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A Mössbauer Study on Behaviors of Tin Deposited on the α-Fe_2O_3 Surface

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The doping process of metallic tin into the α-Fe_2O_3 crystal lattice was studied by using ^{119}Sn Mössbauer spectroscopy. The spectra of the heat-treated samples at 300 °C for 10 h show the existence of Sn_2O_3, remaining β-Sn, and α_2-Sn. The α_2-Sn species is characteristic with the unusually large value of the isomer shift (I.S.=4.5 ± 0.2 mm s^{-1}).

Previously we have reported that metallic tin coated on the surface of hematite powders easily diffuses into the crystal lattice at 1000°C and the incorporated tin exists as Sn^{4+} from the isomer shift value in the ^{119}Sn Mössbauer spectra.[1)] The Sn^{4+} species exhibits the well-resolved six-line due to the supertransferred hyperfine magnetic field, suggesting the substitutional occupation of the Fe^{3+} site in α-Fe_2O_3. The effective internal magnetic field is estimated to be 123 kOe (1 Oe=1000 / 4 A m^{-1}) at 293 K and 131 kOe at 93 K. The results agree with those observed by Fabrichnyi et al.,[2)] who have prepared their samples by means of coprecipitation of hydroxides followed by annealing.

It is interesting to clarify the doping process of the tin atom into the crystal lattice of hematite. The ^{119}Sn Mössbauer spectroscopy is suitable for this purpose, because of providing the information on the local environments and the charge states of the tin atom. In the course of the study we found the existence of a certain tin compound or a metallic tin exhibiting unusually large isomer shift and no quadrupole splitting. In this letter, we report the Mössbauer results on the tin species formed on the surface of hematite.

Powders of α-Fe_2O_3 coated with metallic tin were prepared in a similar manner as our previous paper.[1)] The contents of the metallic tin were adjusted to 5 and 10 mol%. The sample powders sealed in a evacuated quartz tube were annealed at 300 and 350 °C for 10-20 h and quenched in ice-cold water. The ^{119}Sn Mössbauer measurements were carried out in the same way as our previous work.[1)]

Figure 1 shows the Mössbauer spectra at 93 K of the specimens containing 5 mol% tin : a) as-deposited sample, b) heat-treated sample at 300 °C for 10 h, and c) heat-treated sample at 300 °C for 20 h. The spectra of Figs. 1a) and 1b) were analyzed with Lorentzian curves by the least-squares method. The solid lines represent the best-fitted curves. In the spectrum of Fig. 1c), however, attempts to fit were unsuccessful because of overlapping of very broad and complex spectra. The values of the isomer shift (I.S.), the quadrupole splitting (Q.S.), and the line width (2Γ) obtained by the best-fitting are listed in Table 1. The isomer shift values are taken relative to the $BaSnO_3$ standard absorber.

The tin as-deposited on the surface of the α-Fe_2O_3 powders is undoubtedly metallic β-Sn from the I.S. value, consistent with our previous work.[1)] As seen in Fig. 1a), there is no other tin species in the as-deposited sample. Rusanov et al. have studied ^{119}Sn Mössbauer spectra of metallic tin precipitates prepared by the electrochemical reduction of 20% water solution of $SnCl_2$ with Mg.[3)] They found from a Mössbauer line with I.S.=4.3 ± 0.1 mm s^{-1} that "α_2-Sn", in addition to metallic β-Sn, exists in the precipitates obtained with the Mg reductant containing ferromagnetic impurities. The quantity of the α_2-Sn in the precipitates increases with an addition of ferromagnetic materials such as Fe, Co, and Ni fine powders or in the application of external magnetic field of about 0.5 T. The α_2-Sn, one of the modifications of α-Sn, is known to have a diamond cubic lattice identical to silicon and to exist in thin tin films prepared by thermal evaporation in vacuum.[4)] In our measurements for tin deposited on the surface of α-Fe_2O_3 powders any Mössbauer peak is not observed in the velocity range near 4 mm s^{-1}. This implies that the production of the α_2-Sn depends on only the existence of

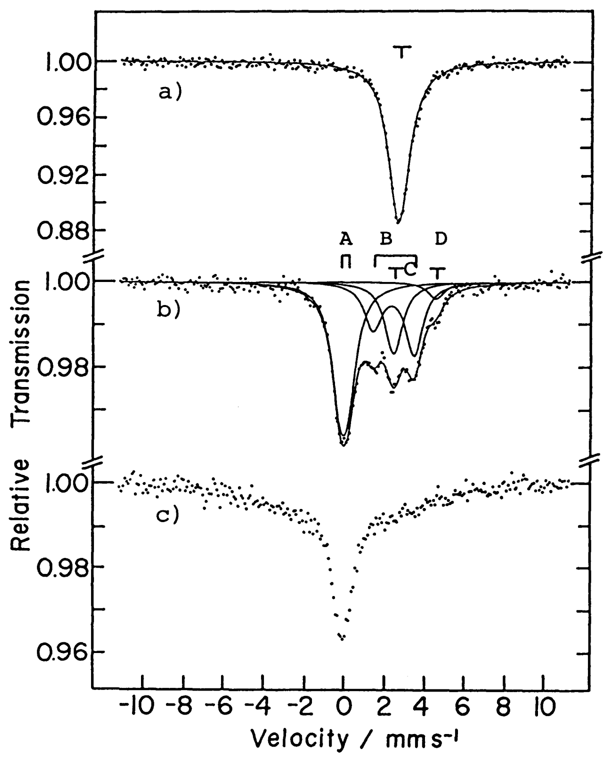

Fig.1. ^{119}Sn Mössbauer spectra at 93 K of a) the as-deposited sample (5 mol% tin), b) the heat-treated sample at 300 °C for 10 h, and c) the heat-treated sample at 300 °C for 20 h.

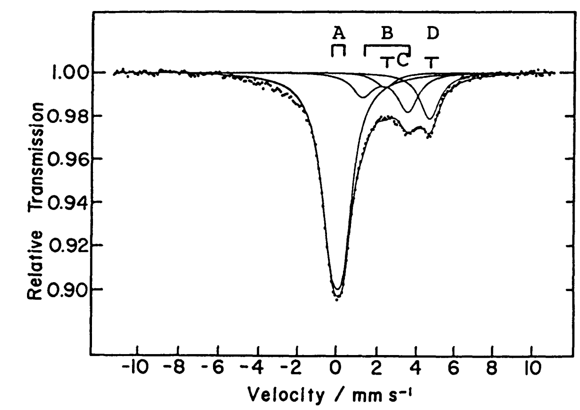

Fig.2. ^{119}Sn Mössbauer spectrum at 93 K of the heat-treated sample (10 mol% tin) at 350 °C for 20 h.

Table 1. The values of the isomer shift (I.S.), the quadrupole splitting (Q.S.), and the line width (2Γ)

Samples	Components	I.S. / $mm\ s^{-1}$	Q.S. / $mm\ s^{-1}$	2Γ / $mm\ s^{-1}$	Assignments
containing 5 mol% tin					
as-deposited		2.62	---	1.24	β-Sn
heat-treated at 300 °C for 10 h	A	0.01	0.39	1.03	Sn(IV)
	B	2.41	1.98	1.03	Sn(II)
	C	2.41	---	1.03	β-Sn
	D	4.48	---	1.03	α_2-Sn
containing 10 mol% tin					
heat-treated at 350 °C for 20 h	A	0.20	0.58	1.22	Sn(IV)
	B	2.50	2.24	1.23	Sn(II)
	C	2.50	---	1.21	β-Sn
	D	4.74	---	1.21	α_2-Sn

ferromagnetic materials : α-Fe_2O_3 is antiferromagnetic at room temperature as well-known.

The spectrum (Fig. 1b)) of the heat-treated sample at 300 °C for 10 h in vacuum is markedly different from that of as-deposited one. The spectrum indicates the existence of four kinds of tin compounds : A) Sn(IV), B) Sn(II), C) β-Sn, and D) unknown tin species. The quadrupole splitting of the Sn(II) species (component B) is larger than that of SnO (Q.S.=1.33 ± 0.04 mm s^{-1} [5] and 1.36 ± 0.04 mm s^{-1} [6]), rather close to those of Sn(II) components of Sn_2O_3 (Q.S.=1.96 ± 0.04 mm s^{-1})[5] and Sn_3O_4 (Q.S.=2.00 ± 0.04 mm s^{-1}),[6] which are formed in the disproportionation of SnO. The unsymmetry of the quadrupole doublet is characteristic of the Mössbauer spectra for the Sn(II) components of Sn_2O_3[5] and Sn_3O_4.[6] The Sn(IV) components of Sn_2O_3 and Sn_3O_4 can not be distinguished from SnO_2 in their Mössbauer spectra : the values of I.S. and Q.S. for the Sn(IV) components are nearly the same as those for SnO_2. Therefore, the Sn(IV) and Sn(II) species found in our Mössbauer spectrum correspond to the Sn(IV) and Sn(II) components respectively of Sn_2O_3 or Sn_3O_4. Judging from the intensity ratio of Sn(IV) to Sn(II), the tin oxide formed on the surface of α-Fe_2O_3 by the heat-treatment is identified to be Sn_2O_3. It is apparent from the Mössbauer spectrum (component C) that a part of metallic β-Sn remains in the specimen at this annealing temperature and time. A small Mössbauer peak with no quadrupole splitting (component D) is observed at 4.48 mm s^{-1}, which is very close to that for α_2-Sn described above. Tin species other than the α_2-Sn can not be considered for such an abnormally large isomer shift. In order to confirm the occurrence of α_2-Sn, the Mössbauer spectra were measured for samples prepared under different conditions of the heat-treatment. Figure 2 shows the spectrum of the 10 mol% tin containing sample annealed at 350 °C for 20 h in vacuum. In this heat-treatment an increase in the Sn(IV) species and a decrease in the metallic β-Sn are observed, indicating the progress of oxidation of the tin species. The peak intensity corresponding to the α_2-Sn obviously increases in this spectrum. These experimental results suggest that the α_2-Sn occurs from the recrystallization of the tin metal on the surface of α-Fe_2O_3 or Fe_3O_4. In our previous Mössbauer study of the tin species deposited on the surface of γ-AgI diamagnetic powders, no α_2-Sn exists in the sample annealed at 300°C for 10 h.[7] It is established that in the (111) plane of the α-Fe_2O_3 crystal electron spins of Fe^{3+} are parallel to each other and are coupled ferromagnetically. The recrystallization of the metallic β-Sn might be magnetically affected on the (111) plane of the α-Fe_2O_3 surfaces. Alternatively, the α_2-Sn is likely formed from the recrystallization on the surface of ferromagnetic magnetite, produced by reduction of α-Fe_2O_3. Oxidation of the tin species must be attended by reduction of Fe^{3+} in α-Fe_2O_3. The ^{57}Fe Mössbauer spectra of these specimens indicate the existence of magnetite Fe_3O_4, in addition to α-Fe_2O_3.

All tin species are oxidized to Sn(IV) at longer annealing times, as shown in Fig. 1c). The weak and very broad spectrum overlapped with the sharp peak of the Sn(IV) species is identified to be Sn^{4+} incorporated into a few surface layers of the substrates. The Sn^{4+} ions are weakly interacting with the magnetically ordered cations of the substrates.

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