Technical Article

Formation of an Fe-Sn Intermetallic Layer During the Reflow Process After Tin Plating

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Tinplate manufacture involves a series of processes that determine the final characteristics of the product. Parameters such as tin coating thickness, passivation film and intermetallic laver thickness contribute to the quality of the final product. It is of particular interest to analyze the intermetallic growth, because the corrosion resistance of tinplate is strongly related to the quantity and quality of the intermetallic layer. The intermetallic is a binary iron-tin alloy that is formed in a fusion tower, where the newly tin-coated material is heated by means of an alternating electrical current. When the tinplate line operates under steady speed conditions, the thickness of the intermetallic layer is maintained within a narrow range. However, when the line speed is changed, undesirable fluctuations in the intermetallic content may occur. For this reason, it is important to study the kinetics of intermetallic growth and its dependency on process variables. In order to perform kinetic studies of intermetallic growth, a flow-melting tower simulator was built. This paper reports on our studies of the effects of the tin coating thickness, initial amount of intermetallic material, quenching temperature and heating rate on the amount and morphology of the iron-tin intermetallic layer.

Introduction

Tinplate is an important product used in the manufacture of food containers.¹⁻³ The tinplate process involves a sequence of steps that determines the final characteristics of the product. The quality of the final product depends on several parameters, including tin coating thickness, crystal morphology and orientation, presence of a passivation film

Nuts & Bolts: What This Paper Means to You

One of the critical aspects of tinplate manufacture is the irontin intermetallic that forms during the flow-melting process. Its nature controls corrosion resistance and a host of other qualities. These researchers studied the nature of the iron-tin intermetallic, studying it on a practical scale by building a flow-melting tower simulator. Presented here is information on the effects of the tin coating thickness, initial amount of intermetallic material, quenching temperature and heating rate on the amount and surface quality of the intermetallic layer. and intermetallic layer thickness. Tinplate is a multilayer system (Fig. 1), where each layer plays a significant role in corrosion protection. In particular, the corrosion resistance of tinplate is strongly dependent on the quantity and quality of the intermetallic layer.^{1,4-6}

The intermetallic layer is an iron-tin (Fe-Sn) binary alloy formed at the iron-tin interface during the flowmelting process. This is accomplished by inductive, radiant tube or electrical resistance heating. The latter process is accomplished by passing an alternating current through the electrotinned steel strip as it passes between two conductor rolls. It can be characterized as a short duration heating (Joule effect) above the melting point of tin. With this treatment, the tinplate surface appearance changes from dull matte to bright.

When the tinplate line works under steady line speed conditions, the thickness of intermetallic layer stays within a narrow range. However, during normal operation, speed changes can and do occur, leading to undesirable fluctuations in the amount of intermetallic material. Accordingly, in order to minimize or avoid these fluctuations, it is important to obtain a better understanding of the kinetics of the intermetallic formation under conditions similar to those of the production line.

Although much study has been devoted to the kinetics of intermetallic growth and its morphology, most have been performed under conditions considerably different from the typical conditions encountered in industrial electrotinning lines.^{4,5,7-14} The main differences pertain to:

- 1. Longer heating times (on the order of hours),
- 2. Materials (usually hot-dipped tin coatings, which are much thicker) and
- 3. Heating method (molten salts, hot oils, lamps, etc.).

In an attempt to obtain more insight into the morphological changes and the kinetics of intermetallic growth, formation of the Fe-Sn intermetallic compound was studied under the actual operating conditions of the flow-melting process. A flow-melting tower simulator was built to this end. We considered the effects of tin coating thickness, the initial

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Figure 1 -Schematic diagram of tinplating.

amount of intermetallic, quenching temperature and heating rates on the amount and morphology of the Fe-Sn intermetallic layer.



Figure 2 -Schematic of the laboratory flow-melting set-up.

Experimental *Materials*

Mattatinplat

Matte tinplate was obtained directly from a production electrotinning line. The tinplate was produced by tin electrodeposition in a phenol sulfonic acid bath and without chemical post-treatment. The steel chemistry and the surface state of the substrate were similar for all tested samples. Before any treatment, all samples were analyzed to confirm the absence of any pre-existing Fe-Sn alloy. The specimens were taken from different unmelted tinplate sheets (thickness: 0.18 - 0.29 mm (0.71 - 1.14 in.), tin coating: 2.8, 5.6, and 8.4 g/m²). The panel size was 80 mm x 200 mm.

Characterization

The physicochemical characterization of the intermetallic layer was accomplished by x-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD spectra were collected using a diffractometer and monochromatic Cu-K_{α} radiation. The morphology was studied using the SEM. Semiquantitative chemical composition was determined by electron dispersive spectroscopy (EDS) with an electron probe (EDAX) attached to the microscope. Prior to examining the intermetallic surface morphology, the free tin was removed by chemical dissolution, using an aqueous solution of KIO₃ (10 g/L; 1.34 oz/gal) and NaOH (50 g/L; 6.68 oz/gal) at room temperature (~25°C; 77°F). Samples were washed thoroughly with acetone, rinsed and dried in warm air.

The amount of alloyed and free tin was determined by galvanostatic dissolution (coulometric method). The evolution of the electrochemical potential of tinplate was determined as a function of time while the tin coating was removed from the sample surface at a constant rate (constant current density). Runs were carried out by means of a potentiostat/galvanostat in an acrylic electrochemical cell. Dissolution current densities were either 0.3 or 0.7 A/dm² (2.79 or 6.50 A/ft²).

The reference electrode was Ag-AgCl and the electrolyte was an aqueous HCl (1:10) solution. The free and alloyed tin contents were calculated by analysis of the potential-time curve.¹

Flow-melting simulation

In order to study the Fe-Sn intermetallic layer formation and the influence of the operating variables during the reflow process, a flow-melting simulator was built,¹⁵ as shown in Fig. 2. Basically, the apparatus allows the tinned sample to be heated by passing a high alternating current over a prescribed period of time (Joule effect). The sample is then quenched in water. The controlled heating current is supplied by an AC power supply source (range 1-1000 A, resolution 1 A) with a timing control system, allowing a resolution of 0.1 sec. The heating rate is varied by varying the current. Once the heating process is complete, the sample is released and allowed to fall into a water tank, held at a controlled temperature, where the sample is quenched.

A series of experiments was performed to study the intermetallic growth of the electrolytic tinplate during flow-melting. The following variables were analyzed:

- 1. Process time, 1 to 30 sec,
- 2. Tin coating weight, 2.3 to 8.0 g/m²,
- 3. Initial weight of Fe-Sn alloy, 0 and 0.25 g/m²,
- 4. Quenching temperature, 25 to 85°C (77 to 185°F) and
- 5. Heating rate, 10 to 50 C°/sec (18 to 90 F°/sec).



Figure 3 -X-ray diffraction pattern of a sample of intermetallic in commercial tinplate.



Figure 4 -Structure of the intermetallic layer in electrolytic commercial tinplate (SEM 6500X).



Figure 5 -Intermetallic growth as a function of time.

In each experiment, the sample was heated at a given rate over different time intervals. Several samples were prepared under given conditions in order to get an accurate mean value of the Fe-Sn alloy thickness.

Results and Discussion

Characterization of the Fe-Sn intermetallic compound

X-ray diffraction was performed on samples from the production line in order to determine the characteristics of the intermetallic compound formed during the actual reflow process. The intermetallic morphology of these samples was observed by SEM. Samples were detinned as described previously.

It is generally accepted that the intermetallic compound consists mainly of FeSn_2 . Even though the presence of other alloys and non-stoichiometric compounds has been reported, such amounts are quite low (trace amounts).¹⁶ The analysis of the XRD pattern for the commercial tinplate samples (after the removal of free Sn) showed the characteristic peaks of FeSn_2 , indicating that this was the main compound in the intermetallic layer (Fig. 3). Based on the Fe-Sn phase diagram, this result was expected because of the low temperatures used (less than 250°C; 482°F).

The iron-tin phase diagram shows that the intermetallic compound FeSn₂, containing 80.95 wt% tin is stable up to 496°C (925°F). The structure of FeSn₂ is tetragonal and the lattice constants are a = 6.520Å and c = 5.312Å. The unit cell contains twelve atoms and its volume is 225.8 Å³.¹⁶

The intermetallic layer formed during the industrial heattreatment cycle (less than 6 sec) had a columnar morphology and

Table 1
Effect of Process Time on the Amount
of Intermetallic Formed

Sample	Process time ^a	Alloyed Tin (g/m²)	Sn _L ^b (wt%)	Fe _K ^b (wt%)
(a)	0	0	0	100
(b)	$t < t_{melt}$	0.11	1.4	98.6
(c)	$t = t_{melt}$	0.65	11.5	88.5
(d)	$t > t_{melt}$	1.36	22.7	77.3

^a t_{melt}, time at which tin melts.

^b determined by EDAX-ZAF, using L and K lines.



Figure 6 -Morphology of the intermetallic layer formed during the reflow process at different treatment times. (a) substrate without heating, (b) $t < t_{meli}$, (c) $t \le t_{meli}$, (d) $t > t_{meli}$.

the crystals appeared to have different orientations. At least on a macroscopic scale, the substrate was completely covered by a cross-linked network (Fig. 4). The continuity of the intermetallic layer is of practical significance because it plays an important role in the protection of the steel from corrosion.^{1,4-6}

Biber and Harter studied the alloy layer formed on iron single crystals and determined that there were actually only three basic alloy-layer structures.¹¹ These occurred on the {111}, {110} and {100} faces of the iron crystal. On the {111} face, the intermetallic layer consisted of small columnar crystallites that projected from the surface at various angles. On the {110} face, the crystallites lay parallel to one another on the surface. On the {100} face, the crystallites were arranged in an approximately orthogonal array. Accordingly, each of the structures present on commercial tinplate could be placed in one of these three classifications.

Laboratory runs in the flow-melting simulator

Several runs were made using different electrical currents, process times and types of material (*i.e.*, steel thickness and tin coating). The quenching temperature was also varied. The laboratory flow-melting simulator allowed us to follow the intermetallic growth as a function of time. Melting was determined by visual inspection. The curve of the amount of intermetallic versus time was found to be sigmoidal (Fig. 5).

The experimental data were fitted with an empirical sigmoidaltype curve (Boltzman's equation), whose mathematical expression had four adjustable parameters:



Figure 7 -Characterization by XRD. Samples prepared at different process



Figure 8 -Intermetallic evolution for different tin coating thicknesses.



In our case, the number of parameters was reduced to three because A_1 , representing the initial amount of intermetallic, was zero.

The different zones of the intermetallic growth curve (Fig. 5) can be interpreted by taking into account the published results on the diffusion mechanism under isothermal conditions.^{5, 7-9,10,12-14} Tin diffusion occurred through the lattice and grain edges of iron, gradually transforming the matrix into intermetallic material. At the begining of the flow-melting process (a non-isothermal process), intermetallic crystallites were formed at a very low rate, primarily through the diffusion mechanism along grain edges, which are the most accessible routes, and therefore the fastest means of diffusion.¹³ Further, this intermetallic layer also acted as a barrier to further intermetallic formation. When temperature was close to the melting point of tin, the continuity of the Fe-Sn interface improved, increasing the contact area and, at the same time, the mobility of tin atoms. This facilitated the interdiffusion of tin and iron and consequently the intermetallic growth rate increased. At this time, the barrier effect of the intermetallic became sluggish, and the diffusion process occurred at a higher rate. Once the intermetallic layer thickness had increased sufficiently, the barrier effect again controlled the growth rate. Thereafter, the intermetallic amount increased very slowly with time, until it leveled off.

The evolution of the morphology of the intermetallic layer as a function of time was observed by SEM (Fig. 6). The intermetallic amounts and compositions of these samples are listed in Table 1. Figure 6b shows that nucleation of the intermetallic occurred



Figure 9 -Effect of the initial amount of intermetallic.

below the melting point of tin, although the steel substrate was not completely covered. When the melting point was reached, the amount of intermetallic increased (Table 1) and a continuous layer was formed (Fig. 6c). Small intermetallic crystallites grew at various angles forming a tight cross-linked network. Over longer treatment times, there was no appreciable change in the intermetallic structure, but diffusion process continued, leading to an increase in the amount of intermetallic material and the formation of larger crystals with rounded edges (Fig. 6d).

Samples processed over several time intervals were characterized by XRD. The XRD patterns of intermetallic are shown in Fig. 7. Analysis of the patterns showed that intermetallic FeSn_2 formed from the very beginning of the flow-melting process.

Effects of the process variables on intermetallic growth

Several experiments were carried out in order to determine the effect of process variables, such as tin coating thickness, initial amount of intermetallic, quenching temperature and heating rate, on the amount of intermetallic formed.

Tin coating thickness. Runs were performed using samples with different tin coating weights (2.8, 5.6 and 8.4 g/m²). Heating rates were similar and lower than those in production. Figure 8 shows the plot of the intermetallic weight formed as a function of time for different tin coatings at a heating rate of 46.9 C°/sec (84.4 F°/sec), while Table 2 shows the effect of heating rate for different tin coating thicknesses. Slight differences in the intermetallic amount were observed over a wide range of tin coating thicknesses. The same behavior was observed at both low and high heating rates. However, at longer treatment times (at high temperatures) (~4 to 5 sec), the amount of intermetallic formed increased with increasing

Table 2Effect of Tin Coating Thickness on Intermetallic Growth Using Different Average Heating Ratesa(Time to reach 0.6 g/m² alloyed tin)

	Times @ 0.6 g/m ² alloyed tin (sec)				
Tin coating thickness, g/m ²	$\beta = 13.1 \text{ C}^{\circ}/\text{sec}$ (23.6 F°/sec)	$\beta = 37.9 \text{ C}^{\circ}/\text{sec}$ (68.2 F°/sec)	$\beta = 46.9 \text{ C}^{\circ}/\text{sec}$ (84.4 F°/sec)		
2.8	14.5	5.1	4.4		
5.6	14.5				
8.4	14.4	5.0	4.4		

^a Defined as $\beta = (232 - 35)C^{\circ}/t_{\text{fusion}}$. (t_{fusion} in sec).

Table 3 Effect of Heating Rates on Intermetallic Growth Rates

Average besting rate	Total tin, g/m²	@ 0.6 g/m ² alloyed tin		
C°/sec (F°/sec)		Average rate, g/m²/sec	Temperature, °C (°F)	Time, sec
8.6 (15.5)	2.88	0.025	237 (459)	23.8
18.3 (32.9)	2.88	0.051	247 (477)	11.7
24.3 (43.7)	3.06	0.072	237 (459)	8.3
30.3 (54.5)	2.88	0.083	254 (489)	7.2
35.8 (64.4)	3.06	0.098	252 (486)	6.1
49.3 (88.7)	3.06	0.130	261 (502)	4.6

* The average growth rate is the amount of intermetallic that has formed (0.6 g/m² alloyed tin) divided by the time required to form that amount.

tin coating thickness (Fig. 8). These results suggest that for process conditions, the intermetallic content was practically independent of the tin coating thickness, and were in agreement with those published by Hoare, *et al.*⁴ These authors observed that for any given flow-melting conditions and with tin coating weights of from 5.6 to 22.4 g/m², the amount of alloy formed increased slightly with increasing total tin. This effect was only obvious at higher temperatures, however, and was not significant at reaction temperatures within the range normally used in industrial practice. For very thin coatings, under 3 g/m², a significant relationship existed between the intermetallic formed and total tin.

Initial amount of intermetallic material. Runs using samples with and without intermetallic material, taken from the same coil, were performed in order to determine whether the initial amount of intermetallic influenced the growth rate. These experiments are relevant because of the subsequent processes that tinplate undergoes, such as lacquering and curing operations. The original matte tinplate was exposed to a heating process in order to obtain samples with a certain initial amount of intermetallic. The treatment consisted of processing the samples with a current of 140 A for 40 sec, and cooling down by free convection in air at room temperature. Several of these samples were analyzed in order to assure that the amount of intermetallic was constant. The initial content of the alloyed tin was 0.25 g/m².

Both types of samples were treated in the flow-melting simulator under identical conditions of heating rate and quenching temperature. Figure 9 shows that the presence of an intermetallic layer delayed the beginning of the reaction and decreased the growth rate. The lag in the growth of the intermetallic can be explained by taking into account what was described earlier. The existence of the thin layer of intermetallic circumvented direct contact between iron and tin. Since atoms should diffuse through this barrier before contact, the increase in the amount of intermetallic occurred later that in the case of tinplate without the initial intermetallic layer.



Figure 10 -Morphology of the intermetallic layer formed during the reflow process from different substrates: (a) substrate with no alloyed tin, (b) substrate with 0.25 g/m² alloyed tin.

Before attempting to explain the final quantity of alloy, one important consideration must be emphasized. In the intersection of both curves (Fig. 9), the intermetallic content and temperature of both samples are the same. From this point on, it would be expected that the intermetallic growth would follow the same pathway. Since this did not occur, it is evident that intermetallic growth depended not only on the initial conditions but also on the pathway along which it is formed.

Figure 10 shows the SEM micrographs for both samples with similar amounts of intermetallic material (~ 0.25 g/m²). The intermetallic structure is totally different. When there is no initial intermetallic on the substrate, the structure is the typical cross-linked network, while an initial amount of intermetallic material on the substrate leads to a layer consisting of small columnar crystallites.

The first 0.25 g/m² of the intermetallic layer was formed under different heating rates on both samples, *i.e.*, they followed completely different pathways. Based on what was seen previously, the intermetallic growth rate should be different, and in fact this is what was observed (Fig. 9).

Quenching temperature. In order to determine the effect of quenching temperature on the amount of intermetallic formed during reflow, different materials were tested (tin coating contents of 2.8 and 8.4 g/m²) varying only the temperature of the water in the quenching tank over the range of 25 to 85° C (77 to 185° F). We



Figure 11 -Effect of the heating rate on the intermetallic growth.

also tried quenching in air (27°C; 81° F), cooling the probes by free convection.

In both materials, a tiny increase, less than 10%, in intermetallic content was observed with increasing quenching temperature. When the probe was air-cooled, its temperature decreased more slowly, and therefore the reaction was not immediately "frozen in place." This led to the formation of a greater amount of intermetallic material. Taking into account the dispersion of alloyed tin values however, it can be said that the amount of intermetallic formed was independent of quenching temperature.

Heating rates. The curves in Fig. 11 show the amount of intermetallic formed as a function of time for different average heating rates. While the heating rate increased, the time required to fuse the tin was reduced and the final amount of intermetallic decreased. These results are in good agreement with those published by other authors within the temperature range employed in this study.^{4,5,8,10,11} They reported that, at temperatures higher than 300°C (572°F), the growth rate arrest was followed by a slower growth process. This arrest was much more marked for lower heating rates and depended on the exposed iron.

Table 3 lists the values of the average growth rate as a function of heating rate. Broadly, the higher the heating rate, the lower the intermetallic formed at the same temperature and the higher the average growth rate. This observation agrees with those published by other authors, and suggest that there is a factor other than time and temperature that affects the amount of alloy formed.^{5,8,10,11}

Previously, it has been shown that when the heating rate was within the range of that in production (\sim 35 C°/sec; 63 F°/sec), the tin coating thickness did not influence intermetallic growth. For this reason, it can be said that heating rate determined the intermetallic content. This implies that at any given values of heating rate and process time, it is possible to find an expression to estimate the intermetallic content.

Conclusions

The main points developed in this paper allow us to conclude that:

- 1. The intermetallic compound formed is mainly FeSn₂.
- 2. The results show that the intermetallic compound begins to form below the fusion temperature of tin (232°C; 450°F).
- 3. The evolution of the FeSn₂ layer during flow-melting can be described in terms of a diffusion-type mechanism.
- 4. The amount of the intermetallic formed on tinplate during the reflow process varies strongly with heating rate, and is practically independent of the tin coating content (2.8 to 8.4 g/ m²) and the quenching temperature (25 to 85°C; 77 to 185°F).
- 5. Additional measurements and further mathematical treatment of the data could lead to an expression to estimate the amount of intermetallic based on process time and heating rate. Furthermore, this expression could be related to operational variables, including strip speed, voltage and the dimensions of the steel strip. Ultimately, it could be used to develop a control loop for the reflow tower.

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