Electroplating of Tin
From Acidic Gluconate Baths

S.S. Abd El Rehim, S.M. Sayyah & M.M. El Deeb

Tin metal has been electroplated from baths containing stannous sulfate, sodium gluconate and potassium sulfate onto steel substrates under different conditions of bath composition, pH, current density and temperature. A detailed study has been made of the effect of these parameters on potentiodynamic cathodic polarization, cathodic current efficiency, microstructure and morphology of the deposit. The throwing power of these baths has been examined under the effect of these parameters. The presence of gluconate ions in the bath improved the quality of the deposits and the throwing power of the bath. The deposits consisted of one phase (β–phase) with tetragonal structure.

Tin is soft, ductile and corrosion-resistant in a variety of atmospheres and easily solderable. It has an attractive appearance and is non-toxic in contact with foodstuffs.[1] Intensive studies were carried out, therefore, to obtain tin electroplates suitable for the above purposes from acidic stannous sulfate,[1,2] sulfamate,[3] fluoborate,[4] and alkaline stannate baths.[5]

Tin electrodeposits obtained from acid stannous sulfate baths are coarse-grained, non-adherent and porous, with formation of dendrites and whiskers.[6] Addition of certain organic molecules to the stannous sulfate electrolyte, however, improves the quality of the deposits. Compact, smooth and fine-grained electrodeposits are obtained from acid stannous sulfate solutions containing various surface active agents[7,8] and aromatic carbonyl compounds.[9-11] Aragon *et al.*[12] studied the electrodeposition of tin from stannous acid baths in the presence of polyethoxylate surfactant. It was found that the additive causes a substantial increase in the overpotential for the discharge of Sn^{+2} ions. The deposits are smooth, homogeneous and no growth of whiskers was observed. Kanenk *et al.*[13] found that the presence of N,N-bis (polyoxy ethylene) octadecyl amine in stannous sulfate solution induces a uniform deposition of tin over the whole surface and produces smooth and compact electrodeposits. Fine-grained and smooth deposits were obtained from acid stannous sulfate solutions containing some kinds of aromatic ketones.[14] It was found that these organic compounds were adsorbed on the cathode surface and enhanced the overpotential.

The aim of this study was to develop baths from which tin metal could be electrodeposited from gluconate solutions. The advantage of these baths is not only their cheapness, but their non-polluting effect on the environment as well. In this study, the effects of some plating and operating variables on the characteristics of the plating, the quality of the deposits and the throwing power of these baths were investigated.

Experimental Procedure

Experiments were carried out in solutions containing $SnSO_4$, $C_6H_{11}O_7Na$ and K_2SO_4. All solutions used were freshly prepared with doubly distilled water and from analytical grade chemicals. The pH was adjusted using sulfuric acid or sodium hydroxide. The experimental set-up used has been described previously[15] and consisted of a rectangular Perspex cell provided with a plane parallel steel sheet cathode and a platinum sheet anode. Each electrode was 3 x 3 cm and filled the cross section of the cell. Before each run, the cathode was mechanically polished with 600-mesh emery paper washed with distilled water, rinsed with ethanol, dried and weighed. The experiments were conducted at the required temperature ±1 °C with the help of an air thermostat. The plating duration was 15 min; at the end of that time, the cathode was withdrawn, washed with distilled water, dried and weighed. X–ray analysis and the morphology of the deposits were exam-
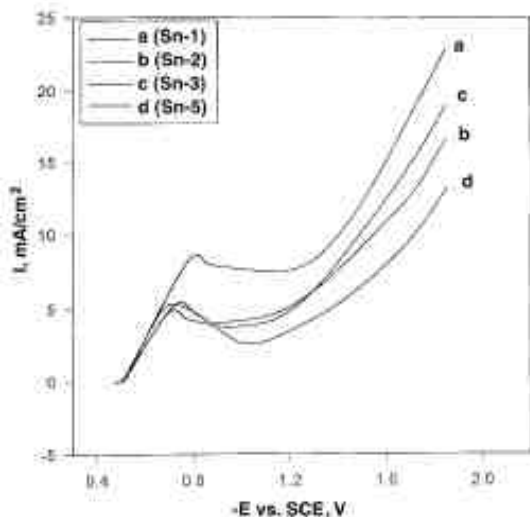

Fig. 1—Effect of concentration of sodium gluconate on the potentiodynamic cathodic polarization curves for tin electrodeposition at T = 31 °C, with scan rate of 25 mV/sec.

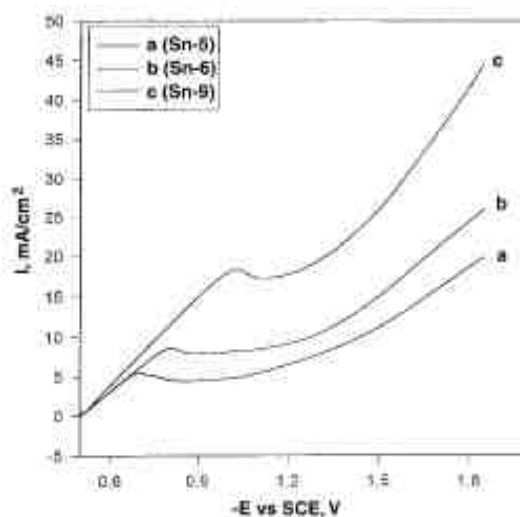*Fig. 2—Effect of concentration of SnSO$_4$ on potentiodynamic cathodic polarization curves for tin electrodeposition at T = 31 °C, with scan rate of 25 mV/sec.*
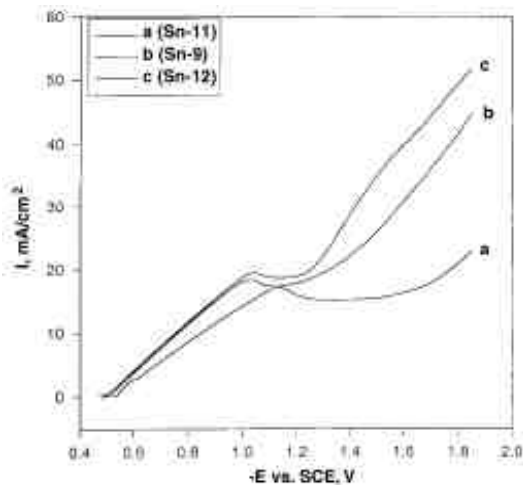
Fig. 3—Effect of pH on potentiodynamic cathodic polarization curves for tin electrodeposition at T = 31 °C, with scan rate of 25 mV/sec.
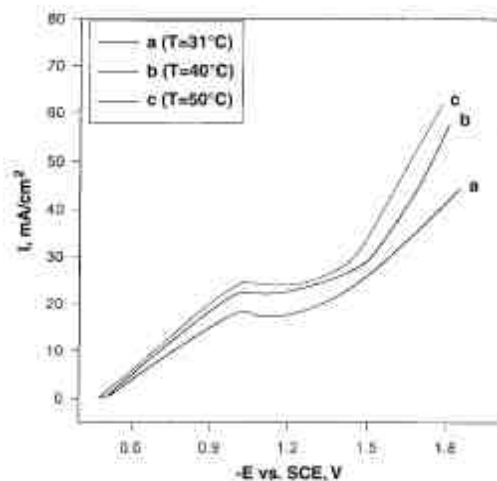

Fig. 4—Effect of temperature on potentiodynamic cathodic polarization curves for tin electrodeposition from bath (Sn-9) with scan rate of 25 mV/sec.

ined by X–ray diffraction using a diffractometer with Cu Kα radiation and nicked filter (40 kV, 30 mA) and scanning electron microscopy. The values of pH were measured by pH meter. Potentiodynamic cathodic polarization measurements were recorded by using a potentiostat/galvanostat. The I–E curves were recorded by computer. The measurements were carried out in a three-electrode cell having a steel cathode, a platinum anode and a reference saturated calomel electrode (SCE). The composition of the baths for the electrodeposition of tin is listed in Table 1.

Results & Discussion

Potentiodynamic Cathodic Polarization Curves

Figure 1 illustrates the potentiodynamic cathodic polarization curves for the electroplating of tin from acidic stannous sulfate solution in the absence and presence of various concentrations of sodium gluconate. The curves were swept from the rest (zero current) potentials toward more negative values. In the absence of sodium gluconate (bath Sn–1), the current increased, starting from the rest potential (about -500 mV vs. SCE) and reaching a maximum (peak) at about -775 mV. Beyond the peak current, the curves show a limiting current in the potential range -885 to -1200 mV. Subsequently, the current increased rapidly with further increase in the potential as a result of hydrogen evolution. The appearance of the limiting current on the potentiodynamic cathodic polarization curve is probably caused by mass-transfer control of Sn^{+2} ions with natural convection.[16] The addition of gluconate ions in

the solution causes remarkable changes of the potentiodynamic cathodic feature. The gluconate ions increase the cathodic polarization and decrease both the peak and the limiting currents. These changes increase with increasing gluconate content in the bath as indicated by curves b-d in Fig. 1. This inhibiting effect of gluconate ions on the deposition of tin could be ascribed to the formation of tin complexes. In an acidic medium, Sn^{+2} ion is present mainly as the $[SnC_6H_{11}O_7]^+$ complex in addition to other complex species.[17] The formation of complex ions may inhibit the deposition of tin because the complex ion cannot be reduced as easily as the free Sn^{+2} ion. In addition to the complexation process, the gluconate ions may be adsorbed on the electrode surface and block the preferential sites for tin deposition. This phenomenon increases the overpotential for the reaction by decreasing the sites available for discharge of metal ions.[18] It is noted that the increase in cathodic polarization is accompanied by progressive evolution of hydrogen as a side reaction. Inspection of the data in Fig. 2 reveals that an increase in Sn^{+2} content in the bath shifts the potentiodynamic cathodic polarization toward the less negative values and increases both the peak and limiting currents. These results may be related to the increase in the relative concentration of Sn^{+2} ions, particularly in the cathodic diffusion layer; this is reflected in the decrease of overpotential associated with tin deposition. An increase in the cathodic current efficiency (CCE) for tin electrodeposition is expected from solution containing high content of $SnSO_4$.

The effect of pH of the gluconate bath on the potentiodynamic cathodic polarization curve was investi-
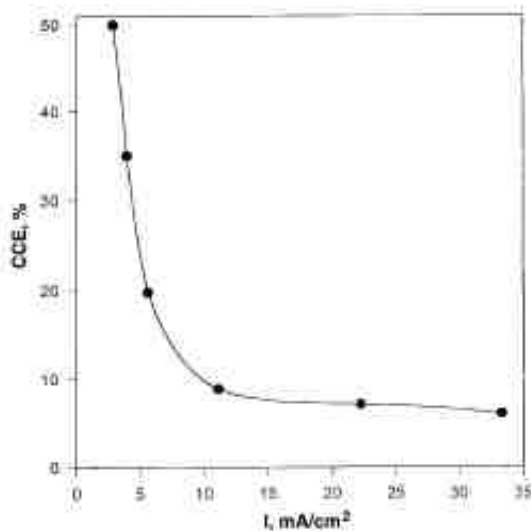

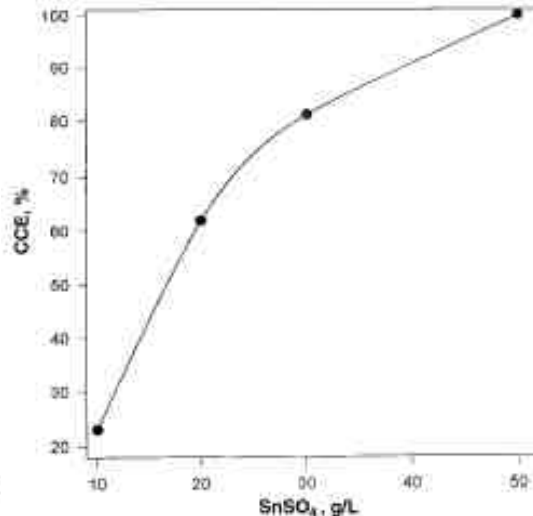Fig. 5—Effect of current density on cathodic current efficiency for tin electrodeposition from bath (Sn-5) at T = 31 °C.

Fig. 6—Effect of concentration of $SnSO_4$ on cathodic current efficiency for tin electrodeposition from baths containing 70 g/L $C_6H_{11}O_7Na$, 10g/L K_2SO_4, at T = 31 °C and I = 5.6 mA/cm².

Table 1				
Composition of Tin Plating Baths				
Bath No.	**Concentration, g/L**			**pH**
	SnSO₄	**Sodium gluconate**	**K₂SO₄**	
Sn-1	10	0	10	1.6
Sn-2	10	10	10	1.6
Sn-3	10	30	10	1.6
Sn-4	10	50	10	1.6
Sn-5	10	70	10	1.6
Sn-6	20	70	10	1.6
Sn-7	30	70	10	1.6
Sn-8	40	70	10	1.9
Sn-9	50	70	10	1.6
Sn-10	50	70	10	3
Sn-11	50	70	10	2.2
Sn-12	50	70	10	1.1
Sn-13	60	70	10	1.6
Sn-14	40	0	10	1.9

Table 2		
Effect of Current Density on Throwing Power & Throwing Index of Gluconate Bath (Sn-4) T = 31 °C		
I mA/cm²	**TP %**	**TI**
5.6	14	1.3
8.3	21	2.0
11.1	74	6.7

Table 3		
Effect of Sodium Gluconate Concentration on Throwing Power & Throwing Index of Gluconate Baths I = 5.6 mA/cm², T = 31 °C		
Bath No.	**TP %**	**TI**
Sn-3	11	1.2
Sn-4	14	1.4
Sn-5	20	1.7

gated and the results are shown in Fig. 3. The polarization curve shifts to less negative potentials with decreasing pH. This shift in polarization is accompanied by an increase in both the peak and limiting currents. In an acidic medium, the Sn^{+2} ions are bound into the complex via a ligand carboxyl group, and the stability constants have relatively low values ($\log k_1 = 3.01$ and $\log k_2 = 2.28$),[17] but increasing pH coordination on the secondary alcohol group is followed by liberation of protons (H^+). Formation of a chelate ring is also possible. This process leads to an increase in the stability constants of the complex and this is reflected in an increase in cathodic polarization. Elevation of the temperature of the gluconate bath, however, decreases the potentiodynamic cathodic polarization and increases both the peak and limiting currents (Fig. 4). Such behavior may be attributed to the depolarization effect of temperature on the activation overpotentials of the reducible ions. Moreover, an increase of temperature enhances the concentration of the reducible ions in the diffusion layer as a result of increasing their diffusion rates. In addition, it is possible that the stability constants of the tin–complex decrease with an increase of temperature.

Cathodic Current Efficiency (CCE)

The effects of applied current density, bath composition, pH value and temperature on CCE for tin electrodeposition from gluconate baths were studied. Figure 5 shows the effect of the applied current density on CCE for tin deposition from bath (Sn–5). The data reveal that CCE decrease markedly with increasing applied current density up to about 10 mA/cm², then tends to level off. This finding implies that hydrogen evolution takes place as a side reaction at especially high current densities. On the contrary, an increase in tin content in the bath greatly improves CCE. Data of Fig. 6 show that CCE increases from 20 to 98 percent with increasing SnSO₄ content in the bath from 10 g/L (bath Sn–5) to 50 g/L (bath Sn–9), respectively. It is obvious from Fig. 7 that an increase in gluconate content in the bath has no significant influence on CCE. Figure 8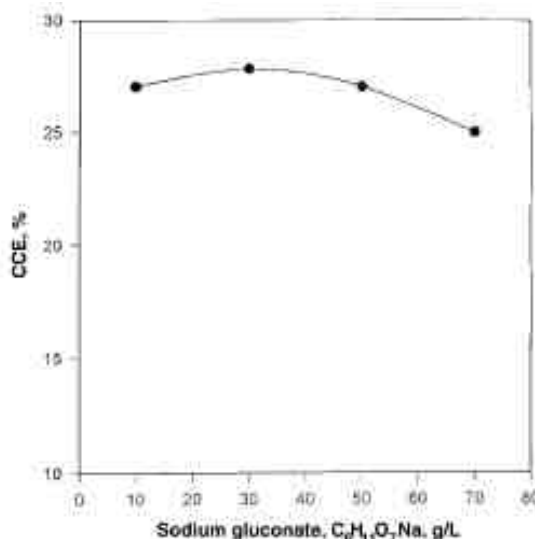 illustrates the influence of pH (from 1.1 to 3), from which it is clear that at low pH values (<1.6), CCE is high and closes to 100 percent. Above this pH value, CCE decreases with increased pH. The increase of pH leads to an increase in the stability constants of the complex ions formed. Reduction of the concentration of the free Sn^{+2} ions in the bath therefore occurs.

The effect of temperature on CCE for tin depo-

Fig. 7—Effect of concentration of $C_6H_{11}O_7Na$ on the cathodic current efficiency for tin electrodeposition from baths containing, 10 g/L SnSO₄, 10 g/L K₂SO₄ at T = 31 °C and I = 5.6 mA/cm².
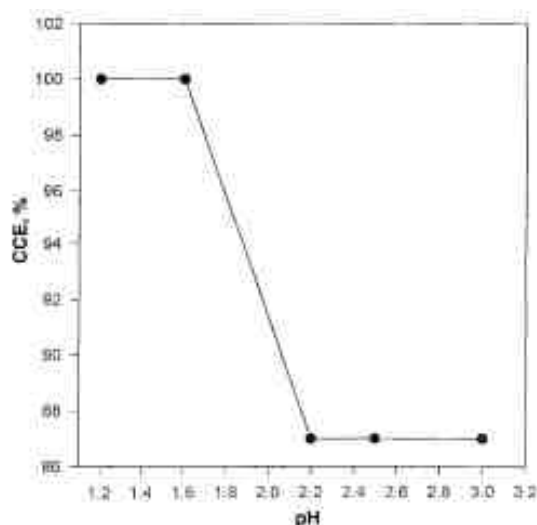

Fig. 8—Effect of pH on the cathodic current efficiency for tin electrodeposition from baths containing 10 g/L SnSO₄, 70 g/L $C_6H_{11}O_7Na$, 10 g/L K₂SO₄ at T = 31 °C and I = 5.6 mA/cm².

Table 4
Effect of SnSO$_4$ Concentration on Throwing Power & Throwing Index of Gluconate Baths
I = 5.6 MA/cm^2, T = 31 _C

Bath No.	TP %	TI
Sn-7	16	2.0
Sn-9	14	1.3
Sn-13	11	1.2

Table 5
Effect of Temperature on Throwing Power & Throwing Index of Gluconate Bath Sn-4
I = 5.6 mA/cm^2

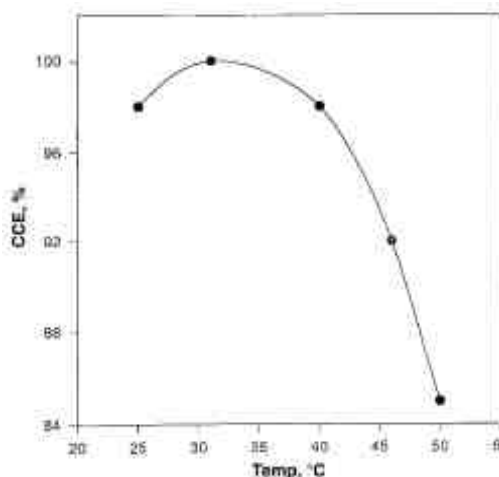| T °C	TP %	TI
31	14	1.1
40	14	1.2
50	14	1.25

Fig. 9—Effect of temperature on the cathodic current efficiency for tin electrodeposition from bath (Sn-9) at I = 5.6 mA/cm^2.

sition from the optimum bath (Sn–9) can be seen in Fig. 9. Increasing the bath temperature decreases the value of CCE from about 100 percent at T = 31 °C to about 84 percent at T = 50 °C. These data agree well with the results obtained from the cathodic polarization curves (Fig. 4).

The optimum plating conditions determined by experiment are: 50 g/L SnSO$_4$, 70 g/L C$_6$H$_{11}$O$_7$Na, 10 g/L K$_2$SO$_4$, pH 1.6, T = 22 to 40 °C and I = 5.6 mA/cm^2.

Surface Morphology & Structure of the Deposits

The surface morphology of the as–deposited tin was examined by scanning electron microscopy (SEM). Figure 10 shows the surface of some tin deposits obtained from a gluconate-free bath (Sn–14), photo (a) and from a gluconate-containing bath (Sn–8), photo (b). It is clear that in the absence of gluconate ions, shapeless and dendritic-grained deposits were obtained. The deposits were rough, not compact and the surface of the substrate was observed. The presence of the sodium gluconate in the bath, however, substantially improved the quality of the deposits as shown in photo (b). In this case, smooth and compact deposits were produced on the whole surface of the substrate and consisted of block–like crystals. It is probable that this improvement in the quality of the deposits is related to complexation of Sn^{+2} ions by gluconate ions that inhibit the outward growth of the grains but allow lateral growth. The structure of the as–
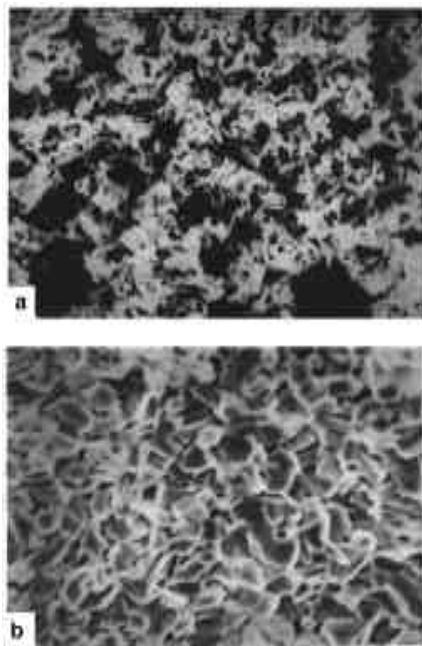
Fig. 10—Photomicrographs of tin deposited from: (a) tin deposited from bath (Sn-14), I = 5.6 mA/cm^2, T = 16 °C, time = 15 min, 2000X; (b) tin deposited from bath (Sn-8), I = 5.6 mA/cm^2, T = 16 °C, time = 15 min, 2000X.

deposited tin produced from the gluconate bath (Sn–8) was also examined by X–ray diffraction (XRD); the result is shown in Fig. 11. The data indicate that the deposits consist of single β–phase with tetragonal structure. It was observed that the highest reflection intensity of this β–phase corresponds to the (204) and (220) preferential orientations, although (101), (301), (321) and (411) orientations were also observed. To gain more information about the phase structure of the as–deposited tin from the bath (Sn–8), however, potentiodynamic anodic stripping voltammograms (ASV) were conducted. In these experiments, tin was electrodeposited potentiostatically on platinum substrate at a given deposition potential for a constant time (4 min). At the end of that time, each potential was swept *in situ* in the same solution by a linear potential scan rate of 20 mV/sec into the anodic potentials. Figure 12 shows the anodic stripping voltammograms for tin deposited at -700 mV, curve (a) and at -1200 mV, curve (b). Each stripping response exhibits a single anodic peak corresponding to tin dissolution. Beyond the peak, no residual tin on the substrate could be detected visually. The charge consumed for tin dissolution increases with increasing negativity of the deposition potential. The appearance of one anodic peak supports the data of XRD: that the deposit consists of one phase (β–phase).

Throwing Power & Throwing Index of the Bath

The throwing power (TP) of the gluconate baths was measured using a Haring–Blum cell under variable conditions, such as current density, bath composition and temperature. The TP values of these baths were calculated using the empirical Field's formula at the distance ratio of (1:3) and the results are given in Tables (2–5). Concerning the results included in Table (2), it is clear that increasing the current density strongly improved the TP of the bath. This trend in the variation of TP could be related to the effect of cathodic polarization on the distribution of current between the two cathodes. An increase in current density enhances the cathodic polarization, which has strong leveling power. This is in agreement with Wagner theory:[19] the current distribution on the two cathodes becomes more uniform (secondary).
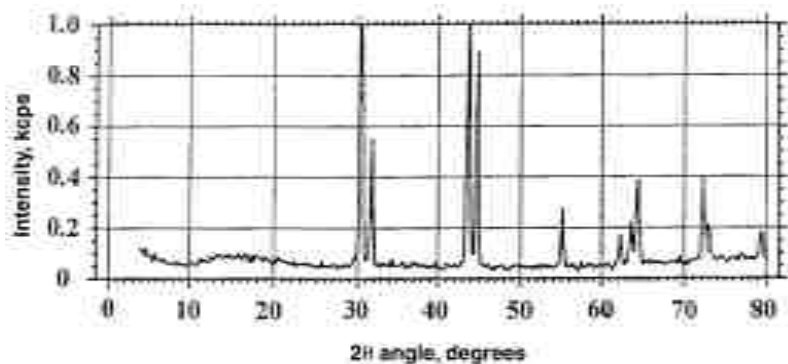
Fig. 11—X-ray diffraction pattern of tin deposited from bath (Sn-8), I = 5.6 mA/cm^{-2}, T = 31 °C, time = 15 min.

Fig. 13—Effect of current density on the throwing index of gluconate baths from bath (Sn-9) at T = 31 °C.
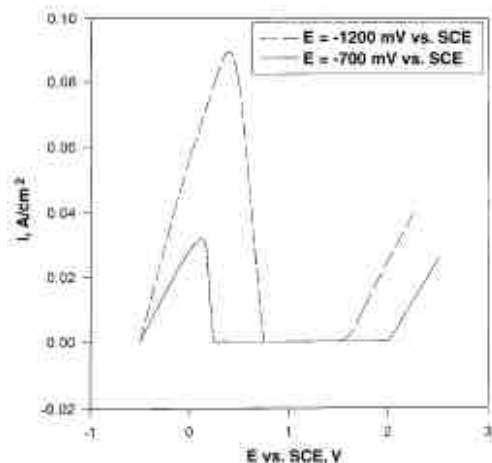

Fig. 12—Anodic stripping voltammograms of a deposit obtained from bath (Sn-8) at T = 31 °C with scan rate of 20 mV sec at different deposition potentials.

Improvement of TP could also be achieved by increasing the gluconate content in the bath (Table 3) because the gluconate ions create an overpotential, resulting in a large polarization resistance having strong leveling power. On the contrary, an increase in tin content in the bath decreases its TP through the decrease in cathodic polarization (Table 4). On the other hand, changing the bath temperature causes no significant influence on TP (Table 5).

A graphical method for expressing the results of the throwing power measurements was suggested by V. Jelink et al.[20] In this method, the metal distribution M was plotted vs. the linear ratio L (within the range from L = 1 to 3), on arithmetic coordinates. The reciprocal of the slope of this plot is called throwing index (TI) and represents a direct measure of bath throwing power.[21] Expressing the results in the form of TI rather than TP is advantageous because several experimental points are taken during the measurements of TI and this minimizes error in the measurement of any one point. Some representative linear plots between M vs. L are given as examples in Fig. 13. The values of TI obtained are listed in Tables (2-5). It is obvious that the values of both TP and T1 are changed in a manner parallel to each other.

Findings

Tin was electrodeposited onto steel substrate from baths containing stannous sulfate, potassium sulfate and sodium gluconate (pH 1.6). The influences of bath composition, pH, current density and temperature on potentiodynamic cathodic polarization, cathodic current efficiency, microstruc-
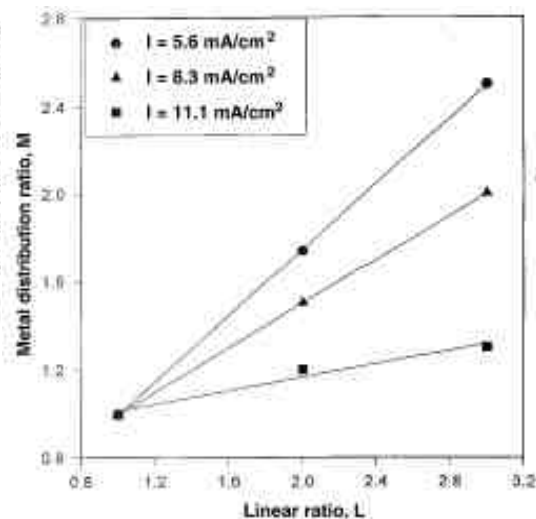
ture and morphology of the deposited tin were examined. It was found that the presence of gluconate ions in the bath increases the cathodic polarization because of the complexation of free Sn^{+2} ions. The cathodic current efficiency increased with increase of the tin content in the bath but decreased with increase in pH, temperature and current density. The presence of the gluconate ions in the bath improves the quality of the deposit and throwing power of the bath. X-ray diffraction analysis (XRD) and anodic stripping voltammetry (ASV) proved that the tin deposit consists of one phase (β-phase) with tetragonal structure. The optimum conditions are: 50 g/L $SnSO_4$, 70 g/L $C_6H_{11}O_7Na$, 10 g/L K_2SO_4, pH 1.6, T = 22 to 40 °C and i = 5.6 mA/cm^2.

References
1. A.C. Tan, *Tin and Solder Plating in the Semiconductor Industry,* Chapman & Hall, 1993.
2. G.S. Tzeng, S.H. Lin, Y.Y. Wang & C.C. Wan, *J. Appl. Electrochem*, **24,** 419 (1996).
3. M.A.F Samel, D.R. Gale & D.R. Eastham, *Metal Fin.*, **64,** 119 (1986).
4. S.M. Silaiman, M. Pushpavanam & K.C. Narasimham, *Plat. and Surf. Fin.*, **83,** 48 (Oct. 1996).
5. S.S Abd El Rehim, A. Awad & A. El Sayed, *Surf. Coat. Technol*, **28,** 139 (1986).
6. S. Meibuhr, E. Yeager, A. Kosawa & F. Hovorka, *J. Electrochem. Soc*, **110,** 190 (1963).
7. Nagaraj & C.K. Mital, *Metal Fin.*,**73,** 76 (1975).
8. N. Dohi, *K.H. Gijutsu*, **21**, 248 (1970).
9. Y. Matsuda, F. Koyama, Y. Hanada & Y. Tanaka, *K.H. Gijutsu*, **29**, 185 (1978).
10. R.M. MacIntosh, *Modern Electroplating*, 3rd Ed., F.A. Lowenheim, Ed., John Wiley & Sons, New York, 1974.
11. N. Kaneko, N. Shinohara, S. Wakabayashi & H. Nezuh, *Denki Kagaku*, **58**, 237 (1990).
12. A. Aragon, M.G. Figueroa, R.E. Gana & J.H.Zagal, *J. Appl. Electrochem*, **22**, 558 (1992).
13. N. Kaneko, H. Nezu & N. Shinohara, *Denki Kagaku*, **50**, 959 (1982).

14. Y. Nakamura, N. Kaneko & H. Nezu, *J. Appl. Electrochem*, **24,** 569 (1994).
15. S.S Abd El Rehim, A.M. Abd El Halim & M.M. Osman, *J. Chem. Technol. Biotechnol*, **35A**, 415 (1985).
16. O. Kardos & D.G. Foulke, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, C.W. Tobias, Ed., Interscience Publishers, New York, 1962; p. 145.
17. T.M. Maskin, B.Z. Zmbova & D.S. Veselinovic, *J. Serb. Chem. Soc,,* **56,** 337 (1991).
18. Y. Nakamura, N. Kaneko, M. Nakamura & H. Nezu, *J. Appl. Electrochem.*, **24**, 404 (1994).
19. C. Wagner, *Advances in Electrochemistry and Electrochemical Engineering*, P.Delahay & C.W. Tobias, Eds., Vol. 2, Interscience, New York, 1962.
20. V. Jelink & H.F. David, *J. Electrochem. Soc.*, **104**, 279 (1957).
21. T.M. Shvets, T.N. Amelichina & E.P. Zelibo, *METALL*, **11**, 8 (1980).

El Rehim   Sayyah   El Deeb

About the Authors

Dr. S.S. Abd El Rehim* is professor of electrochemistry in the Chemistry Department, Ain Shams University, Abbassia, Cairo, Egypt. He holds a PhD from the Hungarian Academy of Science. Prof. Abd El Rehim is an active member of the Egyptian Corrosion Society. He was awarded the State Prize for Encouragement in Chemistry in 1986 from the Egyptian Academy of Scientific Research and Technology. He has published more than 115 papers in international journals. His research interests are in electroplating of metals and alloys and corrosion of metals in aqueous media.
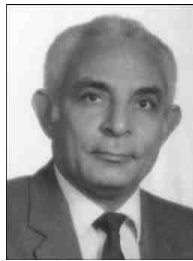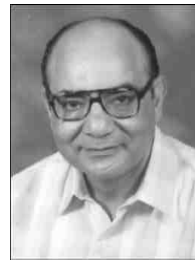
Dr. S.M. Sayyah is professor of physical chemistry of high polymers, Chemistry Department, Cairo University, Beni-Suef Branch. He holds a PhD from the Technical University of Dresden. Prof. Sayyah is an active member of the Egyptian Polymer Society and has published more than 90 papers in international journals. His research interests are in polymer chemistry, characterization of polymers by IR, UV, ^{1}H-NMR, X-ray, TGA, DTA and TLC, as well as applications of water-soluble polymers as corrosion inhibitors, conducting polymers and electropolymerization.

M.M. El Deeb is a doctoral candidate and assistant lecturer at Cairo University, Beni-Suef Branch. He holds an MSc from Cairo University and is an active member of the Egyptian Corrosion Society. His technical interests include electroplating of metal and alloys, preparation and characterization of water-soluble polymers as corrosion inhibitors for metals in aqueous media, as well as electropolymerization and electrochemistry of conducting polymers.
* To whom correspondence should be addressed.