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^{57}Fe and ^{119}Sn conversion electron Mössbauer studies of Fe–Sn phases on tinplate

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^{57}Fe and ^{119}Sn conversion electron Mössbauer spectrometry has been applied to the investigation of the compositional variations of the Fe–Sn intermetallic alloy produced at the surface of 90 nm thick tin electrodeposited steel by the thermal treatment. It was confirmed that the fully alloyed layer of $FeSn_2$, FeSn + $FeSn_2$, FeSn, FeSn + Fe_3SnC and Fe_3SnC was formed by the thermal treatment for 30 min at 300, 400, 500, 600 and 700° C, respectively, and that the thickness of the Fe–Sn layer increased with the elevation of temperature.

1. Introduction

The investigation [1–4] of various low tin-deposited steels, which show sufficient weldability, corrosion resistance, lacquerability and so on, have been carried out in response to the economic demand of cost reduction. The fully alloyed tinplate, the surface of which is composed of a thin Fe–Sn alloy layer, has been reported to have excellent corrosion resistance and is one of the most attractive materials [5, 6]. However, no other detailed study has been reported on the layer structure. ^{57}Fe and ^{119}Sn conversion electron Mössbauer spectrometry (CEMS) has developed as an effective technique for the characterization of such a thin layer and the applications of CEMS to industrial materials has been extensively performed [7]. In ^{57}Fe CEMS, 7.3 keV conversion electrons re-emitted after recoilless resonant absorption of γ-rays in ^{57}Fe nuclei are detected, so that the observed depth, which corresponds to the escape distance of conversion electrons, is estimated to be 300 nm. In ^{119}Sn CEMS, similarly, it is estimated to be 1000 nm because of the detection of 19.6 keV conversion electrons.

Graham *et al.* [8] studied the compositions of Zn–Fe alloy layers produced on hot-dipped galvanized steel by means of ^{57}Fe CEMS and confirmed the presence of the zeta, delta-prime (palisade), delta-prime (compact) and capital gamma phases from the top surface. Godbole *et al.* [9] studied the ion beam mixed Fe–Al interface by ^{57}Fe CEMS and reported the formation of Fe_3Al and $Fe_{55}Al_{45}$ solid solutions. ^{119}Sn CEMS was applied to the identification of Fe–Sn intermetallic alloys on the thermally treated tinplate by Huffman *et al.* [10] and Vértes *et al.* [11]. The former identified $FeSn_2$ at the interface between tin and iron and the latter reported the presence of Fe_3Sn_2 and $FeSn_2$.

In this work, the compositional variations of Fe–Sn intermetallic alloys on the fully alloyed tinplates, which were produced by the thermal treatment, were clarified by applying ^{57}Fe and ^{119}Sn CEM spectrometry.

2. Experimental details

Tin was electrodeposited on a cold rolled steel sheet (0.2 mm thickness, T4CA) with a thickness of 90 nm. The fully alloyed tinplates were

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prepared by heating up to various temperatures within 15 min in an electric resistance furnace of H_2(5 vol%)–N_2(95 vol%) atmosphere, holding for 30 min and cooling down to room temperature. ^{57}Fe and ^{119}Sn CEM spectra were measured at room temperature. 25 mCi ^{57}Co/Rh was used as γ-ray source for ^{57}Fe CEMS and 5 mCi ^{119m}Sn/$CaSnO_4$ for ^{119}Sn CEMS. The re-emitted electrons were detected by the backscatter type gas flow proportional counter, which was connected to the Mössbauer spectrometer. The counting gas was the mixture of He(90 vol %) and CH_4(10 vol %) and flowed at the rate of 10 ml min^{-1}. The Doppler velocity was calibrated with reference to α-Fe for ^{57}Fe CEMS and SnO_2 for ^{119}Sn CEMS.

3. Results and discussion

3.1. ^{57}Fe CEM study

^{57}Fe CEM spectra of the tin electrodeposited steel and the thermally treated tinplates at representative temperatures are shown in Fig. 1. The CEM spectrum of the electrodeposited steel surface consisted only of the sextet due to the substrate and no tin and iron compound could be recognized prior to the thermal treatment, as seen in Fig. 1a. After the thermal treatment below the melting point of tin, 232° C, only the sextet due to substrate was observed in the CEM spectra. However, the formation of the Fe–Sn alloys was confirmed even at 100° C by increasing the period of the thermal treatement to several hours and it was identified as $FeSn_2$ by the analysis of a CEM spectrum. Although Vértes *et al.* [11] reported that the primary product observed at the Fe–Sn interface was mainly Fe_3Sn_2, we could not recognize the peaks as being due to Fe_3Sn_2 in any CEM spectra.

After the thermal treatment at 300° C, the tinplate exhibited another sextet due to an Fe–Sn intermetallic alloy in the CEM spectrum and the Mössbauer parameters (IS = 0.55 mm sec^{-1}, H = 11.4 T) obtained were in agreement with those of $FeSn_2$ [12], which was antiferromagnetic at room temperature. This result corresponded well to that of the commercial tinplate reported by Huffman *et al.* [10] and the primary product was confirmed to be $FeSn_2$. After thermal treatment at 400° C, new sextets due to FeSn, whose average Mössbauer parameters were IS = 0.33 mm sec^{-1}, QS = −0.43 mm sec^{-1} and H = 11.3 T [13], were

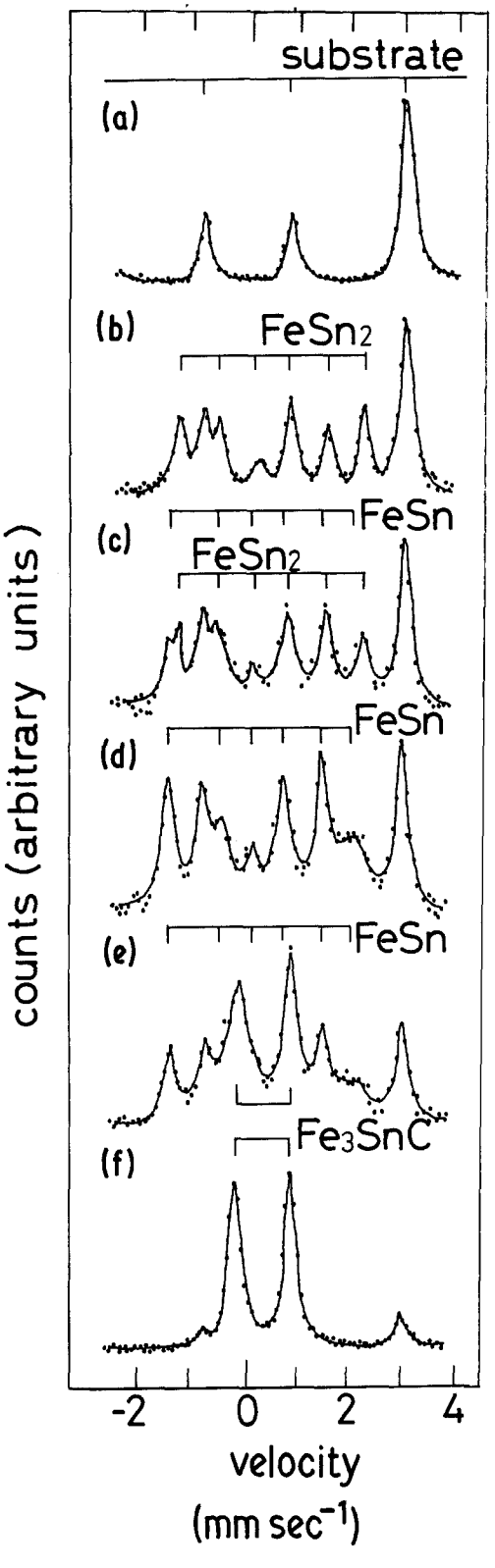

Figure 1 ^{57}Fe CEM spectra of (a) tin electrodeposited steel and thermally treated tinplates at (b) 300° C, (c) 400° C, (d) 500° C, (e) 600° C and (f) 700° C.

superimposed on the sextets due to $FeSn_2$ and the substrate as a result of more tin contribution. It was concluded that the surface layer was composed of FeSn and $FeSn_2$. After thermal treatment at 500° C, only the FeSn layer was confirmed, as seen in Fig. 1d. SEM observation of this specimen revealed that the FeSn layer had a uniform and dense structure as compared with $FeSn_2$ layer formed at 300° C. When the specimen was heated up to 600° C, the doublet peaks with $IS = 0.38\,\text{mm sec}^{-1}$ and $QS = 1.04\,\text{mm sec}^{-1}$ appeared beside the peaks due to FeSn. Furthermore, only the doublet peaks were observed as the Fe–Sn compound for the specimen heated at 700° C and they were assigned to Fe_3SnC. The formation of Fe_3SnC was supported by analysis of an X-ray diffraction pattern. The diffusion of carbon to the surface and the reaction with iron and tin during the thermal treatment are considered to be responsible for this result, while the carbon content in the substrate was 0.04 wt%.

The relative peak intensities of Fe–Sn intermetallic alloys were calculated to be 23, 35, 42, 62 and 73% at 300, 400, 500, 600 and 700° C, respectively, indicating that the Fe–Sn intermetallic alloy layer grew thicker with the elevation of temperature and that the thickness of the Fe_3SnC layer produced at 700° C become as thick as ≈300 nm. It was concluded that the elevation of temperature brought about more and more tin contribution to the iron substrate and an increase in the iron to tin ratio in the intermetallic alloy. After thermal treatment at 800° C, we could not observe any peaks due to the Fe–Sn alloy in the CEM spectrum. The evaporation of tin from the surface is considered to become vigorous at this temperature.

3.2. ^{119}Sn CEM study

The confirmation of the results obtained by ^{57}Fe CEM study and the identification of other tin compounds were performed by applying ^{119}Sn CEMS to the respective specimens. Fig. 2 shows the variations of ^{119}Sn CEM spectra of tinplates subjected to thermal treatment. Prior to the thermal treatment, the ^{119}Sn CEM spectrum of the tinplate showed a doublet due to SnO_2 ($IS = 0.0\,\text{mm sec}^{-1}$, $QS = 0.26\,\text{mm sec}^{-1}$) as well as a singlet due to metallic Sn ($IS = 2.52\,\text{mm sec}^{-1}$), as seen in Fig. 2a. It was found that the top surface of tin film was oxidized to SnO_2. After thermal treatment at 300° C, only the peaks due to $FeSn_2$ were observed in the CEM spectrum. A tin oxide layer several atoms thick was present at the surface of commerical tinplate, whereas the surface was composed of $FeSn_2$ and no oxide layer was observed in the fully alloyed tinplate.

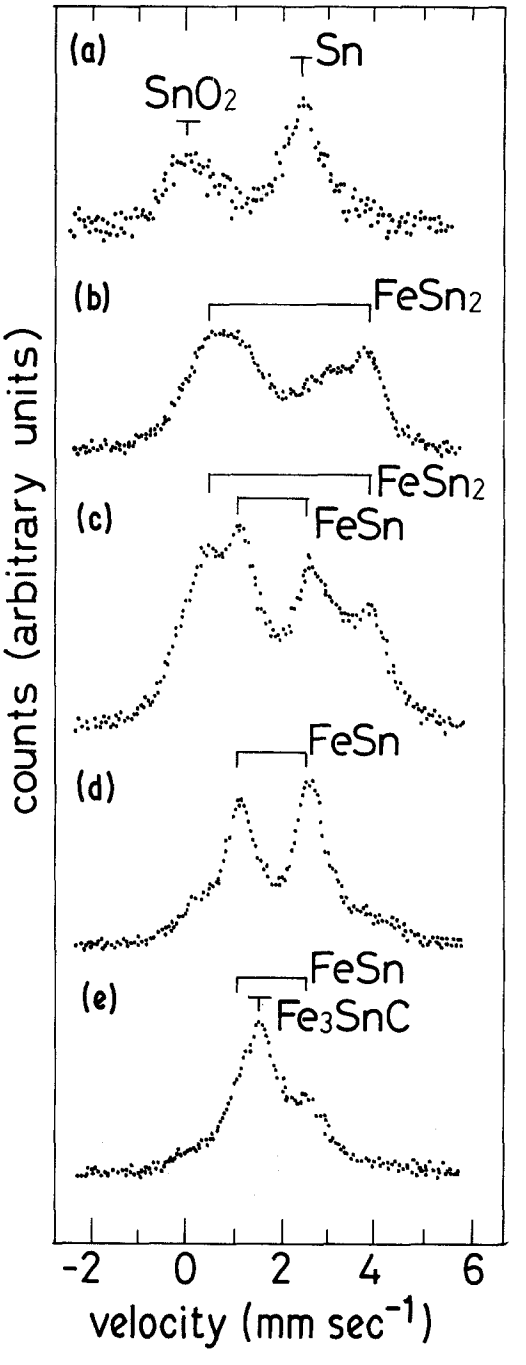

Figure 2 ^{119}Sn CEM spectra of (a) tin electrodeposited steel and thermally treated tinplates at (b) 300° C, (c) 400° C, (d) 500° C and (e) 600° C.

The CEM spectrum of the tinplate heated at 400° C confirmed the existence of the mixed layer of FeSn and $FeSn_2$. After thermal treatment at 500° C, only peaks due to FeSn appeared, as seen in Fig. 2d. Furthermore, thermal treatment at 600° C gave rise to the singlet peak ($IS = 1.46\,mm\,sec^{-1}$), which was identified as Fe_3SnC, as well as the peaks due to FeSn in the CEM spectrum. In a series of these experiments, tin compounds without iron such as SnO_2 were not recognized at the surface. All the tin coated on the substrate contributed to the formation of Fe–Sn intermetallic alloys during thermal treatment. All the results obtained by the ^{119}Sn CEM study coincided well with those of the ^{57}Fe CEM study.

4. Conclusions

The results of CEM studies for the compositional identification of Fe–Sn intermetallic alloys produced at the surface almost followed the phase diagram [15] of the Fe–Sn system except for Fe_3SnC which was formed above 600° C. The layer structure of the commercial tinplate prepared by heating at 300° C was reported to consist of SnO_2, metallic Sn, $FeSn_2$ alloy and Fe substrate from the top surface [10]. On the other hand, further elevation of the temperature brought about increasing diffusion of tin to the substrate and the formation of an FeSn layer, which had a better continuity and corrosion resistance, at the surface.

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