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Characterization of Surface Oxide Layer of Iron Particles for Magnetic Recording II. Surface Oxide Layer of Further Oxidized Iron Particles in High Humidity

Akio MAKISHIMA,† Yukihiro YAMAMOTO,* and Kohji WATANABE
† Institute for Study of the Earth's Interior, Okayama University,
Misasa, Tottori 682-02
R&D Laboratories-I, Nippon Steel Corporation, 1618, Ida, Nakahara-ku, Kawasaki 211

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The surface oxide layer of additionally oxidized iron particles for magnetic recording in high humidity (90%) and at 60 °C was examined by Mössbauer spectrometry. The mechanism of deterioration was concluded to begin with oxidation: the deterioration of the saturation magnetization (**Is**) of iron particles was caused by a deterioration of the **Is** of the surface oxide layer; later deterioration was caused by an increase in the amount of the oxide layer. The specific gravity of the surface oxide layer became gradually reduced during the oxidation.

The surface oxide layer of iron particles for magnetic recording plays a very important role in preventing the core of iron particles from further oxidation. When iron particles are stored in the open air, especially under high humidity, they are gradually oxidized; the magnetic properties, such as saturation magnetization and coercivity, are thus lowered. In this oxidation process the surface oxide layer grows according to the degree of the particle oxidation.

Little is known about the characteristics of the surface oxide layer and the additionally oxidized layer.[1] We have reported a new method for estimating the mean valency and the saturation magnetization of the surface layer by Mössbauer spectrometry.[2]

The purpose of this study was to characterize the oxide layer grown by further oxidation in humidity (90%) and at 60 °C while investigating the deterioration mechanism of the iron particles.

Experimental

The same iron particles which were prepared in a previous study[2] were used. These particles were covered with a thin oxide layer by moderate passivation. The iron powder was oxidized in air at a temperature of 60 °C and a humidity of 90% for three and seven days. These conditions are generally used to test the resistivity of metal powder against oxidation. The iron particles without additional oxidation, those with additional oxidation for three days, and those of seven days are abbreviated as 0D, 3D, and 7D, respectively.

The iron contents of each particle, as well as the silicon and nickel contents of 0D were measured by ICP emission spectrometry. The saturation magnetization of the particles was measured using a TOEI KOGYO VSM-3.

Mössbauer spectra were obtained at room temperature and at liquid-nitrogen temperature. An analytical technique for the Mössbauer spectra was described in a previous paper.[2] The spectra at room temperature were fitted with the superposition of a superparamagnetic doublet of the oxide layer and of a sextet of α-iron. The spectra at 79 K were fitted with the superposition of a doublet and a sextet of the oxide layer, and the sextet of α-iron.

The Debye temperature of the α-iron used in this study was 358 K.[3] Two extreme cases (310 and 421 K [3]) were used as the Debye temperature of α-iron.[2] Instead of the large discrepancy between the two temperatures, the calculation results showed good agreement with each other. In this study 358 K was selected.[3] Consequently, f_m^{RT} and f_m^N are 0.720 and 0.883, respectively. The value of f_m^{RT} is the recoilless fraction of iron in the metal core at 297 K and f_m^N is that at 79 K. The notation is the same as that used in the previous paper.[2] The error in all of the values thus obtained concerning the oxide layer was of the order of ten percent, determined by considering the curve-fitting procedure of the Mössbauer spectra as well as later calculations. The errors in the values of the area fractions, however, are from two to eight percent.

Results and Discussion

The obtained Mössbauer spectra are shown in Fig. 1. As mentioned previously, the superparamagnetic doublet of the surface oxide layer and the sextet of α-iron were observed at room temperature. The peak area of the oxide layer increased according to the degree of oxidation. No other peaks based on α-FeOOH or γ-FeOOH were observed at either room temperature or 79 K, even in 7D which was the most oxidized type particles. The superparamagnetic doublet splits into a sextet at 79 K. The Mössbauer parameters of the doublet at the room temperature and those of the sextets at 79 K, as well as the fraction of the peak area of the oxide layer, are shown in Table 1.

We reported that the surface oxide layer was either amorphous or an aggregation of very small crystals.[2] The further oxidized layer was also amorphous and could not be identified from the Mössbauer parameters.

According to our method,[2] the Debye temperature of the oxide layer and the ratios of the number of metallic iron atoms (N_m) to the number of oxidized iron atoms (N_o) were calculated. The results are shown in Table 2. This decrease in the N_m/N_o ratio is caused by the degree of oxidation.

The results of an elemental analysis of each particle are shown in Table 3. The contents of silicon and nickel in 3D and 7D were calculated from the Si/Fe

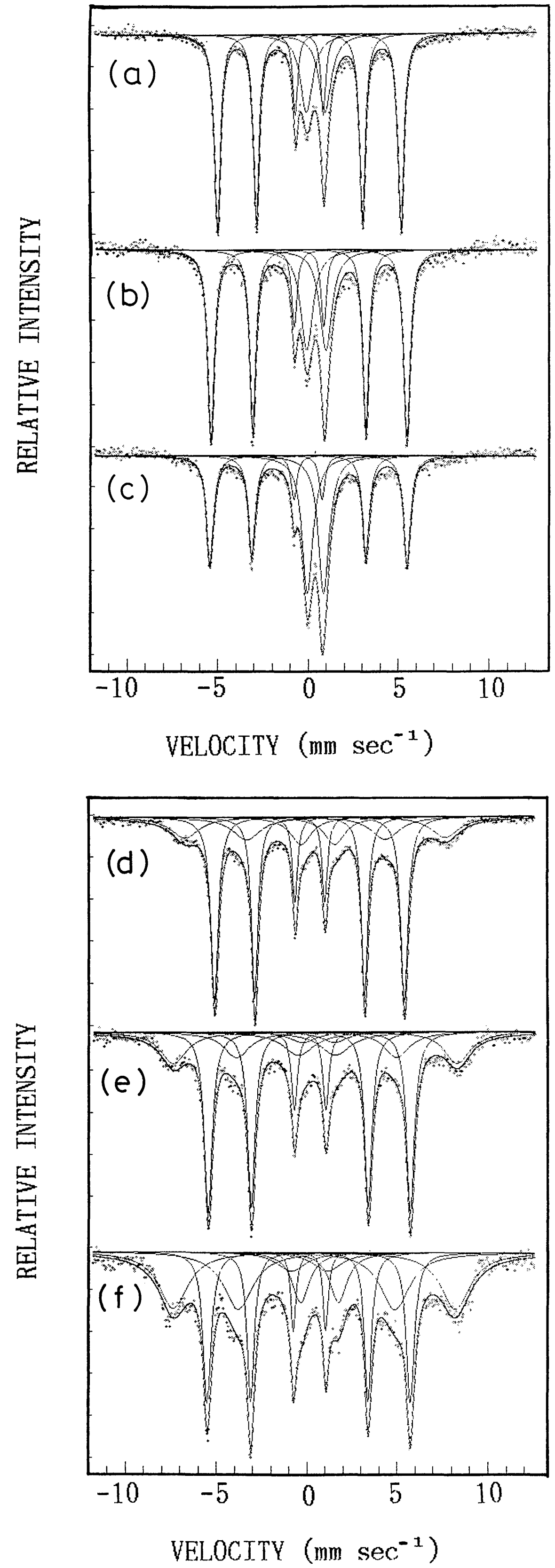

Fig. 1. Mössbauer spectra of iron particles. (a) 0D at 279 K, (b) 3D at 279 K, (c) 7D at 279 K, (d) 0D at 79 K, (e) 3D at 79 K, (f) 7D at 79 K. Curves in figures are fitted lines by lorenzian functions, and indicate total absorption and each component.

and Ni/Fe ratios of 0D, since these ratios are preserved during oxidation. The remaining composition mainly comprise hydrogen and oxygen, indicated as H+O in Table 3. Silicon exists as silicon dioxide, since silicon is not reduced during the preparation of the particles.[2] The amount of oxygen combined with silicon is subtracted from H+O in order to evaluate the amount of hydrogen and oxygen combined with iron. The subtracted H+O is abbreviated as H+O* in the Table.

The chemical composition of the oxide layer can be estimated using this N_m/N_o ratio. The chemical composition of 100 g of iron particles can be represented as

$$x\mathrm{Fe} + l\mathrm{Ni} + y\mathrm{FeO}_m + z\mathrm{H_2O}^* + k\mathrm{SiO_2}, \qquad (1)$$

where x, l, y, z, and k are the moles of each component. The oxide layer comprises FeO_m, H_2O, and SiO_2. Iron hydroxide oxide(FeOOH) is assumed to comprise Fe_2O_3 and H_2O^* in this representation. Oxidized iron in iron oxide and in hydroxide oxide is represented as FeO_m. H_2O^* corresponds not only to the water adsorbed on the particles but also to the water in hydroxide oxide. The weight of H+O* given in Table 3 is the same as that of the oxygen in FeO_m plus the weight of H_2O^*, namely $16my+18z$. By using the data in Table 3, x and y were calculated. We could also calculate how many molecules of H_2O and SiO_2 exist per one FeO_m unit in the oxide layer. These values are expressed as A_W and A_S, respectively, in Table 3. We cannot determine the m values of 3D and 7D only from this experiment. However, since there is H_2O^* in 3D and 7D at every range of the m value, it is considered that FeOOH is formed in these samples. Considering that the m value of 0D is 1.4 and that the samples of 3D and 7D are futher oxidized, the m values of 3D and 7D should be larger than that of 0D; a good approximation for the m value is 1.5. In this case the A_W values of 3D and 7D are 0.22 and 0.31, respectively.

The saturation magnetization (**Is**) of the surface oxide layer can also be calculated. Measurement results of the saturation magnerization of iron particles are shown in Table 3. Assuming that **Is** of the iron core of the iron particles is 220 emu g^{-1}, we obtain **Is** of 0D, 3D, and 7D to be 39, 27, and 26 emu g^{-1}, respectively. **Is** of the iron particles and the oxide layer against the fraction of the number of iron atoms in the oxide layer (r) is shown in Table 2. We know that (1) at the beginning of further oxidation (0D to 3D) saturation magnetization of the iron particles deteriorates mainly by deterioration of that of the surface oxide layer; (2) as the degree of the oxidation increases, the saturation magnetization of the iron particles chiefly depends on the amount of the surface oxide layer.

The specific gravity of the surface oxide layer can be

Table 1. Mössbauer Parameters and Peak Areas of the Oxide Layer

(a) Doublet at 297 K

Iron particles	Isomer shift mm sec^{-1}	Quadrupole splitting mm sec^{-1}	Area fraction
0D	0.38	−0.54	0.27
3D	0.39	−0.53	0.31
7D	0.38	−0.45	0.46

(b) Sextet at 79 K (Area Fraction is the Sum of Areas Based on the Oxide Layer)

Iron particles	Isomer shift mm sec^{-1}	Hyperfine field T	Area fraction
0D	0.44	46.6	0.377
3D	0.44	48.8	0.433
7D	0.41	48.5	0.638

Table 2. Results of Calculations of Debye Temperature and N_m/N_o Ratio of the Iron Particles

Iron particles	F^{RT}/F^{N}	f_o^{RT}/f_o^{N}	Debye temp K	f_o^{RT}	f_o^{N}	F^{RT}	F^{N}	r	N_m/N_o
0D	0.596	0.486	199	0.355	0.730	0.493	0.827	0.423	1.36
3D	0.578	0.471	195	0.340	0.722	0.472	0.818	0.483	1.07
7D	0.485	0.396	176	0.267	0.677	0.371	0.767	0.698	0.43

F^{RT} and F^{N} denote f_m^{RT}/f_m^{RT} and f_o^{N}/f_m^{N}, respectively, f_o^{RT} is the recoilless fraction of iron in the oxide layer at 297 K, and and f_o^{N} that at 79 K.

Table 3-a. Results of Elemental Analysis and Saturation Magnetization of the Iron Particles

Iron particles	Chemical composition wt% Fe	 Si	 Ni	 H+O	 H+O*	Saturation magnetization emu g^{-1}
0D	76.6	3.6	2.1	17.7	13.5	118
3D	73.1	3.4	2.0	21.5	17.7	99.5
7D	66.8	3.1	1.8	28.3	29.8	64.4

Table 3-b. Results of Calculations of x, y, A_W and A_S

Iron particles	x	y	A_W[a)]	A_S
0D	0.790	0.581	1.29—0.889m	0.224
3D	0.677	0.633	1.56—0.889m	0.190
7D	0.362	0.837	1.64—0.889m	0.131

a) In the previous paper,[2)] we neglected the adsorbed water.

calculated using

$$100/(M_m/d_m + (100 - M_m)/d_o) = d_p,$$

where M_m is the weight of metallic iron in 100 g of iron particles, d_m the specific gravity of iron (7.87 g cm^{-3}), d_o the specific gravity of the surface oxide layer, and d_p the specific gravity of iron particles. Since the specific gravities of the samples (3D and 7D) were 5.88 and 4.33 g cm^{-3}, respectively, we obtained the specific gravities of the surface oxide layer of iron particles (3D and 7D) as 5.1 and 3.9 g cm^{-3}, respectively, by using the N_m/N_o ratio. We can further know that the specific gravity of the surface oxide layer is also lowered with the degree of oxidation. Compared with the specific gravities of Fe_3O_4 (5.8 g cm^{-3}),[4)] α-Fe_2O_3 (5.27 g cm^{-3}),[5)] γ-Fe_2O_3 (4.86 g cm^{-3}),[6)] α-FeOOH (4.2 g cm^{-3}),[7)] and γ-FeOOH (3.98 g cm^{-3}),[8)] the specific gravities of the surface oxide layer of the samples (3D and 7D) are nearly equal to that of Fe_2O_3 and FeOOH, respectively, neglecting silicon dioxide.

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