Magnetic Properties of α-Fe_2O_3 Fine Particles

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The spin flipping transition and the weak ferromagnetization of fine particles of α-Fe_2O_3 were experimentally investigated, in relation to particle size, shape or crystal imperfection. Fine particles, having mean sizes ranging from 1μ to 200Å, were prepared by calcination of α-FeOOH and by precipitation from aqueous solution of ferric salts. The transition temperature which is about -15°C for the bulk specimen decreases with decreasing particle size. Particularly, the shift of transition temperature was distinguished in specimens obtained as precipitates from aqueous solutions.

The weak ferromagnetization σ_0 of particle specimens has a value lower than of bulk specimen, when particles were prepared by calcination of α-FeOOH at a temperature below 800°C. The effects of uniaxial pressure squeezing on the magnetism of normal α-Fe_2O_3 were investigated. The values of σ_0 by this squeezing treatment was found to be low. This value resumes its normal value by annealing the specimens at a temperature above 500°C. These phenomena were discussed from the view point of the particle size, shape, or lattice imperfection of fine particles.

I. INTRODUCTION

The present paper deals with characteristics of magnetic properties of α-Fe_2O_3 fine particles, from the view point of the particle size and lattice imperfection.

It is well-known that α-Fe_2O_3 is an antiferromagnet with a weak ferromagnetism caused by the spin canting in the basal plane. Below about 250°K, the spin flipping occurs from the basal to c-axis, and the weak ferromagnetism disappears. Many authors[1] reported that fine particles of antiferromagnetic materials showed paramagnetic behaviors ; it is almost completely analogous to the superparamagnetism of fine ferromagnetic particles. One of the present authors[2] observed that fine particles of α-Fe_2O_3 prepared by thermal decomposition of ferric salt showed the anomalous magnetic behavior. For the elucidation of these phenomena, it seems necessary to examine the magnetic properties in fine particles more precisely in connection with particle size, shape and lattice imperfection on which the preparation method of fine particles may effect. In this experiment, the spin flipping temperature and weak ferromagnetization of α-Fe_2O_3 in fine particles were investigated.

Satisfactory explanation has not been given yet for the mechanism of the "spin flip" transition of α-Fe_2O_3. However, as suggested by Nagamiya *et al.*[3]

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and J. O. Artman *et al*[4], the dipole anisotropy arising from magnetic dipolar interaction and the fine structure anisortropy arising from higher order spin-orbit effect should be comparable in magnitude and opposite in sign. These temperature variations are different. The reversal in the sign of magnetic anisotropy energy K and the consequent "flip over" of spins into the basal plane with increasing temperature are anticipated from this mechanism.

Concerning the weak ferromagnetism, Dzyaloshinsky[5] has pointed out that the low symmetry of the atomic arrangement in this rhombohedral antiferromagnet should result in a spin canting when the spins lie in the basal plane and that this canting is the origin of the weak ferromagnetism.

On the other hand, the morphological and crystallographical properties of various kinds of fine particles have been investigated in our laboratory. Some results[6] have been published. In general, the particle prepared by the thermal decomposition of metallic salt consists of smaller unit particles which are linked each other to form an aggregate ; this aggregate resembles in shape the original crystal of its mother salt. The particle size calculated from the line broadening of X-ray diffraction peaks is that of unit particles, and therefore this unit particle is a single crystal. However, the particle obtained as the precipitates from the aqueous solution of ferric salts is a unit particle of a single crystal. It should be anticipated that crystallographical properties, or imperfections depend on the method of preparation of particles. We studied the effect of these characteristics of fine particles on the magnetic properties of α-Fe_2O_3.

II. EXPERIMENTAL PROCEDURE

1. Preparation and Morphological Properties of Samples

(a) α-Fe_2O_3 obtained by calcination of α-FeOOH. α-FeOOH was precipitated from the $FeSO_4$ solution containing iron scrap by bubbling the air through it. Crystals of α-FeOOH were plate-like with dimension of $1\sim2\mu\times500\sim1000$Å$\times200$Å.

Fig. 1 (a) is the electron microphotograph of α-Fe_2O_3 particles obtained by the thermal dehydration of α-FeOOH at 340°C for 1 hr. This photograph shows that a number of very fine particles of α-Fe_2O_3 with the mean diameter less than 300Å are linked each other to form an aggregate having a shape almost identical with the plate-like shape of α-FeOOH. From the electron diffraction pattern given by the aggregate[6], it is reasonable to infer that these fine particles are crystallographically highly oriented. Consequently, the aggregate possesses a single crystal-like texture. Figs. 1 (b) and (c) show that, despite the growth of unit particles by heating at higher temperature, the shape of aggregate particles is still maintained. The unit particle size was controlled by changing the temperature and the duration of heat treatments. The size of these unit particles is called simply the "particle size" in this paper hereafter.

(b) α-Fe_2O_3 obtained by the precipitation from aqueous solutions These specimens were obtained as precipitates from the aqueous solution of ferric salts. The particle size was controlled by the condition of preparation, such as the temperature, pH and the concentration.

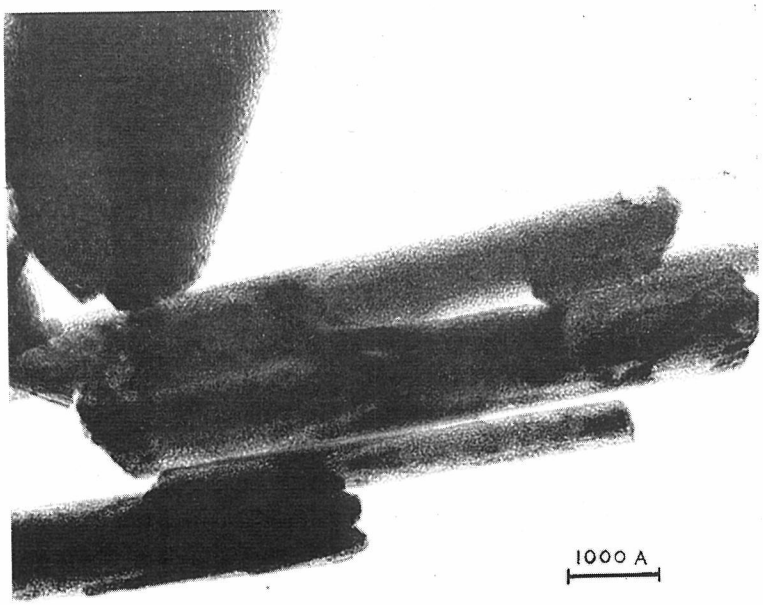

Fig. 1 (a). Electron microphotograph of α-Fe_2O_3 particles prepared by calcination of α-FeOOH at 340°C for 1 hr.

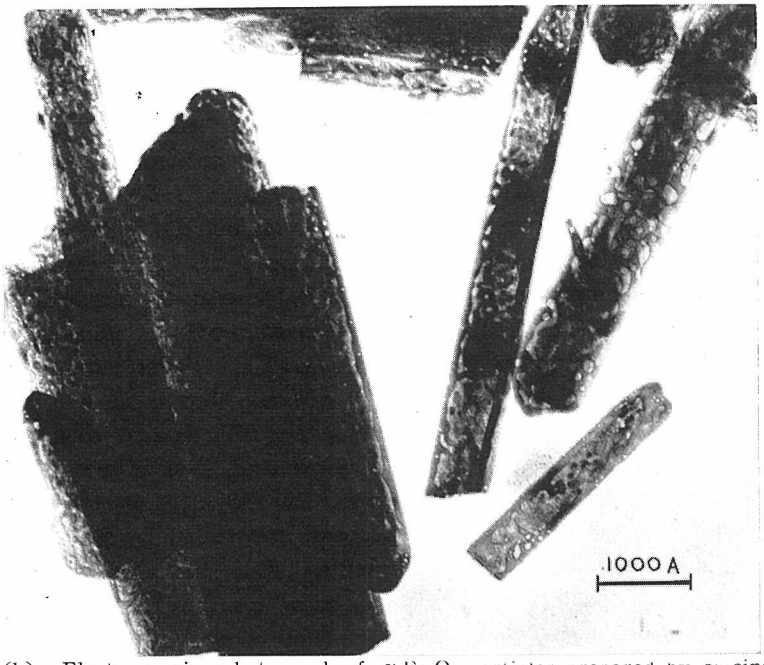

Fig. 1 (b). Electron microphotograph of α-Fe_2O_3 particles prepared by calcination of α-FeOOH at 460°C for 1 hr.

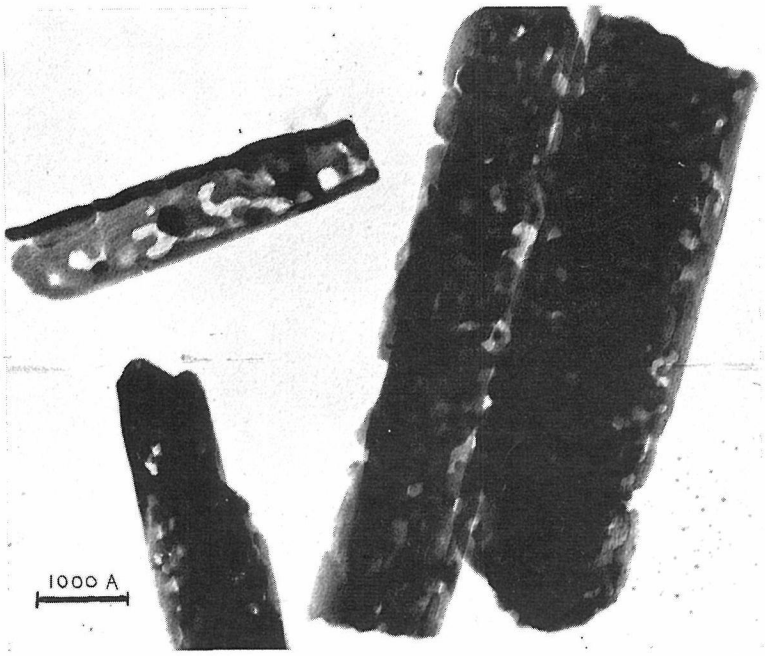

Fig. 1 (c). Electron microphotograph of α-Fe_2O_3 particles prepared by calcination at at 500°C for 1 hr.

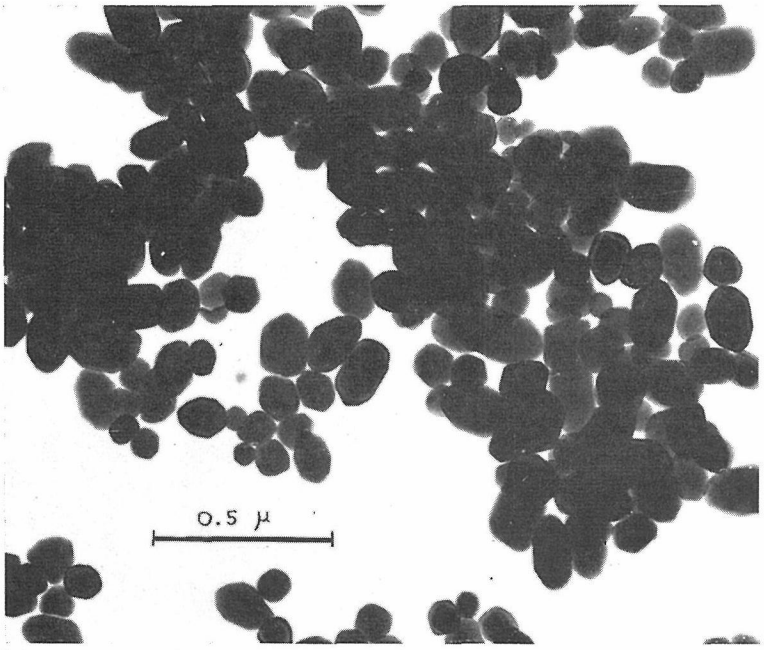

Fig. 2 (a). Electron microphotograph of the sample No. 3 of α-Fe_2O_3 obtained as precipitates from aqueous solution.

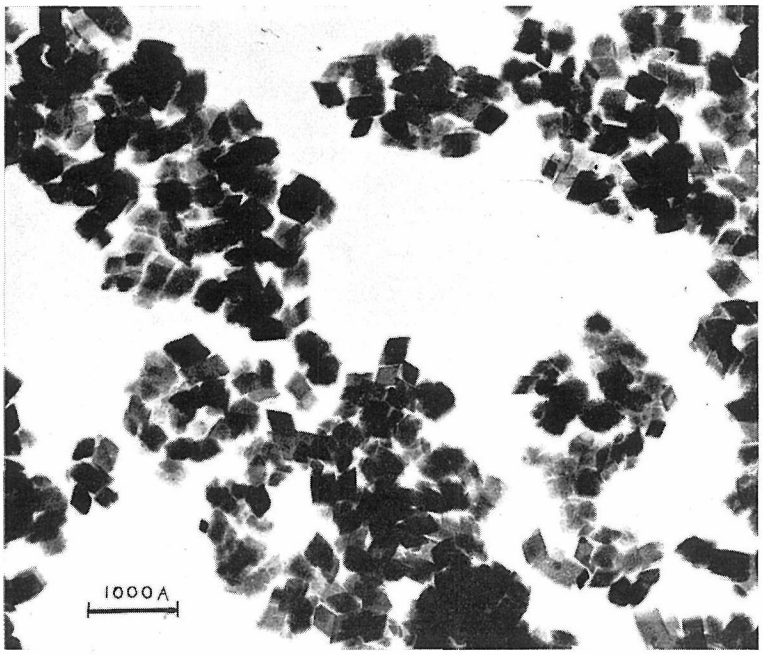

Fig. 2 (b). Electron microphotograph of the sample No. 4 of α-Fe_2O_3 obtained as precipitates from aqueous solution.

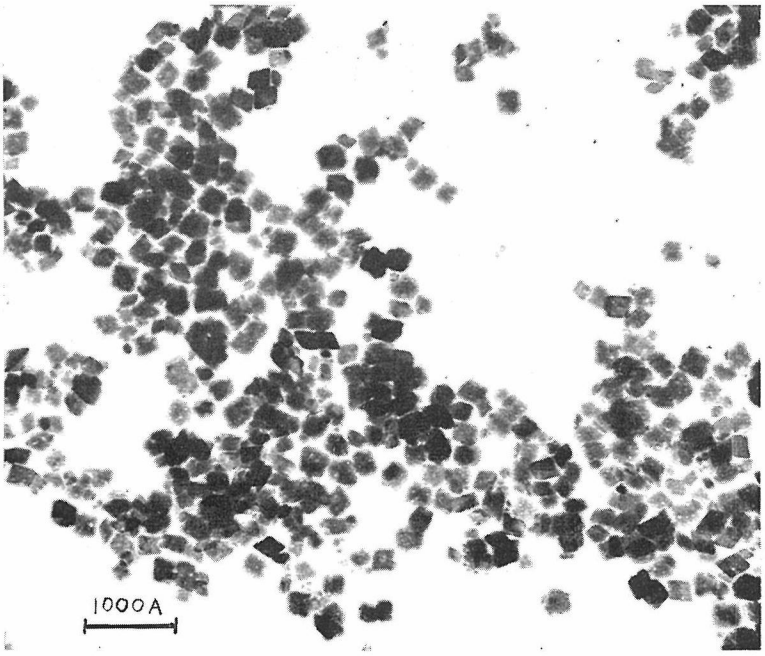

Fig. 2 (c). Electron microphotograph of sample No. 5 of α-Fe_2O_3 obtained as precipitates from aqueous solution.

In Fig. 2, electron micro-photographs of α-Fe_2O_3 particles prepared by the above-mentioned method are shown. Each of these particles has the same crystallographical shape and almost the same particle size, and it seems to be a single crystal. The particle shape of Fig. 2 (a) is different from that of Fig. 2 (b) or (c), because the condition of preparation is different. The examination by the X-ray diffraction and electron microscope showed that no impurity, such as α- or β-FeOOH, was contained in specimens.

All samples were also confirmed by the X-ray diffraction and the particle size was estimated from the broadening of diffraction peaks, and also from electronmicrographs.

2. Magnetic Measurement and Mössabauer Absorption Measurement

The magnetization was measured by the torsion balance at temperatures ranging from the room to the liquid nitrogen temperature. Above about 250°K, the magnetization could be expressed by $\sigma=\sigma_0+\chi H$, where σ_0 is the weak ferromagnetization and χ the susceptibility. In order to obtain these two terms at a given temperature, the magnetization was measured at seven different fields, i. e. 4.1~16.9 KOe.

The optimum thickness of all absorbers used for the measurement of the Mössbauer effect was adjusted to be about 10 mg/cm^2 of natural Fe. The Co^{57} source electroplated onto a palladium plate was used as the source of 14.4 KeV gamma ray. Datails of the measuring system of the Mössbauer effect have already been described by S. Shimizu *et al*[7]. Measurements were carried out at the room, dry ice and liquid nitrogen temperatures.

III. EXPERIMENTAL RESULTS

1. Characteristics of Magnetic Properties of Single-Crystal Fine Particles

Fig. 3 shows the temperature dependence of the spontaneous magnetization σ_0 of fine particles which were obtained as precipitates from aqueous solutions. The spin flipping temperature decreases with the decrease of particle size.

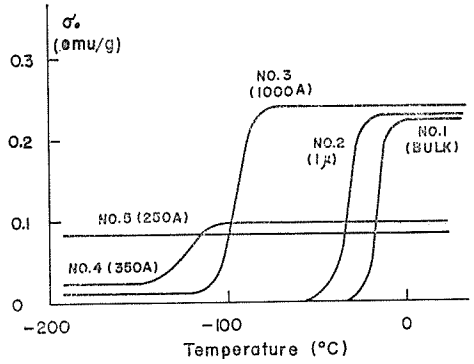

Fig. 3. The temperature dependence of σ_0, of various sized particles which were obtained as precipitates from aqueous solution.

The observation that fine particles of α-Fe_2O_3 prefered the spin direction in c-plane, can also be confirmed directly by the Mössbauer effect. Since the crystal structure of α-Fe_2O_3 has a uniaxial symmetry, the hyperfine interaction at the iron nucleus in this compound must exhibit a quadrupole effect. But the magnetic hyperfine interaction is so strong that the quadrupole interaction can be observed as a small perturbation of the Zeeman splitting. The magnitude and sign of the quadrupole interaction depend on the direction of the internal magnetic field. Therefore the spin direction can be determined from the observed quadrupole interaction. For example, Fig. 4 shows the Mössbauer ab-

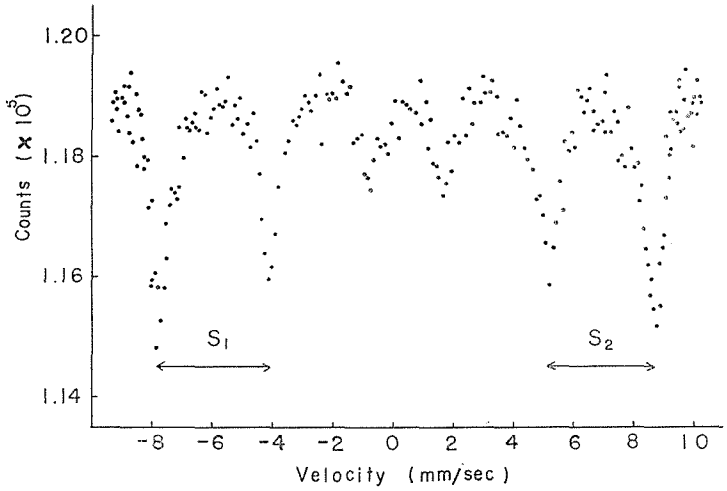

Fig. 4. Mössbauer absorption spectrum of fine particles of α-Fe_2O_3 at dry ice temperature. S_1-S_2 was about 0.3 mm/sec.
S_1-$S_2 = -1/2e^2qQ\ (3\cos^2\theta - 1)$
θ : the angle between the direction of the internal magnetic field and the axis of electric field gradient.
S_1-S_2 in normal α-Fe_2O_3 is 0.35~0.4 mm/sec at the temperature above −15°C and −0.7~−0.8 mm/sec at the temperature below −15°C.

sorption of 350Å sized particle at the dry ice temperature, that is, well below the transition temperature of the bulk sample. The quadrupole interaction was estimated as S_1-S_2 (as indicated in this figure) whose magnitude depend on the direction of the internal field. S_1-S_2 of this specimen at the dry ice temperature is nearly equal to that of the normal α-Fe_2O_3 at the room temperature. It was confirmed that the spin direction in these particles was still retained in the c-plane even at the dry ice temperature. In sufficiently fine particles (250Å), the spin flipping did not occur at temperatures above the liquid nitrogen temperature. In this case, the spin axis in the c-plane was also confirmed by the Mössbauer effect. Values of σ_0 of samples No. 4 and 5 were considerably reduced, but experimental data were not enough to discuss the size dependence of σ_0.

2. Characteristics of Magnetic Properties of Aggregate Particles

Fig. 5 shows the temperature dependence of σ_0 and $\varkappa$ for various sized

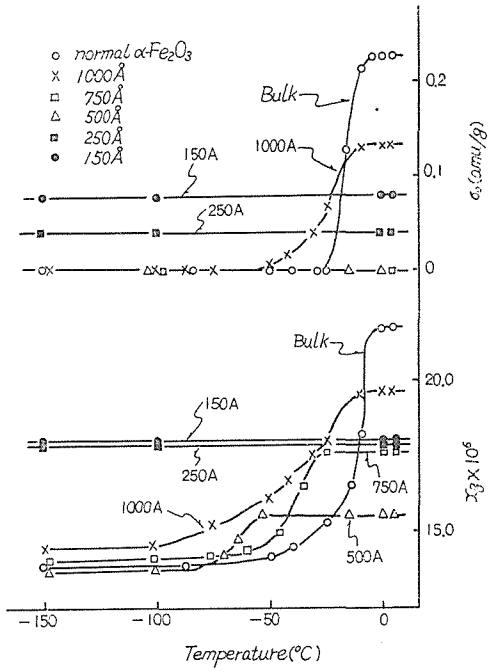

Fig. 5. Variation with temperature of χ_g and σ_0 for various sized particles of α-Fe_2O_3 which were obtained by calcination of α-FeOOH.

particles of α-Fe_2O_3 which were prepared by the calcination of α-FeOOH. The transition temperature decreases with decreasing particle size and in 150Å or 250Å sized particles, the transition does not occur. In this case, it wat also confirmed by the Mössbauer effect[7] that the spin axis remained in the c-plane even at the liquid nitrogen temperature.

We find a more interesting phenomenon as shown in Fig. 5, value of σ_0 of fine particles at temperatures above transition was considerably reduced. Particularly, in the case of particles of 750 and 500Å in size, value of σ_0 became almost zero. In finer particles (250 or 150Å) the weak ferromagnetism slightly remained, although it is not clear whether its origin is due to the spin canting or the sublattice unbalance. Though observed in particles obtained from aqueous solution as well, decrease of σ_0 was particularly remarkable in this case. We thus concluded that the decrease of σ_0 was independent of the particle size.

3. Effect of Uniaxial Pressure Squeezing on Magnetic Properties

Fine particles prepared by the calcination of metallic salt may contain many lattice imperfections or strains which may have an effect on σ_0. To examine these effects, normal α-Fe_2O_3 specimens were treated by the uniaxial pressure squeezing using a die at the room temperature. Fig. 6 shows the temperature dependence of σ_0 for the specimens squeezed by various applied pressures : σ_0 decreased with increasing applied pressure, but the transition temperature was the same for all specimens.

The specimen applied the pressure of 2.9×10^4 kg/cm^2, whose σ_0 was almost

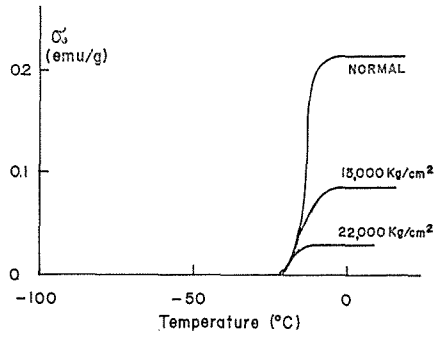

Fig. 6. The temperature dependence of σ_0 of cold-worked α-Fe_2O_3 for various applied pressure.

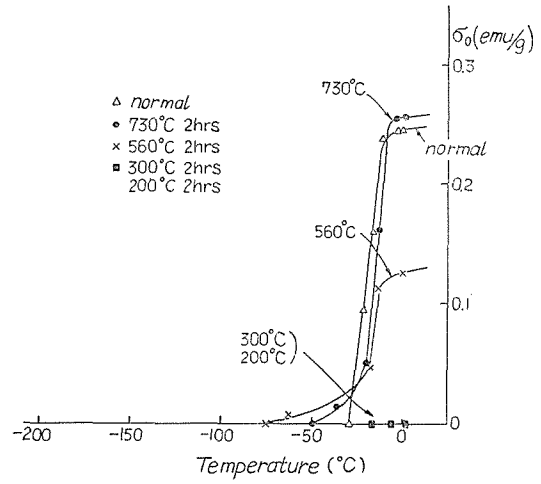

Fig. 7. Variation with temperature of σ_0 of cold-worked α-Fe_2O_3 which were annealed at various temperature for 2hrs.

zero, was annealed at temperatures ranging from 200°C to 800°C, and the temperature dependence of σ_0 was measured, as shown in Fig. 7. The weak ferromagnetism appears by annealing at the temperature above 500°C and completely recovers its normal value by annealing at 720°C for 2 hrs. From these experimental facts, it may be suggested that the occurrence of lattice imperfections or strains in α-Fe_2O_3 reduces the σ_0 value.

IV. DISCUSSION

It is clear from Fig. 3 and Fig. 5 that fine particles of α-Fe_2O_3 prefer the spin axis in the c-plane. The qualitative explanation of the shift of magnetic transition temperature is as follows.

Both of the magnetic anisotropies due to the magnetic dipole field and the crystalline field should have comparable magnitudes, opposite signs and different temperature dependences. The transition occurs as the result of a competition between them. For small particles, the cation near the surface must play an important role. Thus, we can qualitatively conclude that the effect of surface on the dipole field should be different from that on the crystalline field. As a results, the transition temperature is shifted to a lower value with decreasing particle size.

The decrease of σ_0 may directly be related not to particle size but to the lattice imperfection or strain. This conclusion results from the decrease of σ_0 of the α-Fe_2O_3 treated by squeezing and the recovery of σ_0 by annealing of this specimen. Particle obtained by the decomposition of salts contains fine unit particles which are liked each other to form an aggregate particle. These unit particles are in contact with neighboring particles in the aggregate. The unit paritcles grow by sintering between neighboring particles. Therefore, it is in-

ferred that particles contained many imperfection or strains. When either the heating temperature of the duration is increased, the size of unit particle become larger and the imperfection or strain should decrease. Hence, although Fig. 3 appears to suggest that σ_0 increases with increasing particle size, it may rather be explained by the decrease of the lattice imperfection or strain contained in particles.

Particles obtained from aqueous solutions under an appropriate condition (for example, the sample No. 3 in Fig. 1) may contain very few lattice imperfections or strains, σ_0 of this specimen being almost the same as that of the normal α-Fe_2O_3.

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