ELECTROCHEMICAL DEPOSITION OF TIN-ZINC ALLOYS.

Chemist, Grad. scient. Jean Rasmussen[1]
Centre of Advanced Electroplating
The Technical University of Denmark.

Electrodeposition of a tin-zinc alloy is optimized using Taguchi statistics. Interactions between process parameters are investigated. Furthermore the diffusion of hydrogen into the steel substrate during plating, giving rise to hydrogen embrittlement is measured using a sealed Devanathan cell. The type and magnitude of internal stress under various plating conditions is examined by dilatometry. Control of the plating bath is made using Differential Pulse Polarography and Hull cell panels. Results from corrosion tests - field and accelerated - will be presented at the conference. Comparisons will be made with other coatings.

1 INTRODUCTION.

Both tin and zinc are widely used for the protection of steel against corrosion. Each has a different sphere of application and each protects steel by a different mechanism. Tin is more noble 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 the zinc.

The protective properties of the two metals are nicely balanced in a tin-zinc alloy containing about 80 percent of tin. 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 as voluminous white corrosion products as with zinc coatings. The alloy has a solderability which is better than that of cadmium.

A tin-zinc alloy containing about 80 perccent tin has been used because of the superior corrosion protection it affords steel. However, alloys over the complete range of compositions can be deposited if bath parameters are adjusted accordingly. Until recently, plating was mainly done in cyanide-stannate baths. New non-cyanide processes are now available and offer (compared to the cyanide bath), several advantages, such as better bath stability, less parameters to control, and less after treatment of effluents. Furthermore, the alloy is deposited as a bright coating and the composition, contrary to cynide-stannate baths, is less sensitive to current density.

2 FUNDAMENTALS.

The standard electrode potentials of tin and zinc are more than 0.6 volt apart. Consequently, the alloys cannot be deposited readily from acid solutions (1). The deposition potentials of the two metals are much closer in alkaline solutions. Moreover, the presence of a complexing agent is necessary for the deposition of usable tin-zinc alloys.

In a weak acid solution, the complexant is a carboxylic acid (2). Oxidation of tin(II) to tin(IV) by dissolved oxygen is prevented by the addition of an antioxidant. A metallic lustre is obtained by the addition of a brightner.

Compared to normal one-metal processes, several parameters are involved in the deposition of tin-zinc alloys. However, a simultaneous deposition of both metals is relatively unsensitive to the concentration of one of the metals. Use of metals

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[1] *Danfoss A/S, Corporate Production, L3-V127, DK-6430 Nordborg, Denmark.*
Direct dialing + 45 74 88 44 32, telefax + 45 74 45 48 18.

during plating is compensated by an almost balanced dissolution of tin-zinc anodes. Drag out is the main reason for the losses.

3 EXPERIMENTS.

The investigations were based on Taguchi statistic experimental planning (3). It is used to rank the importance of the different parameters and interactions involved in deposition of both zinc and tin in a slightly acidic bath. The composition of the bath was kept inside the tolerance limits listed in table 1.

The first series of experiments was based on a Taguchi L_{18} orthogonal array, which allows variations of 8 parameters - one at two levels and the rest at three. The main reason for using this balanced table is that the number of experiments compared to a total factor investigation is reduced from 729 experiments to 18. Variations associated with uncontrolled conditions is also incorporated in the orthogonal array. The experimential conditions are shown in table 2.

The composition of tin-zinc alloys plated on Hull cell panels, as well as thickness distribution, is determined by X-ray analysis.

Based on the results from the first series of experiments, a Taguchi L_8 orthogonal array is used to examine possible interactions. In this balanced table (see figure 1), interactions between the first two parameters will show up in column III. The fourth column is reserved for the third parameter, and interactions with the first parameter, respectively the second, will show up in column V and VI. The seventh column is reserved for the pH, which does not interact at all with the other parameters. The experimential conditions are shown in table 3. Compared to a total factor investigation, the number of experiments are reduced by 50 percent.

Tin [g/l]	20	± 5
Zinc [g/l]	8	± 5
Complexant [g/l]	120	± 10
Antioxidant [g/l]	60	± 10
Brightner [ml/l]	8	± 1
Current density [A/dm^2]	2	0.5 - 5
Temperature [°C]	25	± 5

Table 1. Dipsol SZ-240®: Concentration of the process parameters and operational conditions for deposition of tin-zinc alloys of 80 wgt-% tin.

		Parameter						
	L_8	I	II	III	IV	V	VI	VII
Experiment no.	1	1	1	1	1	1	1	1
	2	1	1	1	2	2	2	2
	3	1	2	2	1	1	2	2
	4	1	2	2	2	2	1	1
	5	2	1	2	1	2	1	2
	6	2	2	2	2	1	2	1
	7	2	1	1	1	2	2	1
	8	2	2	1	2	1	1	2

Liniar graph

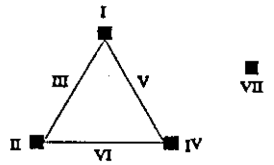

Figure 1.The L_8 orthogonal array and the corresponding liniar graph showing interactions. 7 parameters are investigated at 2 adjustments in 8 experiments (1-8).

Hydrogen embrittlement is investigated using a Dry Hydrogen Contact Cell - HCC 11 (4). This is a contact cell for monitoring hydrogen permeation through a steel substrate. The HCC 11 is a sealed Devanathan cell with a paladium window capable of transmitting hydrogen.Through oxidation, the cell converts the flux of hydrogen into an electrical current, which is registered on a X-Y plotter.

When hydrogen emanates from the steel, the cell will receive a part of this flux giving rise to a current from the cell. This current is measured as a voltage drop across a resistance, and can be expressed as a hydrogen flux instead of a current.

Care must be taken to ensure that the surface conditions of the steel are the same from one plating to another. It is possible to achieve reproducible results within a relative uncertantity of 5-8% by grinding the cell with emery paper before each plating.

Internal stress in the deposits is investigated by a dilatometric method (5), where the length changes of thin straight strips plated on both sides is mea-

					BATH PARAMETERS			
Level	Day	Additive ml/l	Tin g/l	Zinc g/l	Complexant g/l	Antioxidant g/l	pH	N/S
1	Mon	7	15	3	110	40	5	none
2	Thu	8	20	8	120	60	6	none
3	none	9	25	12	130	80	7	none

Table 2. Parameters and levels of adjustments in the Taguchi experiment based on a L_{18} orthogonal array.

sured. Specimens used in the experiments were thin copper strips, 10 ± 0,1 mm wide and 0.055 mm thick. The specimen length is about 210 mm.

From the measured dimensional changes it is possible (in every stage of the plating process) to calculate the value of the average internal stress in the deposit.

The largest single contribution to errors of measurements is the dilatometer reading itself, but this error diminishes rapidly with increasing time and deposit thickness. Above a thickness of 2 µm the errors of measurement are small compared to the measured internal stress. The reproducibility of the method is better than 95%.

4 RESULTS.

In the L_{18} experiment, an analysis of the variance (ANOVA) showed that non-controlled factors did not have an effect upon the results. On the other hand, the only parameters of significant importance are the concentration of zinc, and the noise signal ratio (N/S in table 2). The latter indicates the existence of important interactions between some of the parameters.

A multi regression analysis (assuming liniarity) showed that the following interactions were of importance: the ratio between the concentrations of tin and zinc, tin and complexant and zinc and complexant.

PARAMETER		LEVEL	
I	Tin [g/l]	15	20
II	Zinc [g/l]	3	8
IV	Complexant [g/l]	120	130
VII	pH	6	7

Table 3. Process parameters in the Taguchi experiment based on a L_8 orthogonal array and the level of adjustments. See also figure 1.

There is only a perfect fit to the observed compositions of the tin-zinc alloy, for the highest current density investigated (7.6 A/dm^2). With a confidence limit of 95%, 16 out of the 18 observations can significantly be described by the following formula (concentrations in g/l):

$$\begin{aligned}\text{Zinc content } [\text{wgt-\% at } 7.6\ A/dm^2] = \\ -\,209.85 + 1.13pH - 14.65Sn \\ +\,11.77Zn + 1.87Complexant \\ -\,1.63Sn/Zn - 1218.05Sn/complexant \\ +\,1721.38Zn/complexant\end{aligned}$$

Some of the results from the L_{18} experiment are shown in figure 2. Even though the parameters were kept inside the limits of tolerance (see table 1), the composition along the Hull cell panels varied significantly. Three examples are given in curves a-c. The pH of the bath is an important parameter. A low value causes a pronounced reduction of the zinc-content (curve d) as current density is lowered. A pure tin coating can be deposited at pH = 5 when the zinc concentration in the bath is 3 g/l. At pH values between 6 and 7 the alloy composition is relatively stable over a broad range of current densities. A pH in the higher end of this interval seems to reduce the difference in composition when going from high to low current density (curve e and f).

A high tin content in relation to zinc, causes a displacement of the alloy composition towards higher tin-content. This displacement is almost the same over the total range of current densities (curve g-i).

Interactions between the concentrations of the two metals and the complexing agent are shown in curves j-k. Increasing the concentration of tin relative to the complexant, displaces the alloy

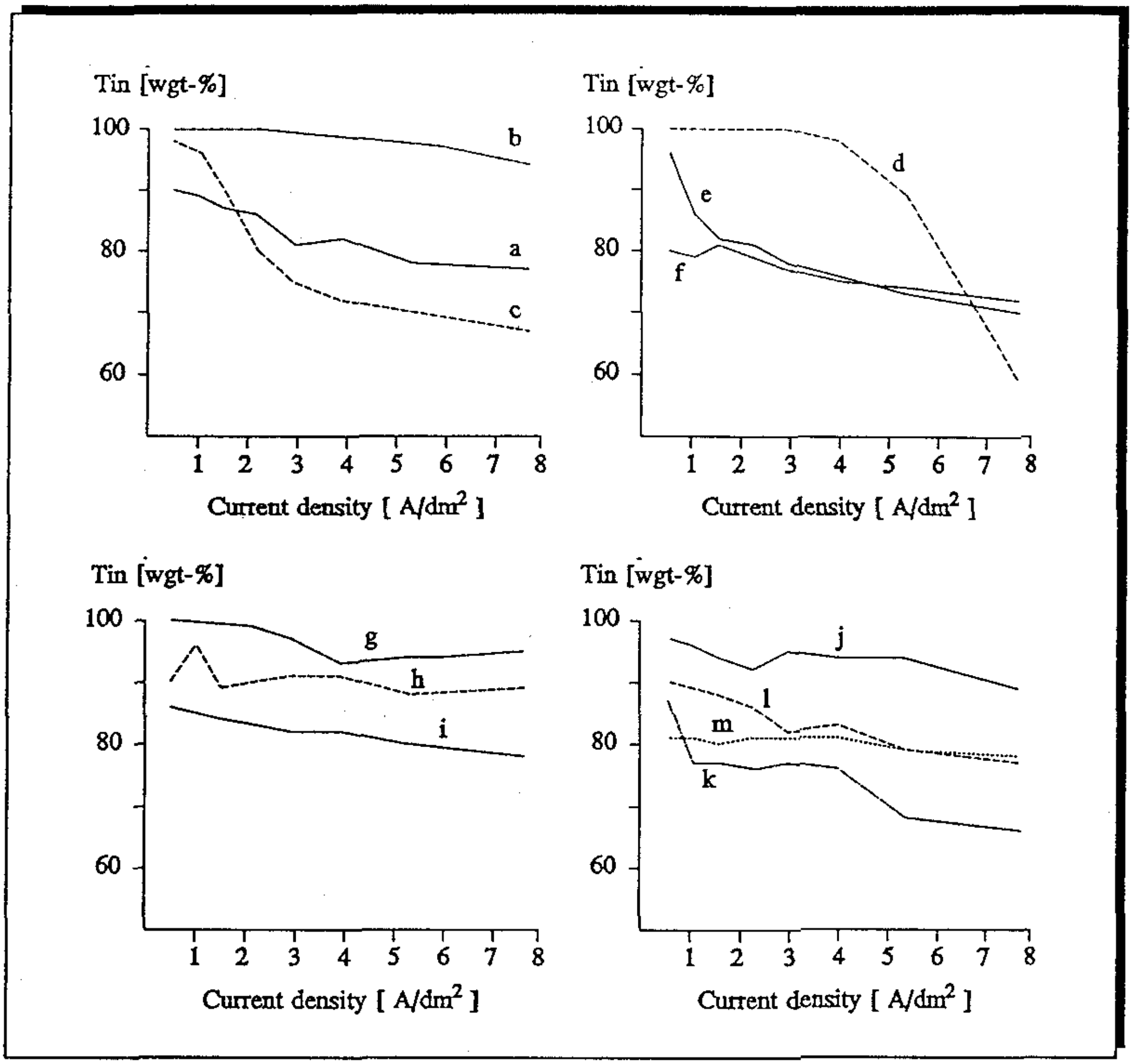

Figure 2. *The composition of alloys plated on the Hull-cell panels versus current density and experimental conditions in the L_{18} experiments.* ***Curves a-c:*** *illustration of variation with the parameters kept inside the limits of tolerance,* ***curves d-f:*** *pH = 5.0 (d), 6.0 (e) and 7.0(f),* ***curves g-i:*** *interaction between tin and zinc, tin/zinc = 6.7 (g), 6.0 (h) and 2.1 (i),* ***curves j-k:*** *interaction between tin and complexant, tin/complexant = 0,13·(j) and 0,18 (k),* ***curves l-m:*** *interaction between zinc and complexant, zinc/complexant = 0,07 (l) and 0,11 (m).*

composition towards lower tin content. Once more the magnitude of the shift is more or less the same over the whole range of current densities (curve j and k). The interaction between zinc and complexant does not have great influence on the alloy composition. The difference in the lower range of current densities is likely to be a result of more important interactions. Comparison of the curves in figure 2 is based on experiments where other interactions are of approximately the same magnitude.

The results from a multi regression analysis (assuming liniarity) on the measured differences in the composition at high and low current density (7.6 and 0.15 A/dm^2) are shown in figure 3. At a confidence limit of 95%, 14 out of the 18 Hull cell panels can significantly be descriebed by the following equation (concentrations in g/l):

$$\begin{aligned}&\text{Variation of tin content [wgt-\%]} = \\ &\quad -\ 448.2 - 21.0\text{Sn} + 3.8\text{Complexant} \\ &\quad +\ 35.6\text{Zn/Sn} + 2467.9\text{Sn/Complexant}\end{aligned}$$

The interactions found are further investigated in an L_8 experiment (see table 3 and figure 1). An analysis of the variance showed that the importance of the parameters and the interaction between

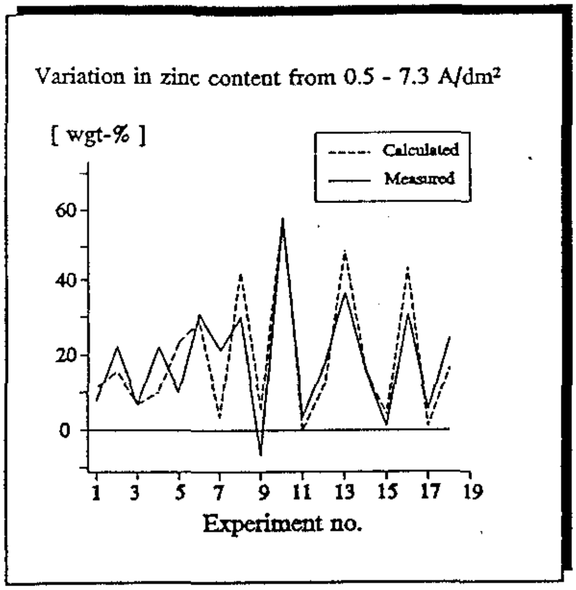

Figure 3. Measured and calculated variation in the alloy composition from high to low current density (A/dm^2). The calculations are based on multi regression analysis (assuming linearity) on the Hull cell panels (from the L_{18} experiments).

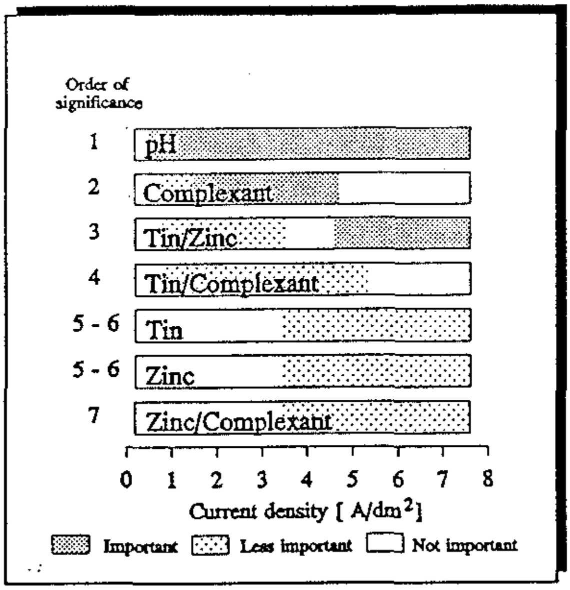

Figure 4. Ranked importance of process parameters and interactions, based on analysis of variance of Hull cells from the L_8 experiment. See text for further information.

them depends on the current density. An attempt to rank them is shown in figure 4. The most important parameter is the pH value of the bath, which is important for the whole range of current densities investigated. The concentration of the complexant is the second most important parameter, especially in the middle and the higher current density range. The two most important interactions are between tin-zinc and tin-complexant.

The relative importance of the bath parameters and the interactions between them (calculated on the basis of a ranking procedure similar to a non parametric Mann-Whitney U-test (6)), is shown in table 4 for the whole range of current densities investigated, and for the range likely to be used in practice.

5 BATH CONTROL

Measurements of the concentration of tin and zinc are easily performed using Differential Pulse Polarography (7). Both metals are electroactive in an ammoniumacetate buffer adjusted to pH=4.5, and simultaneous determination is possible. Concentrations are found using the principles of standard addition. The reduction of tin(II) takes place in the above mentioned supporting electrolyte at -600 mV vs. a saturated calomel electrode. Zinc is reduced at -1000 mV. A total analysis for both metals is performed in approximately 10 minutes (excluding time for deaeration).

The metal concentrations are determined using standard addition and linear regression. The numerical value of the intercept with the x-axis indicates the concentration sought after. An example of metal analysis is shown in figure 5.

Tin(IV) is not electroactive in the above mentioned electrolyte. An analysis of unwanted tin(IV) can be made using a supporting electrolyte of HCl and Na-citrate. The reduction of tin(IV) takes

Parameter/ interaction	Current density [A/dm^2]	
	0.15 - 7.6	1.0 - 4.0
pH	100	100
Complexant	32	44
Tin/zink	29	23
Tin/Complexant	27	31
Tin	23	18
Zinc	23	21
Zinc/Complexant	21	16

Table 4. Relative importance of process parameters and interactions in relation to the operative range of current density. See text for further information.

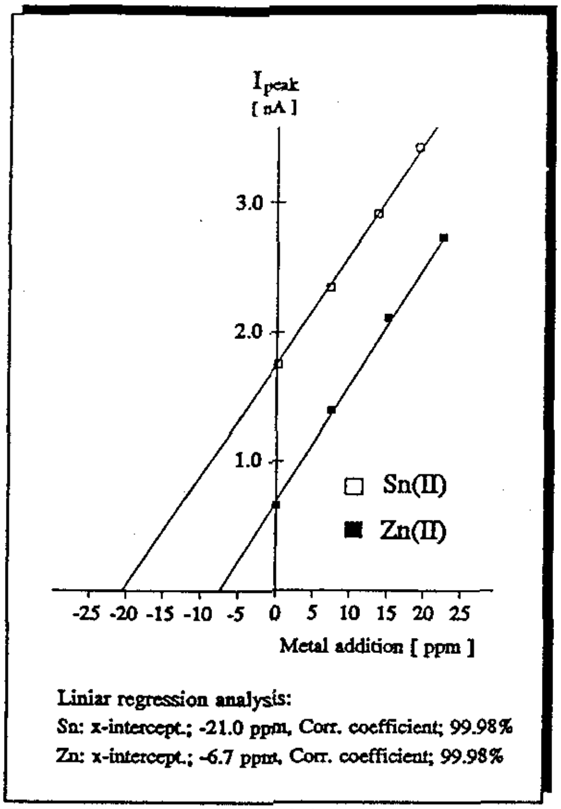

Figure 5. Determination of the concentration of tin and zinc is based upon Differential Pulse Polarography and standard addition.

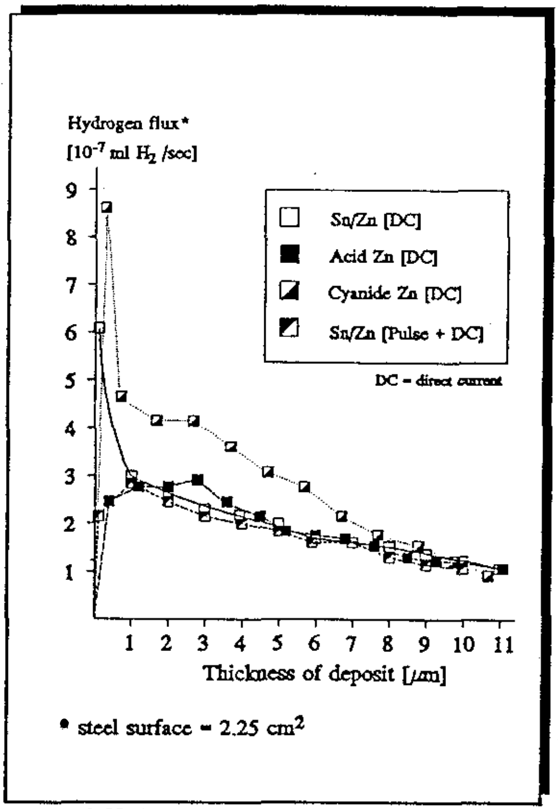

Figure 6. Hydrogen diffusion into steel during plating with cyanide zinc, acid zinc and tin-zinc. Measured with a Devanathan cell.

place at -800 mV.

The pH of the bath is adjusted by the addition of ammonium hydroxide for acidity, and sulfuric acid for alkalinity.

The amount of complexant can be followed using Hull cell panels. Too low a concentration will show up as "burnings" at high current density and loss of brightness at low current density. Pitting at high current density is observed if the concentration is too high.

6 TIN-ZINC PROPERTIES.

Diffusion of hydrogen into steel during plating can lead to hydrogen embrittlement. In the tin-zinc process the hydrogen diffusion is lower than cyanide zinc and comparable to acid zinc. Experiments with pulse plating have shown, that high frequency pulse/reverse causes depositions of tin only. It has been shown that the diffusion of hydrogen into steel in the first minute of plating can be lowered if such a pulse pattern is used at the beginning of plating. Increasing the current density causes a shift of the curves shown towards higher hydrogen flux.

The mean internal stress in electroplated tin-zinc alloys is low and the current density does not have any influence (figure 7). In comparison, measurements of zinc coatings from a cyanide process have a higher internal stress, and the magnitude depends strongly upon the current density. For a 4 μm zinc coating plated at 2 A/dm^2, the internal stress is 2.7 kp/mm^2 and for 10 μm zinc plated at 4 A/dm^2 it is 10.9 kp/mm^2.

The superior protection against corrosion achieved when steel is plated with tin-zinc, depends strongly on the composition of the alloy. The best protection against corrosion is achieved when the composition is 80% tin and 20% zinc. In neutral salt spray tests - ASTM B117 - an unpassivatet coating performs much better than a chromated zinc coating (1,2).

An even better result can be obtained if the tin/zinc coating is chromated (2). Dissolution of zinc leads to changes in the composition of the alloy when chromate treatment takes places in the chromic acid. This should be kept in mind, when the corrosion protective properties are compared to other coatings.

Field tests and accelerated tests (Prohesion (8) and Humidity) are expected to be completed by

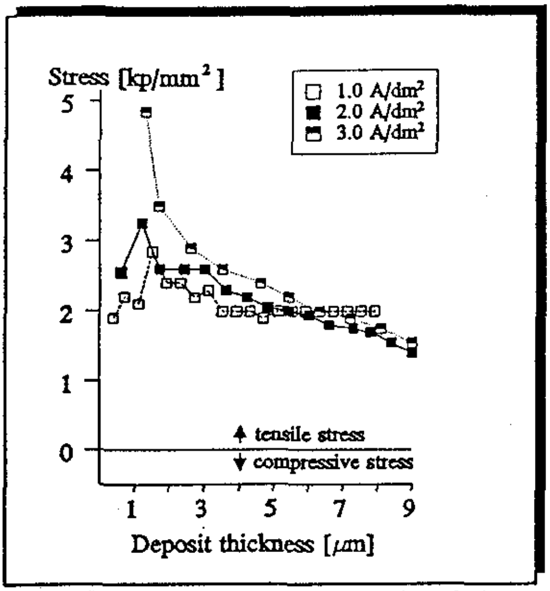

Figure 7. The mean internal stress in relation to thickness and current density, as measured by a dilatometric method.

Spring 1992. The tests involve galvanic and crevice corrosion. Unpassivated and passivated coatings (with chromate and with a new non-chromate process) will be tested and comparisons will be made to acid and cyanide zinc. The results will be presented in the oral presentation of this paper.

7 CONCLUSION.

The experiments show that Taguchi statistics is a very powerful and useful method for optimizing plating conditions and investigating interactions between bath parameters.

The electrochemical deposition of tin-zinc alloys in a slightly acid bath was improved. With an optimized composition of the bath it is possible - over a broad range of current densities - to deposit an alloy with uniform composition. Figure 8 shows the alloy composition in relation to current density before and after the conditions have been optimized using Taguchi statistics.

Bath parameters of main importance are the acidity, the concentration of complexant and the ratio between tin-zinc and tin-complexant. The concentration of the two metals and the ratio between zinc and the amount of complexant is less important.

The composition of the bath does not have a marked influence on the rate of deposition.

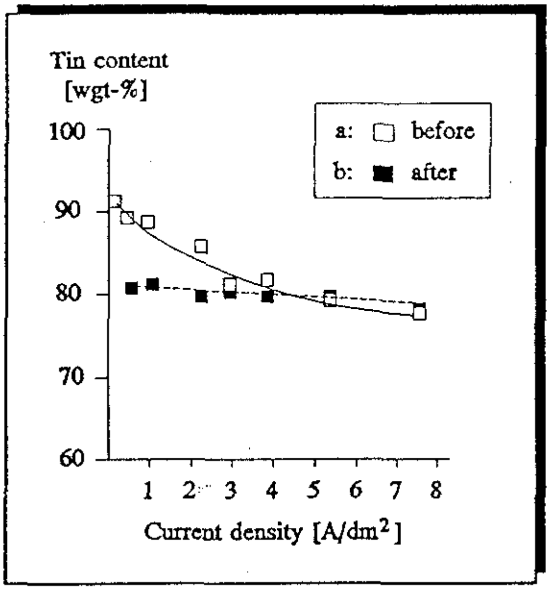

Figure 8. The composition of electrodeposited tin-zinc alloys i relation to current density. Curve a: recommended composition, curve b: after optimization using Taguchi statistics.

Bath control is easily done using Differential Pulse Polarography and Hull cell panels. The need for analysis of the constituents of the bath is reduced when tin-zinc anodes are used. The consumption is almost balanced. Drag out is the main reason for loss.

The general conclusion concerning bath parameters is that the pH should be kept at 7 and that the concentrations of tin, zinc and complexant should be 20, 12 and 110 g/l, respectively.

Changes in the composition of the deposited alloy can take place if the components of the bath are altered. In the lower end of the current density (0.5 - 4 A/dm^2) a reduction of the ratio between tin and zinc will result in a low content of tin in the plated alloy. Lowering the ratio between tin and complexant will have the opposite effect. At high current densities (> 4 A/dm^2) the reduction of the ratio, will result in a deposit low in tin.

The diffusion of hydrogen into the steel during plating is comparable to the acid zinc process. The use of high frequency pulse/reverse plating at the start of a deposition, will reduce the risk of hydrogen embrittlement. The internal stress is of tensile character and is lower than zinc coatings from cyanide-processes. The internal stress is unsensitive towards changes in current density.

8 ACKNOWLEDGEMENTS.

The author is indebted to Dr. Dan Ulrich, NKT Wire Work, Denmark for help and support in the multi regression analysis and interpretation of the results from the Taguchi experiments.

9 NOTES.

Conversion of a hydrogen flux to a current is done using the equation

$$V_H = \frac{4.251 \cdot 10^{-10} \cdot (T + 273) \cdot E}{R}$$

where V_H is the volume of hydrogen, given in ml H_2/sec. T is the temperature measured in centigrade, E is the measured voltage drop (in mV), and R is the shunt resistance (in kΩ). Alternatively, E/R can be replaced by the current I (measured in μA). A current of 1 μA corresponds to a flux of $1.27 \cdot 10^{-7}$ ml H_2/sec at 25 °C.

Calculation of the mean internal stress is done using the equation

$$\Sigma = \frac{E \cdot d \cdot \delta l}{2 \cdot l \cdot t}$$

where Σ is the internal stress (kp/mm^2), E the modulus of elasticity (1.2033 x 10^4 kp/mm^2 for copper), d the thickness and l the plated length of the specimen (mm), t is the thickness of the deposit (mm) and δl the dimensional changes of the specimen (mm).

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