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Analysis of Tin Corrosion Products Using Conversion Electron Mössbauer Spectroscopy, Transmission Mössbauer Spectroscopy, and X-Ray Diffractrometry

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Tin plates corroded by various acids were nondestructively analyzed by a ^{119}Sn conversion electron Mössbauer spectroscopy, a transmission Mössbauer spectroscopy, and an X-ray diffractometry. The conversion electron method was shown to be useful for analysis of some corrosion products which could not be easily observed by the transmission method. By using both the Mössbauer spectroscopy and the X-ray diffractometry, the corrosion products formed by 6.7M-HNO_3, 5.7M-HCl, and 9.0M-H_2SO_4 were determined to be $SnO_2 \cdot nH_2O$, $Sn_4(OH)_6Cl_2$, and $SnSO_4$, respectively.

Since Swanson and Spijkerman reported Mössbauer spectra of thin foil of ^{57}Fe by a conversion electron method,[1] the potential of this technique has been explored and its practical use has been recognized in such investigations as oxidation products,[2–4] corrosion products,[5] ion implantations,[6–8] and metallurgy.[9] The measurement is performed by detecting conversion electrons and Auger electrons. Although a transmission measurement gives information on the total bulk of a sample, the method has the restriction that the sample should be thin. However, the conversion electron method can provide information on the surface layers of a bulky sample because of the limited penetration range of the electrons. In a thick sample, which can be neither destroyed nor transformed in shape, most Mössbauer spectroscopic analyses have been so far made in a reflection geometry by detecting the scattered X- or γ-rays associated with the resonance of nuclei.[10,11] However, the conversion electron method is available for analysis of the chemical compositions and structures in thinner surface layers than can be studied with the scattered X- or γ-ray methods.

In the present paper, we describe the systematic studies of tin metals corroded by a variety of acids by means of the conversion electron method and the transmission method. An X-ray diffractometry was also applied to complement the Mössbauer spectroscopic analysis. Model compounds were synthesized in separate experiments in order to identify the corroded products.

Experimental

In order to detect conversion electrons, we constructed a gas-flow type proportional counter, which is essentially the same as that designed by Swanson and Spijkerman.[1] Our counter is made of a 2 mm thick brass plate and is rectangular in shape, $15 \times 20 \times 15$ cm^3. The anode consists of two tungsten wires of 0.00254 cm diameter which are 7.5 cm apart from each other and symmetrically located with respect to the centerline. The top plate is removable to facilitate placing the sample inside the counter and varying the number and the location of the anode wires.

Conversion electron Mössbauer spectra were determined at room temperature by placing a sample inside the counter. During accumulation of the spectra the anode was kept at a positive potential of 1370V with respect to the grounded brass plate and a helium-methane gas(*e.g.* Q gas) was passed through the counter at the flow-rate of *ca.* 10 cm^3/min. Transmission spectra were recorded by using a NaI(Tl) scintillation counter mounted behind the proportional counter. Both the Mössbauer spectra were measured against a 2 mCi Ca^{119m}SnO$_3$ source moving in a constant acceleration mode at room temperature. X-Ray diffraction data were obtained by using Rigakudenki No. 2001.

Samples studied were prepared by corroding 1 mm thick tin plates in various acid solutions at room temperature and by drying them at room temperature.

Results and Discussion

Mössbauer Spectra. Figure 1 shows Mössbauer spectra of a tin plate corroded by 6.7M-HNO_3 for 5 min. A transmission spectrum (a) gives two peaks, the isomer shift(I. S.) values of which are 0.00 mm/s and 2.56 mm/s with respect to calcium stannate. A conversion electron spectrum (b) consists of only one peak, which corresponds to the less intense line observed in the transmission spectrum. The main peak found in the transmission spectrum is assigned to β-Sn from its peak position. The peak of 0.00 mm/s isomer shift is assigned to the corrosion species formed on the tin

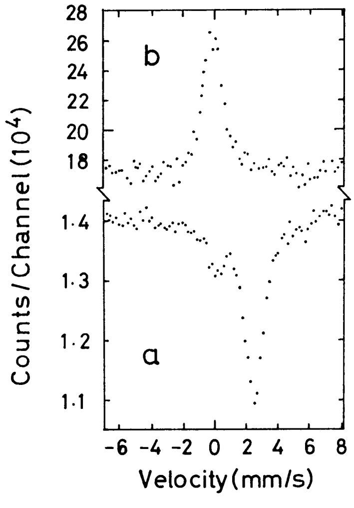

Fig. 1. Mössbauer spectra of a tin plate corroded by 6.7 M-HNO_3 for 5 min. a) Transmission spectrum, b) conversion electron spectrum.

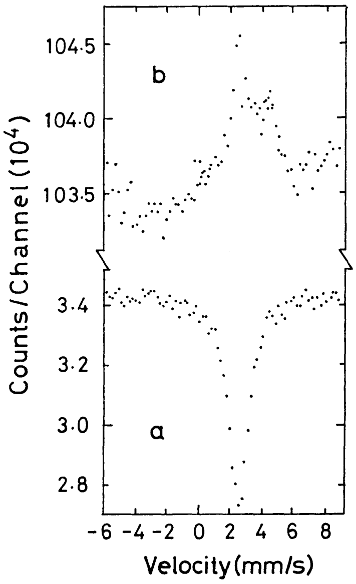

Fig. 2. Mössbauer spectra of a tin plate corroded by 5.7 M-HCl for 6.5 h. a) Transmission spectrum, b) conversion electron spectrum.

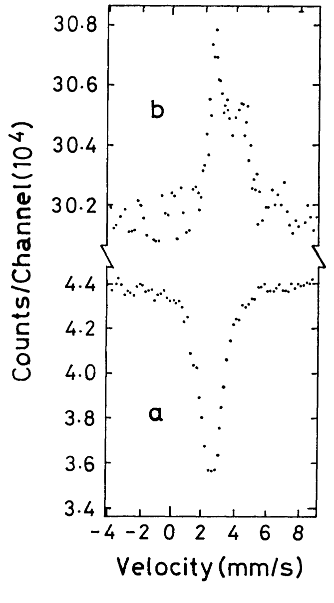

Fig. 3. Mössbauer spectra of a tin plate corroded by 9.0 M-H_2SO_4 for 3.8 d. a) Transmission spectrum, b) conversion electron spectrum.

plate surface by reacting with 6.7M-HNO_3 because the spectrum of an uncorroded tin plate reveals only one peak, with the I. S. value of 2.56 mm/s.

Mössbauer spectra obtained from a tin plate corroded by 5.7M-HCl for 6.5 h are shown in Fig. 2. The transmission spectrum(a) gives a single peak assigned to β-Sn. The conversion electron spectrum(b) shows two peaks, the I. S. values of which are 4.44 mm/s and 2.56 mm/s; the latter peak has a shoulder at the I. S. value of nearly 0.00 mm/s.

As seen in Fig. 3, the transmission spectrum(a) of a tin plate corroded by 9.0M-H_2SO_4 for 3.8 d consists of a single peak, while the conversion electron Mössbauer spectrum(b) gives another peak around 4.40 mm/s.

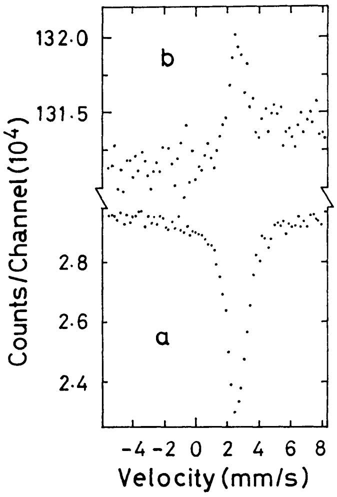

Fig. 4. Mössbauer spectra of a tin plate corroded by 27.0 M-HF for 6.2 d. a) Transmission spectrum, b) conversion electron spectrum.

The conversion electron spectrum of a tin plate corroded by 27.0M-HF for 6.2 d (Fig. 4 b) shows an intensive peak corresponding to β-Sn; no other peak can be clearly observed.

Thickness of Corrosion Layers. It was found from the experimental results that the line width of the substrate observed for the scattered electron is narrower than that for the γ-ray transmission method. For example, the comparsion of the β-Sn peaks observed in the two detection methods for the sample treated by sulfuric acid shows that the line width (fwhm) is 0.85 mm/s for the scattered electron method and 1.56 mm/s for the transmission method. This narrowing is quantitatively explained in terms of the decreased range of the electrons in the substrate, β-Sn. The electrons emitted from the substrate, β-Sn, are scattered through the corroded layers. If the corrosion layers exceed the effective range of the scattered electrons, the peak assinged to the substrate cannot be observed in the conversion electron spectrum. Therefore, it is concluded that corrosion layers for the sample treated by nitric acid nearly exceed the effective range of the conversion electrons. In order to determine the thickness of the corrosion layers, we estimated the effective range of the resonantly scattered electrons from ^{119}Sn for typical inorganic compounds; SnO_2, $CaSnO_3$, and $BaSnO_3$. The line width of a γ-ray transmission spectrum is proportional to an effective thikness, T, which is represented as

$$T = n\sigma tf. \qquad (1)$$

Here n is the concentration of ^{119}Sn atoms in a unit volume; σ, the resonance cross-section; t, the absorber thickness; and f, the recoilless fraction. The experimental line width increases linearly with the increase in the concentration of the resonance atoms. In a previous communication, we demonstrated that the relation between the experimental line width and the effective thickness for γ-rays can be roughly applicable to the scattered electron method.[12] The

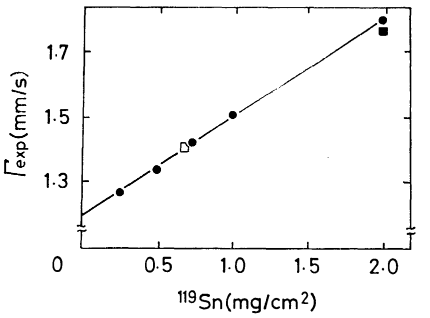

Fig. 5. Experimental line width *vs.* the apparent thickness of ^{119}Sn for SnO_2 by γ-ray transmission method (●). The line width observed by the scattered electron method (□) for the same sample as those by the γ-ray transmission method (■).

thickness dependence of the experimental line width in the γ-ray transmission method is shown in Fig. 5, together with the experimental line width obtained for the scattered electron method. For SnO_2 of 2.0 mg ^{119}Sn/cm^2, the line width found in the γ-ray transimssion method is 1.79 mm/s and that found in the scattered electron method is 1.41 mm/s. The apparent thickness for the electron method obtained graphically from Fig. 5 is 0.72 mg/cm^2 in SnO_2. The value of apparent thickness for each sample is shown in the second column on Table 1. Electrons interact with surrounding atoms and ionize them during their passages. The Bethe's approximated equation concerning the energy loss of electrons shows that the stopping power of materials for electrons is proportional to the atomic number(Z) and inversely to the atomic weight(A) of the interacting atom. By assuming that the value of Z/A is nearly constant for each element concerned, the apparent effective thickness obtained from Fig. 5 is listed in the third column of Table 1. The values are in good agreement with each other, and do not depend on the kind of compounds with which the electrons interact. In the comparison of the line width of the scattered electron spectra with those of the γ-ray transmission spectra, it is found that the apparent cross-section is not identical for the two different kinds of detection methods. The apparent cross-section for emission of conversion electrons is approximately greater than that of γ-ray radiations by a conversion coefficient, α. The values shown in the third column in Table 1 must be divided by the conversion coefficient, 5.12, since the values were taken from the γ-ray transmission method. The value $2.21+0.38$ mg/cm^2 is estimated for the effective range of scattered electrons of ^{119}Sn. Auger electrons are also emitted as a result of the deexcitation of ^{119}Sn atoms, and these electrons will enhance the intensity of the conversion electron Mössbauer spectrum. Moreover, Tricker *et al.* pointed out that non-Mössbauer atoms (chromium or aluminium) enhanced the intensity of a Mössbauer spectrum when these atoms were evaporated on iron foil.[13] They concluded that electrons were emitted from the chromium or aluminium atoms by the X-rays which accompany the Mossbauer effect. Although the effects on the line width of the spectrum remain unsolved, the contribution may be assumed to be small.

Table 1. The effective ranges determined for the resonantly scattered electrons in tin compounds

Compound	^{119}Sn(mg/cm^2)	$\frac{100}{A}\cdot\frac{M}{m}$(mg/cm^2)
SnO_2	0.72 ± 0.06	10.65 ± 0.89
$CaSnO_3$	0.63 ± 0.12	12.79 ± 2.44
$BaSnO_3$	0.36 ± 0.07	10.45 ± 2.09
	Mean value :	11.30 ± 1.81

X-Ray Diffraction Analysis. X-Ray diffractometry is a useful method for assignment of chemical species of a solid sample. In order to compare the characteristics of the X-ray diffractometry with the conversion electron Mössbauer spectroscopy for the corrosion sample, we examined the results obtained by using both these detection methods. For the purpose of the identification of corrosion products, we synthesized the chemically pure tin compounds which can be attributed to the corroded products based on the conversion electron Mössbauer spectroscopy, and measured their X-ray diffraction and transmission Mössbauer spectrum.

The Mössbauer data of the corrosion species produced by nitric acid indicate the presence of tin(IV) species similar to SnO_2. It is also known that a metallic tin plate reacts with diluted nitric acid to form metastannic acid, $SnO_2\cdot nH_2O$. The compound was prepared by according to the procedure of Weiser and Milligan,[14] and was checked by the X-ray diffractometry (see Fig. 7). We found good agreement between the pattern of the prepared sample and that of the tin plate corroded by 6.7M-nitric acid for 5.0 min, although those

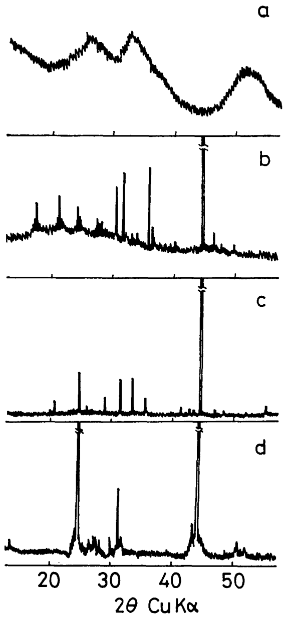

Fig. 6. X-Ray diffraction patterns. a) A tin plate corroded by 6.7 M-HNO_3 for 5 min, b) a tin plate corroded by 5.7 M-HCl for 6.5 h, c) a tin plate corroded by 9.0 M-H_2SO_4 for 3.8 d, d) a tin plate corroded by 27.0 M-HF for 6.2 d.

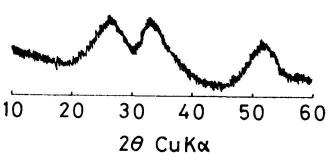

Fig. 7. X-Ray diffraction pattern of metastannic acid.

patterns are very broad, indicating an amorphous state. Transmission Mössbauer spectrum gives the I. S. value of 0.00 mm/s at room temperature for both samples. These results indicate the formation of metastannic acid, $SnO_2 \cdot nH_2O$, on the tin plate treated by 6.7M-nitric acid.

Mössbauer data of the tin plate corroded by 5.7M-hydrochloric acid for 6.5 h indicate a presence of Sn(II) and Sn(IV) corroded species. The X-ray diffraction pattern consists of many sharp lines and a broad line ranging from 20 to 35 deg. In order to identify the corroded products, the X-ray diffraction data were compared with those of Sn(II) compounds such as $SnCl_2$, $SnCl_2 \cdot 2H_2O$, and $Sn_4(OH)_6Cl_2$, and with $SnCl_4 \cdot 5H_2O$. X-Ray diffraction data of $Sn_4(OH)_6Cl_2$ agree the best with those of the corroded sample, as shown in Table 2. Since the Mössbauer parameters have not been reported for the compound, we prepared it by the procedure of Donaldson *et al.*[15] and accumulated the transmission spectrum at room temperature. The I. S. value and the quadrupole splitting (Q. S.) value are found to be 3.76 mm/s and 0.76 mm/s, respectively. The values are in good agreement with those of the corroded product found in a conversion electron spectrum. The conversion electron Mössbauer spectrum shows the presence of Sn(IV)

TABLE 2. X-RAY DIFFRACTION ANALYSIS OF A TIN PLATE CORRODED BY 5.7 M-HCl FOR 6.5 h

Sample 2		β-Sn[a]		$Sn_4(OH)_6Cl_2$[a]		Sample 2		β-Sn[a]		$Sn_4(OH)_6Cl_2$[a]	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
1.67	37	1.659	17	1.675	30	2.71	30			2.70	20
1.83	22			1.828	50	2.82	72	2.793	90	2.82	80
1.91 1.90	20			1.893	30	2.93	63	2.92	100	2.85 2.90	80 40
				1.923	30					3.09	60
				1.937	40	3.18	36			3.18	20
1.96	30			1.969	20	3.27 3.24	40			3.24	30
2.03	100	2.017	74	2.02	20						
				2.14	40	3.45 3.49	35			3.50	30
2.22	19			2.20	20						
2.25	23			2.24	30	3.65 3.71	46			3.64	30
2.29	23			2.28	30						
				2.30	30					4.04	40
2.39	22			2.40	20	4.21	56			4.18	80
2.50	30			2.50	100					4.75	30
2.55	75			2.55	90					4.89	20
2.65	30			2.63 2.64	50	5.07	50			5.09	30

a) JCPDS data.

TABLE 3. X-RAY DIFFRACTION ANALYSIS OF A TIN PLATE CORRODED BY 9.0 M-H_2SO_4 FOR 3.8 d

Sample 3		β-Sn[a]		$SnSO_4$[a]		Sample 3		β-Sn[a]		$SnSO_4$[a]	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
1.45	39	1.458	13			2.46	7			2.454	18
1.49	21	1.484	23			2.68	8			2.660	25
1.66	8					2.82	28	2.79	90		
1.67	10	1.659	17			2.93	15	2.92	100		
1.76	52			1.743 1.735	12	3.09	16			3.06	100
						3.34	8				
1.94	8					3.43	10				
2.04	100	2.017	74			3.57	33			3.55	50
2.08	7			2.089	50	4.28	14			4.25	30
2.10	7			2.101	50	4.42	9			4.39	25
2.14	6			2.130	12						
2.17 2.18	9			2.168	25						

a) JCPDS data.

species with weak intensity in addition to the main peak of $Sn_4(OH)_6Cl_2$; the X-ray diffraction pattern also indicates the presence of amorphous species which may be ascribed to tin(IV) species produced on the tin plate. These observations lead us to the conclusion that $Sn_4(OH)_6Cl_2$ is the main product and some tin(IV) species are produced on a tin plate treated by 5.7M-HCl.

Mössbauer spectra of the tin plate corroded by 9.0M-sulfuric acid for 3.8 d indicate the presence of Sn(II) compound. The X-ray diffraction data were compared with those of Sn(II) compound, as mentioned for the sample corroded by hydrochloric acid. The data of $SnSO_4$ are in good agreement with those of the tin plate corroded by 9.0M-sulfuric acid for 3.8 d (Table 3). The values of I. S. and Q. S. of $SnSO_4$ at room temperature are 3.98 mm/s and 0.95 mm/s, respectively. These values are in good agreement with those of the corroded species. The results indicate the formation of $SnSO_4$ of the tin plate corroded by 9.0M-sulfuric acid.

In the case of the sample corroded by 27.0M-hydrofluoric acid for 6.2 d, the conversion electron Mössbauer spectrum gives no definite peaks, the transmission spectrum gives only the β-Sn peak, and the X-ray diffraction pattern of the sample does not agree with any of the JCPDS data available for tin fluoride compounds.

The present results indicate the following conclusion: In order to determine the thin corrosion products formed on a metal surface, the observed peaks of X-ray diffraction pattern are so weak, as shown in Fig. 6, that the identification of the products is tedious and difficult. The transmission Mössbauer technique gives only the spectrum of the major substrate in a limited time of accumulation of the spectrum. The conversion electron Mössbauer technique, on the other hand, provides information concerning the chemical state of the products through the isomer shift and quadrupole splitting. Although the complete chemical form of the corroded products may not be determined, the conversion electron Mössbauer technique makes it very easy to cross-assign the weak peaks of the X-ray diffractometry to the possible chemical species.

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