

## On the Magnetic Property of Iron Oxides

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# On the Magnetic Property of Iron Oxides

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## Synopsis

Pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder prepared by oxidation of Fe(CO)<sub>5</sub>, was reduced to Fe<sub>3</sub>O<sub>4</sub> by the hydrogen stream containing water vapour. The magnetic properties were measured at each state of reduction and the reduced grade was checked by the chemical and X-ray analysis. Fe<sub>3</sub>O<sub>4</sub> thus prepared, was oxidized again and it was proved that the changes of the magnetic properties during oxidation and reduction, coincide with one another.

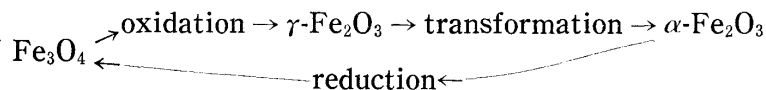
## I. Introduction

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> has a spinel type crystal structure and a ferromagnetic property like Fe<sub>3</sub>O<sub>4</sub>, but  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is rhombohedral and non-magnetic, as shown in Table 1.

Table 1

|  | space group             | lattice constant | magnetic property |
|--|-------------------------|------------------|-------------------|
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | rhombohedral (corundum) | 5.42 Å           | paramagnetic      |
| $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> | cubic (spinel)          | 8.4 Å            | ferromagnetic     |
| Fe <sub>3</sub> O <sub>4</sub>           | cubic (spinel)          | 8.4 Å            | ferromagnetic     |

And it has been recognized hitherto by many researchers that Fe<sub>3</sub>O<sub>4</sub> is oxidized to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by way of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>;  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is reduced directly to Fe<sub>3</sub>O<sub>4</sub> and do not pass through the state of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>; that is, the  $\alpha \rightarrow \gamma$  transformation of Fe<sub>2</sub>O<sub>3</sub> is irreversible and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is reduced directly to Fe<sub>3</sub>O<sub>4</sub> as follows:



However, a few researchers observed that very fine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder on an iron surface changed reversibly to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>(1)(2)</sup>

Fine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powder was prepared from Fe(CO)<sub>5</sub> and it was heat-treated in the range 250°C to 700°C in hydrogen stream with water vapour. Fe<sub>3</sub>O<sub>4</sub>, thus prepared, was gradually oxidized again in vacuum.

The magnetic properties and the ratio of ferrous and ferric ion of these iron oxides were compared. And it was concluded from these experiments that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> might have been changed to Fe<sub>3</sub>O<sub>4</sub> by reduction by way of the state of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>; also in this case the relation between the magnetic properties and the chemical compositions of these oxides was obtained.

(1) T. Iimori, Nature **140** (1937), 278.

(2) T. Iimori, Sci. Pap. I.P.C.R. Tokyo **34** (1937), 60.

## II. Preparation of sample

Very fine, pure  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder was prepared from an iron carbonyl. The oxidation process and apparatus had already been reported by the present author.<sup>(3)(4)</sup> The mixed iron oxides obtained from  $\text{Fe}(\text{CO})_5$  were heated at  $550^\circ\text{C}$  for 2 hrs. in the air, in order to remove ferrous ion and carbon.

The powder thus prepared was dark red and non-magnetic and about  $0.1\mu$  in mean diameter. Fig. 1 shows an electron microscopic photograph of the powder.

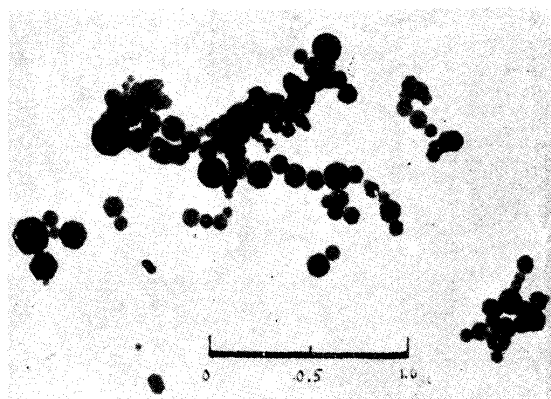


Fig. 1. Electron microscopic photograph for  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder.

## III. Experimental details

The furnace arrangement for oxidation and reduction is illustrated in Fig. 2. For reduction, hydrogen is led to a flask D from a high pressure vessel A, through a gas meter B and a flow meter C. The volume of D is about 1 L and is filled with distilled water about 600 cc. The flask is heated by an electric heater and the temperature of distilled water is kept constant by a thermometer E. The hydrogen is saturated with the water vapour in the flask and then sent to a porcelain tube F. The tube F is about 1 m in length and 30 mm in inner diameter and is heated by a movable electric furnace G. The powder, weighing about 15 g, is heated in the tube F on a porcelain boat. Gas is exhausted through a water seal I. J is a millivoltmeter for a thermojunction. The furnace is evacuated about to  $5/100$  mmHg by a vacuum pump K for oxidation process. L is U tube, containing with  $\text{P}_2\text{O}_5$ , and is used for measuring the vapour content in hydrogen stream.

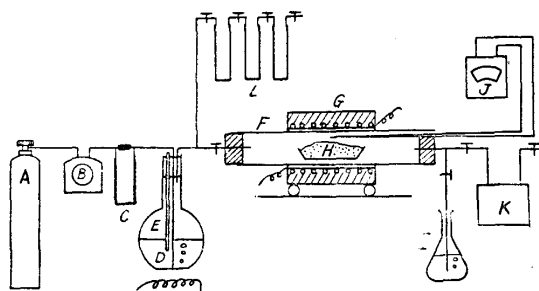


Fig. 2. Schematic view of furnace for oxidation and reduction.

In this furnace,  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder obtained from  $\text{Fe}(\text{CO})_5$  was reduced at various temperatures by the constant hydrogen stream containing water of various ratio. And then,  $\text{Fe}_3\text{O}_4$  thus prepared, was oxidized again in vacuum at various temperatures.

Packed in a glass tube, the magnetic properties for these powder were measured by a solenoid and a ballistic galvanometer. The chemical and X-ray analysis

(3) H. Kojima, Rep. Res. Inst. Sci. Meas., Tohoku Univ. (Japanese) **2** (1952), 101.

(4) T. Okamura, H. Kojima, Y. Kamata, J. App. Phys., Japan. **21** (1952), 9.

were also carried out for all samples.

#### IV. Magnetic behaviour of $\alpha$ - $\text{Fe}_2\text{O}_3$ during reduction

$\alpha$ - $\text{Fe}_2\text{O}_3$  powder, prepared from  $\text{Fe}(\text{CO})_5$ , was reduced in the furnace, illustrated in Fig. 2, and the magnetic behaviour during reduction was observed.

Table 2

| Flow of $\text{H}_2$ | Temp. of $\text{H}_2\text{O}$ | $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ |
|----------------------|-------------------------------|---|
| 300 cc/min           | 90°C                          | 1.11                                    |
| 450 cc/min           | 90°C                          | 0.83                                    |
| 550 cc/min           | 90°C                          | 0.62                                    |

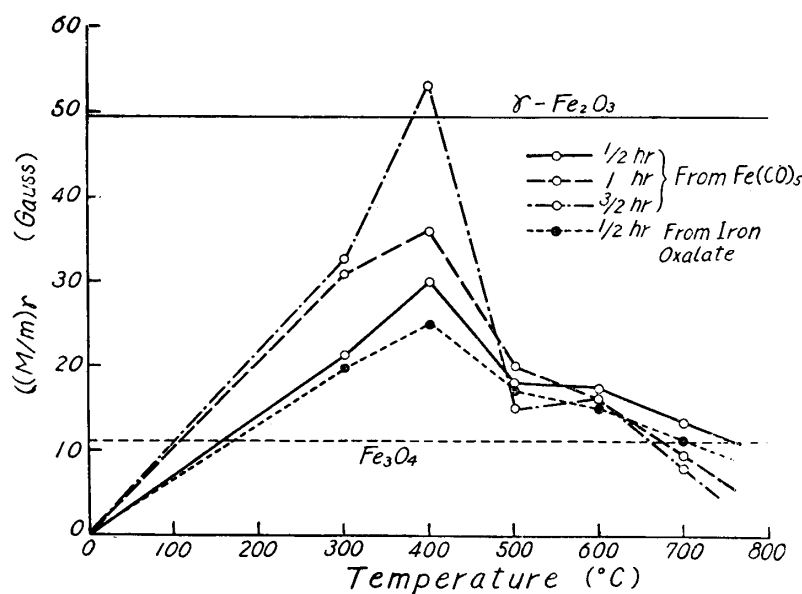


Fig. 3. Magnetic remanence vs reduction temperature for  $\alpha$ - $\text{Fe}_2\text{O}_3$  ( $P_{\text{H}_2}/P_{\text{H}_2\text{O}}=0.83$ )

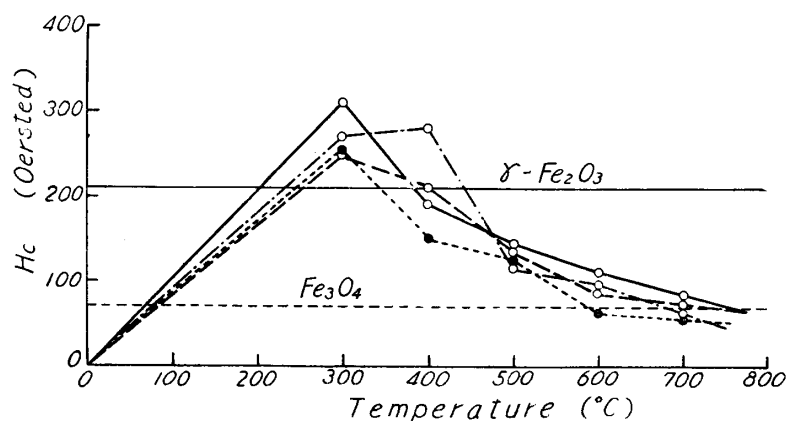


Fig. 4. Corecive force vs reduction temperature for  $\alpha$ - $\text{Fe}_2\text{O}_3$  ( $P_{\text{H}_2}/P_{\text{H}_2\text{O}}=0.83$ )

$\text{Fe}_3\text{O}_4$  powder respectively. And the above notations are common in Figs. 4~10.

In this experiment, the changes of remanence for the oxide powder were shown instead of the saturation value, because the difference of remanence between

That is, the  $\alpha$ - $\text{Fe}_2\text{O}_3$  powder was reduced at 300~700°C in the hydrogen stream of 200~600 cc/min and the temperature of distilled water was varied from 70° to 90°C.

The ratio of  $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$  in hydrogen stream was measured from the change in weight of  $\text{P}_2\text{O}_5$  and illustrated in Table 2.

Fig. 3 shows the change of magnetic remanence per unit mass vs. the reduction temperature of  $\alpha$ - $\text{Fe}_2\text{O}_3$  for  $P_{\text{H}_2}/P_{\text{H}_2\text{O}} = 0.83$ . In the figure, full line, broken line and chain line mean 1/2 hr, 1 hr and 3/2 hrs reduction respectively, and the dotted line illustrates the magnetic property of  $\alpha$ - $\text{Fe}_2\text{O}_3$  for 1/2 hr reduction, which was prepared from iron oxalate. The full and broken parallel lines to the abscissa show the magnetic property of  $\gamma$ - $\text{Fe}_2\text{O}_3$ , prepared from  $\text{Fe}(\text{CO})_5$  and natural

$\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> was more remarkable than the saturation, and the slight change at every reduced state could be easily distinguished from these results.

Fig. 4 shows the change of coercive force due to the reduction temperature. From these figures, we can see that the magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> approach to the properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at 350~450°C, and coincide with that of Fe<sub>3</sub>O<sub>4</sub> at about 600°C. In general, the increase of the reduction hour brings the advance of the reduction, but it seems that the reduction time of 3/2 hrs is almost enough to finish the reduction.

Figs. 5 and 6 show the change of magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> during reduction of  $P_{H_2}/P_{H_2O}=1.11$ , and Figs. 7 and 8 show the case of  $P_{H_2}/P_{H_2O}=0.62$ .

The values were plotted in these figures only for the results of 1/2 hr reduction and they illustrate that the magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> change in the same way in Figs. 3 and 4, but

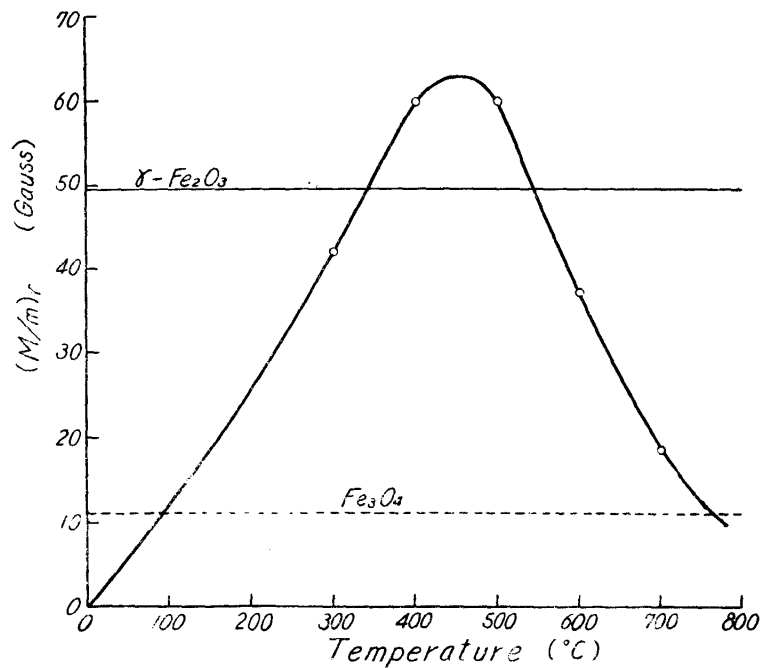


Fig. 5. Magnetic remanence vs reduction temperature for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $P_{H_2}/P_{H_2O}=0.62$ )

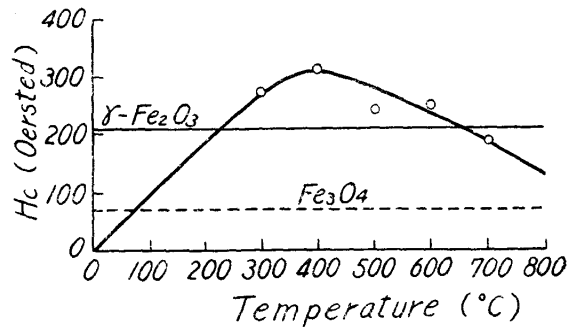


Fig. 6. Coercive force vs reduction temperature for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $P_{H_2}/P_{H_2O}=1.11$ )

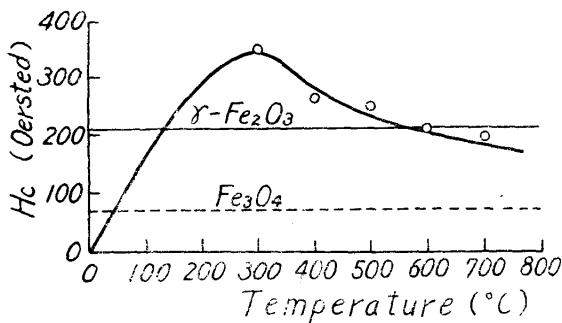


Fig. 8. Coercive force vs reduction temperature for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $P_{H_2}/P_{H_2O}=1.11$ )

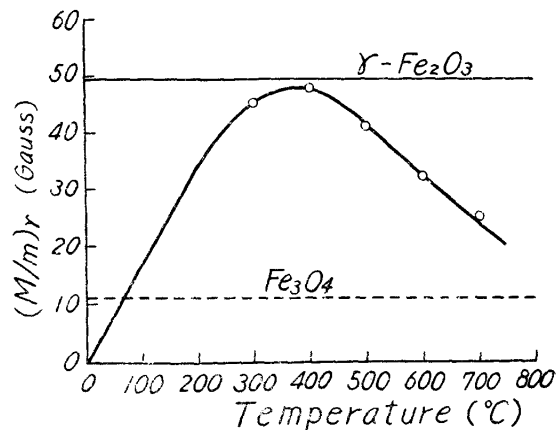


Fig. 7. Magnetic remanence vs reduction temperature for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> ( $P_{H_2}/P_{H_2O}=0.62$ )

the reduction point decreases with the decrease of  $P_{H_2}/P_{H_2O}$ .

### V. Magnetic behaviour of $Fe_3O_4$ during oxidation

It was found from the above experiments that the magnetic properties of  $\alpha-Fe_2O_3$  coincided almost completely with one of  $Fe_3O_4$  by reduction at  $600^\circ C$  for

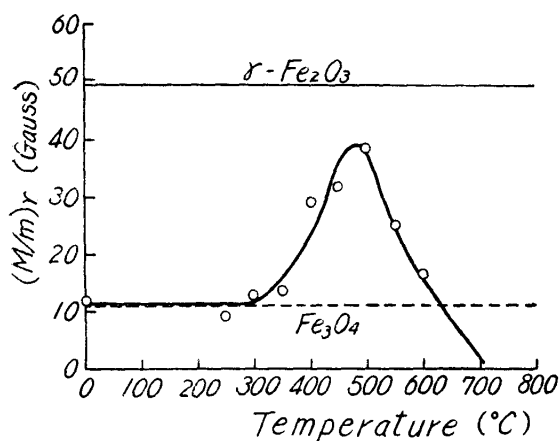


Fig. 9. Magnetic remanence vs oxidation temperature for  $Fe_3O_4$  (vacuum)

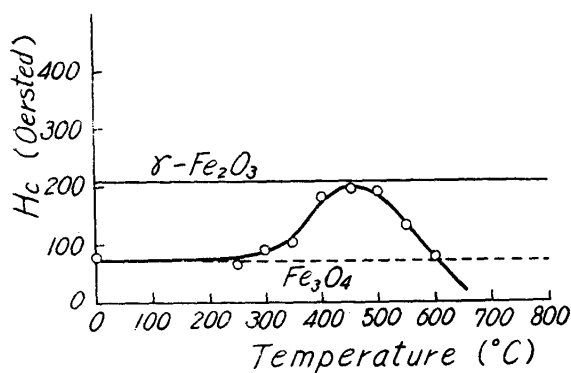


Fig. 10. Coercive force vs oxidation temperature for  $Fe_3O_4$  (vacuum)

3/2 hrs in the gas for  $P_{H_2}/P_{H_2O} = 1.0$ .

And also, it was proved by chemical and X-ray analysis that the powder might be  $Fe_3O_4$ .

Then, pure  $Fe_3O_4$  powder was prepared by this process and gradually oxidized by the use of the apparatus shown in Fig. 2 in the vacuum of 5/100 mmHg. The changes of  $(M/m)_r$  and  $H_c$  by oxidation for 1/2 hr are illustrated in Figs. 9 and 10.

From these figures, it was found that the magnetic properties of  $Fe_3O_4$  approached the properties of  $\gamma-Fe_2O_3$  by oxidation at  $400^\circ C$  for 1/2 hr and it was changed to a paramagnetic state above  $700^\circ C$ . And this may illustrate the oxidation process,  $Fe_3O_4 \rightarrow \gamma-Fe_2O_3 \rightarrow \alpha-Fe_2O_3$ , which has been recognized by many researchers.

The difference of the magnetic properties between  $\gamma-Fe_2O_3$  and the oxidized  $Fe_3O_4$  at about  $400^\circ C$  signifies the co-existence of  $\alpha-Fe_2O_3$ . Then,

$\gamma-Fe_2O_3$ , prepared from these process, may be stable at a lower temperature than  $400^\circ C$ .

In fact, the  $\gamma-Fe_2O_3$  is transformed to  $\alpha-Fe_2O_3$  at about  $300^\circ C$ <sup>(5)</sup>, but very stable  $\gamma-Fe_2O_3$  was also found, which was ferromagnetic even above  $600^\circ C$ .<sup>(5)</sup> And the stability might be due to impurities included, of which we can not give a definite conclusion.

### VI. Chemical analysis

Chemical analysis was carried out on all samples in the course of oxidation or reduction. That is, the sample is first solved in aqueous  $H_2SO_4$  solution in  $CO_2$  atmosphere and ferrous ion is measured by titration of  $KMnO_4$ . Then, the sample is reduced by Zn amalgam and total iron are determined again by the titration.

(5) T. Takei, J. Japan Inst. Metals 16 (1952), A321.

Fig. 11 is the change of the ratio of total iron to ferrous ion in the case of reductin, for which the specimens were treated in the atmosphere for  $P_{H_2}/P_{H_2O} = 0.83$  at various temperature for 1/2, 1 and 3/2 hrs respectively. The ratio is decreased smoothly with higher temperature and  $\alpha$ - $Fe_2O_3$  is partially reduced to  $Fe_3O_4$ , but still ferric ion fairly remains between  $400^\circ \sim 500^\circ C$ , at which the magnetic property shows maximum. For the oxidation of  $Fe_3O_4$  in vacuum, also, the monotonous increase of the value,  $(Fe^{++} + Fe^{+++})/Fe^{++}$ , was observed, as shown in Fig. 12; a fair amount of  $Fe_2O_3$  is recognized at about  $500^\circ C$  at which the magnetic property of  $Fe_3O_4$  approaches one of  $\gamma$ - $Fe_2O_3$  and we cannot find any anomaly on the oxidation curve.

### VII. X-ray analysis

X-ray diffraction patterns were observed for all samples through the whole process. But the Debye-Scherrer's patterns which are now the problem from the results of the magnetic measurements, will only be discussed here. That is to say,  $\alpha$ - $Fe_2O_3$  reduced at  $400^\circ C$  for 1 hr in the mixed gas of hydrogen and water vapour (No. 1) and  $Fe_3O_4$ , oxidized at  $500^\circ C$  for 1/2 hr in vacuum (No. 2) which had both a magnetic property like  $\gamma$ - $Fe_2O_3$ , were compared with  $\gamma$ - $Fe_2O_3$  (No. 3), natural magnetite (No. 4) and  $\alpha$ - $Fe_2O_3$  (No. 5) by X-ray analysis. Here, No. 1, No. 2, No. 3 and No. 5 were respectively prepared from  $Fe(CO)_5$  as mentioned above.

Fig. 13 shows the intensity curves, obtained by a microphotocomparator from the half side of these Debye rings, containing few rings on the opposite side. Experimental conditions and results obtained by X-ray analysis are put in order in Table 3; the relative intensity and radii of Debye rings of No. 1~No. 4 could not be distinguished from one another in these curves.

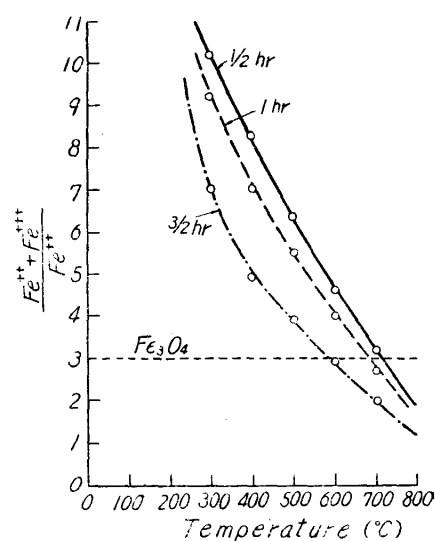


Fig. 11. Chemical composition vs reduction temperature for  $\alpha$ - $Fe_2O_3$  ( $P_{H_2}/P_{H_2O} = 0.83$ )

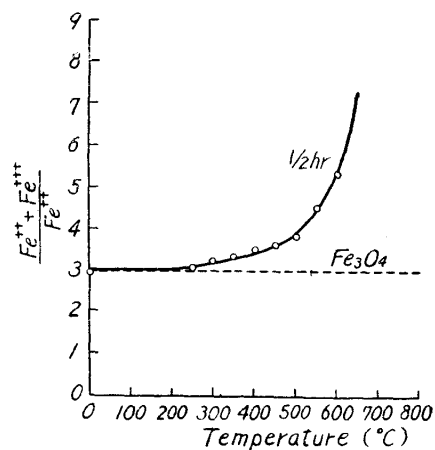


Fig. 12. Chemical composition vs oxidation temperature for  $Fe_3O_4$  (vacuum)

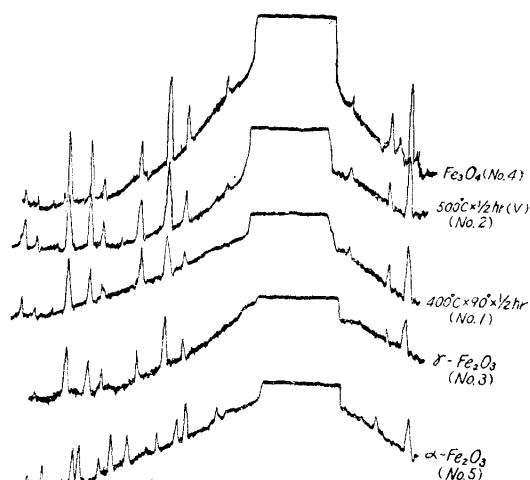


Fig. 13. Intensity curves of Debye rings for various iron oxides.

Table 3

| No. | Material                                 | Atmosphere                       | Heating time | Heating temp. | Crystal structure   |
|-----|--|----------------------------------|--------------|---------------|---------------------|
| 1   | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | H <sub>2</sub> +H <sub>2</sub> O | 1 hr         | 400 C         | cubic (8.4Å)        |
| 2   | Fe <sub>3</sub> O <sub>4</sub>           | Vacuum                           | 1/2 hr       | 500°C         | cubic (8.4Å)        |
| 3   | $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> | —                                | —            | —             | cubic (8.4Å)        |
| 4   | Fe <sub>3</sub> O <sub>4</sub>           | —                                | —            | —             | cubic (8.4Å)        |
| 5   | $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | —                                | —            | —             | rhombohedral (5.4Å) |

### Summary

The following results were obtained from these experiments:-

(1) The magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> get near the properties of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at about 400°C and then coincide with one of Fe<sub>3</sub>O<sub>4</sub> at 600°C by reduction for 1 hr in the mixed gas of H<sub>2</sub> and H<sub>2</sub>O.

(2) The magnetic properties of Fe<sub>3</sub>O<sub>4</sub> approach one of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and then  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by heating for 1/2 hr in vacuum at 500°C and 700°C respectively.

(3) By chemical analysis, these iron oxides, which seem to be  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> from their magnetic properties, are both the mixture of ferrous and ferric ion.

(4) By X-ray analysis, the Debye-Scherrer patterns of these two oxides,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and natural magnetite, cannot be distinguished from one another.

From above results, these oxides may be a mixture of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. At first, they might be reasonably considered as a solid solution of Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, because, if they were a mechanical mixture of Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the Debye rings of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> would have to be found in their X-ray patterns and their remanence

would be smaller than one of Fe<sub>3</sub>O<sub>4</sub>. But from the experimental results, we could not observe the both phenomena.

If they were a solid solution of Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the diameter of Debye rings must be changed gradually with their compositions, and it could not be seen in the present photographs, though it may be found by a more precise experiment. If the oxide were a solid solution of Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the Debye rings would almost coincide with the rings of Fe<sub>3</sub>O<sub>4</sub>. In this case and the case when it was a mechani-

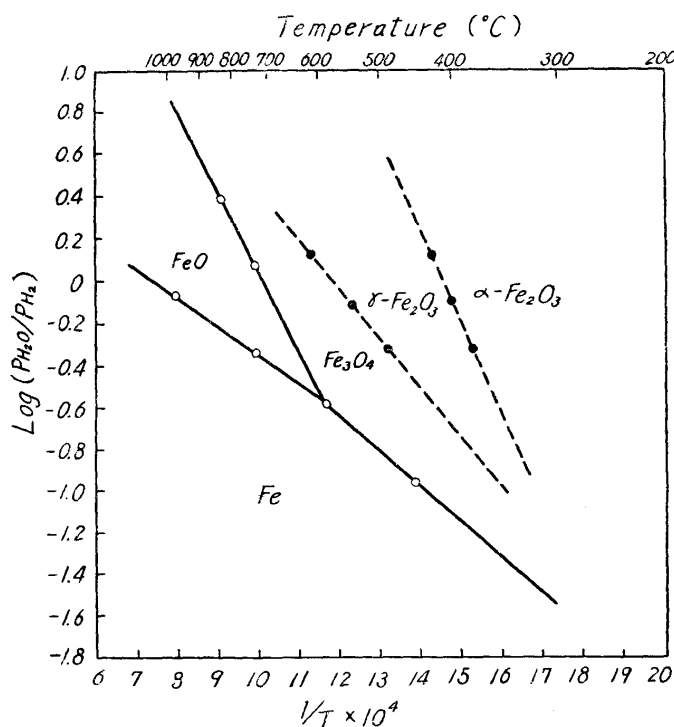


Fig. 14. Equilibrium of the solid phases in the system with iron, iron oxides, hydrogen and steam.



cal mixture of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ , it should be concluded that  $\gamma\text{-Fe}_2\text{O}_3$  was always produced from  $\text{Fe}_3\text{O}_4$  by oxidation or  $\alpha\text{-Fe}_2\text{O}_3$  by reduction.

Hitherto, it has been reported that  $\gamma\text{-Fe}_2\text{O}_3$  could be produced from  $\text{Fe}_3\text{O}_4$  by oxidation at a lower temperature, but it was impossible to obtain from  $\alpha\text{-Fe}_2\text{O}_3$ . That is to say, it has been recognized that the transformation of  $\gamma\text{-Fe}_2\text{O}_3$  to  $\alpha\text{-Fe}_2\text{O}_3$  is irreversible.

On the other hand, it was found by T. Iimori<sup>(1)(2)</sup> from the results of electron diffraction study of iron oxide film, that very fine  $\alpha\text{-Fe}_2\text{O}_3$  powder on iron surface was changed to  $\gamma\text{-Fe}_2\text{O}_3$  by heating at 330°C for 40 min.

In the present experiments, it may be reasonably concluded that very fine  $\alpha\text{-Fe}_2\text{O}_3$  powder, prepared from  $\text{Fe}(\text{CO})_5$  is transformed to  $\gamma\text{-Fe}_2\text{O}_3$  by way of the reduction to  $\text{Fe}_3\text{O}_4$ . And the  $\gamma\text{-Fe}_2\text{O}_3$  has a larger coercive force and remanence but smaller saturation value than  $\text{Fe}_3\text{O}_4$  in powder form.

Then, it may be roughly supposed that the  $\gamma\text{-Fe}_2\text{O}_3$  region should be added in the phase diagram of the iron-oxygen system as shown in Fig. 14.

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