Characterization of the Surface Oxide Layer on Iron Particles for Magnetic Recording by Mössbauer Spectrometry

Akio MAKISHIMA,† Yukihiro YAMAMOTO,* and Kohji WATANABE
R&D Laboratories-I, Nippon Steel Corporation, 1618, Ida, Nakahara-ku, Kawasaki 211

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The average valency of iron in the oxide layer on iron particles for magnetic recording and the saturation magnetization of the oxide layer were estimated to be 2.8 and 39 emu g^{-1}, respectively, by examining the Debye temperature and the recoilless fraction of oxide layer which were calculated with the Mössbauer parameters.

Acicular metallic iron particles are excellent materials for magnetic recording. It is necessary to passivate the iron particles, because those are easily oxidized in air. This passivated oxide layer on the iron particles prevents further oxidation. The layer is thought to be composed of an iron oxide. Many studies have been done to elucidate this oxide layer.[1–7] The acicular iron particles are so small (about 0.2 μm in length) and the oxide layer so thin (about 2 nm in thickness) that only a few analytical methods are available. Both X-ray diffraction and Mössbauer spectrometry are useful techniques for this purpose.

Van Diepen et al.[1] measured X-ray diffraction traces and Mössbauer spectra of such iron particles. They found a broadened cubic spinel pattern from X-ray diffraction studies, and concluded that the oxide layer on the iron particles was an iron-rich iron oxide (FeO) at the metal/oxide interface and an oxygen-rich iron oxide (γ-Fe_2O_3) on the outside. They found only a broadened background in the Mössbauer spectrum except for the spectrum of metallic iron; they found no paramagnetic contribution to the spectrum. Haneda and Morrish[2] also measured X-ray diffraction and Mössbauer spectra. They concluded that the oxide layer was a mixture of Fe_3O_4 and γ-Fe_2O_3. They estimated the oxidized fraction to be 80% by the ratio of the areas of oxide and metallic iron assuming equal recoilless fractions at 78 K. Morrish and Picone[3] measured X-ray diffraction and Mössbauer spectra. They compared the X-ray diffraction pattern with Fe_3O_4 and γ-Fe_2O_3, but they could not assign the iron oxide. They found a central superparamagnetic absorption in the Mössbauer spectrum which split during cooling. From these splitting spectra, they concluded that the oxide layer was a mixture of Fe_3O_4 and γ-Fe_2O_3. The content of metallic iron was calculated to be 83% assuming equal recoilless fractions of iron oxide and metallic iron at 2.2 K. The Debye temperature of the oxide layer was about 100 K using the Debye model. They did not use the Debye temperature for further discussions as we do in this study. Umemura et al.[4] measured the Mössbauer spectra of the iron particles, but they only reported that superparamagnetic iron oxide was observed. Kishimoto et al.[5] observed the iron particles by electron microscopy. They measured the thickness of the oxide layer, and calculated its percentage in weight and its saturation magnetization to be 45% and 40 emu g^{-1} (1 emu g^{-1}= 1.26×10^{-6} Wbm kg^{-1}), respectively. The validity of the microscopic observation is suspect. Brett et al.[6] measured back scattering Mössbauer spectra of iron particles whose surface was enriched in ^{57}Fe, and they concluded that the spectra resembled those of amorphous iron oxide. Kitahata et al.[7] also used the samples enriched in ^{57}Fe and concluded that the oxide layer consisted of ferrimagnetic Fe_3O_4 and superparamagnetic Fe_3O_4. They also calculated their volume ratio, which was 7:3.

Though there are many studies about these iron particles, we have not enough quantitative information, for instance about the average valency of iron in the oxide layer or the saturation magnetization of the oxide layer. There are a few quantitative estimations, but the assumption of equal recoilless fractions of the oxide and metallic iron is not reliable, because the Debye temperature of the oxide layer is considered to be very low.

The purpose of this work is to demonstrate a new method to estimate the amount of oxidized iron. Consequently, we can also calculate the average valency of the iron in the oxide layer and the saturation magnetization of the oxide layer.

Experimental

Acicular goethite particles were prepared by the following method. 139 kg of $FeSO_4\cdot7H_2O$ was dissolved in 2 m^3 of water and 200 cm^3 of concd H_2SO_4 was added to it. 200 kg of NaOH was dissolved in 3 m^3 of water while bubbling with nitrogen gas, the $FeSO_4$ solution was added to the NaOH solution. The slurry containing $Fe(OH)_2$ precipitates was oxidized at 40 °C by bubbling air from the bottom of the cylindrical reactor. The aqueous solution (10000 cm^3) containing 3.7 kg of $NiSO_4\cdot6H_2O$ was added to the reacting solution after 75 min from the starting of oxidation reaction and Nitrogen gas was bubbled for one hour and the oxidation reaction was continued. The reaction time was about 90 min. The goethite obtained was washed with water until the washing water showed pH 7. They were coated with silicon dioxide by hydrolysis of silicone tetraethoxide in the goethite slurry. The goethite powder coated with

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† Present address: Institute for Study of the Earth's Interior, Okayama Univ. Misasa, Tottori-ken 682-02.

silicone dioxide was heated to dryness and dehydrated in air at 923 K for 1 h. The samples were then reduced in a hydrogen atmosphere at 693 K for 4 h. The reduced powder was soaked in toluene stirred in bubbling air at 353 K for 1 h and dried in air at room temperature. The dried powder was considered to have a stable oxide layer.

Chemical analysis of the iron powder gave contents of iron, silicon, and nickel of 76.6, 3.6, and 2.1 wt%, respectively. Water, whose content was determined from the weight loss of the particle when it was heated at 433 K using a Mitsubishi Moisturemeter CA-05, was less than 1%.

The specific surface area (the B.E.T. value), the coercivity and the saturation magnetization were 5.49×10^4 m^2 kg^{-1} (Shimadzu Surface Area Analyzer MIC-2200), 1.22 A m^{-1} and 118 emu g^{-1} (TOEI KOGYO VSM-3), respectively.

The Mössbauer absorption spectra of the iron powder at room temperature (297 K) and at liquid nitrogen temperatures (79 K) were measured with a conventional spectrometer using ^{57}Co in Rh as a source. As the iron powder was very fine and difficult to handle, 20 mg of iron powder and 70 mg of graphite powder were mixed and pressed into a disc of 13 mm diameter and 1 mm thickness. Mössbauer spectra at liquid nitrogen temperatures were obtained with a controlled flow of liquid nitrogen into a cryostat. Mössbauer spectra were fitted to Lorenzian curves using a least-square method, to investigate the structure of oxide layer and to calculate the fraction of the peak area.

An electron micrograph of the iron powder was taken using a JEOL high resolution transmission electron microscope, JEM-2000EX, under an accelaration voltage of 200 keV.

Results and Discussion

Electron Microscopic Observation. An example of the electron micrograph of the iron powder is shown in Fig. 1. The iron powder, on the average, is of needle-like shape of 300 nm in length and 30 nm in width. A core iron and a surface oxide layer exist in each powder. A lattice image is explicitly observed in the core, but not in the oxide layer.

Mössbauer Spectra. The Mössbauer spectrum of the iron powder at 297 K is shown in Fig. 2(a). It is thought to be a superposition of a sextet due to α-iron and a superparamagnetic doublet due to the surface iron oxide. The isomer shift (δ) and the quadrupole splitting (Δ) of the doublet were 0.38 mm s^{-1} relative to iron at room temperature and 1.07 mm s^{-1}, respectively. The area fraction of the doublet was 0.265. The Mössbauer parameters were almost the same with the parameters of the passive film on iron.[6] From the discussion in the literature,[6] this doublet resembles the spectra of amorphous iron oxides and hydroxides more than those of the corresponding bulk crystalline materials. These Mössbauer parameters do not lead to any further characterization.

The Mössbauer spectrum at 79 K is shown in Fig. 2(b). We can conclude that the surface oxide layer is superparamagnetic, as mentioned above, for the doublet due to the oxide layer dissapeared and the magnetically split spectrum was observed at the low temperature. The isomer shift, the quadrupole splitting and the hyperfine field of oxide layer were 0.47 mm s^{-1}, -0.05 mm s^{-1} and 46.6 T, respectively. The area fraction of the oxide layer was 0.377.

Estimation of the Valency of Iron in the Oxide Layer. The area fraction of oxide layer at 297 K (R^{RT}) and that at 79 K (R^{N}) are given by the following equations,

$$R^{\mathrm{RT}} = f_{\mathrm{o}}^{\mathrm{RT}} N_{\mathrm{o}} / (f_{\mathrm{o}}^{\mathrm{RT}} N_{\mathrm{o}} + f_{\mathrm{m}}^{\mathrm{RT}} N_{\mathrm{m}}) \tag{1}$$

$$R^{\mathrm{N}} = f_{\mathrm{o}}^{\mathrm{N}} N_{\mathrm{o}} / (f_{\mathrm{o}}^{\mathrm{N}} N_{\mathrm{o}} + f_{\mathrm{m}}^{\mathrm{RT}} N_{\mathrm{m}}) \tag{2}$$

where $f_{\mathrm{o}}^{\mathrm{RT}}$ is the recoilless fraction of iron in the oxide layer at 297 K, $f_{\mathrm{o}}^{\mathrm{N}}$ is that at 79 K, $f_{\mathrm{m}}^{\mathrm{RT}}$ is the recoilless fraction of iron in the metal core at 297 K, $f_{\mathrm{m}}^{\mathrm{N}}$ is that at

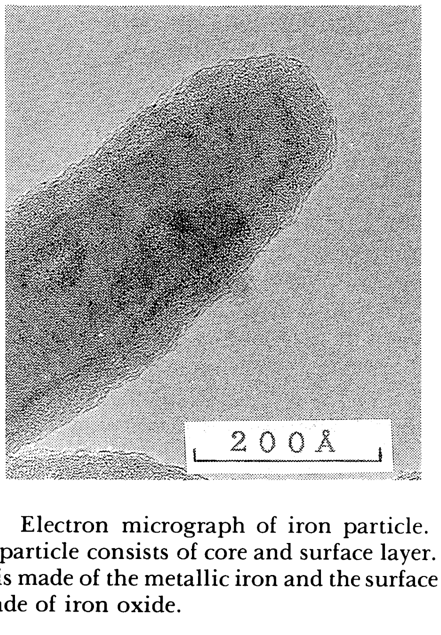

Fig. 1. Electron micrograph of iron particle. The iron particle consists of core and surface layer. The core is made of the metallic iron and the surface layer is made of iron oxide.

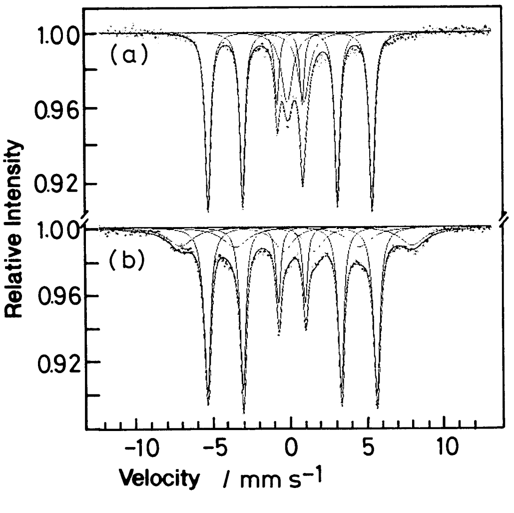

Fig. 2. Mössbauer spectra of the iron particle at 297 K(a), and 79 K(b). The curves are the sum and the components of the computer-fitted patterns.

79 K, N_o is the number of iron atoms in the oxide layer and N_m is the number of iron atoms in the metal core.[8]

The fraction of the number of iron atoms in the oxide layer, r, is given by

$$r = N_o/(N_o + N_m) \qquad (3)$$

By using Eqs. 1 and 2, r is given by

$$\begin{aligned} r &= R^{RT}/(R^{RT} + F^{RT}(1 - R^{RT})) \\ &= R^{N}/(R^{N} + F^{N}(1 - R^{N})) \end{aligned} \qquad (4)$$

where

$$F^{RT} = f_o^{RT}/f_m^{R} \qquad (5)$$
$$F^{N} = f_o^{N}/f_m^{N} \qquad (6)$$

The Eq. 4 gives

$$F^{RT}/F^{N} = R^{RT}(1 - R^{N})/R^{N}(1 - R^{RT}) \qquad (7)$$

The Debye model gives the recoilless fraction (f),[9]

$$f = \exp(-\frac{3E}{2kD}[1 + 4(T/D)^2\int_0^{D/T}\{x/(\exp(x) - 1)\}\mathrm{d}x]) \qquad (8)$$

where E is the recoil energy, D is the Debye temperature, T is the temperature of the absorber, and k is the Boltzmann constant. The relations between the Debye temperature and the recoilless fractions are plotted in Fig. 3. As mentioned previously, Morrish et al. calculated the Debye temperature of the oxide layer to be about 100 K.[3] They did not use the Debye temperature in further discussions. R^{RT} and R^{N} can be measured, and the Debye temperature of metallic iron is known, so we can get the Debye temperature of the oxide layer and the fraction (r) of iron in the oxide layer from the above eight equations and Fig. 3. There exist large discrepancies among the Debye temperatures of the metallic iron, 400 K[10] and 421 K[9] from the thermal-shift measurement, and 310 K[10] and 358 K[9] from the recoilless fraction measurements. Calculations from the Debye temperatures of metallic iron, 310 K and 421 K give the Debye temperatures of the oxide layer, 189 K and 206 K (Table 1), respectively, and r, 0.423 and 0.424 (Table 2), respectively. As mentioned by Morrish et al., the oxide layer is made of small imperfectly crystallized particles which showed the low Debye temperature. The values of r by two calculations showed a good agreement with each other. In later discussions, 0.423 is used as r.

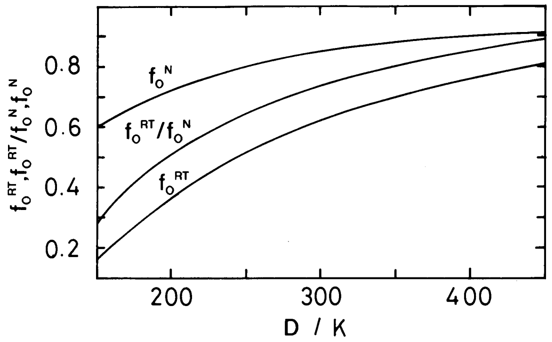

Fig. 3. The relation between the Debye temperature and the recoilless fraction at 297 K and that at 79 K. D is the Debye temperature. f_o^{RT} is the recoilless fraction of the oxide layer at 297 K and f_o^{N} is that at 79 K.

The iron powder consists of 76.6 wt% iron, 3.6 wt% silicon, and 2.1 wt% nickel. Water is less than 1 wt%, so we consider the water content is to be negligible. The rest, 17.7 wt% is thought to be oxygen. Silicon existed as silicon dioxide only on the surface, because silicon dioxide is not reduced and iron silicide is not formed from the reduction of hematite in a hydrogen atmosphere at 693 K. It is considered that nickel is not contained in the surface oxide layer, because of the fact that the reduction of Ni–Fe alloy forms the Fe-rich surface and the Ni-rich bulk.[11] In other words, the core consists of metallic iron containing metallic nickel, and the oxide layer is formed by the iron oxide containing silicon dioxide and is described as $FeO_x \cdot nSiO_2$. Using the fraction of the number of the iron atoms in the oxide layer (r), x and n is calculated to be 1.4 and 0.22, respectively. The average valency of the iron in the oxide layer is 2.8, which is between that of

Table 1. Results of the Calculation of the Debye Temperature of the Oxide Layer

F^{RT}/F^{N}	Debye temp of metallic iron/K	f_m^{RT}	f_m^{N}	f_o^{RT}/f_o^{N}	Debye temp of the oxide layer/K
0.596	310	0.648	0.857	0.451	189
	421	0.778	0.903	0.513	206

Table 2. Results of the Calculation of the Fraction (r) of the Number of the Iron Atoms in the Oxide Layer

Debye temp of the oxide layer/K	f_o^{RT}	f_o^{N}	F^{RT}	F^{N}	r	N_m/N_o
189	0.317	0.707	0.489	0.825	0.423	1.36
206	0.380	0.741	0.488	0.821	0.424	1.36

γ-Fe_2O_3 and Fe_3O_4. The error in the valency so obtained, 2.8, of the iron in the oxide layer is of the order of ten per cent by considering the curve fitting procedure of the Mössbauer spectra and the later calculations.

We can also estimate the saturation magnetization of the iron oxide layer. Because of the low concentration of Ni in the core the effect of Ni on the saturation magnetization is small. Therefore, the saturation magnetization of the iron core should be nearly equal to 220 emu g^{-1}. The saturation magnetization of the iron particle (I_p) is given by the following equation,

$$I_p = (I_o M_o N_o + I_m M_m N_m)/(M_o N_o + M_m N_m) \qquad (9)$$

where I_m is the saturation magnetization of the iron core, I_o is the saturation magnetization of the oxide layer, M_m is the atomic weight of iron and M_o is the formula weight of the oxide layer. Using $I_m=220$ emu g^{-1}, $M_m=55.9$, $M_o=91.5$ and $N_m/N_o=1.36$, I_p is calculated to be 39 emu g^{-1}. This value resembles 40 emu g^{-1} obtained from the microscopic observation.[5] Comparing this value with 90 emu g^{-1} of Fe_3O_4 [12] and 78 emu g^{-1} of γ-Fe_2O_3,[12] it is fairly small. Probably, this is due to imperfection and smallness of the surface oxide crystals.

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