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Mössbauer Study of Iron Oxide Surface Layers Formed on Fine Iron Particles

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Mössbauer studies of iron oxides formed on the surface of fine iron particles (acicular type about 15 nm in diameter and 100 nm long) and of an oxidation process in air have been done in the temperature range from 4.2 to 298 K. The Mössbauer spectra indicate that the main component of the oxide layers 2.1—5.6 nm thick, except for a few oxide layers from the iron surface, is composed of fine particles of γ-Fe_2O_3, and that fine iron oxide particles are produced freshly during the oxidation process at 110 °C in air with the growth of iron oxide particles. It is concluded that an oxide layer 2.1 nm thick is formed on the iron surface if a fresh iron surface is exposed to air at room temperature.

The oxidation or corrosion behavior of iron has yielded a number of interesting results concerning the magnetic properties[1—5] and the corrosion process and products,[6—12] and it has been studied by a number of investigators because iron is an important material in our daily life. However, our knowledge about the corrosion process is far from being sufficient, and the chemical species of the corrosion products formed on the iron surface have not been fully elucidated because the amount of products directly in contact with the metal surface is less that of the corrosion products of relatively thick oxide layers. Sewell and Cohen[13] and van Diepen et al.[14] indicated that the oxides formed up to 175 °C on the surface of iron are cubic Fe_3O_4 and γ-Fe_2O_3. Haneda and Morrish[15] indicated that the oxide layer is a mixture of Fe_3O_4 and γ-Fe_2O_3. Shinjo et al.[16] suggested that the oxide layer is γ-Fe_2O_3. Various methods of preparation (by the evaporation of iron, electrochemical deposition, and chemical reduction from α-FeOOH) for metallic iron were used in these studies, each method produced characteristic result regarding particle size, shape, and micropores in the metal. Furthermore, the corrosive conditions were different, and there has been disagreement as to which part of the oxide layer is actually detected.

Conversion electron Mössbauer spectroscopy (CEMS) is known to be suitable for the study of a surface. However, CEMS gives information of the surface range at a depth 60 nm from the particle surface. Therefore, the information obtained by CEMS is not related to the products directly in contact with the metal surface.[17] Fine samples with a large surface area are needed for a study of the oxide formed on iron. In the present study, corrosion products with a thickness of the order of 2—5 nm on the iron surface have been examined using fine particles of metallic iron.

Experimental

Iron powder was prepared by the reduction of α-FeOOH (doped with aluminium of 1.8 wt%) and stocked in a toluene solution until use because fine particles of iron are very easily oxidized in air at room temperature and are strongly pyrophoric because of their high surface area. The average particle dimensions of the acicular iron powder used here were determined, by means of an analytical electron microscope JEM-2000FX of HVEM Laboratory, Kyushu University, to be 15 nm in diameter and 100 nm in length. The specific surface area was determined by the BET nitrogen adsorption method to be 46.5 $m^2\,g^{-1}$. This value is slightly larger than that of 39.2 $m^2\,g^{-1}$ estimated on the base

Fig. 1. Electron micrograph of the original iron powder (X15000).

of the geometrical values. An electron micrograph for original iron powder is shown in Fig. 1. The particle size is estimated to be uniformly distributed in diameter, but to vary widely in length. The particle forms a single crystal of metallic iron covered with fine oxides, and no micropore was observed in the iron particles. The electron-diffraction patterns for these samples indicated that the sample was composed of metallic α-iron and iron oxide with a spinel structure.

X-Ray diffraction patterns were taken using Cu *Kα* radiations. The data indicate that the iron powder contains a spinel iron oxide phase besides an iron phase. Line broadening for the spinel lines was observed because of the ultrafine particles of iron oxide formed on the surface of the iron particles.

Mössbauer spectroscopy was effected by using a constant-acceleration spectrometer described elsewhere.[18] The spectra were corrected for the curvature of the baseline due to the geometry of the measurement system and then fitted to the Lorentzian line shape, by using a least-squares method, at the Computer Center, Kyushu University. Isomer shifts are reported with respect to the centroid of the spectrum of an iron foil enriched with ^{57}Fe.

Results and Discussion

Oxidation/annealing of the iron powder was done at 110 °C in an air bath. The Mössbauer spectra of samples which has been oxidized/annealed at 110 °C in air for 2, 8, 26, 76, and 220 h were taken at 298 and 78 K; some of them are shown in Figs. 2 and 3. The Mössbauer parameters estimated for the samples are listed in Table 1. The spectrum of the original iron powder at 298 K consists of a superposition of a sextet with a magnetic hyperfine structure of metallic iron and a paramagnetic doublet of iron oxide. Broad lines are added in the spectra for the annealed samples, and the intensities of the broad lines and paramagnetic lines increase at the expense of that for metallic iron with an increase in the annealing time. The full width at a half maximum (fwhm) for metallic iron is narrow, and the hyperfine field coincides with the standard α-Fe value.

The Mössbauer spectra for the samples at 78 K consist of a superposition of the sextets with a magnetic hyperfine structure of both metallic iron and iron oxide. The fwhm for the iron oxide having a larger hyperfine field is wider than that of bulk γ-Fe_2O_3 or Fe_3O_4. A large value of fwhm for iron oxide is usually observed in the case of fine particles.[15] The average hyperfine fields for the iron oxide part were estimated to be 488—492 kOe at 78 K. These values are

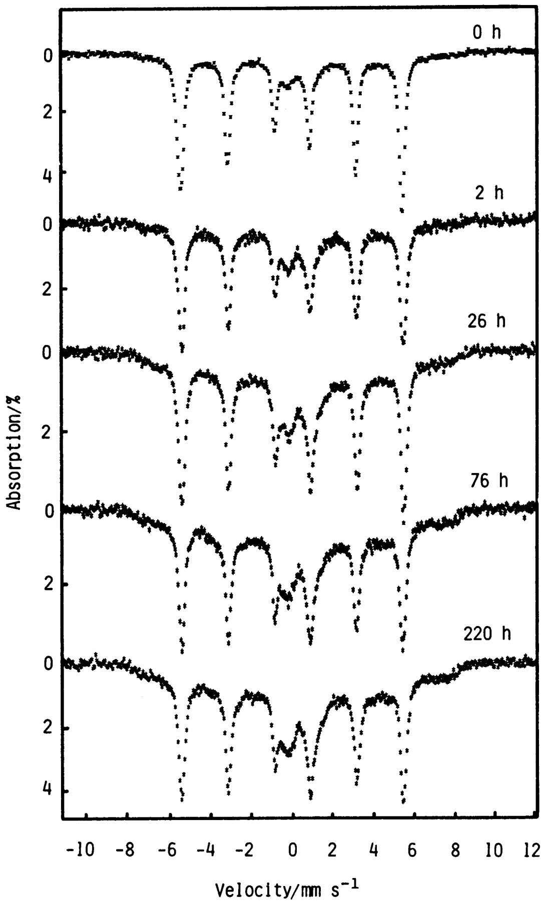

Fig. 2. Mössbauer spectra for the representative samples at 298 K.

Table 1. Mössbauer Data for the Samples at 78 K and the Diameter of the Metallic Iron Part

Sample (annealing time)/h	Metallic iron				Iron oxide					
	δ / mm s^{-1}	H / kOe	Γ_1[a] / mm s^{-1}	δ / mm s^{-1}	ΔE / mm s^{-1}	H / kOe	Γ_1[a] / mm s^{-1}	Γ_6[b] / mm s^{-1}	F[c] / %	d[d] / nm
0 (original)	0.168	345	0.405	0.549	−0.275	492	0.657	0.919	29	12.2
2	0.170	345	0.388	0.585	−0.336	487	1.398	1.222	44	10.6
8	0.163	345	0.440	0.575	−0.245	490	1.199	1.331	51	9.8
26	0.163	345	0.412	0.562	−0.280	489	1.208	1.250	57	9.2
76	0.171	346	0.469	0.487	−0.009	488	1.231	1.315	63	8.4
220	0.170	346	0.542	0.463	+0.079	488	1.315	1.389	61	8.8

a) Fwhm for the lowest energy line. b) Fwhm for the highest energy line. c) The ratio of absorption area for the oxide species to the total absorption area. d) The diameter of the metallic iron part remaining in the sample.

close to 494 kOe (the average of those for A and B sites at room temperature) for bulk γ-Fe_2O_3[19] and less than the value of 527 kOe (78 K) for 18 nm α-Fe_2O_3.[20] That for bulk Fe_3O_4 is known to be 492 kOe for Site A (tetra) and 461 kOe for Site B (octa) above the Verwey temperature (T_v=119 K for bulk).[21] The fields for Fe_3O_4 below the Verwey temperature are reported to be 511 and 499 kOe(at 4.2 K);[22] the line positions of their spectra approach each other, and it becomes difficult to distinguish clearly between γ-Fe_2O_3 and Fe_3O_4 except for a small shoulder in the lowest energy line. The Verwey temperature is reported to lie between 101 and 87 K for 10 nm Fe_3O_4.[23] The spectra show the existence of no Verwey transition above 78 K and no existence of absorption due to iron in the B sites. These facts support the idea that the iron oxides are not Fe_3O_4.

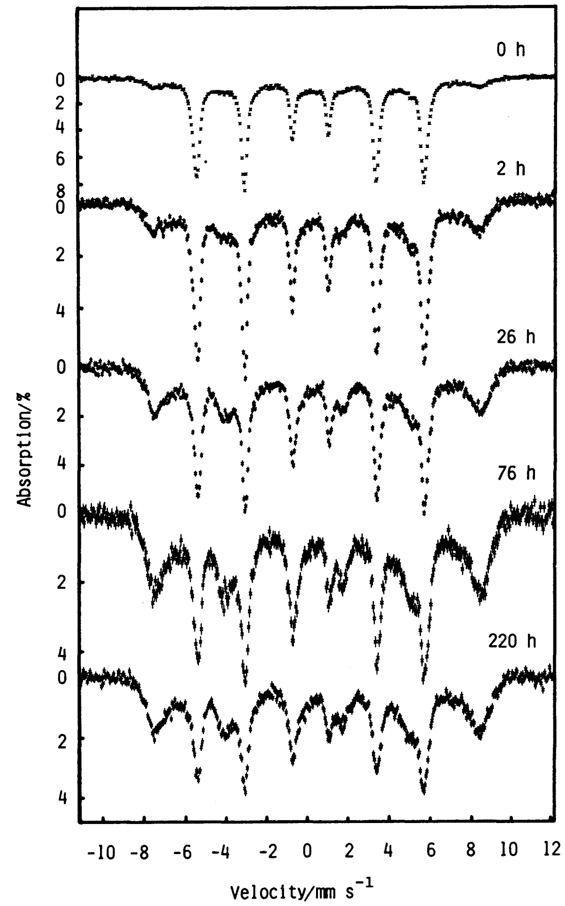

Fig. 3. Mössbauer spectra for the representative samples at 78 K.

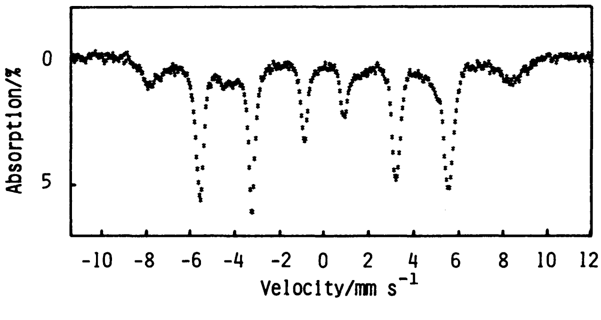

Fig. 4. Mössbauer spectrum for the original iron powder at 4.2 K.

A Mössbauer spectrum for the original sample was measured at 4.2 K; the spectrum is shown in Fig. 4. The spectrum consisted of two simple sextet patterns due to iron oxide and metallic iron, and the hyperfine field for the oxide was estimated to be 498 kOe, close to the value of 500 kOe (at 4.2 K) reported for 0.4 nm thick iron film (actually, this sample was oxidized) by Shinjo et al.[16] The lowest energy line does not split into a doublet, as is observed in the spectra of Fe_3O_4. Our spectra(δ=0.451 mm s^{-1}, ΔE=0.0 mm s^{-1} for the oxide) are in accord with those for γ-Fe_2O_3 and do not resemble the superparamagnetic behavior for Fe_3O_4 observed by Aharoni and Litt,[24] who reported larger isomer-shift values (δ=0.59 mm s^{-1} at 77 K and δ= 0.89 mm s^{-1} at 4.2 K).

The Mössbauer spectra for iron oxides in the original sample are similar to those for the annealed samples. Therefore the chemical structure of iron oxides in the original sample seems to be the same as that for the annealed sample. It is assumed that a minor component (less than 10—20% of the total absorption area in the spectra) can not be detected/resolved because the line positions for γ-Fe_2O_3 are close to those for Fe_3O_4 at 78 K or below. On the other hand, the surface of Fe_3O_4 undergoes a transformation from Fe_3O_4 to γ-Fe_2O_3 which is prominent on fine particles.[25] The thickness of the oxide layer for the original sample is estimated to be 5 monolayers, as will be described later. Therefore, the pattern observed supports the conclusion that the oxide consists of γ-Fe_2O_3. However, it is not possible to reach even a tentative conclusion concerning the mean 1—2 layers from the iron surface, which occupy 10—20% of the total ^{57}Fe in the original sample.

The intensity ratio of the six line patterns at 298 K for metallic iron is close to 3 : 2 : 1 : 1 : 2 : 3, which indicates that the magnetization is orientated at random. The intensity ratio for the spectra at 78 K is different from this ratio. The reason for this is derived from the facts that the samples prepared for low-temperature measurement were pressed to make a disk and that the shape anisotropy of the samples prefers to orientate.

The six lines for the metallic species are clearly observed, and the metallic absorption can be drawn unambiguously. The spectra of Fig. 5 were obtained by the subtraction of the metallic iron peaks from the spectra at 298 K shown in Fig. 2. These spectra show the characteristics of relaxation due to fine iron oxide particles; the superparamagnetic relaxation should also be taken into account. The spectra are symmetric, and the FeO or Fe^{2+} absorptions observed in the spectra of ultrathin Fe_3O_4 film by Terashima and Bando[26] were not visible. A spectrum of the finest iron oxide particle is shown in Fig. 5(a), while a sextet of the magnetic hyperfine structure of iron oxide begins to appear in Figs. 5(c)—(f). However, a strong doublet in the center of the spectra is observed, even in Fig. 5(f), the sample of which was annealed at 110 °C for 220 h.

Interesting variations are found for the line positions. If the lines of the magnetic hyperfine pattern are denoted from low to high energy by the indices from *p*1 to *p*6, the parameter;

$$\Delta E' = p6 - p5 - (p2 - p1),$$

relates to the quadrupole interaction by means of this relationship;

$$\Delta E' = \frac{e^2qQ}{2} \times \frac{3\cos^2\theta - 1}{2}.$$

The parameter $\Delta E'$ for the iron oxide is approximately zero at 78 K. However, the quadrupole splitting ($\Delta E = e^2qQ/2$) for the paramagnetic components at 298 K is about 1.10 mm s^{-1}. The difference between $\Delta E'$ and ΔE is caused by the angle θ, which specifies the orientation of the V_{zz} axis with respect to the direction of the magnetic hyperfine field. It has been established that the spin structure is canted at temperatures below 300 K in the surface layer and/or in particles smaller than about 10 nm.[15,20,23]

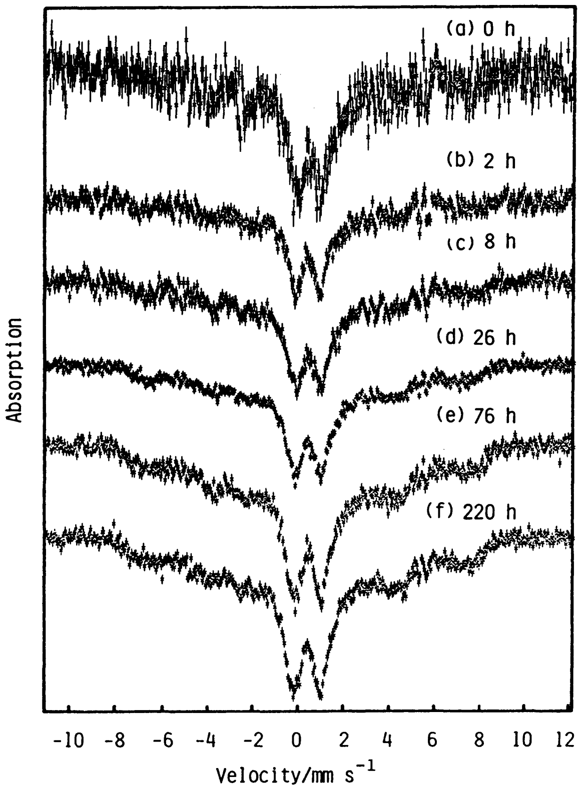

Fig. 5. Mössbauer spectra subtracted metallic iron peaks from the spectra at 298 K.

Figure 6 shows a spectrum simulated for Fig. 5(e) using the motional narrowing formula derived by Wickman et al.[27] although fitting a theoretical curve is quite difficult and it is impossible to get a unique solution. The relaxation time of $3\tau_L$ (τ_L is the Larmor precession time 2×10^{-8} s) was obtained, the other parameters (positions, intensity ratio, and fwhm of the sextet of the magnetic hyperfine structure) used for the fitting were determined with reference to the spectra at 78 K. The fit is not good because of the reasons described above and because of the distribution of the particle size of the iron oxide. It should be noted that the paramagnetic components are observed in the spectra of samples annealed for a long time and that their intensities do not decrease with the annealing time, although the absorption lines with the magnetic hyperfine structure due to larger particles of the iron oxides do increase in intensity. These facts imply that very fine particles are always produced newly on iron surface during the annealing process. The oxide of the first monolayer on the iron surface is different from that of other layers, and an increase in the mole volume upon further chemical transformation leads to a disruption of the next first oxide layer into fine particles which grow over the iron surface. The following simple model of corrosion is considered (Fig. 7): I. In a first step, oxygen is adsorbed on the metal surface. The metal is now covered by one or two monolayers (these layers are considered to consist of Fe^{2+} and O^{2-}, but there has not yet been experimental proof of this.) II. Further oxidation leads to the formation of layers of γ-Fe_2O_3 up to about 5 nm. New fine iron oxides are formed on iron during the progress of the corrosion.

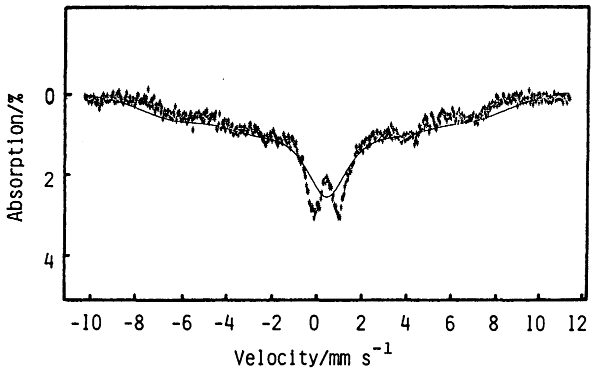

Fig. 6. Mössbauer spectrum for oxide species in the sample annealed at 110 °C for 220 h. The experimental spectrum is compared with a theoretical curve calculated on the basis of a simple model discussed in the text.

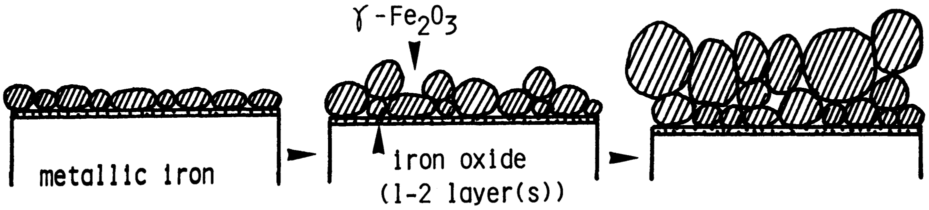

Fig. 7. A model proposed for corrosion of iron.

The recoilless fraction (f) of fine particles is of great interest. The Mössbauer spectrum of the original iron powder was measured at 4.2K in order to evaluate the fraction of metallic iron or iron oxide in the sample, for the recoilless fraction of iron oxide can be supposed to be equal to that of metallic iron at 4.2K. The metallic iron components in the original sample were estimated to be 86% of the total ^{57}Fe. From the relation of this value to the absorption area for individual chemical species at 78K, the ratios of residual metallic iron part to the total ^{57}Fe were evaluated for all the samples; they are shown in Table 1. The recoilless fraction of our sample is not very small; the $f(78\text{ K})/f(4.2\text{ K})$ ratio for iron oxide was 0.78. It has been reported that $f(300\text{ K})/f(4.2\text{ K})$ is 0.43 for very fine oxide (corresponding to 0.4 nm thick iron) and 0.78 for the oxide on 2.0 nm thick iron film.[16] Our datum supports the idea that recoilless fraction for very fine oxides is not so small as was suggested by Belozerskii et al.[28]

Taking a model that iron is oxidized uniformly from the surface of metallic iron and that metallic iron forms a continuous solid without micropores, the thickness of the metallic iron is estimated to be as listed in Table 1. The thickness of the oxide layer for the original sample is evaluated to be 2.1 nm. This thickness corresponds to the case formed if 1.4 nm of an iron layer (corresponding to 5 monolayers) is oxidized. Haneda and Morrish[15] have reported, from the line-broadening observed in the X-ray diffraction pattern using the Scherrer relation, that the average size of oxide is 2.7 nm. However, the Mössbauer spectrum reported by Haneda is similar to that for the sample annealed at 110 °C for 76 h in our experiment. Shinjo et al.[16] have reported that the oxide part is 59% of the total ^{57}Fe in 2.0 nm-thick iron film (corresponding to the thickness of 1.2 nm of metallic iron for a very thin layer of iron). From the kinetic study of oxygen absorption into iron metal, Quinn and Roberts[29] reported that oxidation to 6 layers occurs at 78 K. Fromm[30] and Fromm and Mayer[31] investigated the kinetics of oxygen absorption on evaporated metal film and reported that sorption-layer formation plus molecular chemisorption take place in the O_2/Fe system, that the initial sticking probability is not dependent on the temperature, and that layer formation is thermally activated at a higher coverage sorption. Although the sample treatment was not described in detail in these papers, our value (2.1 nm of iron oxide) is in accordance with the values they reported. This layer may be the thinnest one necessary to prepare metallic iron without severe autoxidation at room temperature in air.

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