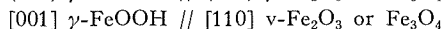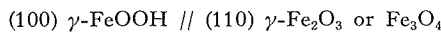# Morphological and Crystallographic Studies on the Oriented Transformation in γ-FeOOH and its Decomposed Oxides

Toshio Takada, Masao Kiyama and Shigeki Shimizu*

(Takada Laboratory, Institute for Chemical Resaerch, Kyoto Univasity)

Lepidocrocite crystals (γ-FeOOH) have been chemically, prepared thermally dehydrated to γ-Fe_2O_3 and reduced to Fe_3O_4. Electron microscopic observations, electron and X-ray diffractions analysis have been undertaken before and after the above mentioned stages of decomposition. Electron microscopy shows that, within each lepidocrocite cyrstal, very fine γ-Fe_2O_3 or Fe_3O_4 particles are formed, which link together to form an aggregate, whose shape closely resembles that of the initial crystal. From the electron diffraction pattern given by the aggregate, it is reasonable to infer that these fine particles are considered to be from the crystallographical viewpoint. Consequently, the aggregate possesses a single-crystal-like texture. The crystallographic relationships between the mother salts and their products are as follows:

(100) γ-FeOOH // (110) γ-Fe_2O_3 or Fe_3O_4

[001] γ-FeOOH // [110] v-Fe_2O_3 or Fe_3O_4

On the basis of these results, explanations are given to the mechanism of the transformation from γ-FeOOH to γ-Fe_2O_3 or Fe_3O_4.

INTRODUCTION

Since 1945 the morphological and crystallographic properties of various kinds of fine metallic oxide particles which were obtained by the thermal decomposition of metallic salts, have been investigated in our laboratory and some results were published.[1][2][3]

In general, the oxide particle thus obtained consisted of the smallest unit particles which were linked with each other, to form an aggregate. And these aggregates resemble in shape the original crystals of their mother salts. Some of these aggregates, for example, the aggregate of α-Fe_2O_3 which was obtained by the thermal decomposition of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) gave a pattern of single crystal structure in electron diffraction. Sawkill[4] studied on the thermal decomposition of silver azide to silver and Goodman[5] studied on that of $Mg(OH)_2$ to MgO and they reported that the aggregate of the product gave a pattern of single crystal structure in electron diffraction. Bernal and Mackey[7] also studied on the dehydration of γ-FeOOH to γ-Fe_2O_3 by means of X-ray method using somewhat rare mineral lepidocrocite, γ-FeOOH as starting specimen. And they found that a single crystal of lepidocrocite was transformed to an oriented texture of a spinel phase and also reported the nature of the mutual crystallographic orientation between lepidocrocite and the spinel phase.

γ-FeOOH has been synthetically prepared by various method, but it was extremely difficult to prepare pure γ-FeOOH witbout contamination by α-FeOOH. In our laboratory we studied on the formation of the precipitate of iron oxides and oxyhydrates from the aquous solutions of iron salts, and we found that it was possible to prepare pure γ-

---

* 高田利夫, 木山雅雄, 清水恵己

Toshio TAKADA, Masao KIYAMA and Shigeki SHIMIZU

FeOOH without contamination by α-FeOOH from aqueous solution of ferrous salt bearing iron powder by passing air bubbles through the solution. Some of the crystals of γ-FeOOH thus obtained were thin and plate-like in shape which were suitable for the morphological and crystallographic studl s by electron microscope and diffraction. In this paper the morphological and crystallographic properties of γ-FeOOH and its dehydrated product γ-Fe$_2$O$_3$ and also the mutual crystallographic orientation between them are described. Some discussions are also given on the results obtained.

EXPERIMENTAL

The particles γ-FeOOH were precipitated from FeSO$_4$ solution bearing metallic iron scraps by heating at 60°C and simultaneously by passing air bubbles through the solution. The precipitates were washed with distilled water and dried at 110°C in air. The powder thus obtained was found to be pure γ-FeOOH by means of X-ray diffraction. The particles of γ-Fe$_2$O$_3$ were prepared by dehydration of γ-FeOOH particles, heating in air at 240°C$\sim$400°C in electric furnace. Fe$_3$O$_4$ particles were also prepared by reducing γ-FeOOH at 350°C$\sim$400°C in the flow of hydrogen. The shape of these particles were observed by an electron microscope and the crystallographic properties were determined by electron diffraction method.

RESULTS

The followings are the results of electron diffraction and electron microscopic observations on the crystallographic structure and particle shape of γ-FeOOH, γ-Fe$_2$O$_3$ and Fe$_3$O$_4$.

(1) γ-FeOOH

The particles obtained by the above-mentioned method of precipitation are yellow and are very uniform in size. X-ray and chemical analyses also indicate that the substance can be identified as pure γ-FeOOH. Other authors[6] report that the crystals are needle-shaped but (see Fig. 1(a)), in most cases, the crystals we obtained are thin and plate-like with dimensions of about 2-5 $\mu \times$0.2-0.5 $\mu \times$0.01-0.02 μ. These differences in shape depend, perhaps, on the different experimental conditions for precipitation.

(a) Electron microphoto-
graph.

(b) Corresponding electron
diffraction pattern.

(c) Dark field image photograph
of the corresponding Bragg
reflection.
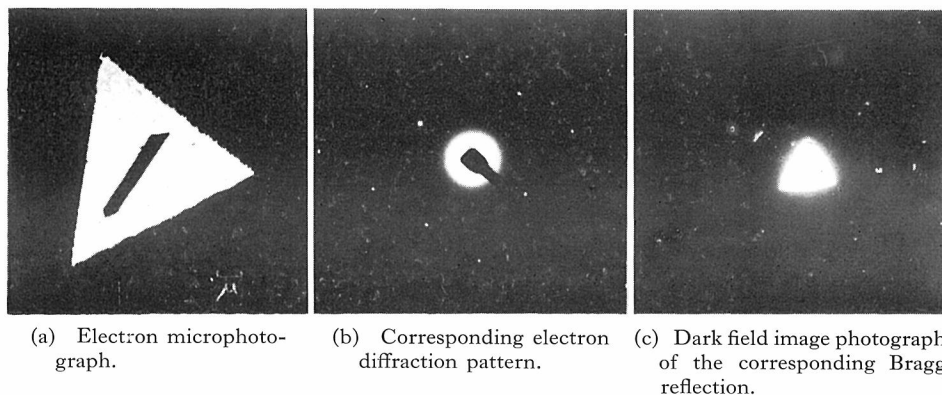
Fig. 1. Electron diffraction pattern of γ-FeOOH.

The electron diffraction pattern and the dark field image, from a single particle of γ-FeOOH are shown in Figs. 1(b) and (c) respectively. Despite the fact that the length and width of the particles in question considerably varied, the obtained electron diffraction patterns were all the same.

An analysis of the diffraction pattern in Fig. 1(b) indicates that this pattern arises from an electron beam which enters the crystal in a direction perpendicular to the (100) plane of γ-FeOOH. The (100) plane therefore lies on a surface parallel to the plane of the photograph in Fig. 1(a). Moreover, a comparison of electron diffraction patterns and electron micrographs identifies the longest crystal axis of γ-FeOOH as the [001] direction.

(2) γ-Fe$_2$O$_3$

Photographs were taken with powders obtained by dehydration of γ-FeOOH in air at a temperature of 30°C for 300 minutes. The powders are brown and possess strong ferrimagnetism. X-ray and chemical analyses show that they are pure γ-Fe$_2$O$_3$.

Fig. 2.1(a) is a typical electron micrograph of the resulting aggregate, while Fig. 2.1 (b) illustrates very fine particles of diameter about 60 Å and which link together to form the aggregate. For the sake of convenience we shall simply describe these ultra-fine particles as unit particles.
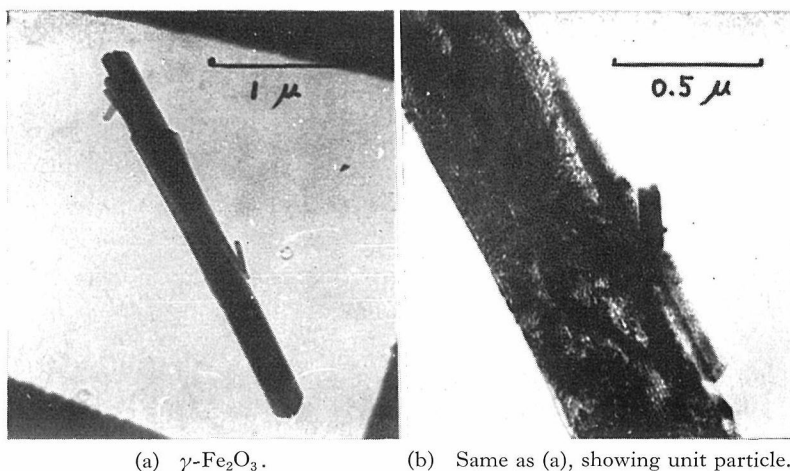

(a) γ-Fe$_2$O$_3$.   (b) Same as (a), showing unit particle.

Fig. 2.1. Electron microphotographs of γ-Fe$_2$O$_3$ particle obtained by dehydration of γ-FeOOH at 300°C for 30 min.

The size of the unit particle was determined by carrying out direct measurements on the enlarged photographs of the unit particles and also, using X-rays, by the method of the line-broadening of a Debye-Scherrer ring. The two methods show fairly good agreement.

Figures 2.2(b) and (c) are the electron diffraction pattern and the dark field image photograph of the corresponding Bragg reflection taken for the aggregate, respectively. From these two photographs it is reasonably inferred that the unit particles are so highly orientated that the aggregate possesses a single-crystal-like structure.
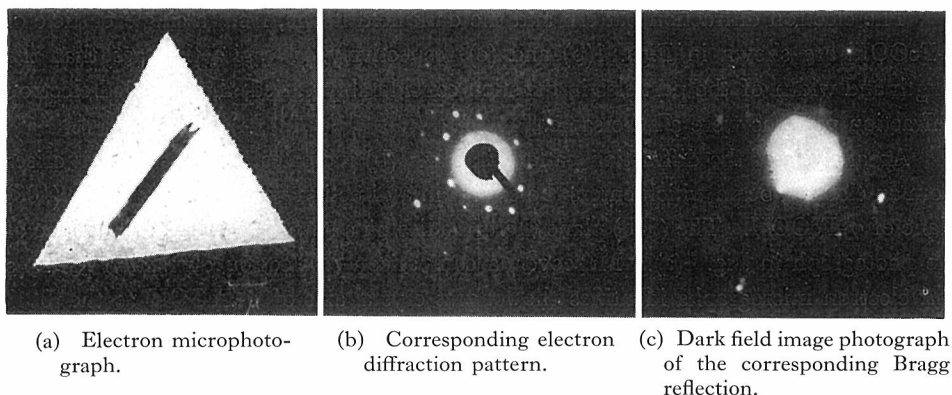
| (a) Electron microphoto-
graph. | (b) Corresponding electron
diffraction pattern. | (c) Dark field image photograph
of the corresponding Bragg
reflection. |

Fig. 2.2. Electron diffraction pattern of γ-Fe_2O_3 particle obtained by dehydration of γ-FeOOH at 300°C for 30 min.

From the results of the electron diffraction analysis of the aggregate (Fig. 2.2. (b)) it is inferred that the diffraction pattern corresponds to that due to the beam entering in a direction of the normal to the (110) plane of the spinel structure in γ-Fe_2O_3. Patterns such as in Fig. 2.2(b) are a characteristic of γ-Fe_2O_3.

Consequently it follows that the orientation of the unit particles of γ-Fe_2O_3 is such that the (110) plane lies in a plane parallel to the photograph and the direction of the longest axis of the aggregate corresponds to the [110] direction of γ-Fe_2O_3.

(3) Fe_3O_4

The powders are black and strongly ferrimagnetic. From X-ray and chemical analyses they are identified as pure magnetite.

γ-FeOOH crystals were reduced in a current of hydrogen at 400°C for 15 minutes. The reduced particles are aggregates whose shapes resemble those of the initial crystals before reduction and in which there remain a number of small pore spaces. The unit particles have shape somewhat different from those in γ-Fe_2O_3 and this would seem attributable to the further stage of sintering.

It is also evident from the photographs in Figures 3(a), (b) and (c) that the aggregate
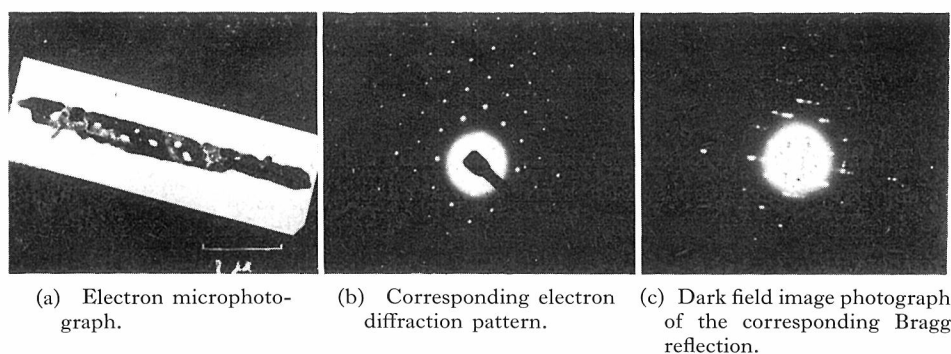

| (a) Electron microphoto-
graph. | (b) Corresponding electron
diffraction pattern. | (c) Dark field image photograph
of the corresponding Bragg
reflection. |

Fig. 3. Electron microphotograph and corresponding electron diffraction photograph of Fe_3O_4 obtained by reduction of γ-FeOOH at 350°C for 20 min..

possesses a single-crystal-like structure as in the case of γ-Fe_2O_3. The results of the electron diffraction work are directly comparable with those obtained in the case of γ-Fe_2O_3; the plane of the photograph of the aggregate corresponds to the (110) plane and the longest axis of the aggregate corresponds to the [110] direction of Fe_3O_4.

DISCUSSION

Dehydrated γ-Fe_2O_3 and reduced Fe_3O_4 from γ-FeOOH are discovered to form aggregates, plate-like in shape, very closely resembling the initial γ-FeOOH. In γ-Fe_2O_3 ultra-fine unit particles are linked whilst in Fe_3O_4, in addition to the linking, a number of small pores can be found generally. Electron diffraction observations of the aggregates, in spite of the variable shapes of the latter, show that the crystallographic structure as well as the axis of each unit particle is common throughout the aggregate. The unit particles are so highly orientated in the aggregate that the diffraction pattern is a cross-grating pattern and, therefore, the aggregate, can be considered as a single crystal. The mechanism by which such single crystallographic structure arises would appear to be identical to that reported by Bernal and Mackay who have proposed that if the mother salt changes into the oxide by dehydration or decomposition there is only the least displacement of the cation and anion networks.

We now consider in more detail the crystallographic differences and the relationships of the networks between the mother salt and its products. Our data yield the following crystallographic parallelisms:

(100) γ-FeOOH // (110) γ-Fe_2O_3 or Fe_3O_4

[001] γ-FeOOH // [110] γ-Fe_2O_3 or Fe_3O_4

Figure 4 diagrammatically shows the structuure of γ-FeOOH whilst Figure 5 depicts the layered structures of both γ-FeOOH (viewed at right angles to [100]) and γ-Fe_2O_3 (viewed at right angles to [110]).

In γ-FeOOH there is a characteristic repetition of the layers; two OH layers (C) and (D) are sandwiched between Fe, O layers (B) and (E). When the decomposition of γ-FeOOH occurs, water molecules are expelled from the (C) and (D) layers, the one layer of oxygen necessary for the formation of γ-Fe_2O_3 being left in the (C¹) layer. Fe ions required here are supplied from neighbouring layers. This results in a considerable
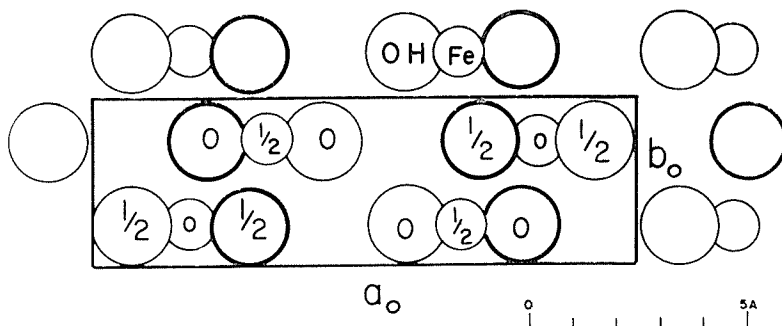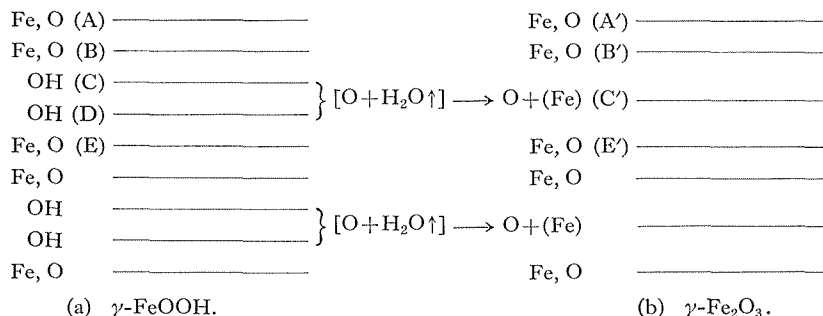

Fig. 4. A projection along C_0 of γ-FeOOH.

Fig. 5.   Schematic diagram of γ-FeOOH and γ-Fe$_2$O$_3$ lattices viewed at right angle to the [100] axis and [110] axis respectively.

shortening of the distance between the (A) and (E) layers; from 6.2Å in γ-FeOOH to 4.41 Å in γ-Fe$_2$O$_3$ (see the figure).   The changes of the network within the layers, however, are quite small.   If we assume only a 4.5 % contraction of the oxygen network of γ-FeOOH in the [001] direction and, simultaneously, a 7.5 % elongation in the [010] direction we can account for the transformation of the γ-FeOOH network into γ-Fe$_2$O$_3$. Displacements in the Fe ion network which accompany the above explusion are similarly small.   These considerations are helpful in making the crystallographic parallelisms discussed above appear to be quite reasonable.

It is to be concluded that the transformation of γ-FeOOH into γ-Fe$_2$O$_3$ is a characteristic one, the former changing into the latter with only the slightest deformations, without any irregular disturbance in the networks..   Hence the product occurs in the form of an aggregate which possesses extremely high orientation.   This same conclusion was reached by Goodman in the case of dehydration of Mg(OH)$_2$ into MgO.

REFERENCES

(1)   K. Iwase, K. Ogawa and T. Takada, *J. Japan Inst. Met.*, **17**, 467 (1953).
(2)   T. Takada, *Science of Powders*, **4**, 120 (1958).
(3)   K. Iwase, T. Takada and T. Hayashi, "Powder Metallugy", Interscience Publishers, New York, 1961, p. 173.
(4)   J. Sawkill, *Proc. Roy. Soc.*, **A229**, 135 (1955).
(5)   T. F. Goodman, *Proc. Roy. Soc.*, **A247**, 346 (1958).
(6)   R. Fricke, G. Weitbrecht, *Z. anorg. allg. Chem.*, **251**, 424 (1943).
(7)   J. D. Bernal, D. R. Dasgupta and A. L. Mackay, *Nature*, **180**, 645 (1957).