Hydrogen in Electrodeposited Tin-Zinc Alloy

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Tin-zinc alloy is finding increased interest in the electronics industry. An alloy with 70 percent tin is said to be a high-performance alternative to zinc deposits in high humidity conditions and to cadmium under marine conditions. The alloy is used in the chassis for electrical and electronic equipment, automobile, fuel and brake lining components and for steel fasteners for aluminum panels in the aerospace industry.

The major problem associated with zinc and cadmium electrodeposition is the result of hydrogen entrapment in the substrate metal. The occluded hydrogen leads to premature failure of the components. Having been considered as a substitute for cadmium, a comparative study of the hydrogen content of the above deposits was felt equally as important as other physico-mechanical properties. The results obtained are presented in this paper.

The increasing threat of environmental pollution has led to the development of numerous substitutes for cadmium. Tinzinc alloy is one of the best; zinc deposits in conditions of high humidity and cadmium deposits under marine conditions are being replaced by Sn-Zn electrodeposits.

The major problem associated with zinc and cadmium plating is embrittlement, caused by hydrogen entrapment in the deposit. This paper presents a comparative study of the permeation of hydrogen during electroplating of zinc, cadmium from conventional baths and tin-zinc alloy plating from a neutral gluconate bath.

Experimental Procedure

Plating bath composition and conditions are listed in Table 1. Mild steel panels, $7.5 \times 5 \times 0.1$ cm, were used for the porosity tests. They were electrocleaned and acid-dipped prior to plating. The porosity test was carried out by electrographic technique at 0.3 A/dm², using an aluminum cathode at a load of 10 g. A solution of 5-percent NaCl was used. The pores developed were identified by a dip in 5-percent potassium ferricyanide solution and reported as the percentage defective area.

Hydrogen permeation during deposition was studied by the standard method consisting of measuring the current required to ionize hydrogen occluded in the substrate. A steel specimen was inserted in the cell to expose an area of one cm². The palladized side was placed in the ionization (degassing)



Fig. 1—Hydrogen permeation cell.

compartment (Fig. 1). The specimen was kept at -300 mV vs. Hg/HgO/0.1 N NaOH for one hr to allow the permeation current to reach a steady value. Deposition took place in the polarizing compartment, with the required plating conditions maintained. The change in the permeation current was recorded, using an X-Y-Z recorder.

The permeation current initially reached a maximum (i_{max}) , then decreased to a steady value (i_{res}) . The time required to reach maximum (t_{max}) and the time to reach steady current value (t_{crit}) were noted. The total charge (coulombs) required to ionize hydrogen was taken as a measure of the hydrogen incorporated in the substrate during deposition. Experiments were conducted for deposition of various metals and alloys and the results compared (Table 2).

Table 1 Composition & Conditions of Electrodeposition

Electrodeposit A—Tin	Composition g/L Sodium stannate, 100 Sodium hydroxide, 10	Conditions Current dens., A/dm ² 1, 70 °C
B—Tin	Stannous sulfate, 10 Sulfuric acid, 20 Phenol sulfonic acid, 16.2 B-naphthol, 0.2 Gelatin, 0.4	2, 30 °C 2
C—Tin	Stannous sulfate, 50 Sodium gluconate, 160 Sodium acetate, 20 Peptone, 1	2, 70 °C pH 7
D—Zinc	Zinc cyanide, 60 Sodium cyanide, 23 Sodium hydroxide, 53	2, 30 °C
E—Zinc	Zinc sulfate, 300 Boric acid, 30 Sodium chloride, 15 Aluminum sulfate, 15 Dextrin, 5	2, 30 ℃ pH 3
F—Cadmium	Cadmium fluoborate, 22 Ammonium fluoborate, 5 Boric acid, 20	0 2, 30 °C 5 pH 2.5
G—80% Zinc 20% Tin	Zinc sulfate, 30 Stannous sulfate, 30 Sodium gluconate, 169 Sodium acetate, 20 Peptone, 1.5	2, 60 ℃ pH 7
H—70% Zinc 30% Tin	Stannous sulfate, 30 Zinc sulfate, 45 Sodium gluconate, 160 Sodium acetate, 20 Peptone, 1.5	2, 60 °C pH 7



Fig. 2—Variation of permeation current density for several deposits with time: (a) tin; (b) zinc and cadmium; (c) Zn-Sn alloy.

Results and Discussion

Tin Deposition

The alkaline stannate bath showed i_{max} at the end of 40 sec (Fig. 2). It progressively decreased and attained a steady value in 10 sec. The high i_{res} that resulted in high Q, indicated that the deposits obtained from this bath induce greater hydrogen inclusion in the substrate. The very low t_{crit} suggests that the deposits become pore-free and compact within a short time. The permeation current observed in tin deposition from the acid bath was lower and attained a steady value of 5.5 _A after 220 sec. The values of i_{max} , t_{max} , t_{crit} and Q were

 Table 2

 Parameters Derived from Permeation Studies

Deposit A	Current de Max.	ensity, A/dm ² Residual	Time, Max. 100	sec Crit.	Q Coulombs
В	41	5.5	225	60	225
С	27	1.5	180	10	53
D	39	20.0	240	70	425
E	13.25	1.5	520	40	106
F	21.5	12.0	140	40	247
G	19	0.25	90	5	28
Н	16.25	0.75	100	10	31

 Table 3

 Porosity Values for Various Tin Deposits

Deposit	Thickness, µm	Porosity, %
A	3	35
В	3	15
С	1.5	35
	3	10
	6	5
	12	2

found to be considerably less during deposition from a gluconate bath compared to the other baths.

The porosity (Table 3) of the tin deposit obtained from the acid bath was greater compared to that in the deposits obtained from the alkaline bath. The permeation characteristics of the deposit from the gluconate bath revealed that the deposit is less porous than those obtained from other baths.

Zinc and Cadmium Deposition

For zinc deposition, the cyanide bath offered higher permeation currents (i_{max} and i_{res}), suggesting lower porosity. The acid bath offered moderate permeation current and the deposits were moderately porous. For cadmium deposition, the i_{max} values were higher than for zinc deposition and, after 140 sec, the residual current was obtained.

Zinc Alloy Deposition

The permeation currents (i_{max}) are minimum in the deposition of 70- and 80-percent tin alloy deposition compared to zinc and cadmium. The i_{res} and Q values were low in the alloy baths, suggesting that the deposits were less prone to hydrogen embrittlement than zinc and cadmium electrodeposits.

Conclusion

The tin and tin-zinc alloy-deposits obtained from gluconate baths are less prone to hydrogen embrittlement than zinc and cadmium electrodeposits. It is thought that formation of finegrained, coherent, compact alloy deposits has made this possible, as evident from the low residual current and low critical time, irrespective of i_{max} higher than that of the acid zinc bath. *Editor's Note:* Manuscript received, September 1994; revisions received, April 1995.

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