

MORPHOLOGY AND X-RAY DIFFRACTION PATTERN OF DIHYDRATES OF COBALT (II) OXALATE

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ABSTRACT

Depending on the mode of preparation three different dihydrates of cobalt (II) oxalate exist, which can be distinguished by means of X-ray diffractometry (XRD). There is a good correlation between the morphology of the crystallites and the peak heights of the maxima in the XRD-pattern. The morphology of the crystallites is determined by the precipitation procedure rather than by the crystallographic structure. The structure of the β -dihydrate has not been elucidated as detailed as stated in the literature.

Introduction

To produce ferromagnetic materials of a high remanent magnetization, the coercive force of the material must be sufficiently elevated. Small acicular ferromagnetic particles can exhibit high coercive forces, provided the particles can be well dispersed into a non-magnetic or less magnetic phase. Direct production of the required small acicular (single-domain) particles from a ferromagnetic metal is not possible. Consequently an acicular precursor must be produced, which has subsequently to be reacted to the desired ferromagnetic metal. To retain the acicular morphology of the particles, the precursor must be capable of being converted to the desired ferromagnetic metal at a low temperature. At more elevated temperatures the metal particles are sintering to more spherical particles and generally to irregular aggregates.

Cobalt oxalate is an interesting precursor, as it can be decomposed to metallic cobalt at relatively low temperatures. Moreover, some carbon remaining in the metal decreases the mobility of cobalt atoms over cobalt surfaces and thus strongly impedes sintering. The crystallization of cobalt oxalate to acicular crystallites is therefore interesting to investigate. The defect density of the resulting cobalt oxalate crystallites is also important, since the initial decomposition of inorganic salts is often governed by the defect structure.

Cobalt (II) oxalate can be crystallized either as a tetrahydrate or as different dihydrates. In a previous paper (1) we showed that the tetrahydrate and the dihydrates can be distinguished by their X-ray diffraction pattern (fig. 1 of ref. 1).

In the literature three different dihydrates of cobalt (II) oxalate have been described; the crystal structure of these dihydrates is still debated. Lagier et al. (2-5) considered the most stable dihydrate to be isostructural with oxalite (natural iron (II) oxalate dihydrate) that crystallizes in a monoclinic lattice (space group C2/c). They considered this crystal structure to be build up by stacking identical layers in the sequence ABCDABCD, etc. Solid state transformation of the tetrahydrate of cobalt oxalate leads to another dihydrate of a structure in which the stacking order is ABABABAB.

Besides the above two dihydrates, Lagier et al. mentioned the existence of dihydrates of a crystal structure in which the two stacking orders are present side by side. These dihydrates are relatively unstable. However, a structure in which about equal amounts of both stacking orders are present, displays a relatively high stability. The above authors associated this structure with the third different type of oxalate dihydrate. This structure should result when during crystallization in solution both stacking orders are equally probable.

Deyrieux et al. (6), on the other hand, distinguished only two dihydrates, which they designated by α and β . They did not mention a specific structure of a dihydrate resulting from the solid state dehydration of the tetrahydrate. When boiling solutions of oxalate and cobalt (II) ions were mixed, the β -dihydrate (with an orthorhombic lattice and space group Cccm) showing acicular crystallites initially precipitated. In an aqueous suspension containing an excess of oxalate ions, the β -dihydrate should recrystallize to the most stable phase, α -dihydrate, with dipyrimidal crystallites (monoclinic lattice, space group C2/c).

The two groups of authors agree on the structure of the most stable phase, the α -dihydrate. However, Deyrieux et al. could not detect any intermediate dihydrate and the two dihydrates they observed had a different space group. They therefore rejected Lagier's theory of stacking faults and concluded to polymorphism of two cobalt oxalate dihydrates not considering a third crystallographically different dihydrate. Neither Lagier nor Deyrieux investigated the influence of the conditions during the precipitation, such as temperature, concentration and rate of precipitation. We will demonstrate that these parameters are appreciably affecting the morphology and structure of the resulting crystallites.

In view of the importance of producing acicular oxalate particles as precursor for permanent magnets, we investigated the influence of the procedure of preparation on the morphology of the crystallites. Moreover, we investigated how far the morphology of the crystallites can be assessed by means of XRD. Finally, Deyrieux's results will be considered critically.

Experimental

The samples were prepared by the three procedures described in detail earlier (1).

Procedure 1

Relatively rapid addition of a solution of oxalate ions to a solution with cobalt (II) ions.

Procedure 2

Precipitation from a homogeneous solution of cobalt (II) chloride and dimethyl oxalate.

Procedure 3

Procedure 1 but with very slow dropwise addition of the solution containing oxalate ions (about 1 or 2 days).

The X-ray diffractometry and the scanning electron microscopy were done as described earlier (1).

Results and discussion

In our former paper (1) we have published three different XRD-patterns of cobalt (II) oxalate dihydrate. The dihydrate not mentioned by Deyrieux et al. results from solid state dehydration of the tetrahydrate. A β -dihydrate can be obtained either indirectly from recrystallization of suspended tetrahydrate or directly, when solutions containing Co^{2+} and $\text{C}_2\text{O}_4^{2-}$ ions are mixed at temperatures above about 60 °C. When the β -dihydrate is kept in an aqueous suspension, eventually the α -dihydrate results. As for the designation of the α - and β -dihydrate we shall follow Deyrieux.

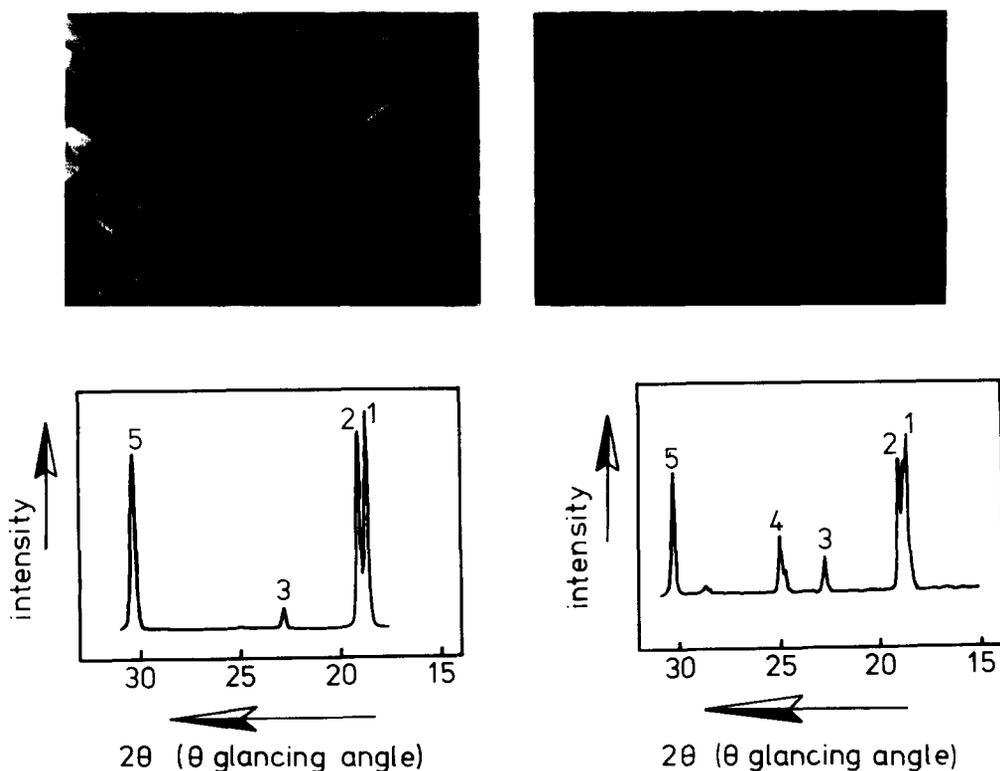


FIG. 1

Correlation between the morphology and the XRD-pattern of α -Cobalt (II) oxalate dihydrate.

Left: sample 78, procedure 1 at 80 °C, kept in aqueous suspension for 2.0 h.
 Right: sample 19g, procedure 1 at 100 °C, kept in aqueous suspension for 833 h.

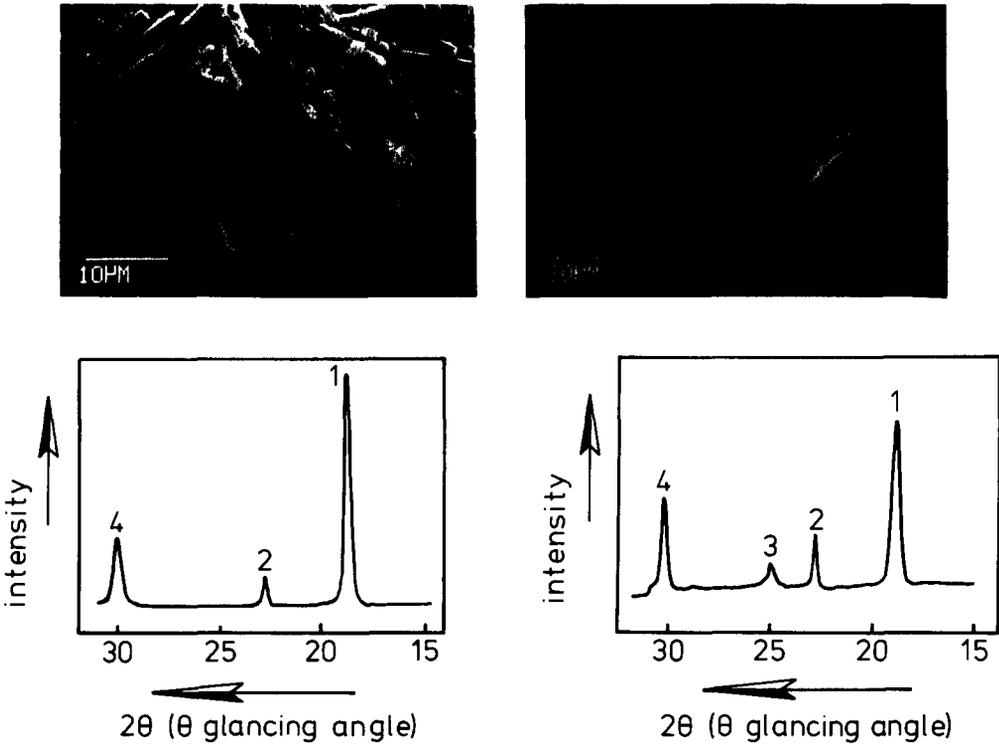


FIG. 2

Correlation between the morphology and the XRD-pattern of β -cobalt (II) oxalate dihydrate.

Left: sample 85, procedure 1 at 60 °C, kept in aqueous suspension for 1.0 h.
 Right: sample 40b, procedure 3 at 53 °C with addition rate 0.21 ml min⁻¹; filtered off 75 h after the onset of the precipitation.

TABLE I

Relative Peak Height and Standard Deviation of XRD-maxima of α -Cobalt (II) Oxalate Dihydrate.

peak number in fig. 1	Preparation according to							
	procedure 1				procedure 3			
	number of patterns used	d (nm)	I/I ₀	standard deviation	number of patterns used	d (nm)	I/I ₀	standard deviation
1	17	0.476	1.00	--	10	0.475	1.00	--
2	16	0.466	0.84	0.08	10	0.466	0.94	0.10
3	17	0.390	0.22	0.12	10	0.390	0.35	0.08
4	17	0.356	0.17	0.11	10	0.356	0.33	0.04
5	16	0.295	0.68	0.18	10	0.295	0.70	0.09

TABLE II-A

Relative Peak Height and Standard Deviation of XRD-maxima of β -Cobalt (II) Oxalate Dihydrate, prepared according to Procedure 1

peak number in fig. 2	moderately high temperatures with precipitation times of a few minutes				room temperature with precipitation times of a few hours			
	number of patterns used	d (nm)	I/I ₀	standard deviation	number of patterns used	d (nm)	I/I ₀	standard deviation
1	14	0.474	1.00	--	27	0.472	1.00	--
2	14	0.390	0.19	0.04	27	0.390	0.16	0.05
3	--	--	--	--	27	0.357	0.10	0.05
4	14	0.297	0.24	0.03	27	0.296	0.36	0.11

TABLE II-B

Relative Peak Height and Standard Deviation of XRD-maxima of β -Cobalt (II) Oxalate Dihydrate, prepared according to Procedure 3 (precipitation times of a few hours)

peak number in fig. 2	number of patterns used	d (nm)	I/I ₀	standard deviation
1	8	0.472	1.00	--
2	8	0.390	0.27	0.09
3	8	0.356	0.04	0.02
4	8	0.296	0.31	0.05

Figure 1 and 2 demonstrate the correlation between the peak height of the XRD-pattern and the morphology of both the α -dihydrate and the β -dihydrate. Table I and II show the variation in the relative peak height of the maxima with the preparation procedure. The standard deviation significantly exceeds the value of about 0.01 or 0.02 obtained when the XRD-measurement was repeated 10 to 20 times with the same sample. When an acicular habit was observed the peak at $d = 0.356$ nm appeared to be absent or very badly developed. This was found after precipitation according to procedure 1 at moderately high temperatures (about 60 °C up to about 80 °C). Then the β -dihydrate originates without recrystallization of the tetrahydrate. After recrystallization generally a more symmetrical habit was found (1). When procedure 3 was followed adding exceptionally the solution with Co^{2+} ions to the solution containing $\text{C}_2\text{O}_4^{2-}$ ions, the peak at $d = 0.356$ nm was also absent. Presumably, the large excess of oxalate ions favours the growth rate of the nuclei in the direction of the periodic bond chain (PBC), which is present in the model of Lagier (4). Consequently, the resulting crystallites have a more acicular habit.

The electronmicrographs reveal that the morphology of the crystallites is determined by the preparation procedure rather than by the crystallographic structure. This is in contrast to Deyrieux *et al.* (6) who discerned an acicular habit for the β -modification and a more cubical habit for the α -modification. Possibly they erroneously considered cobalt (II) oxalate to be analogous to iron (II) oxalate. Taskinen *et al.* (7) reported that the β -modification has not always an acicular habit and the α -modification has not always a cubical habit. They do not give any information on the procedure of the preparation of the samples they used.

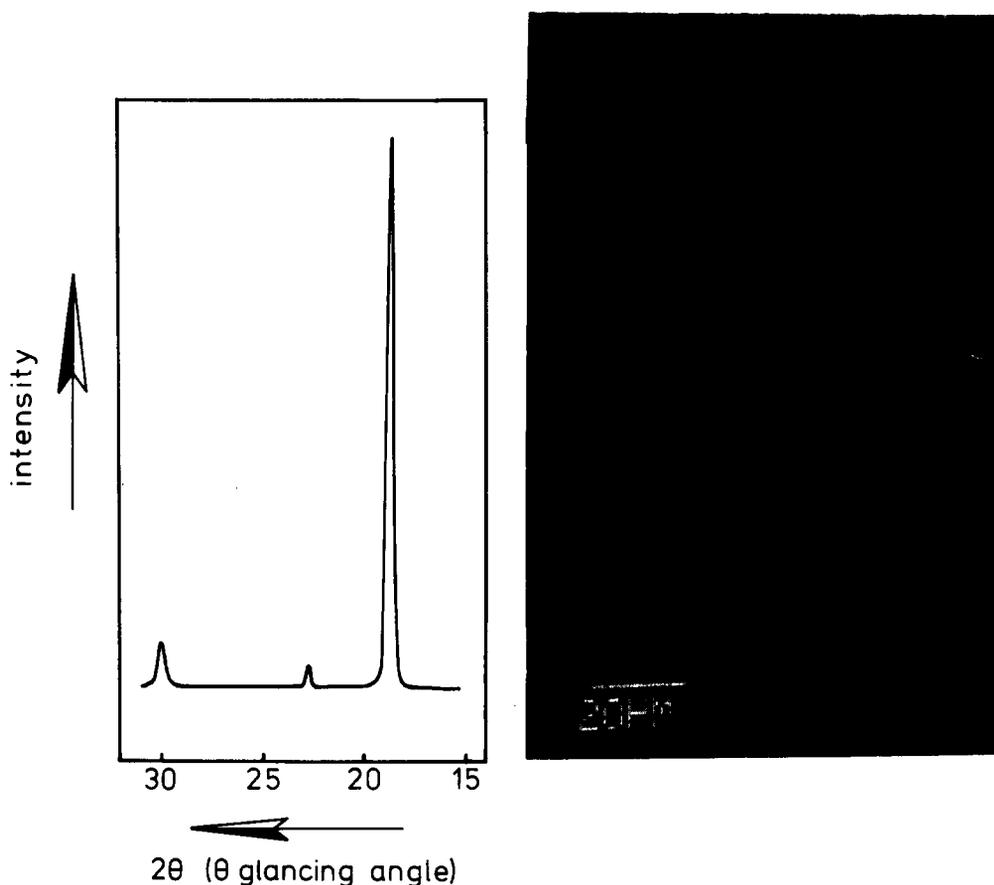


FIG. 3

Change towards a pronounced acicular habit when the concentrations are reduced to 10% of the usual values as shown by sample 81b, prepared by procedure 1 at 100 °C kept in an aqueous suspension for 0.5 h. The left part of the figure demonstrates the disappearance of the XRD-maximum at $d = 0.356$ nm.

The relation between the morphology of the crystallites and the preparation procedure is also demonstrated by the large difference in morphology observed on varying the absolute concentrations of the oxalate and cobalt (II) solutions. When the concentrations are reduced to 10% of the usual values, we can see from figure 3 a pronounced change in morphology towards an acicular habit accompanied by a total disappearance of the maximum at $d = 0.356$ nm in the XRD-pattern.

When we compare the upper graph of figure 8 of ref. 6 with the XRD-patterns we recorded on our numerous samples of the various dihydrates, we believe that Deyrieux et al. did not isolate a pure sample of a β -dihydrate (see XRD-patterns of fig. 1 of ref.1). Firstly his (112) reflection is only present in our patterns of the tetrahydrate dehydrated in the solid state, whereas the (113) reflection is only met with samples obtained from aqueous suspensions. The best match with his pattern is obtained with a sample that we got from an aqueous suspension at room temperature kept continuously stirred for several days. Then the recrystallization of the tetrahydrate has already begun. After filtering off and drying a mixture of the two dihydrates resulted. Both acicular and more symmetrical crystallites were observed. Secondly, from a filtrate obtained at 87°C and left at room temperature, the tetrahydrate appeared to be precipitated exclusively after two weeks.

Since detailed XRD-analysis is beyond the scope of our investigations, we here only state that the crystal structure of the less stable dihydrate of cobalt (II) oxalate obtained in aqueous suspension is not elucidated as yet.

Like we did earlier (1), we shall designate the dihydrate obtained in aqueous suspension and displaying XRD-pattern III of fig. 1 of ref. 1 as the β -cobalt (II) oxalate dihydrate. The modification which can be obtained by solid state dehydration of the tetrahydrate, on which we reported earlier (1), will be denoted henceforth as γ -cobalt (II) oxalate dihydrate.

From the results mentioned above and in our previous paper (1) we can see that the modifications α , β and γ can be obtained all with an acicular habit. By choosing the proper conditions during the preparation of the cobalt (II) oxalate it should thus be possible to optimize the catalytic and magnetic properties of small metal or metal oxide particles resulting from thermal decomposition.

We intend to report on the transformation of the β -dihydrate to the α -dihydrate and on the thermal decomposition of both the α -dihydrate and the β -dihydrate exhibiting different morphologies in subsequent papers.

Conclusions

1. The three modifications of cobalt (II) oxalate dihydrate can all be prepared with an acicular habit.
2. A missing XRD-maximum at $d = 0.356$ nm points to an acicular habit of the crystallites of the dihydrate.
3. The morphology of the crystallites of cobalt (II) oxalate dihydrate depends on the conditions during the precipitation, rather than on the crystal structure. An excess of oxalate ions favours an acicular habit.
4. The crystal structure of the β -dihydrate is not elucidated as detailed as stated in the literature.

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