Russian Journal of Applied Chemistry, Vol. 74, No. 11, 2001, pp. 1842–1845. Translated from Zhurnal Prikladnoi Khimii, Vol. 74, No. 11, 2001, pp. 1787–1790.

APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrodeposition of Tin from Sulfate Electrolyte with Organic Additives

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Received June 7, 2001

Abstract—Electrodeposition of tin from sulfate electrolytes containing $SnSO_4$, H_2SO_4, Synthanol, formalin, and benzyl alcohol was studied.

It was shown in [1, 2] that dihydric alcohols (1,4-butynediol, 1,4-butenediol, and 1,4-butanediol), present in sulfate tin-plating electrolyte simultaneously with Synthanol and formalin, favor formation of lustrous tin coatings. Proceeding with these studies, we considered in this work electrodeposition of tin from a sulfate electrolyte in the presence of Synthanol, formalin, and benzyl alcohol.

The study was carried out in the electrolyte of the following composition (g l^{-1}); $SnSO_4$ 5–50, H_2SO_4 90–100. The organic substances were introduced in the following amounts: Synthanol DS-10 1–4 g l^{-1}; formalin (37% solution) 1–10 and benzyl alcohol 1–10 ml l^{-1}.

Tin coatings 6–24 μm thick were deposited onto copper samples. Polarization curves were obtained potentiodynamically with a P-5878 potentiostat. The leveling power of the electrolyte was measured on a flat sinusoidal microprofile. The leveling power P was calculated using the equation [3]

$$P = \log[(H_0 \times 2.3a)/(H_\tau \times 2\pi h_{av})],$$

where H_0 and H_τ are, respectively, the microprofile amplitudes before and after deposition of tin; a is the sinusoid wavelength, and h_{av} is the coating thickness (10 μm).

The coating luster was measured with an FB-2 photoelectric luster meter.

Our experiments showed that matte coatings with coarsely crystalline structure are formed in tin-plating electrolyte ($SnSO_4$ 30 and H_2SO_4 100 g l^{-1}) containing 1–4 g l^{-1} of Synthanol. In the presence of formalin and benzyl alcohol (in amount of 1–10 ml l^{-1} each), matte coatings with unsatisfactory quality are obtained. Addition of benzyl alcohol to an electrolyte with Synthanol does not lead to any significant change in the coating quality. In an electrolyte with Synthanol and formalin, silvery coatings are formed. The outward appearance of the coatings is much improved if benzyl alcohol (6–8 ml l^{-1}) is added to an electrolyte with Synthanol (2–3 g l^{-1}) and formalin (6–8 ml l^{-1}). In this case, lustrous tin coatings are obtained in the current density range i_c = 4–12 A dm^{-2}. When the concentrations of formalin and benzyl alcohol are beyond the above limits, semilustrous or silvery coatings are obtained, depending on i_c. At Synthanol concentrations lower than 2 g l^{-1}, the working range of current densities at which lustrous coatings are obtained becomes much narrower. At Synthanol concentrations exceeding 3 g l^{-1}, the interval of current densities in which lustrous coatings are obtained remains unchanged, but electrolyte foaming is much enhanced, which hinders the electrodeposition process. It should be noted that lustrous coatings can only be obtained with electrolyte stirring. We have examined the influence of the $SnSO_4$ concentration on the range of working current densities for preparing lustrous coatings. We found that raising the $SnSO_4$ concentration from 5 to 50 g l^{-1} in an electrolyte containing H_2SO_4 (90–100 g l^{-1}), Synthanol (2–3 g l^{-1}), formalin (6–8 ml l^{-1}, and benzyl alcohol (6–8 ml l^{-1}) makes higher the current density necessary for obtaining lustrous coatings. For example, lustrous coatings are formed in the following ranges of current densities (A dm^{-2}) at indicated $SnSO_4$ concentrations in the electrolyte: 1–7, 5 g l^{-1}; 1–8, 10–20 g l^{-1}; and 4–12, 30–50 g l^{-1}.

Data on current efficiency (CE) in tin-plating electrolyte with additives are presented in Fig. 1. It can be seen that CE grows with increasing $SnSO_4$ concentration in the electrolyte and decreases when i_c becomes

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higher. The highest CE is observed in an electrolyte containing 50 g l^{-1} of $SnSO_4$. Lustrous tin coatings have finely crystalline structure and firmly adhere to the base metal.

To reveal the influence of organic substances on electrodeposition of tin, cathodic polarization curves were measured with immobile and rotating disk electrodes (Fig. 2). It can be seen that organic additives (curves *1* and *2*) make the deposition of tin slower and the cathodic polarization stronger. With increasing speed of electrode rotation, the overvoltage of tin deposition also grows (curves *2–4*).

The inhibiting action of organic substances in a tin-plating electrolyte is presumably due to their adsorption onto the electrode surface. This assumption is confirmed by measurements of the electrical double layer capacitance *C*. As seen from Fig. 2 (curves *5*, *6*), introduction of organic substances into the electrolyte leads to a decrease in the double layer capacitance in the potential range from –0.3 to –0.4 V from 32 to 8 μF cm^{-2}. At higher potentials, organic substances are desorbed from the electrode surface, which leads to higher capacitance of the double layer.

To reveal the effect of organic substances on the microdistribution of electrodeposited tin, we studied the dependence of the leveling power *P* of the electrolyte on the cathode current density upon addition of organic substance to the electrolyte. As seen from Fig. 3 (curve *1*), introduction of Synthanol into the tin-plating electrolyte leads to a certain leveling of the surface ($P = 0.1$) only at $i_c = 1$ A dm^{-2}. With the current density increasing further, surface antileveling is observed. On addition of formalin to an electrolyte with Synthanol (curve *2*), the leveling ($P = 0.14$–0.05) occurs at $i_c = 1$–10 A dm^{-2}. Introduction of benzyl alcohol into the electrolyte leads to more pronounced surface leveling (curve *3*). The leveling power of the mixture reaches its maximum value $P = 0.83$ at $i_c = 7$ A dm^{-2}.

Thus, the leveling additives in a mixture of organic substances are formalin and benzyl alcohol, with the latter ensuring the strongest surface leveling. A study of the influence exerted by the concentration of benzyl alcohol on the extent of leveling demonstrated that, with increasing concentration of benzyl alcohol (Fig. 3, curve *4*), the *P* value grows to reach a maximum of 0.69 at $C = 6$ ml l^{-1}. According to the adsorption–diffusion theory of surface leveling [3], the leveling additives inhibit electrodeposition of metals, with the extent of inhibition controlled by diffusion of an additive in the course of electrodeposition. The polarization curves measured on a rotating disk electrode at

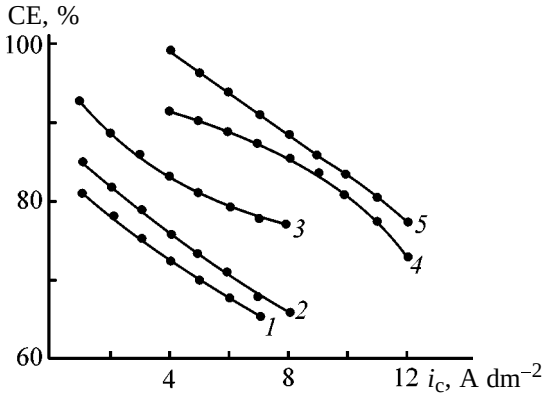

Fig. 1. Current efficiency CE vs. current density i_c at different $SnSO_4$ concentrations in the electrolyte. Mechanical stirring; the same for Fig. 2. Electrolyte composition: H_2SO_4 100, Synthanol 2 g l^{-1}; formalin 6, benzyl alcohol 6 ml l^{-1}. Electrolyte + $SnSO_4$ (g l^{-1}): (*1*) 5, (*2*) 10, (*3*) 20, (*4*) 30, and (*5*) 50.

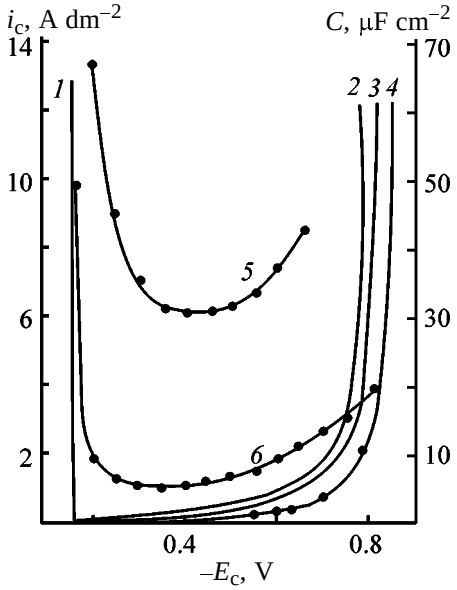

Fig. 2. (*1–4*) Cathodic polarization curves and (*5*, *6*) dependences of the capacitance of the electrical double layer, *C*, on the electrode potential E_c (vs. s.h.e), obtained in tin-plating electrolyte. Electrolyte composition (g l^{-1}): $SnSO_4$ 30, H_2SO_4 100; the same for Fig. 3. (i_c) Current density. (*1*, *5*) Electrolyte; (*2–4*, *6*) *1* + Synthanol, 2 g l^{-1}; formalin, 6 ml l^{-1}; and benzyl alcohol, 6 ml l^{-1}. Speed of electrode rotation (rpm): (*3*) 200 and (*4*) 2000.

different speeds of rotation can qualitatively model the cathodic process at microprojections (high speeds of electrode rotation) and at microdepressions (low speeds) [3]. The uneven accessibility of the microprofile is the reason for the nonuniform distribution of the rates at which additive is delivered to different parts of the microprofile. Since the inhibiting effect exerted by the leveling additives on electrodeposition

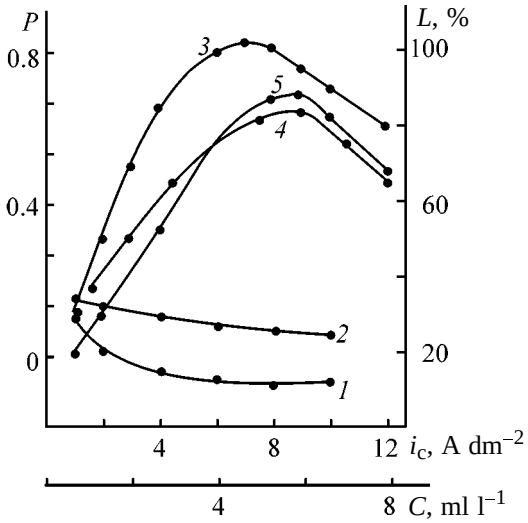

Fig. 3. Leveling power P vs. (*1–3*) current density i_c and (*4*) benzyl alcohol concentration C, and (*5*) coating luster L vs. current density for tin-plating electrolyte. (*1*) Electrolyte + Synthanol, 2 g l^{-1}; (*2*) *1* + formalin, 6 ml l^{-1}; (*3*, *5*) *2* + benzyl alcohol, 6 ml l^{-1}.

of metals becomes stronger with increasing rate of additive diffusion toward the cathode (high speed of rotation), this effect is more pronounced at microprojections, and less so at microdepressions, which leads to nonequilibrium distribution of the electrodeposition rates.

Analysis of the polarization curves measured in electrolytes with organic additives (Fig. 2, curves *2–4*) shows that the cathodic polarization curves measured at different speeds of rotation qualitatively model the distribution of the tin electrodeposition rate over the surface microprofile [3]. With increasing i_c, the leveling power first grows and then, at comparatively high current densities, the surface concentration of the additive and its inhibiting action decrease even at microprojections, which makes the leveling effect weaker. At too low content of additive in the electrolyte, when there occurs weak inhibition of tin electrodeposition, one cannot expect a pronounced leveling effect. At the same time, at too high concentrations of additive, the leveling power decreases because of the termination of the diffusion control over the rate of consumption of the additive and its inhibiting action. The phenomenon of leveling is related to the luster of electroplated coatings, since luster formation is also governed by leveling of submicrometer surface irregularities. According to [4], large microirregularities, from 0.2 to 100 μm and more in size, are eliminated in leveling, and very fine submicroirregularities of about 0.15 μm and less, in luster formation. Comparison of samples differing in luster and extent of leveling (Fig. 3, curves *3*, *5*) shows that these parameters are correlated: the higher the extent of leveling, the stronger the luster. Thus, leveling of submicro- and microirregularites on the cathode surface occurs in the course of electrolysis in a tin-plating electrolyte containing Synthanol, formalin, and benzyl alcohol.

On the basis of the performed investigations, a sulfate electrolyte of the following composition was developed for obtaining lustrous tin coatings (g l^{-1}): $SnSO_4$ 5–50, H_2SO_4 90–100, Synthanol DS-10 2–3; formalin 37% solution 6–8, benzyl alcohol 6–8 ml l^{-1}; deposition mode: i_c = 1–12 A dm^{-2}, CE = 65–98%. The process is carried out with mechanical stirring of the electrolyte. To obtain high-quality lustrous coatings, it is necessary to use anode made of pure tin. In order to prevent electrolyte contamination with sludge, the anodes are to be placed in sheaths made of polypropylene, before being submerged in the electrolyte. The electrolyte temperature is 20–25°C. At higher temperatures, the electrolyte rapidly turns turbid, and a large amount of precipitate is formed at the bath bottom, which impairs the coating quality. Long-term tests with the electrolyte demonstrated its high stability in operation. However, it should be noted that, during prolonged operation, a light yellow precipitate impairing the coating quality is formed on the bath bottom. The precipitate should be filtered off at regular intervals. The adjustment of the $SnSO_4$, H_2SO_4, and formalin content relies upon the results of chemical analysis [5]. The adjustment of the Synthanol content of the electrolyte should be done after passing 100 A h l^{-1} of electricity, by introducing 1 g l^{-1} of the additive into the bath. Since there is no technique for determining the concentration of benzyl alcohol in a tin-plating electrolyte, a spectrophotometric method was developed for this purpose. A 50-ml sample of a tin-plating electrolyte containing Synthanol, formalin, and benzyl alcohol was extracted with octanol (50 ml) under vigorous stirring in the course of 10 min. During this time, complete extraction was achieved. Part of the obtained organic phase was placed in a cell 10 mm thick, and spectra were recorded in the optical density–wavelength coordinates with an SF-26 spectrophotometer in the range 220–310 nm. As blank sample was used a solution obtained by extraction with octanol of a tin-plating electrolyte containing no benzyl alcohol. It was found that for all of the solutions studied the peak of the absorption band is observed at 252 nm, with the peak growing in height with increasing concentration of benzyl alcohol. It should be noted that the absorption is zero or very low in the employed wavelength range for all other components.

The obtained spectra were used to plot the calibration curve describing the dependence of the concentration of benzyl alcohol on the optical density at the maximum at 252 nm. This calibration curve can be used to monitor the concentration of benzyl alcohol in a tin-plating electrolyte. The scatter of measurement results in separate series does not exceed 5%.

CONCLUSIONS

(1) A study of tin electrodeposition from a sulfate electrolyte in the presence of organic substances demonstrated that high-quality lustrous deposits of tin are obtained in an electrolyte containing Synthanol, formalin, benzyl alcohol, $SnSO_4$, and H_2SO_4.

(2) A sulfate electrolyte and a deposition mode were developed for obtaining lustrous tin coatings with leveled surface.

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