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The Coercive Force of γ-Fe_2O_3 Prepared from γ-FeOOH

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Synopsis. The γ-Fe_2O_3 with a high coercive force was prepared by reducing the acicular γ-FeOOH at 300 °C and by then reoxidizing it at 250 °C. A conversion from γ-FeOOH to γ-Fe_2O_3 at lower temperatures was effective in obtaining acicular particles without pores because of the large mobilities of ions in the crystal.

The γ-Fe_2O_3 with a high coercive force has usually been prepared from the acicular α-FeOOH through complex processes: dehydration, reduction, and reoxidation, especially by the heat treatment of the α-Fe_2O_3 before the reduction.[1] These three processes were also effective in obtaining the γ-Fe_2O_3 with a high coercive force when the γ-FeOOH was used as the starting material, while the γ-Fe_2O_3 obtained by only the dehydration of the γ-FeOOH exhibited a very low coercive force. In this work, the effect of this heat treatment on the coercive force was examined for the γ-FeOOH.

Experimental

Two kinds of γ-FeOOH were prepared as the starting materials by the method described in a previous paper.[2] Three kinds of α-FeOOH were also prepared by the method reported by Nakajima *et al.*[1] in order to compare them with the γ-FeOOH as follows: a solution of iron(II) chloride or sulfate was made alkaline (pH 13.1—13.7) after the dissolved oxygen had been removed, and then the iron(II) ions were oxidized at 45 °C by bubbling air at the flow rate of 2.5 l/min, while the pH value of the reaction mixture was not controlled. The preparative conditions are shown as follows:

Sample No.	Product	Initial concn mol/l	pH	Temp °C
L-1	γ-FeOOH	0.064 ($FeCl_2$)	6.5	25
L-2	γ-FeOOH	0.096 ($FeCl_2$)	6.5	25
G-1	α-FeOOH	0.064 ($FeCl_2$)	13.7→12.8	45
G-2	α-FeOOH	0.064 ($FeSO_4$)	13.5→12.5	45
G-3	α-FeOOH	0.257 ($FeCl_2$)	13.1→12.2	45

These iron(III) hydroxide oxides were then converted to γ-Fe_2O_3 in the following manners:

Process 1.

$$\left.\begin{array}{l}\gamma\text{-FeOOH}\\ \alpha\text{-FeOOH}\end{array}\right\}\xrightarrow[\text{440—800°C (60 min)}]{\text{Heat treatment, in air}}\alpha\text{-}Fe_2O_3$$

$$\xrightarrow[\text{360°C (30 min)}]{\text{Reduction in }H_2}Fe_3O_4\xrightarrow[\text{250°C (30 min)}]{\text{Reoxidation in air}}\gamma\text{-}Fe_2O_3$$

Process 2.

$$\left.\begin{array}{l}\gamma\text{-FeOOH}\\ \alpha\text{-FeOOH}\end{array}\right\}\xrightarrow[\text{300—340°C (30 min)}]{\text{Dehydration and reduction in }H_2}$$

$$Fe_3O_4\xrightarrow[\text{250°C (30 min)}]{\text{Reoxidation in air}}\gamma\text{-}Fe_2O_3$$

The coercive force, ${}_BH_C$ (maximum applied field; H_m= 2 KOe), of the γ-Fe_2O_3 was measured at 25 °C at the packing density of 0.1 with an automatic B-H curve tracer, model BHH-5, from the Riken Denshi Co.; the packing density, p, was expressed as follows: $p=d/d_0$, where d is the apparent density of a cylindrical specimen, and d_0, the intrinsic density of γ-Fe_2O_3 (5.24 g/cm^3).[3]

The particles were observed at magnifications of from 24000 to 36000 times with an electron microscope, model HU-200F, from Hitachi Seisakusho.

The crystallite sizes of the heat-treated α-Fe_2O_3 were estimated by the Scherrer method[4] at the directions of [012], [104], [110], and [113] by using Fe$K\alpha$ radiation.

Results and Discussion

Figure 1 shows the relationships between the coercive force of the γ-Fe_2O_3 and the reduction temperature in Process 2 or the heat-treatment temperature in Process 1. The γ-Fe_2O_3 was found to exhibit sufficiently high coercive forces when the samples were prepared from the γ-FeOOH by Process 2 at the reduction temperature of 300 °C. The γ-FeOOH was not reduced completely into the Fe_3O_4 below 300 °C. The coercive force, however, was lowered abruptly with the rise in the reduction temperature in Process 2 and in the heat-treatment temperature in Process 1. On the contrary, a remarkable effect on the coercive force was observed by heat treatment at 600 or 700 °C in Process 1 when the α-FeOOH was used as the starting material. This effect has previously been reported by Nakajima *et al.*[1]

The DTA pattern of the γ-FeOOH showed an endothermic peak near 270 °C based on the dehydration of structural water and an exothermic peak near 440 °C based on the transformation to α-Fe_2O_3 from γ-Fe_2O_3.

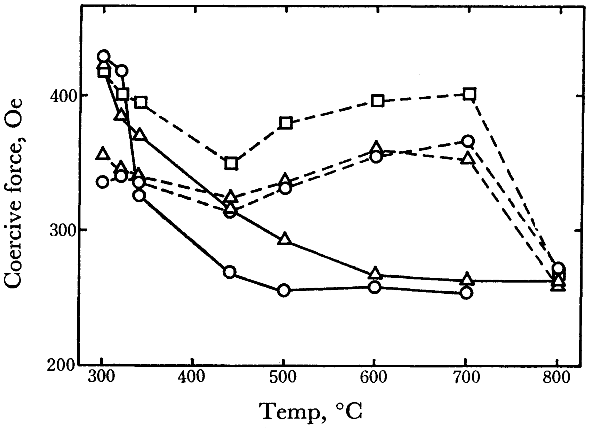

Fig. 1. Relationships between coercive force of γ-Fe_2O_3 and reduction or heat-treatment temperature.
—○—: L-1, —△—: L-2, ---○---: G-1, ---△---: G-2, ---□---: G-3.

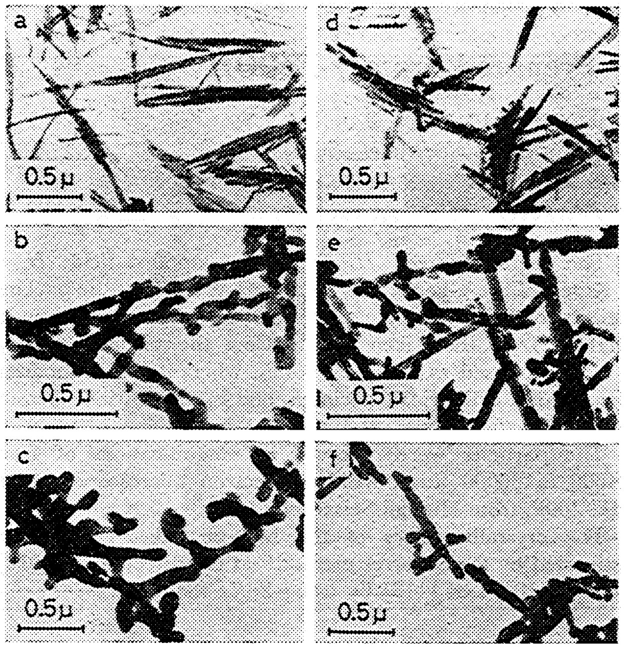

Fig. 2. Particles of γ-, α-FeOOH and γ-Fe_2O_3.
a: γ-FeOOH(L-1), b: γ-Fe_2O_3, reduced L-1 at 300°C in Process 2, c: γ-Fe_2O_3, heat-treated L-1 at 600°C in Process 1, d: α-FeOOH(G-1), e: γ-Fe_2O_3 reduced G-1 at 300°C in Process 2, f: γ-Fe_2O_3, heat-treated G-1 at 600°C in Process 1.

Figures 2a and 2d show the original γ- and α-FeOOH particles with acicular shapes. When the γ-Fe_2O_3 was obtained only by the dehydration at 300 °C, countless number of fine pores were observed, while the particles kept the original shapes of the γ-FeOOH. This γ-Fe_2O_3 exhibited very low values of the coercive force, 126 and 129 Oe.

Figure 2b shows the γ-Fe_2O_3 particles obtained from the γ-FeOOH by Process 2. Few pores were observed in the particles thus prepared, while the shapes were deformed in some degree compared with the original ones. Much deformation and sintering were, however, observed among the particles prepared by the heat treatment at 600 °C in Process 1, as is shown in Fig. 2c. On the contrary, several pores were observed in the particles, though there was less deformation, when the γ-Fe_2O_3 was prepared from the α-FeOOH by Process 2, as is shown in Fig. 2e. The pores, however, were scarcely detectable by heat treatment, especially at 600 or 700 °C, in Process 1, as is shown in Fig. 2f. Remarkable deformation and sintering among the particles were observed by heat treatment at 800 °C, even when the α-FeOOH was used as the starting material as well as the γ-FeOOH.

In the acicular particles of γ-Fe_2O_3 with a single domain size,[5] the shape anisotropy is well known to dominate their coercive force; $H_c=(1/2)\Delta N \cdot M_s$ in random-oriented powders,[6] where ΔN is the difference between the demagnetizing factors along the minor and major axes of the acicular particles, which can take 2π as the maximum value in the CGS-Gauss unit system, and M_s, the saturation magnetization. Therefore, the coercive force depends mainly on the acicularity of the particles. On the other hand, the existence of pores in the particles lowers the coercive force.[5] The coercive force of the γ-Fe_2O_3 varies reasonably according to the degree of deformation and the existence of the pores, as Figs. 1 and 2 show.

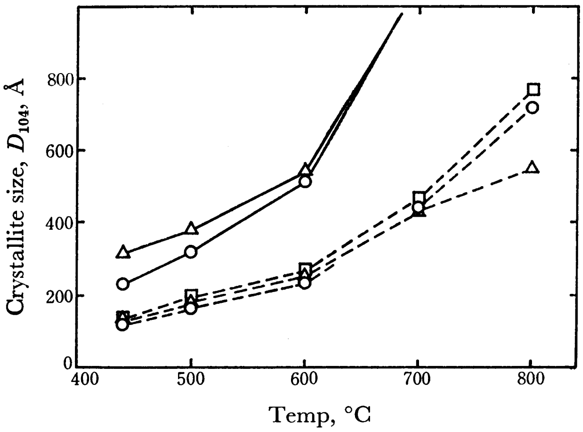

Fig. 3. Plots of crystallite size, D_{104}, of α-Fe_2O_3 against heat-treatment temperature.
—○—: L-1, —△—: L-2, ---○---: G-1, ---△---: G-2, ---□---: G-3.

The crystallite size, D_{104}, for [104] of the α-Fe_2O_3, the intermediate in Process 1, grew as the heat-treatment temperature increased, as is shown in Fig. 3. The crystallite of the α-Fe_2O_3 obtained from the γ-FeOOH grew much extensively than that obtained from the α-FeOOH. Similar tendencies were confirmed for the other directions of the α-Fe_2O_3 lattice. Such a clear difference between them is considered to be due not to the absorbed Cl^- ions, but to the difference in the structural arrays of ions in the iron(III) hydroxide oxides, judging from the corresponding results between the G-1 and G-2 samples. This fact indicates that the ions in the lattice moved easily when the α-Fe_2O_3 was obtained from the γ-FeOOH. It can be considered that the large mobilities of ions in the lattice carry a positive effect which serves to abolish the pores, but also a negative effect which serves to keep the acicularity of the particles, when the γ-FeOOH is converted into the γ-Fe_2O_3.

References

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