Electrochemical Deposition of Sn/Zn Alloys

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Abstract.
A new proprietary process for deposition of tin/zinc alloys is described. The corrosion protective properties of tin/zinc alloys are highly correlated with the amount of alloying zing in the coating. The composition of the deposited alloys in the new process is constant between 20 and 25 wgt-% zinc when the current density is higher than 0.1 A/dm^2.
Compared to the state of the art, the improved alloying uniformity versus current density has been achieved without sacrificing the depositing rate. As a consequence, plating can be made at higher current density (less processing time) and still achieve maximum corrosion protection because alloy composition is independent on current density.

Introduction.
Both tin and zinc are widely used for the protection of steel against corrosion. Each has a different range of applications and they protect steel by different mechanisms. Tin is nobler than steel and, under ordinary atmospheric exposure, protects steel by forming a corrosion resistant envelope around it. However, rusting takes place in pinholes or imperfections in the tin coating, and is accelerated galvanically by the difference in potential between steel and tin. Zinc is less noble than steel and protects by a sacrificial action. Even when steel is exposed through faults in the coating, it is protected galvanically by zinc.

The protective properties of the two metals are nicely balanced in a tin-zinc alloy containing about 75 - 80 percent of tin (1). The coating protects steel by a sacrificial action similar to that of zinc. Consequently, steel does not rust through pinholes and yet the coating does not form voluminous white corrosion products as with zinc coatings. Deposits may be plated onto parts, which are subsequently bent, crushed or deformed in their regular service life, without substantial reduction in corrosion protection. A Tin/zinc coating is crack free and has been reported to do better than zinc coatings in moist SO_2 testing.

Alloy compositions outside the above range, results in reduced corrosion resistance, especially if the tin content is higher than 80 percent. Additional data from accelerated corrosion test show that the resistance decreased significantly when the amount of alloying tin exceeds 20% by weight (Figure 1). The overall corrosion resistance of Sn/Zn coatings is highly dependent on the relation between alloy composition and current density. At present, electrochemical processes for deposition of tin/zinc coating shows high amounts of tin in low current density areas and high amounts of zinc at high current density.

This paper describes a new proprietary process for deposition of tin/zinc alloys from a neutral bath where the alloy composition is uniform from low to high current density, unlike past technology, which has been commercially marketed. Hence, the new process ensures optimal corrosion protection under a variety of plating conditions and especially for part of complex shapes.

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Results.

The new process for deposition of tin/zinc alloys with optimal alloy composition over a larger range of current densities is shown in Table 1. The alloy composition versus current density is shown in Figure 2. Obviously, the new process for Sn/Zn alloy deposition is not dependent on current density. The alloy composition is constant between 20 and 25 wgt-% Zn when current density is higher than 0.1 A/dm^2. For comparison, the alloy composition of an existing process versus current density is shown as a dashed line in Figure 2.

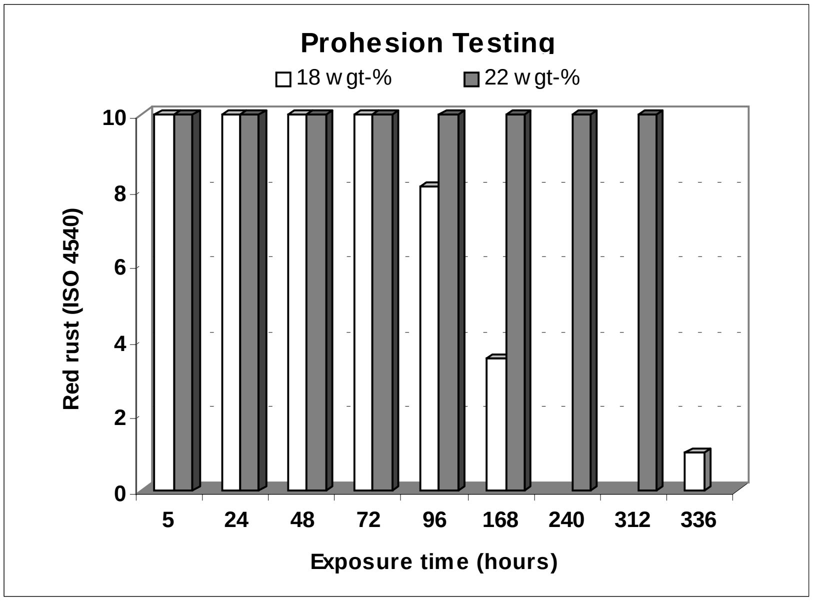

Figure 1. *Prohesion® testing. Amount of red rust according to ISO 4540 during accelerated corrosion testing of 5 µm thick Sn/Zn coatings (2).*

Metals:	Sn(2+) 22 g/L (range 20-24 g/L) added as $SnSO_4$
	Zn(2+) 5 g/L (range 4.5 – 6.0 g/L added as $ZnSO_4$
Complexant:	140 g/L (range 130 – 160 g/L)
Additives:	6 ml/L (range 4-8 ml/L)
Antioxidant:	1 g/L (range 1-2 g/L)
Current density:	0.1 – 4 A/dm2
Temperature:	Room temperature
Agitation:	Mild
Filtration:	Yes
Anodes:	Sn/Zn 70/30% alloy. Anode bags required

Table 1. *Process composition and operation conditions for a new proprietary process for deposition of Sn/Zn alloys.*

The new proprietary Sn/Zn alloy process is ensuring optimal alloy composition in areas exposed to low and high current densities, which no commercial available process has been able to do today. The formation rate of the new process is comparable depositions rate of commercially available processes (Figure 3).

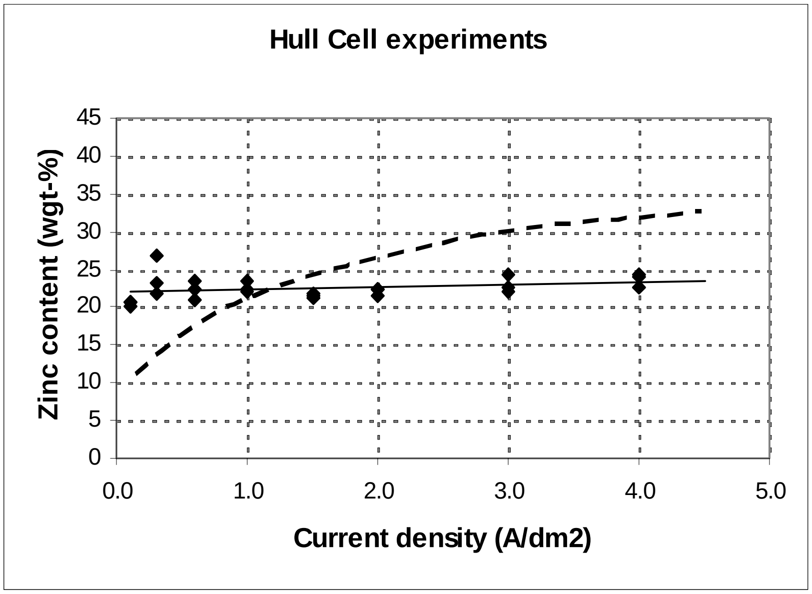

Figure 2. *Alloy composition versus current density compared to the state of the art (dashed line).*

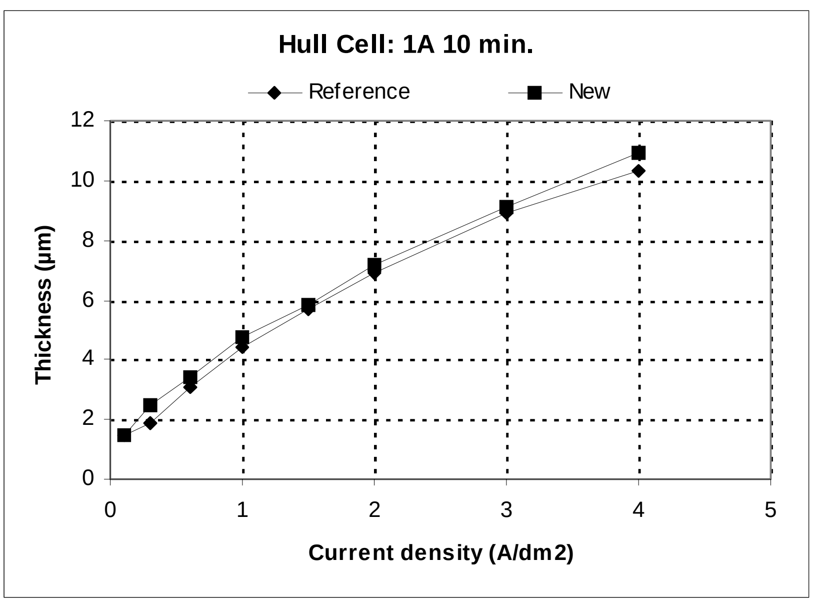

Figure 3. *Coating thickness versus current density compared to the state of the art (reference).*

Complexant.
The Complexant developed for this new process ensures the composition of the alloying elements in the coating is close to optimal conditions and that the composition is fairly independent of current density. The operational range is 130 – 160 g/L, with a recommended concentration between 140 – 150 g/L (Table 2).

Wgt-% Zn	Hull Cell Current density (A/dm^2)							
Complexant	0.05	0.15	0.30	0.50	0.75	1.00	1.50	2.00
120 g/L	16	21	22	22	22	22	22	22
126 g/L	18	21	21	22	22	21	22	24
140 g/L	22	24	23	24	24	24	23	24
150 g/L	20	23	23	23	22	23	24	24
160 g/L	20	24	25	24	25	24	24	25

Table 2. *Alloy composition versus current density for various concentrations of Complexant. Hull Cell experiments at 0.5 A 10 minutes.*

Acidity (pH).
The operational pH range is 6.3 – 7.2 with a recommended adjustment between 6.6 and 7.0 (Table 3). Below the recommended lower limit, the amount of alloying zinc in low current density areas decreases. Little variation in alloy composition versus current density has been observed at pH values above the upper limited. However, if pH is too high precipitation phenomena occurs. Adjustment of pH is made with H_2SO_4 and NH_4OH.

The measurements of pH must be made with a pH-meter and prior to each measurement the calibration has to be checked. Exposed contact between the pH-probe and the electrolyte causes too low pH readings.

Wgt-% Zn	Hull Cell current density (A/dm^2)							
pH	0.05	0.15	0.30	0.50	0.75	1.00	1.50	2.00
6.0	16	22	26	26	24	24	24	25
6.3	20	24	25	23	24	24	25	25
6.6	21	24	23	24	24	24	23	24
6.8	20	22	23	22	23	24	23	24
7.0	19	19	21	22	25	22	24	24

Table 3. *Alloy composition versus current density for various adjustments of pH. Hull Cell experiments at 0.5 A 10 minutes.*

Additives.
The use of additives in the new process for Sn/Zn alloy deposition have two main objectives: first of all they ensure an uniform appearance of the alloy coating (main brightener) and secondarily they suppress the amount of tin in the coating at low current densities and enhance tin deposition at high current densities.

The additive system developed for the new Sn/Zn was optimized using a Taguchi L8 orthogonal array. The results regarding the theoretically best additive combination are compared to the best experimental results in Figure 4.

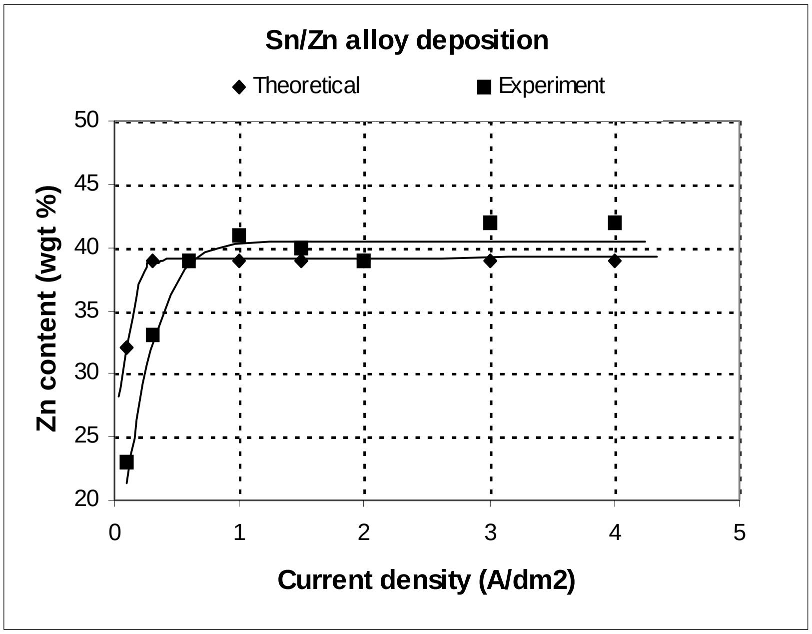

Figure 4. *Alloy composition versus current density for Taguchi calculated optimum and best experimental combination of additive system.*

Metal concentrations.

The operational range of metal concentrations is for Sn 20-24 g/L (optimal 22 g/L) and for Zn it is 4.5 – 6.0 g/L (optimal 5.0 g/L). The relation between alloy composition and current density for different concentrations of Sn and Zn is shown in Table 5 and 6.

As long as the ratio between the two metals (22 g/L versus 5 g/L) is constant, the relation between alloy composition and current density is not changed if the concentration of the two metals reached values below the operational range.

Wgt-% Zn	**Hull Cell current density (A/dm2)**							
Sn g/L	**0.05**	**0.15**	**0.3**	**0.5**	**0.75**	**1.0**	**1.5**	**2.0**
22.0	20	24	25	24	25	24	24	25
24.0	22	24	23	24	24	24	23	24

Table 5. *Amount of zinc in the coating versus concentration of electrolytic Sn(2+). The amount of electrolytic Zn(2+) is 5 g/L.*

Wgt-% Zn	**Hull Cell current density (A/dm2)**							
Zn g/L	**0.05**	**0.15**	**0.3**	**0.5**	**0.75**	**1.0**	**1.5**	**2.0**
4.6	21	23	22	24	23	24	24	24
5.0	23	25	26	25	25	25	26	27

Table 6. *Amount of zinc in the coating versus concentration of electrolytic Zn(2+). The amount of electrolytic Sn(2+) is 22 g/L.*

Barrel plating.

The alloy composition and plating rate of Sn/Zn alloys barrel plating in the new proprietary process has been investigated by plating of different sizes of nuts, bolts and washers. The average alloy composition after various plating conditions (current and time) and adjustment of pH is shown in Figure 5. A current of 6A corresponds to an average current density of $1A/dm^2$.

Within the recommended pH range, alloy composition is independent on current. As expected pH values at the lower operational range results in a small decrease in the amount of alloying zinc, especially at low current density (45minutes of plating at 4 A). Depending on current and process time, thickness ranging from 3µm to 20µm was measured.

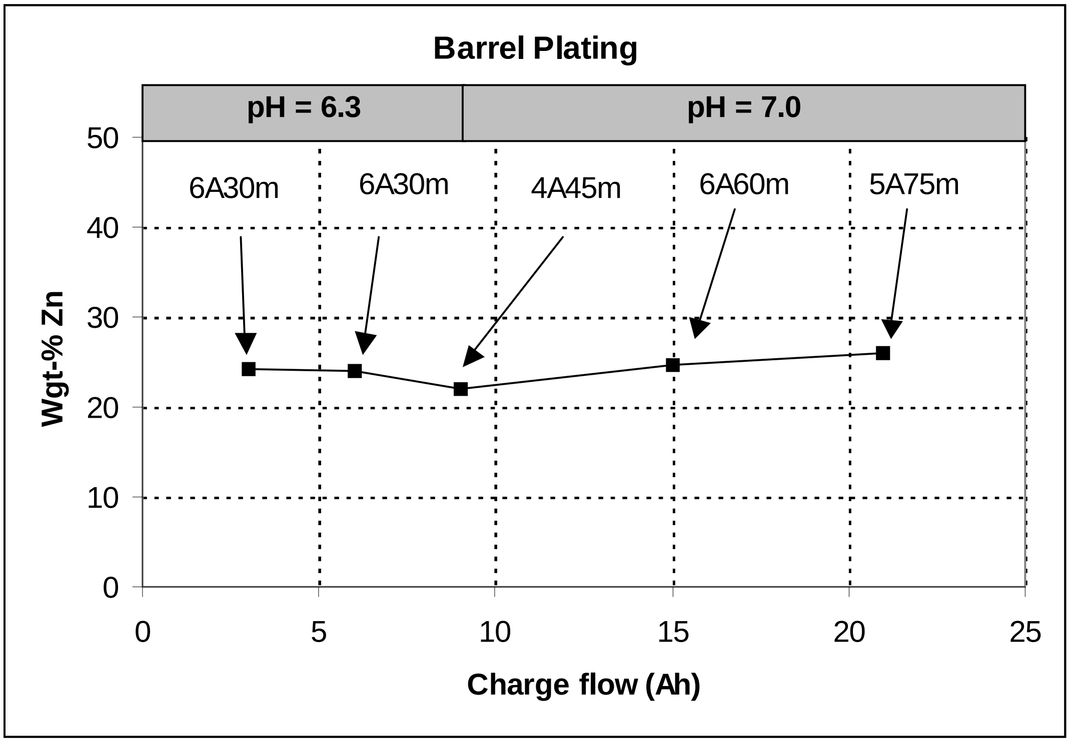

Figure 5. *Alloy composition of barrel plated nuts, screws and washers under various process conditions.*

Summary.

A new process for deposition of tin/zinc alloys has been developed. The alloy composition of the coating is within the optimal range for optimum corrosion resistance, which is 25 wgt-% zinc. Furthermore, the alloy composition is constant if the current density is higher than $0.1A /dm^2$.

References.

1. Edward Budman & Robert R. Sizelove: "Zinc alloy plating". Metal Finishing, 99 Guidebook and directory issue, p. 344.
2. J. Rasmussen: "Tin/Zinc Alloy Plating". 2000 Aerospace/Airline Plating & Metal Finishing Forum, March 27-29, 2000 Cincinnati, OH.