# A Comparative Study of Halogen & Methanesulfonic Acid Electrotinning Processes

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The characteristics of a typical halogen and a patented methanesulfonic-acid-based electrotinning process were studied, using laboratory tests. The stability of the bath and its corrosiveness toward the steel substrate were evaluated simultaneously by a "spinning disc" experimental technique. The results show that the MSA bath is very stable, with a low oxidation rate of stannous ions, but is much more corrosive to the steel substrate. The effects of operating conditions, such as line speed and current density, on the plating efficiency, coating morphology and preferred crystal orientation were investigated, using a rotating cylinder cathode. Comparison of the plating efficiencies obtained from the rotating cylinder cathode and production identified a window of test conditions that is representative of production conditions. Within this window, the MSA process offers a higher plating efficiency at high current densities, but different microstructure and preferred crystal orientation compared with those of the halogen process. The coating morphology in the MSA bath also exhibits a greater variation at low current densities, resulting in a narrower operating window. In both processes, the grain size increases in the directions parallel as well as normal to the steel substrate. This three-dimensional grain growth is accompanied by a continuing change in crystal orientation, suggesting that recrystallization takes place during these two electrotinning processes.

The halogen electrotinning process, developed by E.I. du Pont de Nemours & Co.<sup>1</sup> and Weirton Steel Co., has been used successfully in the production of tin plate in continuous steel strip plating lines for more than 50 years. Because of increasing environmental concerns about the ferrocyanidecontaining sludge generated by the halogen process, users of



*Fig. 1—Schematic top view of concentric plating cell with rotating cylinder cathode and insoluble anode.* 

the process are considering other, environmentally friendly processes. The methane-sulfonic acid-(MSA) based process has been used for years in the electronics industry and has been developed recently as a viable alternative for continuous steel strip plating lines.<sup>2-4</sup> In addition to being influenced by the proprietary chemical additives in MSA baths, the plating efficiency and the coating quality also depend on the operating conditions of line speed and current density.<sup>5,6</sup> It was necessary, therefore, to compare the characteristics of these two processes under the operating window of a halogen line, where the steel strip travels at speeds between 2 and 10 m/s (400 and 2,000 fpm) and where the current density can vary from 11 to 65 A/dm<sup>2</sup> (100 to 600 A/ft<sup>2</sup>) to encompass the product mix. The hydrodynamic conditions created by the fast-moving steel strip could not be simulated easily in a laboratory test. Accordingly, for a reasonable comparison, it was also desirable to establish a correlation between the conditions of a laboratory test and those of production.

# Experimental Procedure

## Plating Bath Makeup

A patented MSA process,<sup>7</sup> was selected for this study. The bath consisted of 50 mL/L stannous methanesulfonate,<sup>a</sup> 30 mL/L methanesulfonic acid,<sup>b</sup> 100 mL/L grain refiner,<sup>c</sup> and 20 mL/L anti-oxidant.<sup>d</sup> Because the grain refiner has a cloud point of 55 °C, the MSA bath was evaluated at 52 °C (125 °F).

The halogen bath consisted of 16.5 g/L stannous fluoride  $(SnF_2)$ , 44.3 g/L stannic chloride  $(SnCl_4 \cdot 5H_2O)$ , 43.4 g/L sodium bifluoride  $(NaHF_2)$ , 21.5 g/L sodium hydroxide

<sup>a</sup> Ronastan TP Tin Concentrate 300, LeaRonal

<sup>b</sup> Ronastan TP acid 70, LeaRonal

° Ronastan TP additive, LeaRonal

<sup>d</sup> Ronastan TP anti-oxidant, LeaRonal



Fig. 2—Distribution of primary current density along normalized width  $(Z/Z_{max})$  of the rotating cylinder cathode.



Fig. 3-Effect of temperature on bath conductivity.

(NaOH), 3 g/L sodium ferrocyanide (Na<sub>4</sub>Fe(CN)<sub>6</sub>  $\cdot$  10H<sub>2</sub>O), often referred to as Addition Agent 55, and 2 mL/L brightener, known as Addition Agent 20. The bath concentrations were within the typical ranges for halogen lines.<sup>8</sup>

The halogen process is often operated at 60 to 70 °C because of its low conductivity and/or other constraints from production (such as water balance), therefore, the halogen bath was evaluated at 60 °C (140 °F).

The conductivity of the baths was measured using a conductance meter,<sup>e</sup> and the kinematic viscosity was measured using a glass capillary kinematic viscometer according to ASTM Standard D455-88.

# Bath Stability/Corrosiveness: Spinning Disc Experiment

In a halogen line, the steel strip is plated only on the bottom side as it travels through the horizontal plating cells. As a result, the topside of the steel strip is subject to corrosion by the plating solution in the cells on the first tier of the halogen line. The dissolved iron ions greatly increase the oxidation rate of the stannous ions in the halogen bath. A "spinning disc" experiment was designed, therefore, for simultaneous evaluation of a plating bath for its corrosiveness toward the steel substrate, as well as its stability in the presence of the



Fig. 4-Effect of temperature on bath viscosity.

dissolved iron. Because iron is introduced through dissolution of the steel substrate by the plating bath, the resulting oxidation rate of stannous ions is intrinsic to the plating bath tested.

For the "spinning disc" experiment, a 700-mL plating bath was placed in a one-liter plastic beaker, heated and maintained at the test temperature by a constant-temperature water bath. The plating bath was sparged with air at 120 mL/min throughout the test period. The stannous ion concentration was measured by titration at the beginning of each test and every 30 min thereafter. The oxidation rate of stannous ions was determined by the decrease in concentration after two to four hr of testing.

Within each of the 30-min intervals, a 15-min corrosion test was conducted. A steel disc, 5.72 cm (2.25 in.) in diameter, was degreased, dried and weighed. Immediately prior to the test, the disc was electrolytically cleaned in an alkaline solution<sup>f</sup> (25 g/L, 82 °C), rinsed in distilled water, activated in a five-percent sulfuric acid solution and rinsed in distilled water. The disc was attached to the shaft of a rotator,<sup>g</sup> then immersed in the plating bath and spun at 3,500 rpm. After 15

<sup>e</sup> Model 35, Yellow Springs Instrument Co. <sup>f</sup> Pennwalt 92L



Fig. 5—Effects of current density and rotation speed on plating efficiency of the MSA bath.



Fig. 6—Effect of current density and rotation speed on plating efficiency of the halogen bath.



*Fig.* 7—*Comparison of plating efficiency between production line trial and rotating cylinder cathode in the halogen bath.* 

min, the disc was removed from the bath, rinsed in distilled water, dried in acetone vapor and weighed again. The corrosion rate was determined by the weight loss.

#### Electroplating: Rotating Cylinder Cathode

A rotating cylinder cathode (RCC) was selected for this study because it provides a well-defined hydrodynamic condition for mass transfer.<sup>9</sup> Figure 1 shows the layout of the concentric cylindrical electrodes in the plating cell. The plating cell consisted of a two-liter plastic graduated cylinder cut to 920 mL, 20 cm tall. The inside diameter of the cylinder was 8.1 cm (3.18 in.). The cathode was a steel coupon, 2.86 x

Table 1 Concentration, Mobility & Transport Number For Ionic Species in MSA Bath					
Ions	Conc., C	Mobility, <i>u</i>	Transport		
	mol/L	x 10 <sup>-4</sup> cm <sup>2</sup> /sV	number, t*		
$Sn^{+2}$	0.13	2.3	0.035		
$H^+$	0.34	36.3	0.713		
MS <sup>-</sup>	0.60	7.3	0.252		
$*t = \frac{u \int z_j / C_j}{1 - \frac{u}{2}}$					

*	+	_				·
	ij	_	2	$u_k$	$ z_k $	$C_k$
				k	•~k•	- k

Table 2
Concentration, Mobility & Transport Number
For Ionic Species in Halogen Bath

Ions	Conc., C	Mobility, u	Transport
	mol/L	x 10 <sup>-4</sup> cm <sup>2</sup> /sV	number, t
$Na^+$	1.262	5.19	0.4744
$H^+$	0.0002	36.3	0.0005
F-	0.276	5.7	0.1137
Cl <sup>-</sup>	0.506	7.91	0.2898
$HF_2^-$	0.094	6.0*	0.0408
SnF <sub>3</sub> <sup>-</sup>	0.106	2.3*	0.0176
$SnF_6^{-2}$	0.127	2.3*	0.0423
$Fe(CN)_{6}^{-4}$	0.006	11.51	0.0207

\* Estimated values



*Fig.* 8—*Comparison of plating efficiency within the window representative of production conditions.* 

5.70 cm (1.125 x 5.70 in.), wrapped around the shaft, 1.93 cm (0.76 in.) in diameter, of the rotating cylinder electrode.<sup>g</sup> The anode was a cylinder made of platinum mesh, 4.95 cm (1.95 in.) in diameter and 3.02 cm (1.19 in.) tall. A baffle was placed inside the plating cell so that the rotation speed could reach 3,000 rpm without causing a vortex. Plating current was supplied by a 10-ampere DC power supply.<sup>h</sup>

The symmetrical arrangement of the electrodes in the plating cell allows calculation of the primary current density distribution on the cathode. A finite element simulation package,<sup>i</sup> was used for this calculation. Figure 2 shows that the primary current density distribution on the RCC is almost a symmetrical U-shape. It is fairly uniform-about 90 percent of the average current density  $(i_{ave})$  in the middle 50 percent of the cathode, but much higher, more than 120 percent of the average, within five percent width from the edges. The actual coating weight distribution measured by Xray fluorescence showed a similar U-shape at low currents and/or high rotation speeds, but became more uniform over the entire width at high currents and/or low rotation speeds. Therefore, the discussion on morphology and crystal structure is based on examination of coating from the middle section of the coupon.

The steel coupon was weighed first and then mounted on the rotating cylinder cathode. The assembled electrode was electrolytically cleaned, rinsed in hot water, activated in a five-percent sulfuric acid solution at ambient temperature,

g Model AFASR, Pine Instrument Co.

<sup>h</sup> Model MSK 10-10M, Kepco Inc.

<sup>i</sup> FIDAP, Fluent Inc.

Table 3
Properties of the Two baths
at Respective Test Temperatures

Properties	Halogen	MSA
Temp °C	60	52
Conductivity, mS/cm	129	176
Kinematic Viscosity Centistokes	0.524	0.626
Density, g/mL	1.06	1.04
Stannous ion conc. molar	0.106	0.132
Transport number for Sn <sup>+2</sup>	0.0176	0.035
pH	3.4	0.47



Fig. 9-Effect of current density and rotation speed on morphology of tin deposited from the halogen bath.

and rinsed in hot water again. After the assembly was immersed in the plating solution and set in rotation at a chosen speed, from 0 to 3,000 rpm, a predetermined current, from 0.1 to 10 A, was applied until a total charge of 30 coulombs was transferred. This would produce an average coating weight of 11.16 g/m<sup>2</sup> (1.0 lb/BB [Base Box])at 100 percent plating efficiency. After plating, the assembly was rinsed in hot water; the steel coupon was then dismounted, quenched in acetone, dried in air and weighed again. The plating efficiency was calculated from the weight gain.

The coating weight was measured by X-ray fluorescence (XRF).<sup>j</sup> The coating morphology was examined by scanning electron microscopy (SEM).<sup>k</sup> To study the growth of tin crystals during deposition, coated coupons were fractured in liquid nitrogen and the cross sections were examined by SEM. The crystallographic texture of the coating was determined by X-ray diffraction<sup>m</sup> (XRD) using an X-ray diffractometer with Cr K $\alpha$  radiation of 2.291 Å wavelength. The preferred crystal orientation was determined by using the inverse-pole figure technique.<sup>10,11</sup>

## Results & Discussion

# Plating Bath Chemistries & Properties

In the MSA bath, the grain refiner and anti-oxidant were nonionic. There were, therefore, only the three ionic species of hydrogen ion, stannous ion and methanesulfonate (MS<sup>-</sup>) in the bath. Table 1 shows the concentrations, the standard values of mobility<sup>12</sup> and the calculated transport numbers of these three species. According to the transport numbers, 71.3 percent of the current in the bulk electrolyte is carried by hydrogen ions migrating to the cathode, while only 3.5 percent is carried by stannous ions. The remaining 25.2 percent is carried by methanesulfonate ions migrating to the anode.

The chemistry of the halogen bath is much more complicated. Based on the assumption that the stannous and stannic ions exist primarily in the forms of  $\text{SnF}_3^-$  and  $\text{SnF}_6^{-2}$  complexes,<sup>1,8</sup> the equilibrium concentrations of all the species (including the non-ionic HF) were calculated. Then, with the estimated mobilities for the complex ions, the transport numbers were calculated. Table 2 shows the results of these calculations.

Unlike the MSA bath, the halogen bath contained excess amounts of non-reactive ions in Na<sup>+</sup>, Cl<sup>-</sup> and F<sup>-</sup> that carry the majority of currents in the bulk electrolyte. The two reactive ions, stannous and hydrogen, account for only 1.76 percent and 0.05 percent of the total current, respectively. Thus, the majority of the currents are carried by diffusion of stannous

<sup>&</sup>lt;sup>j</sup> Model SFT-157, Seiko Instruments

<sup>&</sup>lt;sup>k</sup> Model 3200-C, AMRAY

<sup>&</sup>lt;sup>m</sup> Model N8711, DEXCO



statution observations

Fig. 10-Effect of current density and rotation speed on morphology of tin deposited from the MSA bath.

ions through the concentration gradient across the boundary layer. Since the migration current carries the negatively charged  $SnF_3^-$  complex away from the cathode, diffusion would be even more critical for the halogen process.

Figure 3 shows the conductivity of the two baths as a function of temperature. While the conductivity for both baths increases linearly with increasing temperature, the



Fig. 11—Comparison of the operating window of the two processes.

conductivity of the MSA bath is about 60 mS/cm higher than that of the halogen bath at a given temperature between 35 and 60 °C. The halogen process, therefore, generates more heat and would be operated at a higher temperature in a plating line without appropriate cooling capability. At their respective test temperatures, the conductivity is 176 mS/cm for the MSA bath and 129 mS/cm for the halogen bath.

Figure 4 shows the viscosity of the two baths as a function of temperature. While the viscosity of both baths decreases with increasing temperature, similar to pure water, the viscosity of the halogen bath is only slightly lower than that of the MSA bath at a given temperature between 40 and 60 °C. However, at their respective test temperatures, the viscosity is 0.524 centistokes for the halogen bath and 0.626 centistokes for the MSA bath. A lower viscosity generally enhances the rate of mass transfer and increases the diffusion-limiting

Table 4 Results of Spinning Disc Experiment				
Baths	Oxidation Rate of Stannous Ions g/(L · hr)	Corrosion Rate of Steel Disc g/(m <sup>2</sup> · hr)		
Halogen with AA-55	0.45	3.0		
Halogen w/o AA-55	3.30	4.4		
MSA	-0.07	34.9		



Fig. 12-Effect of rotation speed on crystal orientation of tin plated at (a) 18 A/dm<sup>2</sup>, and (b) 42 A/dm<sup>2</sup> in the MSA bath.

current density. The densities of the baths are insensitive to the change of temperature within the range studied (*i.e.*, 1.06 g/mL for the halogen bath and 1.04 g/mL for the MSA bath).

The properties of these two baths at their respective test temperatures are summarized in Table 3. As will be discussed later, the higher operating temperature of the halogen bath offsets the effect of its lower stannous ion concentration on the diffusion-limiting current density by decreasing the viscosity and increasing the diffusion coefficient.

#### Bath Stability/Corrosiveness

Table 4 shows the results of the spinning disc experiment. For the halogen bath with sodium ferrocyanide (AA-55), the oxidation rate of the stannous ions is 0.45 g/(L · hr), and the corrosion rate of the steel disc is 3.0 g/(m<sup>2</sup> · hr). In the absence of ferrocyanide, the corrosion rate of the steel disc increases to 4.4 g/(m<sup>2</sup> · hr) but the oxidation rate of the stannous ion increases drastically to 3.3 g/(L · hr). This comparison clearly demonstrates the deleterious effect of iron on the stability of the halogen bath, and the importance of ferrocyanide, which removes all ferrous and ferric ions by forming sodium ferrous ferrocyanide and sodium ferric ferrocyanide precipitates. These ferrocyanide precipitates and the precipitate of sodium fluostannate ( $Na_2SnF_6$ ), generated by the oxidation reaction of stannous ions, form a heavy sludge at the bottom of the plating cells and the recirculation tank. Consequently, a halogen line must be shut down approximately every eight weeks to remove the accumulated sludge.

For the MSA bath, the oxidation rate of the stannous ions is extremely low, about 0.07 g/(L  $\cdot$  hr), but the corrosion rate of the steel disc is much higher at 34.9 g/(m<sup>2</sup>  $\cdot$  hr). This low oxidation rate allows the use of filtration to continuously remove the precipitate of stannic oxide (SnO<sub>2</sub>), thus eliminating the sludge operation. This low oxidation rate in the MSA bath, however, requires the use of several insoluble anodes with the soluble tin anodes normally used in a halogen line so that the stannous ion concentration can be maintained. Its high corrosiveness to the steel substrate requires constant removal of dissolved iron from the bath and protection of the structure and equipment in the production line.



Fig. 13—Effect of rotation speed on crystal orientation of tin plated at (a) 18 A/dm<sup>2</sup>, and (b) 42 A/dm<sup>2</sup> in the halogen bath.



*Fig.* 14—*Effect of plating time on crystal orientation of tin deposited at 42 A/dm<sup>2</sup> and 2,000 rpm in the MSA bath.* 

### PlatingEfficiency

Figure 5 shows the plating efficiency in the MSA bath as a function of the current density and the rotation speed. Without agitation of the electrolyte (i.e., at 0 rpm), the plating efficiency decreases monotonically from 97 to 25 percent as the current density increases from 0.6 to  $60 \text{ A/dm}^2$  (5.6 to 562 A/ft<sup>2</sup>). As the rotation speed increases from 0 to 3000 rpm, the plating efficiency decreases from 97 to 27 percent at the extremely low current density of 0.6 A/dm<sup>2</sup>. As the current density increases from  $0.6 \text{ A/dm}^2$ , the plating efficiency increases sharply, reaches a maximum above 95 percent, then gradually decreases. Depending on the rotation speed, the maximum plating efficiency occurs somewhere between 12 and 30 A/dm<sup>2</sup>. At current densities less than about 18 A/dm<sup>2</sup>, the plating efficiency decreases as the rotation speed increases from 500 to 3000 rpm. This decrease in plating efficiency is caused by the cathodic reduction of dissolved oxygen, as its diffusion limiting current density increases with increasing rotation speed. With limited solubility, however, oxygen reduction becomes insignificant as the applied current density increases. Above 30 A/dm<sup>2</sup>, the plating efficiency increases as the rotation speed increases from 0 to 2,000 rpm, then slightly decreases as the rotation speed further increases to 3,000 rpm.

Figure 6 shows the plating efficiency in the halogen bath as a function of the current density and the rotation speed. At 0 rpm, the plating efficiency also decreases monotonically from 94 to 17 percent as the current increases from 0.6 to 60 A/dm<sup>2</sup>. Unlike the MSA bath, however, the plating efficiency at 0.6 A/dm<sup>2</sup> decreases only slightly from 95 to 90 percent as the rotation speed increases from 0 to 3,000 rpm. Moreover, between 500 and 3,000 rpm, the plating efficiency remains relatively constant as the current density increases from 0.6 to about 18 A/dm<sup>2</sup>, then begins to decrease gradually as the current density increases further. The current density, at which the plating efficiency begins to decrease, increases as the rotation speed increases. Above 30 A/dm<sup>2</sup>, the plating efficiency increases as the rotation speed increases.

To compare these two processes in a more meaningful way, it is necessary to identify a window of test conditions that is representative of the production line. Figure 7 compares the plating efficiencies in the halogen bath from the RCC experiments and those obtained from a production trial.



Fig. 15—Three-dimensional crystal growth of tin deposited at  $42 \text{ A/dm}^2$  and 2,000 rpm in the MSA bath.

It can be seen that the current density has the same effect on the plating efficiency (*i.e.*, the plating efficiency decreases at the same rate as the current density increases. Moreover, the plating efficiencies from production at 3 to 9 m/sec (600 to 1800 ft/min) linear speed fall in line with those from the RCC experiments with 500 to 2,000 rpm rotation speed. Thus, it appears that the operating conditions in the halogen line could be reasonably simulated by the rotating cylinder setup used in this study.

Figure 8 compares the plating efficiency of these two processes at two representative rotation speeds of 1,000 and 2,000 rpm. It can be seen that the plating efficiency in the MSA bath could be up to 10 percent higher than that of the halogen bath at high current densities (*i.e.*, above 30 A/dm<sup>2</sup>). The plating efficiency in the halogen bath is higher, however, at low current densities (*i.e.*, below 12 A/dm<sup>2</sup>). (Note that redissolution of the tin coating as the steel strip travels through the plating efficiency with the MSA bath.) The higher plating efficiency and the higher conductivity of the MSA bath would result in less power consumption.

#### Coating Morphology

Figure 9 shows the SEM photomicrographs of the coatings plated in the halogen bath as a function of the rotation speed (X-axis) and the current density (Y-axis). In general, the morphology of the coatings could be divided into two groups diagonally in Figure 9. In the lower right half (i.e., high rotation speeds and low current densities), the deposits are compact, fine grains with little variation. In the upper left half (i.e., low rotation speeds and high current densities), the deposits are predominantly columnar dendritic.

Figure 10 shows the morphology of the coatings plated in the MSA bath. A similar effect on morphology can be seen from the rotation speed and the current density. There is, however, a greater variation in morphology within the finegrain region. For instance, at 6 A/dm<sup>2</sup>, the coating is rough at 0 rpm and becomes angular as the rotation speed increases to 500 rpm. In addition, at 0.6 A/dm<sup>2</sup>, the deposit gradually becomes less compact with increasingly visible porosity as the rotation speed increases to 2,000 rpm. This increase in porosity parallels the decrease of plating efficiency as shown in Fig. 5.

The dependence of coating morphology on the current density and agitation (*i.e.*, rotation speed), observed from these two baths is similar to that found with a SnCl<sub>4</sub> electrolyte by Lempereur *et al.*<sup>13</sup> and that found with a phenolsulfonic acid (PSA) based electrolyte by Longley *et al.*<sup>14</sup> As suggested by Winand, <sup>15</sup> this dependence could be related to one parameter, the ratio of the applied plating current density and the diffusion-limiting current density (*i*<sub>1</sub>), which is given by:

 $i_L = nFCk$ 

where n is the number of electrons transferred, F the Faraday constant, C the concentration of reactive ions in the bulk electrolyte, and k the mass transfer coefficient.

The mass transfer coefficient depends on the hydrodynamic conditions. In the rotating cylinder set-up used in this study, it can be correlated by the relationship developed by Eisenberg:<sup>9</sup>

$$k = 0.0791 V Re^{-0.3} Sc^{-0.64}$$

where *V* is the peripheral speed of the cylinder, *Re* the Reynolds number based on the cylinder diameter d (*i.e.*, Re = dV/v), and *Sc* is the Schmidt number (= v/D) of the electrolyte. By substituting *Re* and *Sc* with their definitions, the above equation becomes:

$$k = 0.0791d^{-0.3}V^{0.7}v^{-0.34}D^{0.64}$$

where D is the diffusion coefficient, and v the kinematic viscosity. In general, the diffusion coefficient increases with increasing temperature, while the kinematic viscosity decreases with increasing temperature. Thus, the effects of concentration, agitation and temperature on coating morphology could be reflected through the diffusion-limiting current density:

 $i_L \propto CV^{0.7}T^{0.98}$ 

Therefore, increasing the stannous ion concentration, the rotation speed or the temperature, increases the diffusion limiting current density and widens the current range for a good coating. Apparently, the higher temperature of the halogen bath offsets the lower stannous concentration noted in this study. The MSA process would benefit from a grain refiner of a higher cloud point.

At a given rotation speed, the current density above which the deposit becomes dendritic is defined as the critical current density,  $i_C$  As shown in Fig. 11,  $i_C$  increases as the rotation speed increases in both baths, but is higher in the halogen bath at rotation speeds up to 2,000 rpm. Because the MSA bath has porous deposits and low plating efficiencies at current densities below 6 A/dm<sup>2</sup>, it has a narrower range of current density at a given line speed. For these reasons, the current density in the MSA process should be kept above 10 A/dm<sup>2</sup>, which may require shutting off plating cells for the production of light coatings. Moreover, because of the greater variation in coating morphology within the operating window, the MSA process could be problematic for production lines without looping towers to maintain the line speed.

Table 5 Determination of Preferred Orientation of Tin Crystals by Inverse-Pole Figure Technique

	Observed				
Plane	Intensity	A*	B**	A/B	C***
	cps				
(200)	76	78	95	0.83	0.10
(101)	269	280	83	3.38	0.39
(220)	656	726	33	22.00	2.53
(211)	226	251	61	4.12	0.47
(301)	0	0	18	0.00	0.00
(112)	580	712	30	23.74	2.74
(321)	501	622	29	21.45	2.47
(420)	208	269	33	8.15	0.94
(411)	63	82	33	2.48	0.29
(312)	50	67	100	0.67	0.08

\* Transparency corrected intensity,

$$A = Observed / (1 - e^{-2\left(\frac{\mu}{\rho}\right)w/\sin\theta}).$$

\*\* Theoretical relative random intensity,

$$B = \left|F\right|^2 p\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \, \cos \theta}\right).$$

\*\*\* Normalized intensity ratio (preferred orientation),

$$C = \frac{A}{B} / \sum \frac{A}{B}$$

Crystallography & Preferred Crystal Orientation From the peaks in X-ray diffraction spectra, all the deposits were identified as  $\beta$ -Sn, body-centered tetragonal. To quantify the relative importance of the 11 possible peaks between 40 and 150 degrees 2 $\theta$ , the inverse-pole figure technique was used. Table 5 shows an example for determining the preferred orientation by this technique. The observed intensity, already subtracted by the background intensity, was first corrected for the penetration depth of X-rays relative to the coating thickness and the diffraction angle (*i.e.*, transparency correction). Note that the degree of correction increases as the diffraction angle  $2\theta$  increases. The transparency-corrected intensity (A) was then compared with the peak intensity calculated from the random diffraction theory (B). The intensity ratios (A/B) of the primary and secondary pair of (200) - (400) were combined and represented by (200). Finally, the intensity ratios were normalized to give preferred orientations (C). Such a preferred orientation is essentially equivalent to "percentage of crystal grains" with a particular orientation parallel to the surface of the steel substrate.<sup>10</sup>

Figure 12a shows the preferred orientation of coatings plated at 18 A/dm<sup>2</sup> in the MSA bath as a function of the rotation speed. At 0 rpm, the dendrite is characterized by the preferred orientation of (200) with three times the theoretical intensity, followed by (220), (420), (101), etc. As the rotation speed increases to 500 rpm, (200) diminishes and (220) becomes the preferred orientation, accompanied by the emergence of (321) and (112). As the rotation speed further increases to 3,000 rpm, (112) gradually becomes the preferred orientation, primarily at the expense of (220). Compared with the coating morphology in Fig. 10, the diminishing of (200) coincides with the disappearance of dendrites.

Figure 12b shows a similar trend in the change of preferred

orientation with increasing rotation speed at 42 A/dm<sup>2</sup> in the MSA bath. The diminishing of (200) also coincides with the change in morphology occurring between 1,000 and 2,000 rpm. Also, within the dendritic region, (200) decreases slightly from 3 to 2.3 times the theoretical intensity as the rotation speed increases from 0 to 1,000 rpm. It appears that moving away from the mass transfer limit (*i.e.*, decreasing current density and/or increasing rotation speed), favors (112) orientation in the MSA bath.

Figures 13a and 13b show the preferred orientation under the same plating conditions from the halogen bath. One noticeable difference is the prevalence of (101) orientation immediately after the transition from dendritic to polycrystalline. At 18 A/dm<sup>2</sup>, (101) is four times the theoretical intensity at 500 rpm, but gradually decreases to equal theoretical intensity as the rotation speed increases to 2,000 rpm. In the meantime, (112) and (321) become the preferred orientations. At 42 A/dm<sup>2</sup>, (101) is more than five times the theoretical intensity with (112) as the only other preferred orientation at three times the theoretical intensity after the transition at 2,000 rpm.

Within the window of test conditions representative of production conditions (i.e., 500 rpm, 18 A/dm<sup>2</sup>, and 2,000 rpm, 42 A/dm<sup>2</sup>), the halogen process favors (101) and (112), while the MSA process favors (220), (321) and (112). This difference in preferred orientation could cause differences in reflectance and reflow characteristics. The results of an MSA trial conducted at a halogen line at Weirton Steel also indicated there was a difference in crystal orientation between these two processes.<sup>16</sup> The difference found on the light coatings of 1.1 and 3.3 g/m<sup>2</sup> (0.1 and 0.3 lb/BB [base box]) in the production trial was less, however, than what was found on the heavy coatings of 8.9 to  $11.2 \text{ g/m}^2$  (0.8 to 1.0 lb/ BB) in this study. It has been reported that, as the coating thickness increases, the coating roughness increases and the reflectivity decreases.<sup>17</sup> Nevertheless, the effect of coating weight was further studied by adjusting the plating time.

#### Electrocrystallization

Figure 14 shows the effect of plating time on the preferred crystal orientation of coatings plated at  $42 \text{ A/dm}^2$  and 2,000 rpm in the MSA bath. In the early stage of deposition, two seconds, the crystal orientation is fairly random, showing nine of the 10 orientations with (321), (112) and (220) as the three major orientations. As the plating time increases, the (220) orientation continues to increase to more than five times the theoretical intensity at the expense of other orientations except for (321) and (420), both of which remain constant.

Figure 15 shows the SEM photomicrographs of the cross sections from cryofractured samples. The grains are about 0.4  $\mu$ m thick and 1  $\mu$ m in diameter after two seconds of plating. They increase to about 2  $\mu$ m thick and 4  $\mu$ m in diameter after 10 sec; then to about 4  $\mu$ m thick and 5  $\mu$ m in diameter after 20 sec. The grain size increases not only in the direction of plating current, normal to the substrate, but also laterally, parallel to the substrate. While the increase in thickness is proportional to the plating time, the increase in diameter gradually slows, resulting in near-equiaxed grains. The same pattern of grain growth has also been observed on coatings plated from the halogen bath. This three-dimensional grain growth, accompanied by the continuing changes in preferred orientation, suggests that the deposited tin recrystallizes during the plating process.

An equiaxed grain has been observed in coatings plated in an MSA bath and a SnCl<sub>4</sub>/SnCl<sub>2</sub>/HCl bath by Colinet,<sup>18</sup> whereas a fibrous structure has been found in coatings plated in a stannous sulfate bath by Kaneko and Nezu.<sup>19</sup> Whether the deposited tin recrystallizes during subsequent plating may depend, therefore, on the process. As a result of the coatingweight dependence of the crystal orientation, it is necessary to specify the coating weight as well as the operating conditions in comparing the preferred orientation obtained from different processes.

#### Conclusions

- 1. The results of the spinning disc experiments show that the MSA bath is very stable with a low oxidation rate of stannous ions, but is much more corrosive to the steel substrate.
- 2. Comparison of the plating efficiencies obtained from the RCC tests and production identified a window of test conditions that is representative of production in a halogen line.
- 3. Within this window, the MSA process offers a higher plating efficiency at current densities above 30 A/dm<sup>2</sup>, but a lower efficiency at low current densities.
- 4. The coating morphology and preferred crystal orientation from the two baths are different, which could cause a difference in reflectance and reflow characteristics.
- 5. The coating morphology in the MSA bath also exhibits a greater variation with operating conditions, especially at current densities below 6 A/dm<sup>2</sup>. Thus, the MSA process has a slightly narrower window of operation.
- 6. Because of low plating efficiency and irregular morphology at low current densities, the current density for the MSA process should be kept above 10 A/dm<sup>2</sup>.
- 7. In both processes, the preferred crystal orientations depend on the coating weight as well as the operating conditions.
- 8. The three-dimensional grain growth, together with the continuing change in crystal orientation, suggest that recrystallization takes place during both processes.

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