JOURNAL OF MATERIALS SCIENCE 9 (1974) 772–776

Oxidation of cobalt (II) hydroxide to oxide hydroxide: solids evolution during reaction

M. FIGLARZ
Université de Picardie, Laboratoire de Chimie des Solides Pulvérulents, 33 rue St Leu, 80039 Amiens, France

J. GUENOT, J.-N. TOURNEMOLLE
Université Paris VI, Laboratoire de Chimie des Solides, 4 Place Jussieu, 75230 Paris, Cedex 05, France

Studies of solids evolution during oxidation of powdered $Co(OH)_2$ to CoOOH by oxygen in air flow or water suspension have been carried out at different temperatures by electron microscopy and diffraction.

Although the same mechanisms are operating, changes of habit and texture of reacting particles are temperature and medium dependent. As the case may be, the particles will be porous without habit change or broken up into flakes with or without orientation relationships.

1. Introduction

By adding a basic solution to a solution of a cobaltous salt, out of contact with air to prevent oxidation, a precipitate of cobalt II hydroxide is formed. This rose compound is called β form because of the transitory formation of a blue compound (α form) during the precipitation [1].

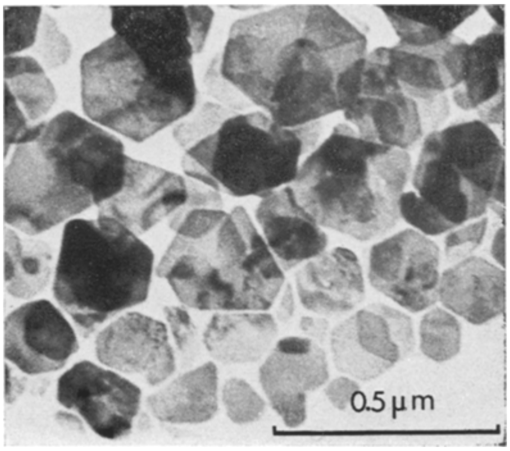

Figure 1 Set of $Co(OH)_2$ particles.

With suitable concentration of reagents, the dried hydroxide is a powder the particles of which are seen by electron microscopy as non-porous hexagonal thin platelets with regular shape (Fig. 1). Their largest dimensions are 50 to 500 nm and their mean thickness 40 nm.

The selected-area electron diffraction (SAED) pattern of an isolated grain corresponds to a single crystal pattern with (0001) plane perpendicular to the electron beam (Fig. 2).

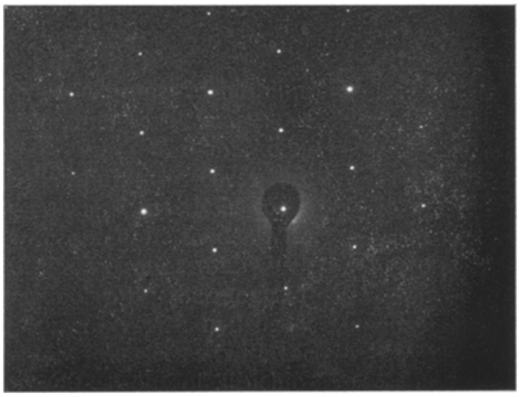

Figure 2 SAED of a $Co(OH)_2$ single particle lying on the (0001) plane.

On account of its morphological properties this cobalt hydroxide is a suitable material for the study of the solid phases evolution during reactions of $Co(OH)_2$ with a gas or a liquid: the ultrafine character of the particles permits an easy reaction after dispersing into an appropriate medium, their single crystal state and their geometrical shape make it possible to follow the change of their habit, texture [2] and structure by electron microscopy and diffraction.

Some studies on dehydration have already been conducted with this material [3]. The present investigation was initiated to study its oxidation into CoOOH by oxygen in a gaseous medium or in hydrothermal conditions.

2. Experimental

2.1. Hydroxide sample

$Co(OH)_2$ was precipitated in the absence of air by the action of a 1M solution of KOH on a 0.1M solution of cobaltous chloride. After centrifugation and drying a rose powder is obtained.

A sample of commercial hydroxide (Riedel-de Haën) was also used. With this sample the same results were obtained in spite of a slight oxidation not detectable by X-ray and electron diffraction but which gave a beige tinge to the hydroxide.

2.2. Electron microscopy

The observations were made by transmission electron microscopy. We used a 100 kV SOPELEM microscope and, in addition, a Philips EM 300 microscope equipped with a tilting stage and operating at 100 kV.

To permit good observation, the powders were dispersed on a thin vacuum-deposited carbon film on a specimen holder grid. To obtain this dispersion, a small quantity of powder was suspended in about 5 cm^3 of distilled water to which were added several drops of a surface-active foaming agent and placed in a test tube. The grid was then plunged into the foam produced by shaking the tube. The resulting dispersion easily allowed the SAED pattern of an isolated particle to be obtained.

2.3. X-ray diffraction

The X-ray diffraction patterns were obtained by means of a CGR diffractometer using the $K\alpha_1$ monochromatized radiation of cobalt. The scanning speed of the counter was $1°\theta\ min^{-1}$ for the patterns of phase identification and of $1°\theta\ (20\ min)^{-1}$ for the crystallite size analysis.

3. Oxidation of $Co(OH)_2$ to CoOOH in an oxygen or air flow

3.1. Reaction features

3.1.1. Earlier investigations

Kondrashev and Fedorova [4] indicated that a freshly prepared cobalt hydroxide is easily oxidized to oxide hydroxide by air at 100° C. Ammann *et al* [5] observed that a particle of dried $Co(OH)_2$ oxidized by heating in oxygen gives rise to a three phases electron diffraction pattern ($Co(OH)_2$, CoOOH and C_3O_4). Pirmatov [6] claimed after a study of thermal decomposition of $Co(OH)_2$ by differential thermal analysis and X-ray diffraction that the transformation $Co(OH)_2 \rightarrow Co_2O_3, H_2O$ occurs at 170° C whereas Co_3O_4 appears at 250° C.

3.1.2. Hydroxide stability

If the rose hydroxide is maintained in air at room temperature, its colour changes fairly rapidly to beige, showing that $Co(OH)_2$ is not a stable compound in those conditions; this is confirmed by X-ray analysis which shows the presence of CoOOH after a sufficiently long time.

If the powdered hydroxide is heated in air flow (fixed bed reactor) with an elevating temperature ($5° C\ h^{-1}$), one can observe by making X-ray diffraction patterns of samples taken out at regular intervals between 100 and 110° C that CoOOH and Co_3O_4 are formed at the same time.

To obtain CoOOH in a pure state, isothermal heating is necessary and the temperature must stay under 100° C. In those conditions, no traces of Co_3O_4 can be detected.

3.2. Texture studies of the reaction products

A distinction must be made between the reaction products according to their reaction temperature.

3.2.1. Reaction products obtained at 60° C and higher

At 60° C the duration for total reaction was about 20 h. Electron microscopy reveals that the oxide hydroxide obtained by isothermal heating at 60° C and above consists of particles of the same habit as the initial hydroxide. However, those particles are finely porous with some cracks (Fig. 3). Particles are lying on the (0001) plane as we can see through SAED patterns. The arcing of diffraction spots results from an azimuthal misorientation of about ± 10° (Fig. 4).

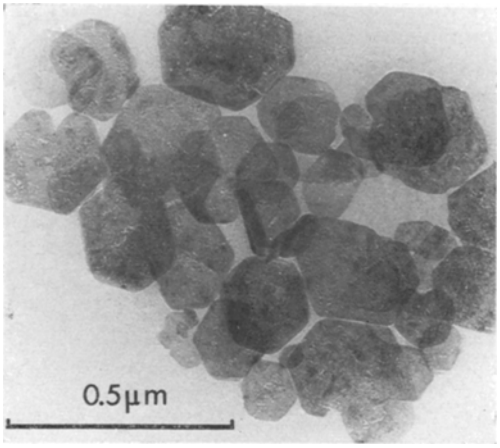

Figure 3 Set of CoOOH particles obtained by isothermal heating of $Co(OH)_2$ at 60°C in an air flow.

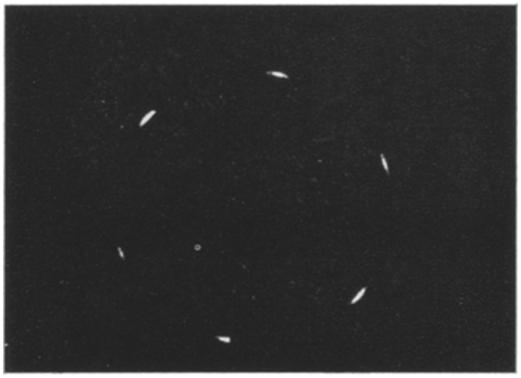

Figure 4 SAED of a single particle of Fig. 3 lying on the (0001) plane.

The oxide hydroxide crystallite size has been inferred from X-ray diffraction (Scherrer formula). Contrary to other reactions [3, 7] for which a notable increase in crystallite size upon heating was noted, our observations showed a slight tendency to decrease. For instance, crystallite sizes deduced from the $10\bar{1}1$ line are 8, 6 and 7 nm at 60, 80 and 100°C respectively.

By SAED of a reacting particle (Fig. 5), the reaction is revealed to be topotactic: the axes of a hexagonal unit cell of CoOOH are parallel to the unit cell axes of $Co(OH)_2$. But, even at the beginning of the reaction, the CoOOH crystallites are more misoriented.

3.2.2. *Reaction products obtained at room temperature*

At room temperature the reaction is very slow; after a few months the oxidation is still incomplete. When a particle at the beginning of reaction is observed by electron diffraction, the same orientation relationships are observed as in the first case but the crystallite misorientation of CoOOH is much weaker (Fig. 6). As the reaction progresses, crystallite misorientation remains weak but the particle habit is broken up (Fig. 7). A more detailed study of the reaction mechanism will be published in the future.

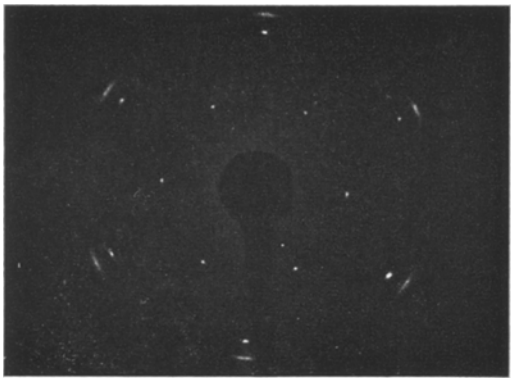

Figure 5 SAED of a $Co(OH)_2$ particle during oxidation at 60° C in an air flow.

4. Oxidation of $Co(OH)_2$ to CoOOH with molecular oxygen in hydrothermal conditions

4.1. Experimental procedure

The powdered solid was suspended into water within an autoclave, the desired oxygen pressure was set up and the autoclave was heated up to the reaction temperature. During the isothermal

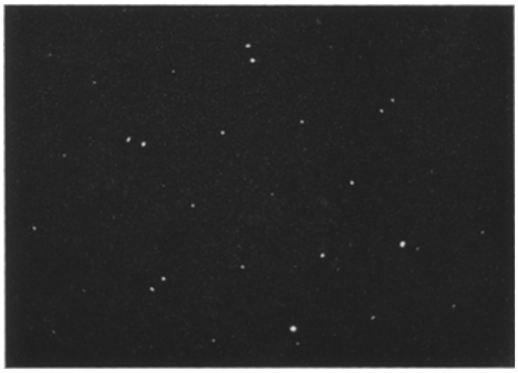

Figure 6 SAED of a $Co(OH)_2$ particle at the beginning of oxidation in an air flow at room temperature.

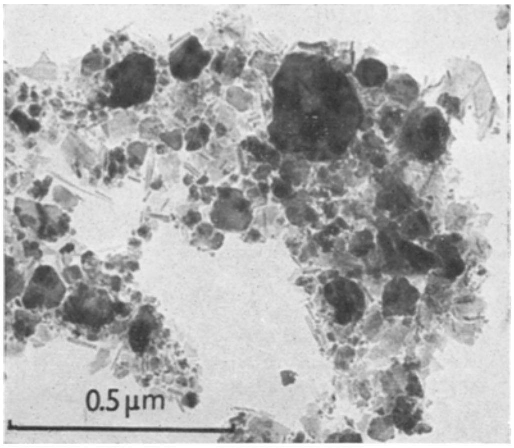

Figure 7 Set of $Co(OH)_2$ particles during oxidation to CoOOH at room temperature (the habit is breaking up).

reaction, the liquid was continually stirred with a magnetic rotary stirrer. The operating oxygen pressure before heating was 5 bar.

It was observed that the compound CoOOH is obtained in a pure state (without Co_3O_4) only under a temperature threshold (same observation as in gaseous medium) which was 85° C. Accordingly, the reaction was effected at 80° C; the duration for total reaction was 7 h.

4.2. Textural study of reaction products

By electron microscopy, the CoOOH particles can be seen as clusters of thin flakes without any definite form (Fig. 8a). Contrary to all expectations the SAED of such a cluster gives a single crystal pattern (Fig. 8b). This pattern shows the following features:

1. it is consistent with that expected from a single crystal lying on (0001) plane;
2. diffraction spots are almost punctual, and so indicate only a slight azimuthal misorientation between the clustered flakes;
3. some spots appear in the pattern centre which are precluded by the space group $R\bar{3}m$ of CoOOH [4, 8].

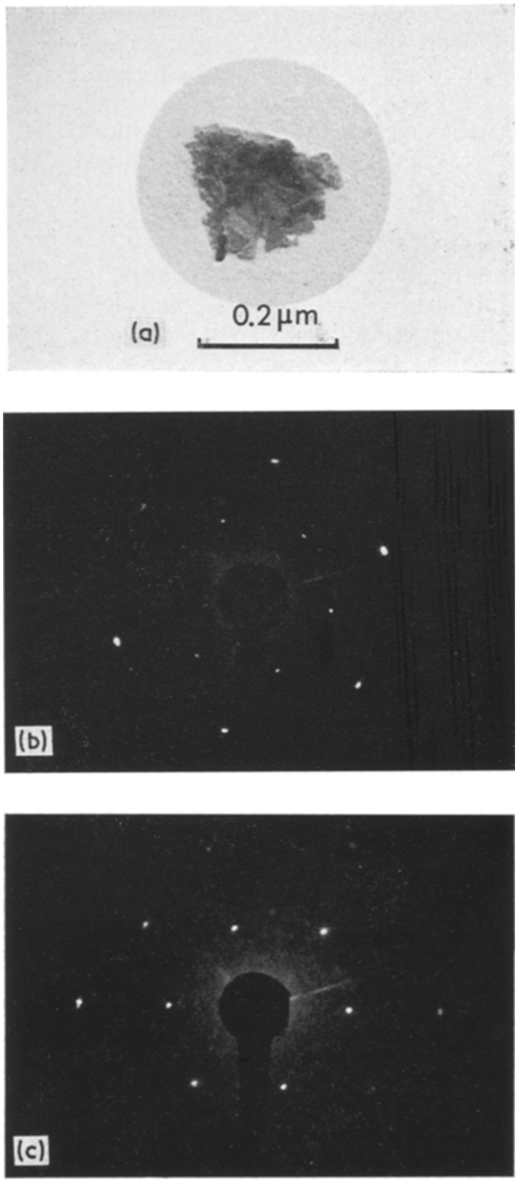

Figure 8 (a) Cluster of CoOOH flakes obtained by oxidation of $Co(OH)_2$ in hydrothermal conditions. (b) SAED of the same cluster: pattern of a single crystal lying on the (0001) plane with central extra spots. (c) SAED after 36° tilting around an axis of the (0001) plane.

These reflections cannot be explained as a consequence of multiple diffraction. Their origin must be searched among factors from which Laue zones can arise: shape effect and crystallite misorientation [9]. In the present case the first factor is operating. Indeed, when a particle is tilted around any axis of (0001) plane, it may be observed that a pattern is present throughout the tilting operation with progressive pattern deformation (Fig. 8c). Therefore the reciprocal lattice consists of continuous streaks instead of points [9]. Such a reciprocal lattice exists when the particle is built with irregular stacking of flakes [10],which is consistent with the electron microscopy image. However, this conclusion is not definitive because the flake thickness determined by X-ray diffraction is about 10 nm, this value being too large to explain the observed effect.

The SAED of a particle at the beginning of the reaction reveals the same orientation relationships as in the air flow reaction. The central spots are already observable.

5. Discussion

The observed phenomena can be tentatively explained in the following manner. For the reaction occurring in an air flow, the strains resulting from the misfit between the networks of $Co(OH)_2$ and CoOOH and from the accumulation of water vapour are reduced at 60° C, when the reaction is fast, by the formation of relatively small and misoriented crystallites and the appearance of pores and cracks. At room temperature the reaction is much slower, the crystallites attain larger dimensions and the reduction of strains can only occur through the breaking up of the initial particle of $Co(OH)_2$. Similar phenomenon could certainly be observed with other reactions if they could be carried out at a sufficiently low temperature.

A comparison between habit of oxidation products obtained in an aqueous medium at 80° C and in a gaseous medium at room temperature leads to the following conclusion: whatever the medium is, one can observe a breaking up of particles but, in the first conditions, the formed flakes are not misoriented. It can be concluded that similar mechanisms are operating in the two cases with possibility of a greater reaction rate in an aqueous medium (higher temperature) and fragmentation along the cleavage plane (0001) of CoOOH.

6. Conclusion

$Co(OH)_2$ particle have been treated by oxygen between room temperature and 100° C and within two different media. Evolution of those particles has been observed by transmission electron microscopy and SAED. It may be concluded that the textural modifications of particles is greatly related to the reaction conditions. In particular, by varying these conditions, the obtained particles will be porous without habit change or broken up into flakes with or without orientation relationships.

References

1. G. BRAUER, "Handbook of Preparative Inorganic Chemistry" (Academic Press, New York, 1965) p. 1521.
2. M. FIGLARZ, F. VINCENT, C. LECAILLE and J. AMIEL, *Powder Technol.* **1** (1967) 121.
3. M. FIGLARZ and F. VINCENT, *Compt. Rend. Acad. Sci. (Paris)* **266** (1968) 376; F. VINCENT, M. FIGLARZ and J. AMIEL, in "6th Int. Symp. Reactiv Solids, Schenectady, 1968" (edited by J. W. Mitchell, R. C. Devries, R. W. Roberts and P. Cannon) (Wiley-Interscience, New York, 1969) p. 181.
4. YU. D. KONDRASHEV and N. N. FEDOROVA, *Dokl. Akad. Nauk SSSR* **94** (1954) 229.
5. R. AMMANN, W. FEITKNECHT and R. GIOVANOLI, in "7th Congr. Int. Microsc. Electron., Grenoble, 1970" (edited by P. Favard) (Soc. Franç. Microsc. Electron., Paris, 1970) Vol. 1, p. 467.
6. A. P. PIRMATOV, *Uch. Zap. Biol. Fak. Osh. Gos. Pedagog. Inst.* (1968) 3; (*Chem. Abs.* 72-115 227 h).
7. D. COLAÏTIS, F. FIEVET-VINCENT, J. GUENOT and M. FIGLARZ, *Mat. Res. Bull.* **6** (1971) 1211.
8. P. N. BITYUSKII and V. I. KHITROVA, *Z. Strukt. Khim.* **9** (1968) 1034.
9. B. K. VAINSHTEIN, "Structure Analysis by Electron Diffraction" (Pergamon Press, Oxford, 1964) pp. 32 and 42.
10. A. GUINIER, "X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies" (W. H. Freeman, San Francisco, 1963) p. 169.

Received 5 October and accepted 19 November 1973.