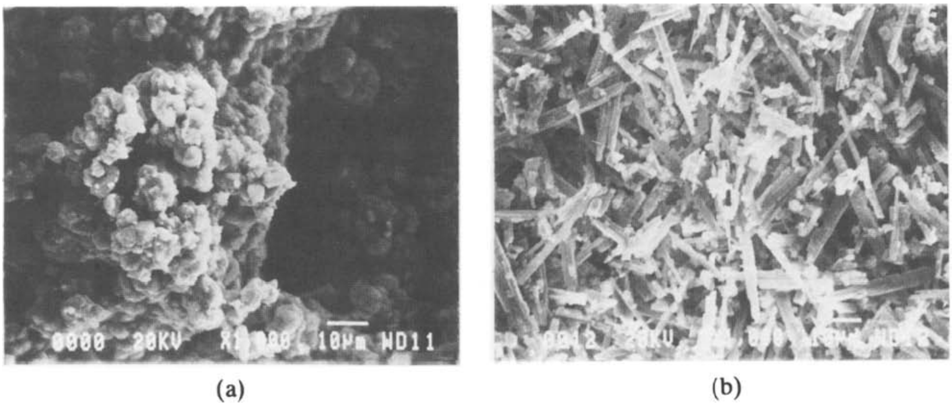
Fig. 3. The separation of the overlap peak at about $2\theta = 30.2°$ for the mechanical mixture of cobalt oxalate dihydrate and nickel oxalate dihydrate in the mole ratio 7:3.

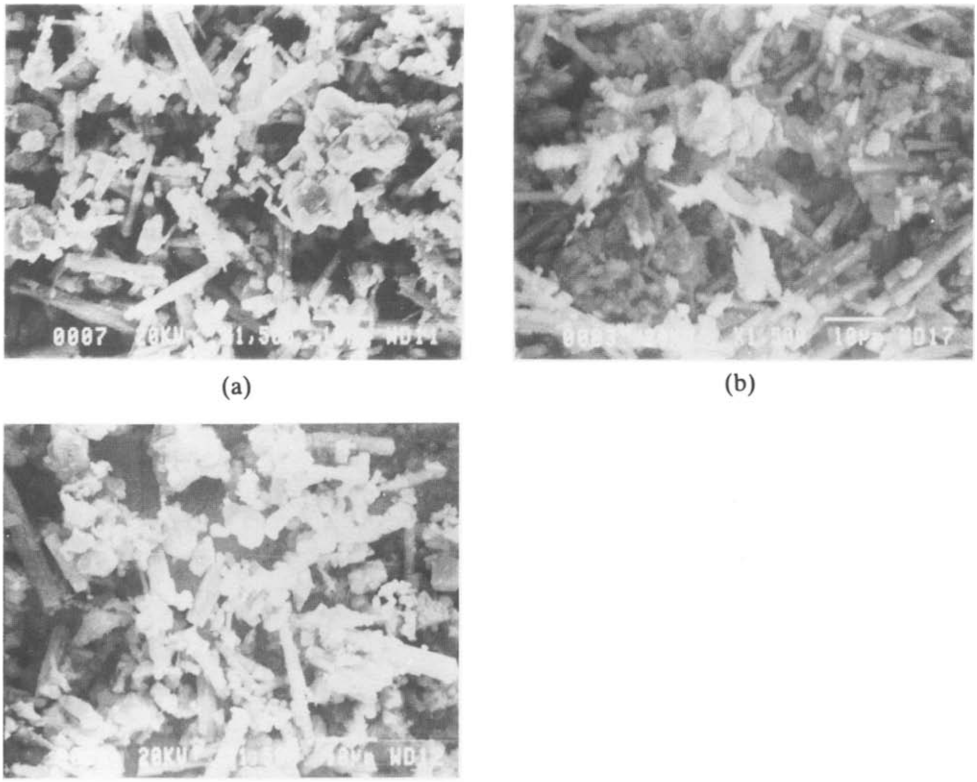
respectively. From Fig. 5, it can be seen that these are simply a mixture of the round and rod crystals, which supports the above conclusion.

Figure 6 shows the TG traces of samples No. 1 and No. 5, and of the mechanical mixture of these two samples in a mole ratio of 6:4. From Fig. 6, it can be seen that the TG trace of the mechanical mixture has two DTG



(a) (b)

Fig. 4. Scanning electron micrographs of: a, xalate dihydrate; and b, cobalt oxalate dihydrate.



(a)

(b)

(c)

Fig. 5. Scanning electron micrographs of mechanical mixtures of cobalt oxalate dihydrate and nickel oxalate dihydrate: a, mole ratio 7:3; b, mole ratio 5:5; c, mole ratio 3:7.

peaks in the range 100–200°C, which correspond to the dehydration peak in the range 100–170°C of the cobalt oxalate (Fig. 6a), and the dehydration peak in the range 145–205°C of the nickel oxalate (Fig. 6b). In the range 285–380°C, two distinct DTG peaks also appear in the mechanical mixture corresponding to the decomposition peak (320–380°C) of cobalt oxalate and the decomposition peak (280–340°C) of nickel oxalate.

Figure 7 shows a comparison of the X-ray patterns of samples Nos. 2–4 which were prepared by coprecipitation, and the mechanical mixtures of samples No. 1 and No. 5 of the same stoichiometry. It is very difficult to use the differences between these patterns because the significant peaks are almost the same. However, if the peak at about 30.2° is investigated in detail, the difference is revealed. Figure 8 shows the detailed structure of the peak at about $2\theta$ 30.2° for the same compositions as in Fig. 7. It can be seen from Fig. 8 that the peaks at about $2\theta$ 30.2° are all symmetrical for the three coprecipitate samples Nos. 2–4, which means that the peak at this $2\theta$ angle could be a single peak; but the peaks at this angle are all unsymmetrical for the three mechanical mixtures, and as mentioned above,

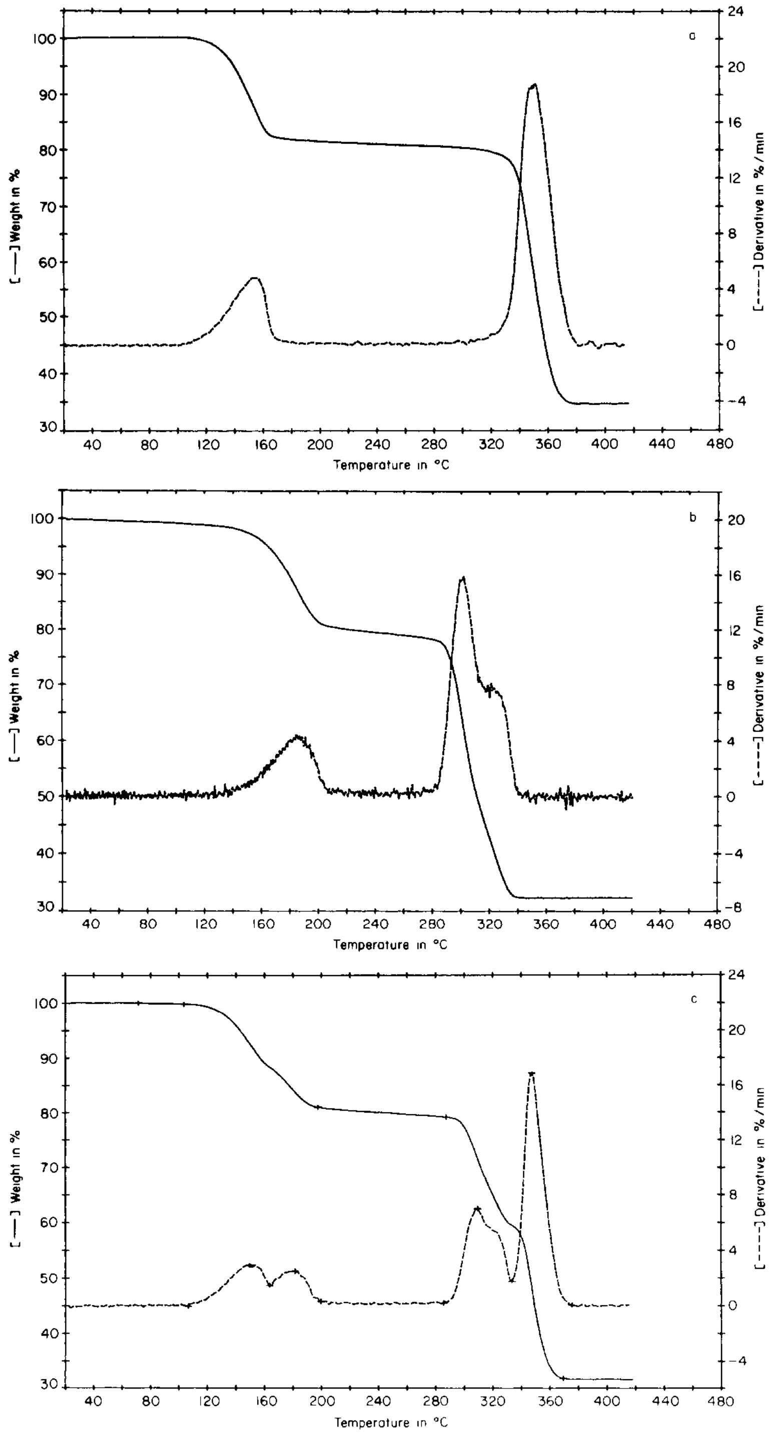


Fig. 6. The TG and DTG curves: a, cobalt oxalate dihydrate; b, nickel oxalate dihydrate; c, the mechanical mixture of $NiC_2O_4 \cdot 2H_2O$ and $CoC_2O_4 \cdot 2H_2O$ in the mole ratio 6:4.

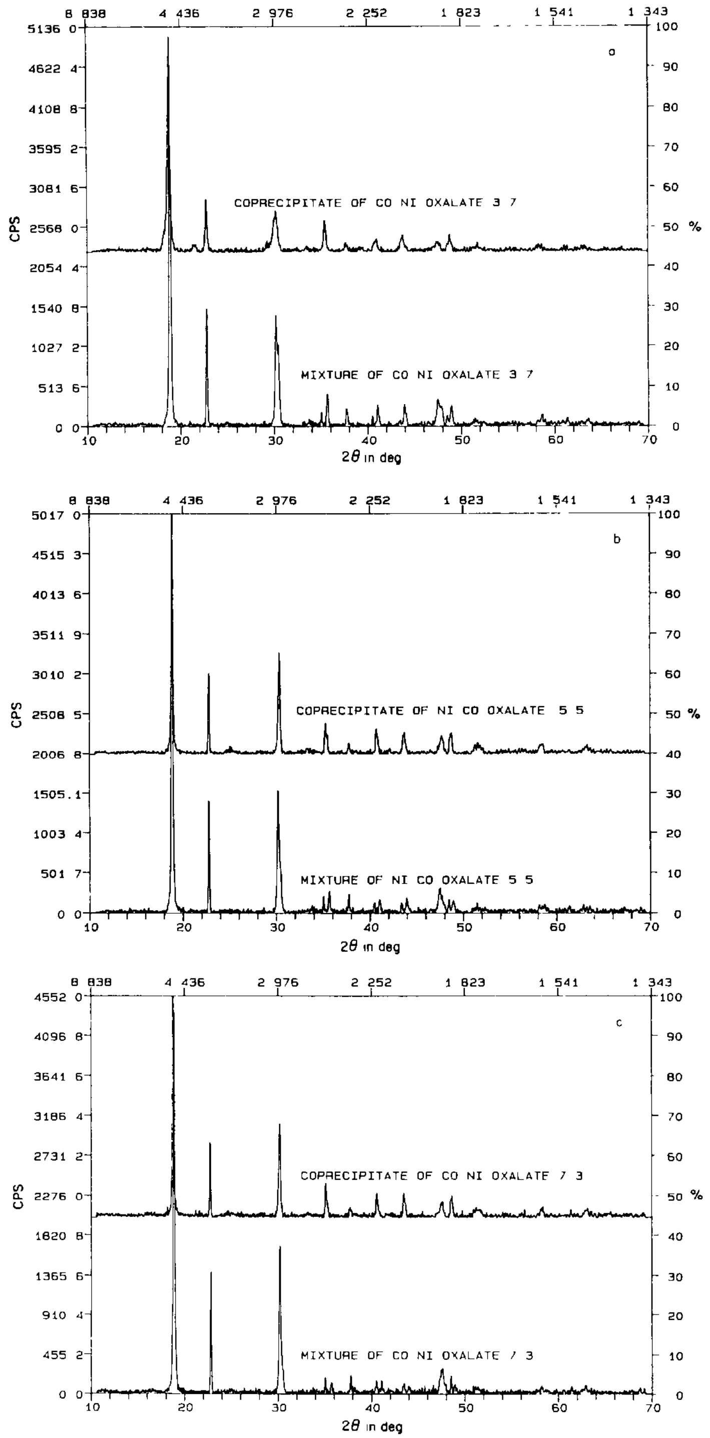


Fig. 7. The comparison of the X-ray diffraction patterns of the coprecipitates and the mechanical mixtures with the same stoichiometry: a, mole ratio Ni:Co = 3:7; b, mole ratio Ni:Co = 5:5; c, mole ratio Ni:Co = 7:3.

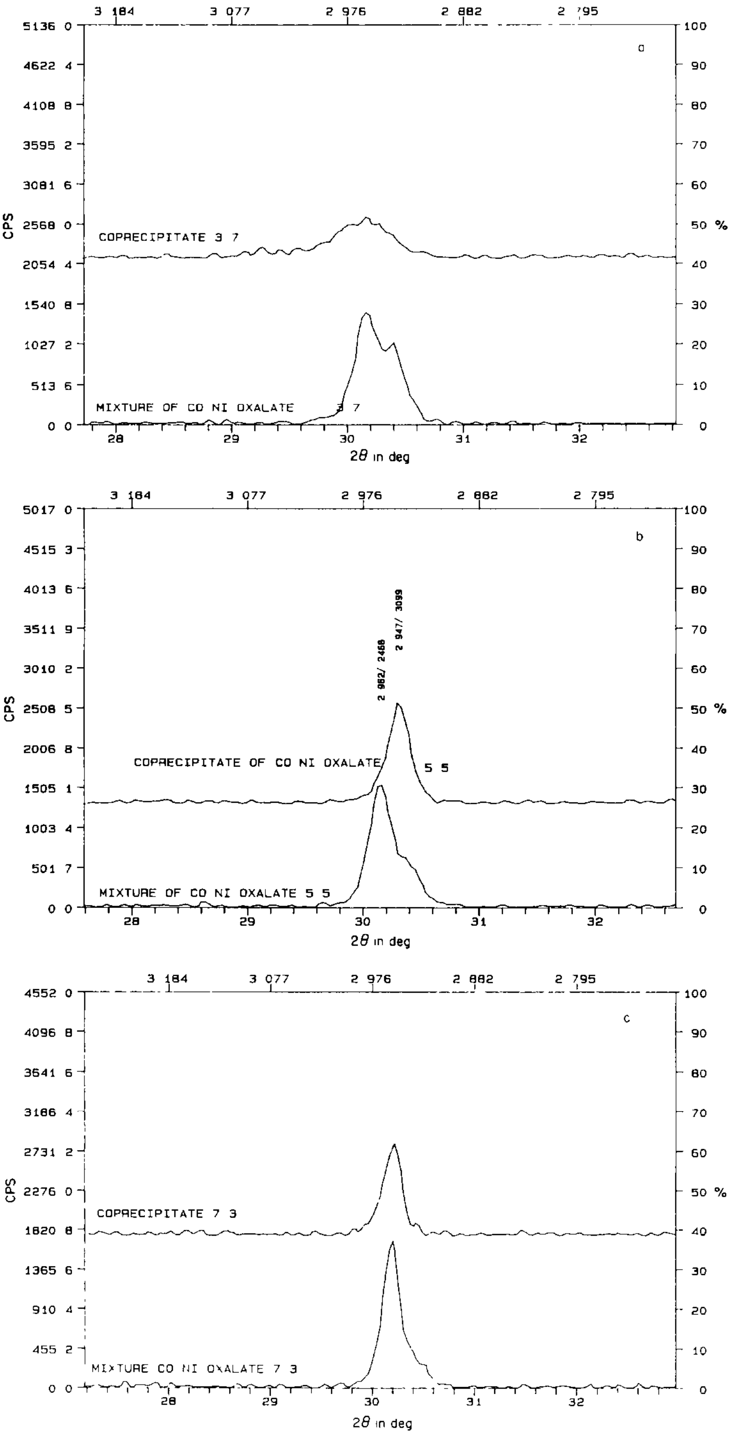
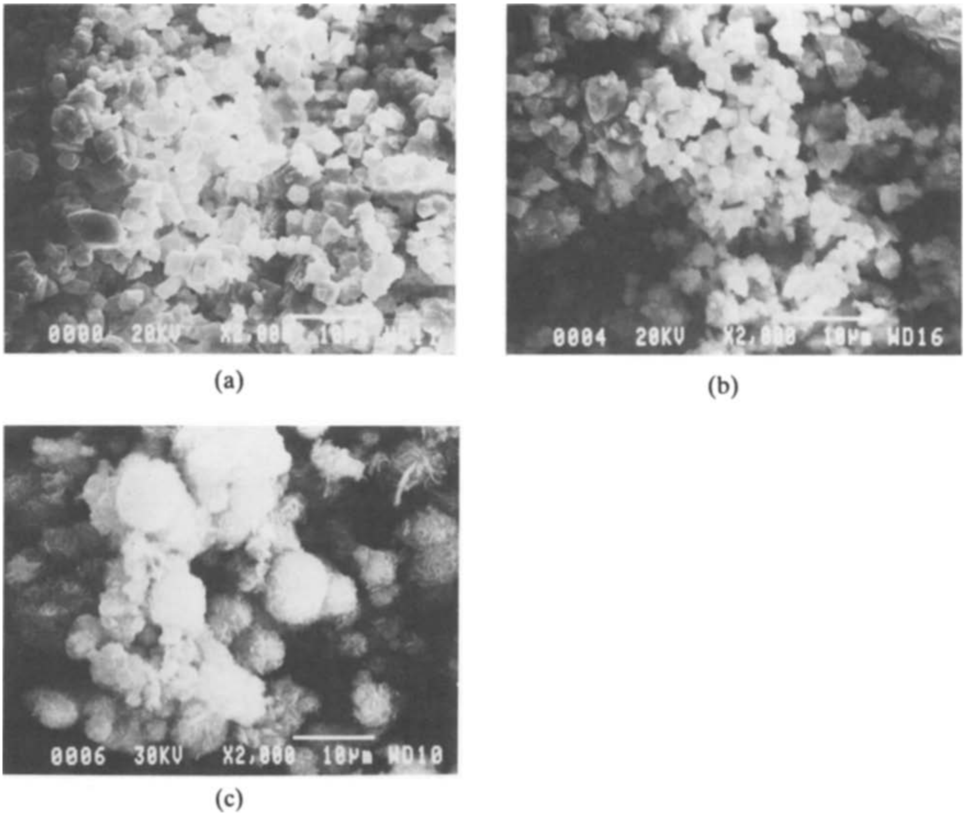


Fig. 8. The comparison of the detailed structure of the X-ray diffraction peaks at about $2\theta = 30.2°$ of the coprecipitates and the mechanical mixtures with the same stoichiometry: a, mole ratio Ni:Co = 3:7; b, mole ratio Ni:Co = 5:5; c, mole ratio Ni:Co = 7:3.



(a)

(b)

(c)

Fig. 9. Scanning electron micrographs of coprecipitates of cobalt oxalate dihydrate and nickel oxalate dihydrate; a, mole ratio Ni:Co = 3:7; b, mole ratio Ni:Co = 5:5; c, mole ratio Ni:Co = 7:3.

it can be verified from Fig. 3 that these peaks are the overlaps of the two peaks of nickel oxalate and cobalt oxalate. Therefore, it can be concluded that the coprecipitates have a crystal structure which definitely differs from that of the mechanical mixtures. From Fig. 8, it can be seen that sample No. 4 has a much broader peak than the other two coprecipitates. This may result from the effect of imperfect crystallization.

Figure 9 shows the SEM photos of sample Nos. 2–4. From Fig. 9, it can be seen that samples No. 2 and No. 3 have a uniform well-crystallized, cubic shape of size about $2.5 \times 2.5 \times 2.5\ \mu m^3$. However, sample No. 4 is poorly crystallized, rounded in shape, of radius about $3\ \mu m$, and the surface is porous. This could explain why the X-ray diffraction peak at $2\theta = 30.2°$ is much broader for this sample. When compared with Fig. 5, Fig. 9 confirms that the three coprecipitates are a solid solution.

Figure 10 shows the TG traces of the three coprecipitates. From Fig. 10, it can be seen that all the dehydrations present a single peak, unlike the mechanical mixture which has two separated peaks (see Fig. 6). The

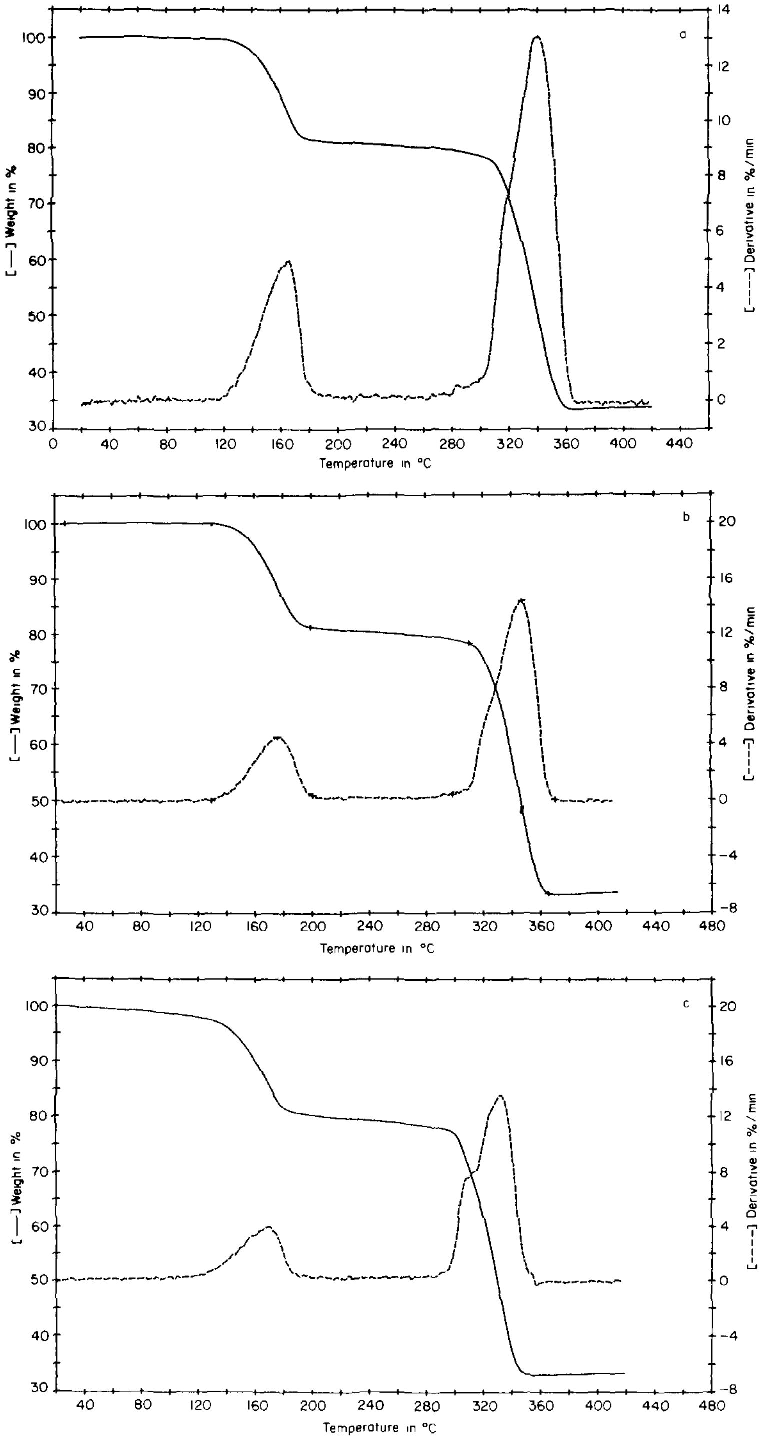


Fig. 10. The TG and DTG curves for the thermal decomposition of coprecipitates of cobalt oxalate dihydrate and nickel oxalate dihydrate: a, mole ratio Ni:Co = 3:7; b, mole ratio Ni:Co = 5:5; c, mole ratio Ni:Co = 7:3.

TABLE 1

The comparison of the experimental weight losses of single oxalates, coprecipitates, and the mechanical mixture with the theoretical weight losses of the substances in the same stoichiometry during their thermal decomposition

| Sample | Weight loss in % | | |
|---|---|---|---|
| | Dehydration | Decomposition to | |
| | | Oxide | Metal |
| *Theoretical* | | | |
| $NiC_2O_4 \cdot 2H_2O$ | 19.71 | 40.88 | 48.16 |
| $CoC_2O_4 \cdot 2H_2O$ | 19.68 | 37.12 | 48.11 |
| *Mixtures of Co and Ni oxalates* | | | |
| Mole ratio 3:7 | 19.70 | 38.72 | 48.14 |
| Mole ratio 5:5 | 19.69 | 38.27 | 48.14 |
| Mole ratio 6:4 | 19.69 | 38.01 | 48.13 |
| Mole ratio 7:3 | 19.68 | 37.81 | 48.12 |
| *Experimental* | | | |
| $NiC_2O_4{:}2H_2O$ | 19.25 | | 48.14 |
| $CoC_2O_4 \cdot 2H_2O$ | 18.43 | | 48.01 |
| *Coprecipitates of Co and Ni oxalates* | | | |
| Mole ratio 3:7 | 18.90 | | 48.12 |
| Mole ratio 5:5 | 18.63 | | 48.01 |
| Mole ratio 7:3 | 18.52 | | 48.08 |
| *Mechanical mixture of Co and Ni oxalates* | | | |
| Mole ratio 6:4 | 18.70 | | 48.25 |

decomposition peaks are also different from those of the mechanical mixture in Fig. 6.

From all the above evidence, it can be concluded that the coprecipitates prepared are solid solutions.

Table 1 gives a comparison of the experimental weight losses of the coprecipitates, single oxalates and the mechanical mixture, with the theoretical weight losses in the dehydration and decomposition of nickel oxalate, cobalt oxalate, as well as of their mixtures in different ratios, assuming that the final decomposition products are either oxides or metals. From Table 1, it can be seen that all the coprecipitates, single oxalates and mechanical mixture lost about 48% in weight in nitrogen atmosphere during the decomposition step, which is consistent with the theoretical weight loss if one assumes that the coprecipitated oxalates were decomposed to metals. When it was cooled to room temperature and air was admitted, the weight of the residue increased, and the powder was black, suggesting the formation of oxides. This means that very reactive (very high surface area) metal powders were produced and, even at room temperature, they were oxidized by air. This agrees with the phenomena described by Broadbent et al. [11]. However, it is not in accordance with the results obtained by Pease et al. [12], who reported that nickel oxide was produced when nickel oxalate was decomposed in $N_2$ atmosphere. During the dehydration step, the experimental weight loss was about 1% less than the theoretical one; this phenomenon was also observed by Konieczny [13] when studying the thermal decomposition of beryllium oxalate. The explanation is that the crystallized water is very readily partially lost, especially when the synthesized powder has a very small particle size; thus, water has a greater chance of being lost from a surface of greater area.

From the Figs. 5 and 10, it can be seen that the DTG peaks for the decomposition step of nickel oxalate and the three coprecipitates all have a shoulder; however, the shoulder is on the left for the coprecipitates and on the right for the nickel oxalate. This may indicate that some intermediate is formed in the decomposition step. Pease et al. [12] claimed that the intermediate in the decomposition of nickel oxalate is nickel carbonate, but they did not detect it; their conclusion rested on the production of nickel oxide. In our case, nickel was produced, not nickel oxide. Hence, it is necessary to determine the intermediate experimentally. For the coprecipitates, the shoulder may indicate two separate steps, one for nickel oxalate and one for cobalt oxalate respectively, or it may indicate the existence of an intermediate. The residues for the coprecipitates and mechanical mixtures may be either nickel and cobalt, or an alloy of these two metals. The study of this problem is in progress.

## CONCLUSIONS

A technique to synthesize the fine powder of the solid solution of nickel and cobalt oxalates was developed by coprecipitating the two corresponding metal nitrate solutions with oxalic acid solution.

From the XRD, SEM and TG results mechanical mixtures of nickel oxalate and cobalt oxalate have different characteristics from their coprecipitates. This suggests that the coprecipitates are solid solutions.

The final residues from the thermal decomposition in nitrogen atmosphere are either metals or alloys.

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