Morphological and topotactical aspects of the reactions $Co(OH)_2$ → $CoOOH$ and $CoOOH$ → Co_3O_4

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Studies of the thermal decomposition to Co_3O_4 of particles of $CoOOH$ with different textures and porosities were carried out by electron microscopy and diffraction. A comparison of topotactical relationships, crystallite misorientation and porosity between these results and those previously obtained for the reaction $Co(OH)_2$ → $CoOOH$ has permitted significant conclusions to be drawn about the interaction of these parameters. In particular, a reaction can be topotactical even without a good fit between the lattices of the starting and final products provided that an easy texture reordering is observed in the reaction conditions.

1. Introduction

In a previous paper [1] we studied the solid evolution during oxidation by oxygen of powdered $Co(OH)_2$ to $CoOOH$. The present study deals with thermal decomposition of $CoOOH$ to Co_3O_4 and comparison between the morphological aspects of both reactions. From this comparison some interesting conclusions can be drawn, in particular about the phenomenon of topotaxy. The same experimental methods as in the previous study [1] were used here.

2. Oxide hydroxide formation

The oxide hydroxide used in our experiments is obtained from a powdered $Co(OH)_2$, the particles of which are seen by electron microscopy to be hexagonal non-porous thin platelets (diameter: 50 to 500 nm, mean thickness: 40 nm) with rather large, well oriented crystallites.

When the oxidation of this hydroxide to $CoOOH$ is achieved with oxygen in a gaseous medium, two different kinds of materials are obtained according to the reaction temperature [1]. Between 60 and 100°C the particles of $CoOOH$ which are formed keep the habit of the starting material, but their texture is very different: their crystallites are small and somewhat misoriented and some cracks and irregular pores are present (Fig. 1a and b). At room temperature in oxygen, the hydroxide particles are broken up during the reaction, so the oxide hydroxide particles have very irregular shapes; no major changes in texture occur.

The oxide hydroxide obtained at 60°C can be used to study the decomposition of $CoOOH$ to Co_3O_4 in the same way as for $Co(OH)_2$ to $CoOOH$. However, in order to achieve a comparative study and also to appreciate the influence of the texture of the starting material, it would have been advisable to use an oxide hydroxide and an hydroxide of comparable texture. Unfortunately, although the particles obtained at room temperature have a texture similar to that of $Co(OH)_2$, their very irregular shapes make the observation by selected-area electron diffraction very difficult. On the other hand, we have as yet not succeeded in

obtaining, by a different method, a material with a suitable shape and texture; in particular, the particles formed by precipitation in an oxidizing medium are always too thick to be used in transmission electron microscopy and diffraction. Accordingly, the oxide hydroxide obtained at 60° C (material I) was the main material used in our experiments to study the decomposition of CoOOH; nevertheless, the examination of the decay products of the oxide hydroxide obtained at room temperature (material II) brought us some further information.
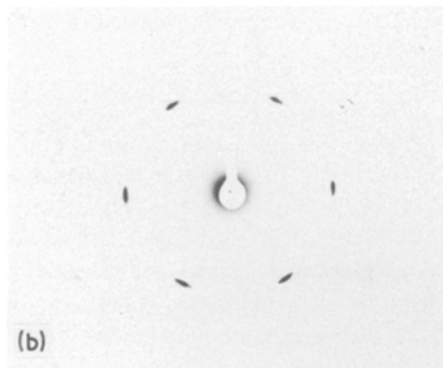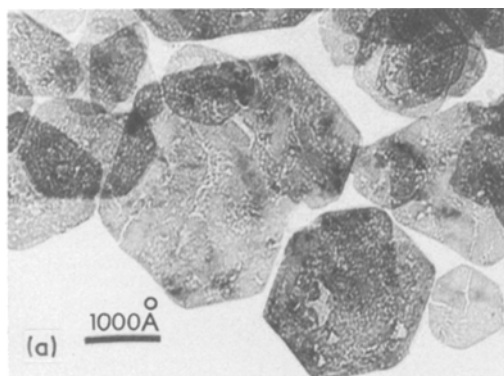

(a)

1000Å

(b)

Figure 1(a) CoOOH particles (material I). (b) SAED of a CoOOH particle.

## 3. Decomposition of CoOOH to Co_3O_4 at 250° C

The oxide hydroxide was heated in an air flow (fixed-bed reactor) with a rising temperature of $5°\,C\,h^{-1}$. At 250° C, the decomposition reaction to Co_3O_4 was total according to analysis by X-ray diffraction.

Examination by electron microscopy of the Co_3O_4 obtained from material I shows that the habit of the starting particles is preserved, whereas the porous texture undergoes an important change. The starting porosity of CoOOH (Fig. 1a) is inhomogeneous with cracks; on the other hand,

the porosity of Co_3O_4 (Fig. 2a) is very regular with tiny round pores and can be compared to the porosity of CoO obtained by dehydroxylation of $Co(OH)_2$ [2, 3].

Selected-area electron diffraction (SAED) of a particle of Co_3O_4 gives the pattern of a single crystal lying on the (1 1 1) plane (Fig. 2b) except for the presence of extra weak spots with irrational indices which may be explained by a crystallite misorientation in relation to this plane (zenithal misorientation) and a size effect [4].

Diffraction of a reacting particle gives a similar pattern. This observation can be easily explained if we admit that the reaction is a topotactical one with the relationships:

$$[0\,0\,1]\ CoOOH\,/\!/\,[1\,1\,1]\ Co_3O_4\ \text{and}$$
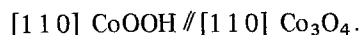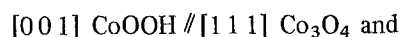
$$[1\,1\,0]\ CoOOH\,/\!/\,[1\,1\,0]\ Co_3O_4.$$

As a matter of fact, in this case, the $\{1\,1\,0\}$ CoOOH reflections are not separate from the $\{4\,4\,0\}$ Co_3O_4 ones, owing to the interplanar spacings:

$$CoOOH\quad d_{1\,1\,0} = 1.425\,\text{Å}$$
$$Co_3O_4\quad d_{4\,4\,0} = 1.429\,\text{Å}$$

which are too close to each other. The particle has
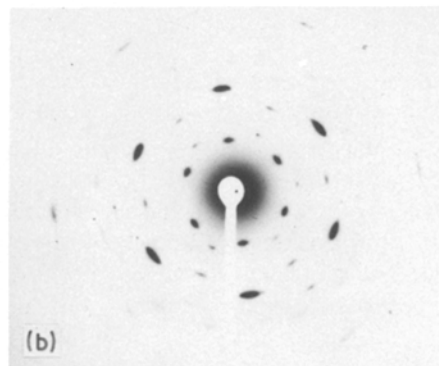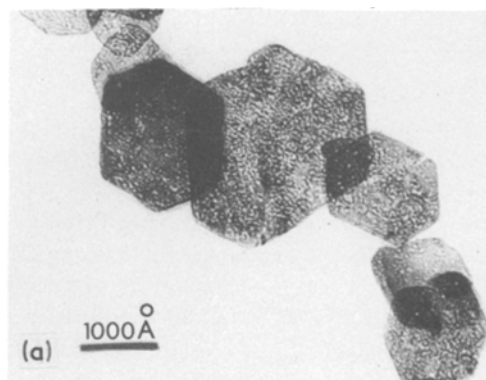

(a)

1000Å

(b)

Figure 2(a) Co_3O_4 particles obtained from material I at 265° C. (b) SAED of a Co_3O_4 particle (265° C).

2268

to be tilted by a rather large angle to give quite distant spots.

The spots of the SAED pattern of Co_3O_4 resulting from the material I exhibit the same spreading as the starting oxide hydroxide (Fig. 2b). This observation shows that no extra misorientation is generated by the reaction as was the case in the reaction of $Co(OH)_2$ to CoOOH when this was carried out at 60 to 100° C. This is confirmed by examination of Co_3O_4 obtained from material II. This oxide hydroxide exhibits practically no spot spreading and the resulting Co_3O_4 only a rather low one.

There is no difference in the porosity of Co_3O_4 obtained from materials I and II.

4. Development of texture with temperature of Co_3O_4 oxide

Oxide Co_3O_4 issuing from the decomposition of CoOOH (material I) was heated to 850° C. One could then observe:

(a) with X-ray diffraction, a regular growth of crystallite size, from 8 to 24 nm between 350 and 850° C (as measured on the 1 1 1 line);
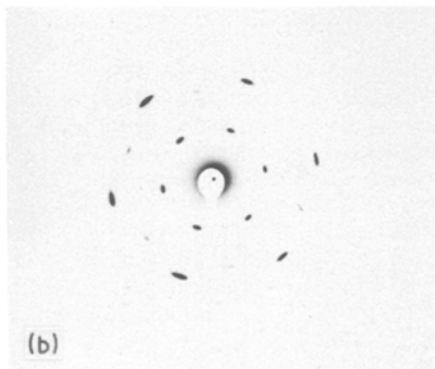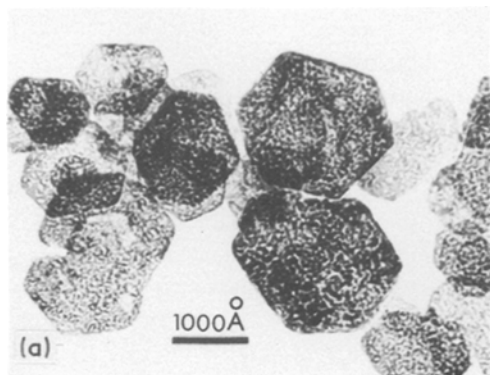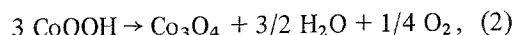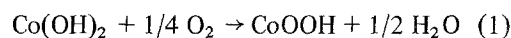
(b) with electron microscopy, a gradual increase in the sizes of the pores which simultaneously show a tendency to become hexagonal while the grains of oxide still retain the habit of the parent oxide hydroxide (Figs. 3a and 4a);

(c) with SAED, a thinning down of the spots – and a vanishing of the extra weak spots – arising from crystallite growth (Figs. 3b and 4b). The results concerning the Co_3O_4 oxide obtained from material II are the same except, of course, as far as the crystallite misorientation is concerned.

5. Comparison between the morphological aspects of the reactions $Co(OH)_2 \rightarrow$ CoOOH $\rightarrow Co_3O_4$

These two reactions

$$Co(OH)_2 + 1/4\ O_2 \rightarrow CoOOH + 1/2\ H_2O \quad (1)$$

$$3\ CoOOH \rightarrow Co_3O_4 + 3/2\ H_2O + 1/4\ O_2, \quad (2)$$

which are chemically very different, are both topotactical, i.e. the solid products of the reactions show to a greater or lesser extent orientation relationships with the starting solid. Some significant differences must be noted.

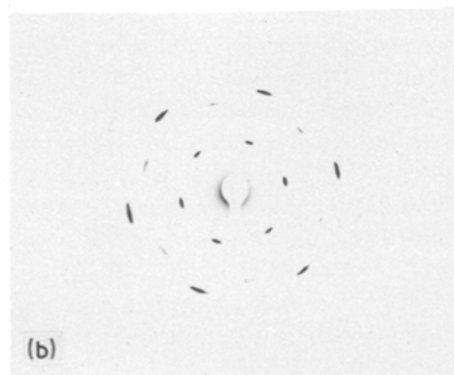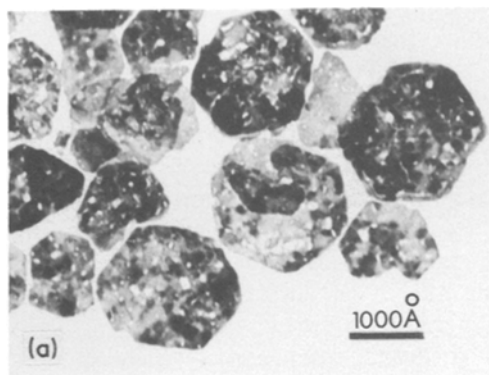The solid product of reaction 1, CoOOH, looks

Figure 3(a) Co_3O_4 particles after heating to 345° C. (b) SAED of a Co_3O_4 particle (345° C).

Figure 4(a) Co_3O_4 particles after heating to 410° C. (b) SAED of a Co_3O_4 particle (410° C).

2269

like a pseudomorphous one provided that the reaction is fast enough (60° C), but in this case the topotactical relations are approximate: the crystallites of CoOOH are tiny and misoriented. One can note an inhomogeneous porosity with small pores and cracks. If reaction 1 is achieved slowly (room temperature), the topotactical relationships which are very clear at the beginning cannot be seen during the rest of the reaction owing to the breaking out of the starting particles [1].

These first observations can be explained by [5, 6]:

(a) the existence of large strains at the reaction interface level which are produced by a misfit between hydroxide and oxide hydroxide lattices;

(b) the difficulty of relieving those strains which, according to the reaction conditions, lead either to a somewhat large crystallite misorientation or to the particle disruption.

Reaction 2, being carried out with material II (non-porous particles with irregular shapes, large and slightly misoriented crystallites), yields a pseudomorphous Co_3O_4 with rather strict topotactical relationships and still well oriented crystallites; on the other hand, a regular small porosity appears in Co_3O_4 particles. If the starting solid is material I (inhomogeneous porosity with small pores and presence of cracks, tiny misoriented crystallites) the disappearance of its irregular porosity can be observed at the same time that a new regular porosity is expanding; crystallite misorientation, important in the starting material, remains unchanged. These results point out that, under these experimental conditions, the strain relief is easy; as a result the final porous texture is homogeneous and an extra crystallite misorientation does not occur.

6. Discussion
Quite general conclusions can be drawn from the results obtained from these two reactions. Effectively, we are able to conclude that an essential condition for keeping fairly good topotactical relationships is the ease with which the strains that necessarily appear at the reacting interface are lessened in the reaction product by the formation of crystallites which will be, in this case, tiny and quite well oriented. A small regular porosity is a token of the ease with which the matter reorganizes.

If strain relief is, on the contrary, more difficult, topotactical relationships which are present

at the beginning of the reaction will disappear more or less quickly as the reaction progresses. When the habit is not broken up, the presence of cracks is a sign of a difficult textural reorganization in the matter.

On the other hand, it is noted that the crystallite misorientation is maintained in the case of the crystallite growth during development of texture of Co_3O_4 as well as in the case of the chemical reaction CoOOH → Co_3O_4.

This phenomenon is normally expected in the case of the development of texture; the vanishing of some crystallite boundaries during crystallite growth does not involve a modification of the reciprocal orientation of the remaining ones. An opposite result might be expected when a chemical reaction is carried out with an easy textural reordering. The fact that the crystallite misorientation is maintained, points out that the crystallite boundaries of the starting solid act on the boundary formation in the final product. However, this phenomenon has no influence on the crystallite sizes; when material II is used (large crystallites) the crystallites of the resulting Co_3O_4 oxide are as small as in the case of Co_3O_4 obtained from material I but only a little misoriented.

7. Conclusion
The textural evolution of the solid phases during the reaction CoOOH → Co_3O_4 has been studied. This work and the comparison with the results on the $Co(OH)_2$ → CoOOH reaction have enabled us to draw some conclusions of general significance on the importance of the textural reordering with regard to the topotaxy phenomenon.

References
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