Electron Microscopic Observation of the Oriented Transformation Process in γ-FeOOH and its Decomposed Oxides

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For the purpose of clarifying the crystallographic and morphological relationships between γ-FeOOH and its decomposed product, the thermal transformation of a γ-FeOOH particle was investigated by an electron microscope equipped with an electric furnace. Application of electron beams was also attempted to heat the sample. Electron microscopic images and the selected area electron diffraction patterns were obtained as the sample were heated. A γ-FeOOH particle heated at 350°C showed the electron diffraction pattern consisting of two kinds of net patterns corresponding to γ-FeOOH and γ-Fe₂O₃ or Fe₃O₄, respectively. From the analysis of these net patterns, the crystallographic relationships between γ-FeOOH and γ-Fe₂O₃ or Fe₃O₄ were derived as follows;

$$(100)_{\gamma\text{-FeOOH}} \;//\; (110)_{\gamma\text{-Fe}_2\text{O}_3 \text{ or } \text{Fe}_3\text{O}_4}$$
$$[100]_{\gamma\text{-FeOOH}} \;//\; [1\bar{1}0]_{\gamma\text{-Fe}_2\text{O}_3 \text{ or } \text{De}_3\text{O}_4}$$

A γ-FeOOH particle partially decomposed into γ-Fe₂O₃ by application of intense electron beams gave the same relationships.

I. INTRODUCTION

γ-FeOOH has an orthorhombic structure whose lattice spacings are $a_o = 12.50$ Å, $b_o = 3.86$ Å and $c_o = 3.06$ Å. It is known that the product obtained by dehydration of γ-FeOOH in air is γ-Fe₂O₃. γ-Fe₂O₃ has a spinel structure whose lattice spacing is $a_o = 8.30$ Å. γ-Fe₂O₃ is a metastable phase and transforms to α-Fe₂O₃ above about 350°C in air. In reducing atmosphere, however, γ-Fe₂O₃ transforms easily to Fe₃O₄ which has the same spinel structure as γ-Fe₂O₃ and whose lattice spacing is $a_o = 8.40$ Å. In the present study, the thermal decomposition of γ-FeOOH to γ-Fe₂O₃ or Fe₃O₄ was observed continuously by an electron microscope.

Topotaxy, that is, "any chemical solid state reaction that leads to a product with crystal orientation correlated with crystal orientation of the initial material", has been studied by electron microscope or x-ray measurements.[1,2,6] For example, the thermal decomposition of γ-FeOOH was investigated by several investigators; Bernal[3] and Mackay[4] studied the thermal decomposition of mineral lepidocrocite single crystal (γ-FeOOH) using x-ray and electron diffraction methods, while Takada[5,6] treated that of synthetic γ-FeOOH particle using electron microscope. On heating, the crystal decomposed to give the pattern of a spinel crystal with the (110) and [1̄10] replacing, respectively, the (100) and [001] of the γ-FeOOH.[5] No direct observation

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of the transformation process was made, however, in these investigations.

In the present study, the particles of γ-FeOOH were heated in the electron microscope by two methods; in one method the specimen was heated in the furnace which was set in the specimen chamber of an electron microscope and in the other heated by application of intense electron beams. These methods of heating made it possible to follow the transformation process closely and, as a result, investigate crystallographic and morphological relationship between γ-FeOOH, a starting material, and γ-Fe₂O₃ or Fe₃O₄, a resultant product.

II. EXPERIMENTAL

The particles of γ-FeOOH were synthesized from aqueous solution of ferrous salt bearing iron powder by passing air bubbles through it. The precipitates obtained were filtered and washed. The particles (γ-FeOOH) dispersed in water were mounted on platinum mesh with a thin film of evaporated carbon. Each particle of γ-FeOOH was a thin flake of about 1.2 μ in length and 0.5 μ in width as shown in Fig. 1. The selected area electron diffraction was used for examination of this particle. For the electron microscopic observation an instrument equipped with the transmission hot stage type attachment, that is, two heaters in the specimen chamber, was used. The platinum mesh was inserted between these two heaters. The temperature was calibrated against the heater voltage beforehand so that the temperature of the specimen could be known by reading the voltage supplied to the heater in the actual runs. The temperature of the specimen was raised to 800°C. During the heating, the electron microscopic image and the corresponding selected area diffraction pattern of γ-FeOOH were observed continuously by paying attention to the one and the same particle. Photographs were taken at room temperature, 300°C, 350°C, 400°C, 700°C and 800°C.

Another particle of γ-FeOOH was heated with intense electron beams in the electron microscope and the transformation was observed in the same way.
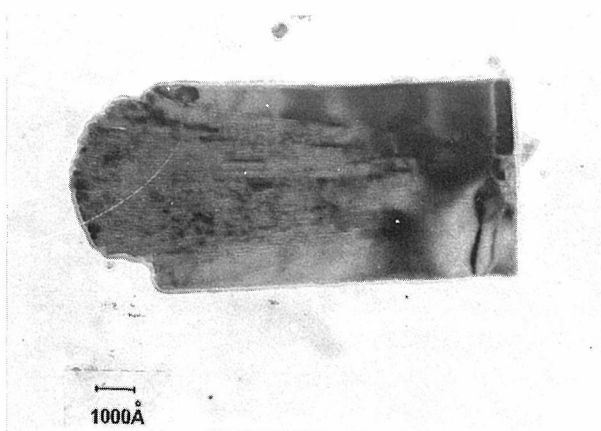

Fig. 1. Electron micrograph of γ-FeOOH

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III. RESULTS AND DISCUSSION

The electron diffraction pattern of the γ-FeOOH particle and the dark field image are shown in Fig. 2. The electron diffraction pattern in Fig. 2(a) consists of a net pattern indicating that the particle is a single crystal. Moreover, analysis of the electron diffraction pattern and the corresponding dark field image indicates that electron beams enter in a direction perpendicular to the (100) plane of γ-FeOOH, and that the longest crystal axis is parallel to the [001] direction, as shown schematically in Fig. 3. As shown in Fig. 4, the diffraction pattern of the particle at 300°C is the same as that at room temperature, suggesting that γ-FeOOH remains unchanged up to 300°C. At 350°C, however, a new net pattern is observed in addition to the old one, as can be seen in Fig. 5. The new pattern corresponds to the net pattern which is obtained when the beams enter in a direction perpendicular to the (110) plane of the such spinel structure as γ-Fe$_2$O$_3$ or Fe$_3$O$_4$. This is shown schematically in Fig. 2. As shown in Fig. 6, the orientation relationship is such that

(a)   (b)
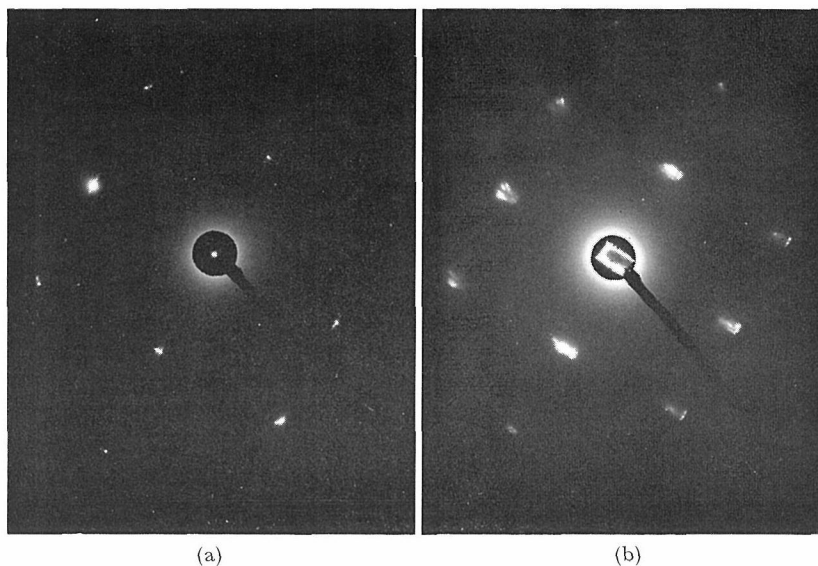
Fig. 2. (a) Electron diffraction pattern, (b) dark field image of γ-FeOOH at room temperature.
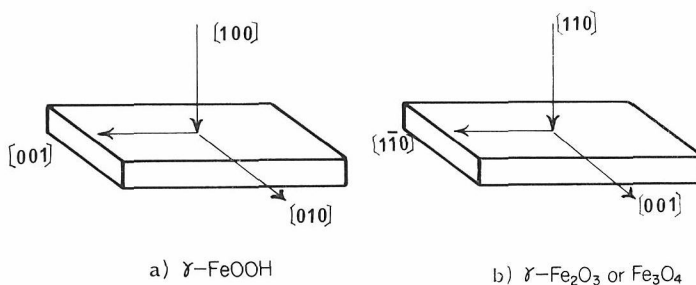

a) γ-FeOOH   b) γ-Fe$_2$O$_3$ or Fe$_3$O$_4$

Fig. 3. Orientation of (a) γ-FeOOH and (b) γ-Fe$_2$O$_3$ or Fe$_3$O$_4$

(a)   (b)
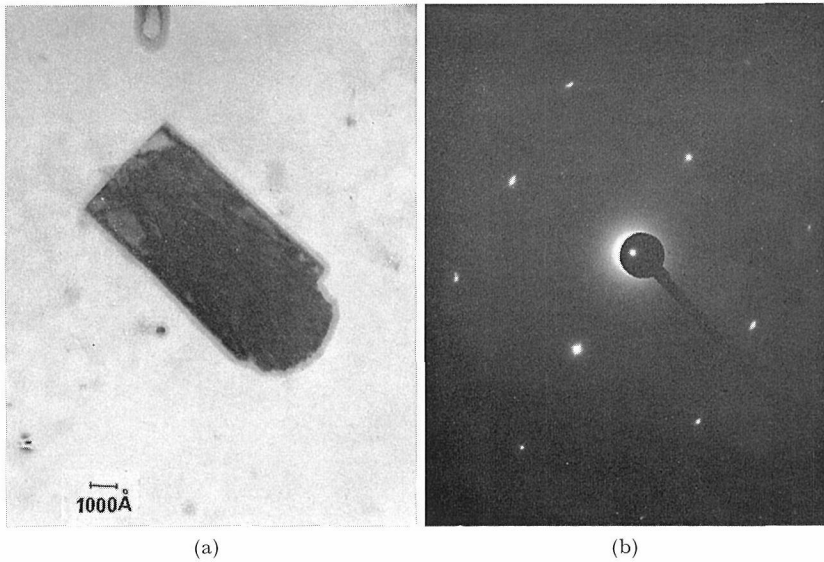
Fig. 4. (a) Electron micrograph (b) diffraction pattern of the particle
heated at 300°C.
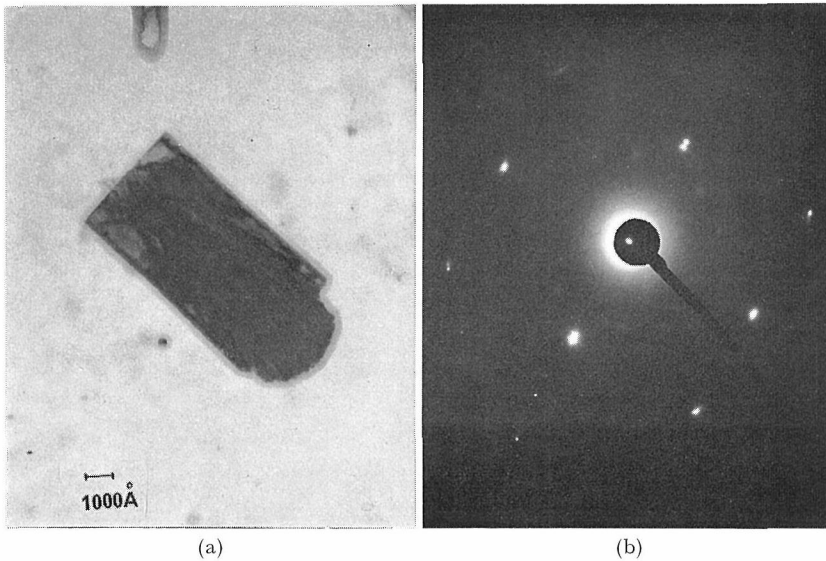
(a)   (b)

Fig. 5. (a) Electron micrograph (b) diffraction pattern of the
particle heated at 350°C.

$$(100)_{\gamma-\text{FeOOH}} \quad // \quad (110)_{\gamma-\text{Fe}_2\text{O}_3 \text{ or } \text{Fe}_3\text{O}_4}$$
$$[001]_{\gamma-\text{FeOOH}} \quad // \quad [1\bar{1}0]_{\gamma-\text{Fe}_2\text{O}_3 \text{ or } \text{Fe}_3\text{O}_4}$$
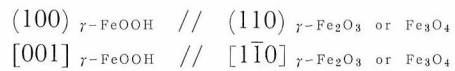
The appearance of the spinel structure in addition to originally present γ-FeOOH
in electron diffraction pattern means that two phases of γ-FeOOH and γ-Fe$_2$O$_3$ or
Fe$_3$O$_4$ coexist in one particle at this temperature. It should be noted also that the
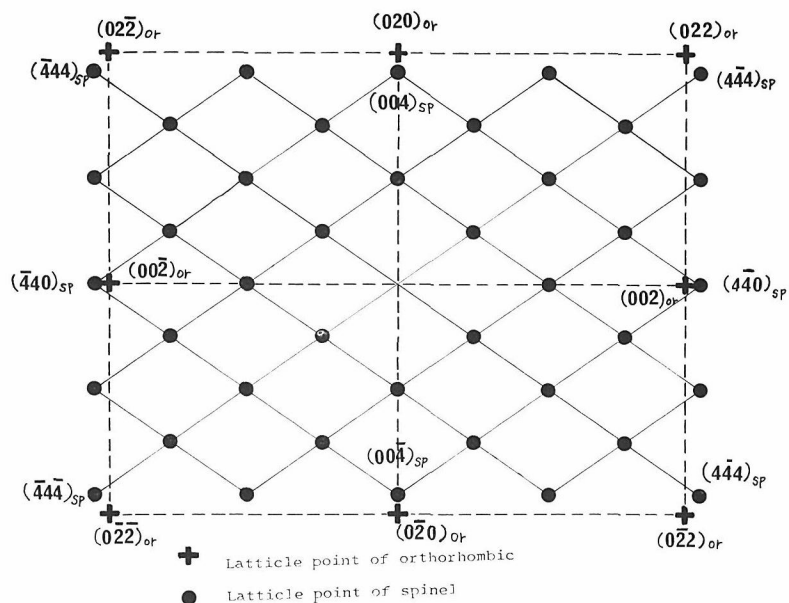shape of the particle is not changed when it is heated at 350°C. It can be said from
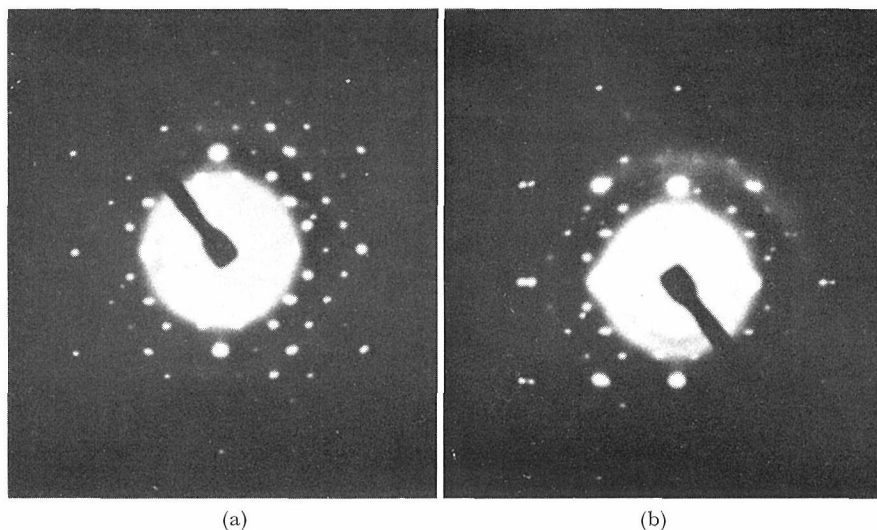
Fig. 6. Illustration of Fig. 5 and Fig. 7.

(a)   (b)

Fig. 7. (a) Diffraction pattern of a particle which consists of γ-FeOOH
and spinel phase, (b) diffraction pattern of the particle which consists
of one phase of spinel. The particle was decomposed with strong
electron beams.

these observations that a γ-FeOOH particle is partially transformed to γ-Fe$_2$O$_3$ or
Fe$_3$O$_4$ as a result of decomposition and that the particle is now a highly oriented
crystalline aggregate. As shown in Fig. 7, diffraction pattern of another particle heated
with intense electron beams also shows the same orientation relationship.

As shown in Fig. 8, the electron diffraction pattern corresponding to γ-FeOOH
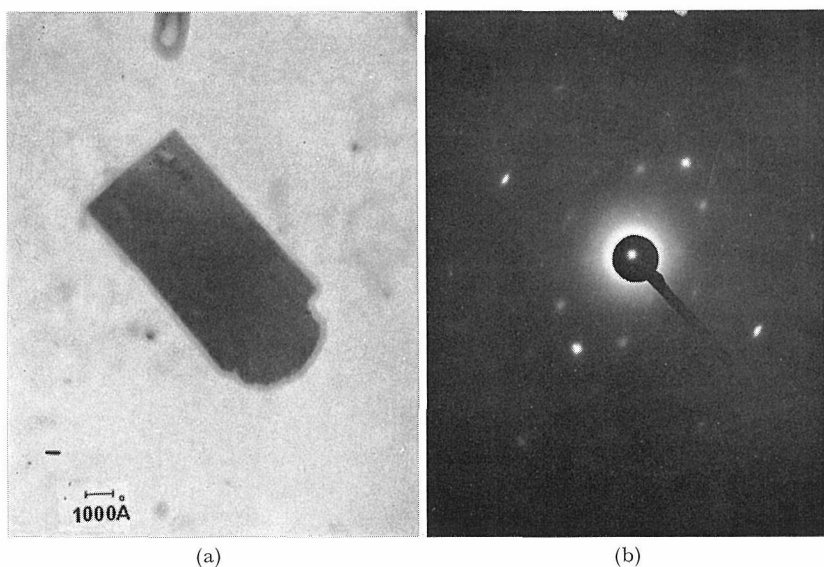
Fig. 8.　(a) Electron micrograph, (b) diffraction pattern of the
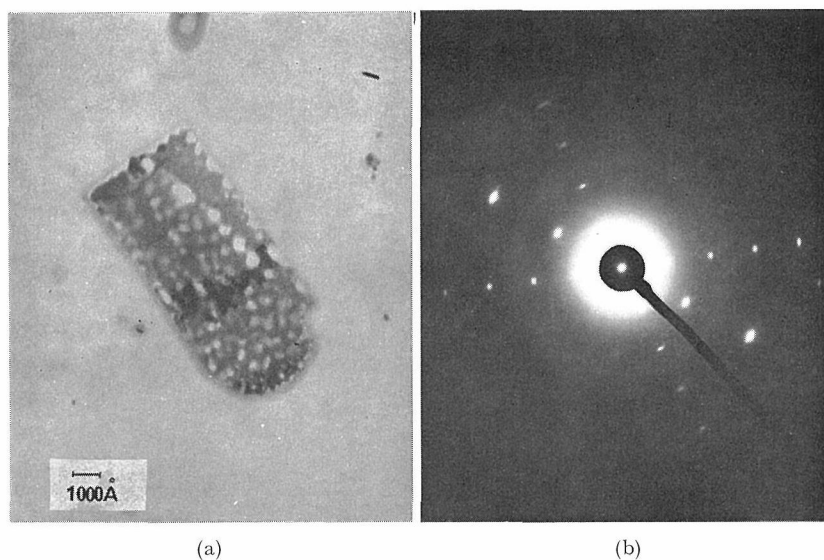particle heated at 400°C.

Fig. 9.　(a) Electron micrograph, (b) diffraction pattern of the
particle heated at 800°C.

disappears at 400°C, indicating that γ-FeOOH has perfectly transformed to γ-Fe$_2$O$_3$ or Fe$_3$O$_4$ over the whole regions of the particle.　Up to 800°C the diffraction pattern corresponding to spinel structure is still observed as shown in Fig. 9.　In our experiment, it was impossible to distinguish γ-Fe$_2$O$_3$ from Fe$_3$O$_4$ by the selected area electron diffraction because the lattice constant of γ-Fe$_2$O$_3$ is nearly equal to that of Fe$_3$O$_4$.　Generally, however, γ-Fe$_2$O$_3$ obtained from γ-FeOOH transforms to α-Fe$_2$O$_3$ above 400°C in air. Therefore, the material corresponding to spinel structure above 400°C would be Fe$_3$O$_4$.

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IV. SUMMARY AND CONCLUSION

The thermal decomposition of γ-FeOOH was observed continuously by heating it in the specimen chamber of an electron microscope. It remained unchanged from room temperature to 300°C. When heated at 350°C, γ-FeOOH coexisted with γ-Fe_2O_3 or Fe_3O_4 in one particle. The same phenomenon was observed when γ-FeOOH was heated with electron beams. It was concluded that the crystallographic relationships between the mother salt and their product were as follows:

$$(100)_{\gamma\text{-FeOOH}} \quad // \quad (1\bar{1}0)_{\gamma\text{-Fe}_2\text{O}_3 \text{ or } \text{Fe}_3\text{O}_4}$$
$$[001]_{\gamma\text{-FeOOH}} \quad // \quad [1\bar{1}0]_{\gamma\text{-Fe}_2\text{O}_3 \text{ or } \text{Fe}_3\text{O}_4}$$

This relationship was identical to that reported by Takada.[5] Above 400°C, γ-FeOOH transformed completely to the spinel phase corresponding to γ-Fe_2O_3 or Fe_3O_4. The shape of the particle, however, remained unchanged from room temperature to 800°C. Therefore, it was concluded that γ-FeOOH topotaxially transformed to γ-Fe_2O_3 or Fe_3O_4 with the parallelism as mentioned above.

ACKNOWLEDGMENT

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