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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrodeposition of Tin from Sulfate Electrolyte in the Presence of Syntanol, Formaldehyde, and Allyl Alcohol

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Abstract—The elecrodeposition of tin from a sulfate solution containing $SnSO_4$, H_2SO_4, Syntanol, formaldehyde, and allyl alcohol was studied.

Organic substances ensuring formation of lustrous tin coatings can be chosen taking into account their first ionization potentials I [1]. It was established that obtaining lustrous tin coatings requires the presence of organic substances, luster-producing additives (LA), with I = 7.25 or 8.95–10.50 eV in an electrolyte containing Syntanol DS-10 and formaldehyde (37% solution).

We studied the influence exerted by allyl alcohol having I = 10.17 eV on the tin electrodeposition from a sulfate solution containing Syntanol and formaldehyde.

The study was performed in an electrolyte containing (g l^{-1}) $SnSO_4$ 10–50 and H_2SO_4 90–100. Organic substances were added into the electrolyte in the following amount: Syntanol DS-10 1–4 g l^{-1}, formaldehyde (37% solution) 1–10, and allyl alcohol 1–20 ml l^{-1}.

A 9–12-μm-thick tin layer was deposited onto copper samples. The polarization curves were taken with a P-5828 potentiostat. The degree of the coating luster was determined on an FB-2 photoelectric brightness-measuring device. The leveling power P of the electrolytes was determined by a direct method involving a profilographic measurement of the sample surface with a sine-shaped microprofile and calculation by the formula [2]

$$P = 2.3a/2\pi h_{av} \log (H_0/H_i),$$

where a is the amplitude of the wave of the sine-shaped microprofile; h_{av}, average thickness of the coatings (10 μm); H_0 and H_i, initial and final wave amplitudes of the sine-shaped profile, respectively.

The capacitance of an electrical double layer was measured in the course of electrolysis with a P-5021 ac bridge at a frequency of 30 kHz in a series equivalent chain.

The electrodeposition was performed at 18–25°C with and without agitation of electrolytes with a magnetic stirrer.

The influence exerted by organic additives on the outward appearance of the coatings was studied in an electrolyte containing (g l^{-1}) $SnSO_4$ 50 and H_2SO_4 100. It was found that the addition of Syntanol (1–4 g l^{-1}) to the electrolyte results in dull coatings. In the presence of formaldehyde (1–10 ml l^{-1}) or allyl alcohol (1–20 ml l^{-1}), or of both simultaneously, poor coatings are formed. The coatings with a considerably better outward appearance are formed in an electrolyte containing Syntanol (2–3 g l^{-1}), formaldehyde (6–8 ml l^{-1}), and allyl alcohol as additive. The influence of allyl alcohol is demonstrated in the table.

Influence of the allyl alcohol concentration c on the outward appearance of the tin coatings at various current densities. Electrolyte composition, g l^{-1}: $SnSO_4$ 30, H_2SO_4 100, Syntanol DS-10 2, formaldehyde (37% solution) 6 ml l^{-1}. Mechanical agitation

c, ml l^{-1}	j_c, A dm^{-2}	Outward appearance of coatings
1–5	1–2	Dull
	3–5	Semilustrous
	6–10	Dark gray
10–15	1–3	Dull
	4	Semilustrous
	5–10	Lustrous
	11–12	Lustrous with burn-on
20	1–4	Dull
	5–7	Lustrous
	8–10	Lustrous with burn-on

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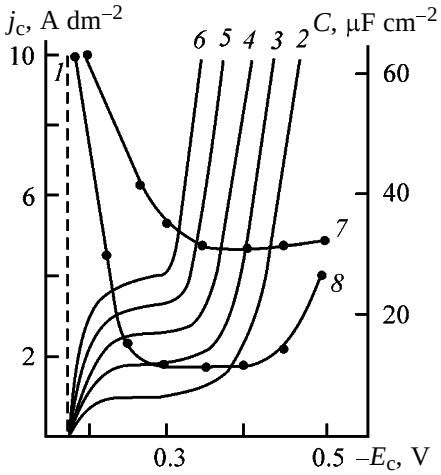

Fig. 1. (*1–6*) Cathodic polarization curves taken on a rotating Sn disk electrode and (*7, 8*) dependences of the electrical double layer capacitance C on the electrode potential relative to a standard hydrogen electrode E_c in the tin-plating electrolytes. (j_c) Current density. Electrolyte (g l^{-1}): $SnSO_4$ 30 and H_2SO_4 100. (*1, 7*) Electrolyte, (*2, 8*) *1* + 2 g l^{-1} Syntanol, 6 ml l^{-1} formaldehyde (37% solution), and 10 ml l^{-1} allyl alcohol; (*3, 4, 5, 6*) *2* at a rotation rate of the disk electrode (rpm) of 200, 500, 1000, and 2000, respectively.

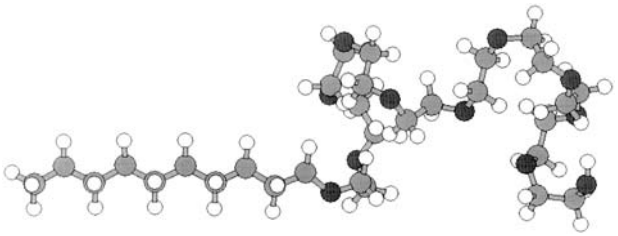

Fig. 2. Structure of Syntanol molecule according to quantum-chemical calculation. Hydrogen, carbon, and oxygen atoms are colored white, gray, and dark, respectively.

As seen, lustrous coatings can be obtained in the presence of allyl alcohol in certain modes of the electrolysis. The widest range (5–10 A dm^{-2}) of the current densities j_c ensuring formation of lustrous deposits is observed at an allyl alcohol concentration of 10–15 ml l^{-1}.

Deviations of the formaldehyde concentration from the above limit result in silvery coatings. At a Syntanol concentration below 1–2 g l^{-1}, the working interval ensuring formation of lustrous coatings is considerably narrower. At a Syntanol concentration above 3–4 g l^{-1}, the current density range in which lustrous coatings are obtained is the same, but foam formation in the electrolyte increases considerably, which complicates electrodeposition in the agitated electrolyte.

We studied the influence of the $SnSO_4$ concentration on the current density range ensuring formation of lustrous coatings. The study was performed in an electrolyte containing 2 g l^{-1} Syntanol, 6 ml l^{-1} formaldehyde, and 10 ml l^{-1} allyl alcohol. It was found that decreasing the $SnSO_4$ concentration makes j_c range ensuring formation of lustrous coatings narrower. For example, at a $SnSO_4$ concentration of 10–20 g l^{-1} lustrous coatings were formed in the current density range 2–4 A dm^{-2}, whereas at 30–60 g l^{-1}, they were formed in the 5–10 A dm^{-2} range. The H_2SO_4 concentration in the electrolyte must be within 90–100 g l^{-1}. Below 90 g l^{-1}, the electrolyte operation is instable, and the j_c range ensuring formation of lustrous coatings is narrower. At the H_2SO_4 concentration above 100 g l^{-1}, the range of the current densities ensuring formation of lustrous coatings does not vary.

It should be noted that high-quality lustrous coatings are obtained solely in an agitated electrolyte, and dull coatings are formed without agitation.

The current efficiency (CE) by tin in the electrolytes ensuring obtaining lustrous coatings decreases with increasing j_c and increases with increasing $SnSO_4$ concentration. At a $SnSO_4$ concentration varied within 10–20 g l^{-1} and at j_c = 2–4 A dm^{-2}, CE = 95–75%, and at the $SnSO_4$ concentration within 30–50 g l^{-1} and j_c = 5–10 A dm^{-2} CE = 95–90%.

The cathodic polarization curves on a rotating-disc electrode were obtained. As seen from Fig. 1, in the presence of organic substances, the cathodic polarization increases and the plateau of the limiting current appears on the cathodic polarization curve (curves *2, 3*). As the rate of rotation of the disc electrode increases, the limiting current density increases, whereas the cathodic polarization decreases (curves *2–6*). The limiting current in the polarization curves is due to adsorption of organic substances and formation of an adsorption layer on the cathode surface. This suggestion is confirmed by the results of measuring the capacitance of the electrical double layer. As seen from Fig. 1, curves *7* and *8*, the introduction of organic substances into the electrolyte results in the decrease of the double layer capacitance. In the potential range E from –0.3 to –0.4 V, the capacitance decreases from 32 to 11 μF cm^{-2}. At higher cathodic potentials, the organic substances desorb from the electrode surface, which makes the adsorption layer nonuniform and results in increased double layer capacitance.

To ascertain the nature of the adsorption layer formed on the cathode surface in electrochemical tin plating, we calculated the optimal structure of the

Syntanol molecule by the PM3 semiempirical quantum-chemical method [3, 4].

As seen from Fig. 2, the molecule consists of fibrillar hydrophobic nonpolar moiety (hydrocarbon radical $C_{10}H_{21}$) and hydrophilic moiety [globular oxyethylated fragment $(C_2H_4O)_{10}OH$]. The maximum size of the molecule lies within 2000 × 900 × 500 pm.

The surface of tin electrode was simulated by a rectangular cluster consisting of 48 tin atoms. The cluster was chosen as recommended in [5].

It was established that an adsorption layer on the tin surface is formed with planar orientation of the Syntanol molecule. In the process, formaldehyde, allyl alcohol, and Sn^{2+} ions are distributed in its globular moiety (Fig. 3). The calculation results show that, with the system Syntanol + allyl alcohol + Sn^{2+}, the interaction with the cluster surface is the strongest (E = 1009 kJ mol^{-1}). With formaldehyde introduced into this system, the interaction energy decreased by a factor of approximately 3 (E = 384 kJ mol^{-1}).

As known [6], formation of lustrous coatings is associated with the adsorption of organic substances on the electrode surface and with the complex physicochemical processes occurring in the near-cathode layer. The diffusion-hydrodynamic mode of delivery (removal) of ions changing the structure and properties of an adsorption layer on the cathode surface is also important [7]. The possibility of the electrochemical transformation of organic molecules must also be taken into account. In such a case, the products of transformation of the additive on the electrode, rather than the additive itself, can exert a luster-producing effect. Taking into account the experimental data obtained, the luster production in electrochemical tin plating can be explained by the adsorption–diffusion mechanism.

Unequal accessibility of different regions of the submicroprofile to LA is due to the adsorption film on the cathode [8]. The thickness of this film must be comparable with the size of ridges and pits, typical of lustrous surface.

As already noted, in a tin-plating electrolyte, the adsorption layer on the cathode is formed by Syntanol, formaldehyde, LA, and Sn^{2+}. Without agitation of the electrolyte, the thickness of the adsorption layer is large owing to polymolecular adsorption of organic substances (Fig. 4a). The layer formed in an agitated electrolyte has a smaller thickness, comparable with the size of ridges and pits (Fig. 4b). In this case, the adsorption layer plays the role of a diffusion layer in which a gradient of LA concentration is created. After

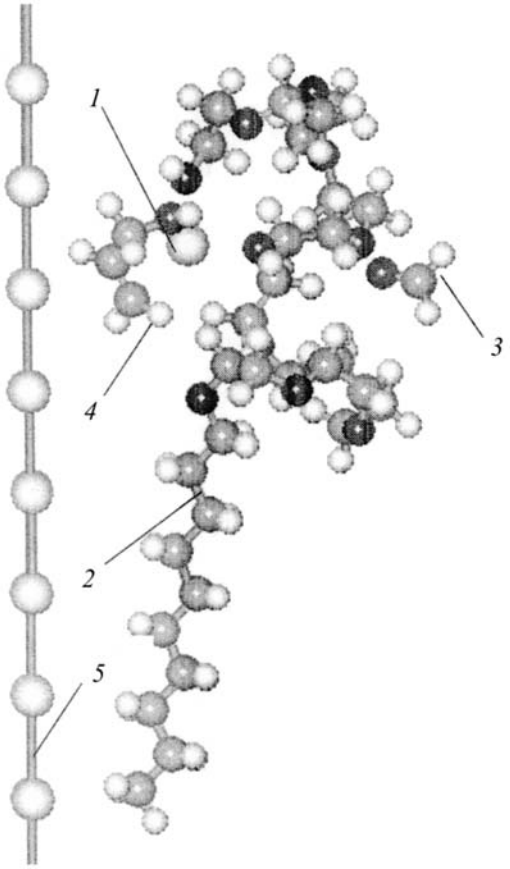

Fig. 3. System of (*1*) Sn^{2+}, (*2*) Syntanol, (*3*) formaldehyde, (*4*) allyl alcohol, and (*5*) Sn_{48} cluster. Planar orientation of the Syntanol molecule with respect to the cluster plane.

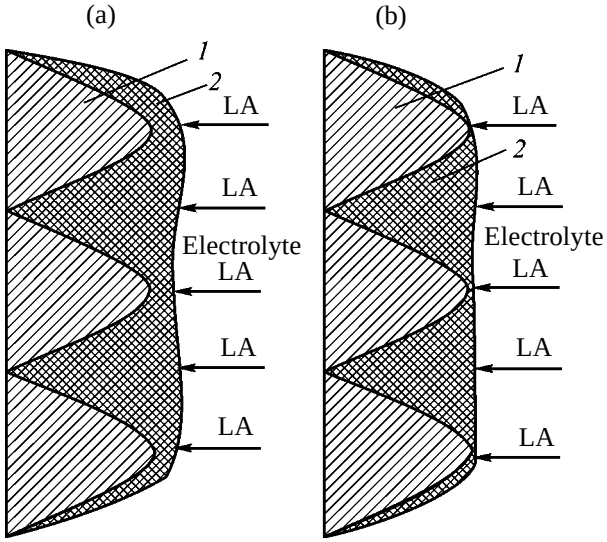

Fig. 4. Scheme of (*1*) ridges and pits of the submicroprofile in the presence of (*2*) adsorption layer (a) with and (b) without agitation of the electrolyte. Diffusion flow of LA is indicated by the arrows.

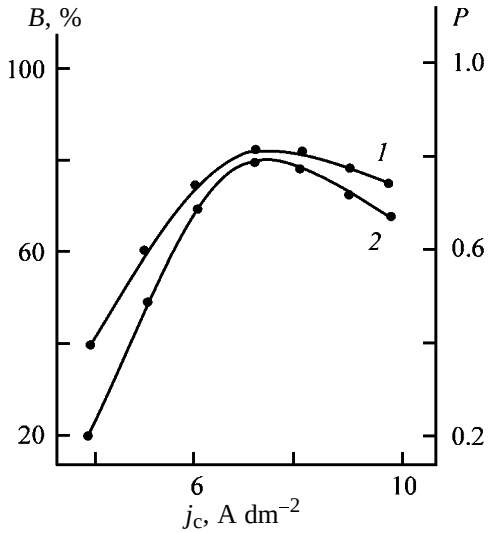

Fig. 5. (*1*) Degree of luster *B* and (*2*) leveling power *P* of the coatings vs. the cathodic current density j_c. Electrolyte: $SnSO_4$ 30 g l^{-1}, H_2SO_4 100 g l^{-1}, Syntanol 2 g l^{-1}, formaldehyde (37% solution) 6 ml l^{-1}, and allyl alcohol 7 ml l^{-1}; mechanical agitation.

the certain agitation rate is attained, the diffusion to the cathode will result in stronger adsorption of LA on ridges than in pits. As in adsorption–diffusion leveling theory [2], unequal accessibility of different regions of the microprofile is provided by consumption of LA in the diffusion-limited process, i.e., when the rate of LA consumption is equal to the limiting rate of its delivery to the cathode, with the consumption mechanism (incorporation of molecules into the deposit or their electrochemical reduction) insignificant. Since with increasing rotation rate of the disk electrode (and rate of the electrolyte agitation) the limiting current increases and the cathodic polarization decreases, it appears that inhibition on the ridges occurs to a lesser extent than in pits.

At the same time, despite the presence of the adsorption layer in them, a larger amount of tin will be deposited in pits than onto ridges (Fig. 4b). This is due to incorporation of tin ions Sn^{2+} into the adsorption film. Such redistribution of the metal makes the submicroprofile relief smoother and hence makes the surface lustrous.

We studied the leveling power of tin-plating electrolytes for obtaining lustrous coatings. It was found that they have the positive leveling power. The degree of luster and degree of leveling were studied in relation to the cathodic current density. Comparison of these parameters revealed their interrelation, i.e., the higher the degree of leveling, the higher the degree of luster (Fig. 5).

The phenomenon of leveling is associated with the luster of electrolytic coatings, since the luster production is also the process of the surface leveling. In the course of leveling, coarse microroughnesses, from 0.2 to 100 μm and larger, are removed. In the course of the formation of lustrous surface, very small submicroroughnesses, about 0.15 μm and smaller, are removed [9]. Thus, in a tin-plating electrolyte containing Syntanol, formaldehyde, and allyl alcohol, in the course of the tin electrodeposition the submicro- and microroughnesses of the cathode surface are smoothed.

Thus, we have developed a sulfuric acid tin-plating electrolyte of simple composition for obtaining lustrous coatings with a leveled surface. The electrolyte contains $SnSO_4$ 10–50 g l^{-1}, H_2SO_4 90–100 g l^{-1}, Syntanol (DS-10) 2–3 g l^{-1}, formaldehyde (37% solution) 6–8 ml l^{-1}, and allyl alcohol 10–15 ml l^{-1}. The process is performed with mechanic agitation of the electrolyte at the current density j_c = 2–10 A dm^{-2}. The current efficiency is 75–95% and the electrolyte temperature, 18–25°C. Above 25°C, the operation region of j_c in which lustrous coatings are obtained is narrower, the electrolyte becomes turbid wihtin a short time, and the deposit appears on the bath bottom. All the above impairs the quality of the coatings obtained. Anodes must be made of pure tin. To prevent the contamination of the electrolyte with sludge, it is necessary to place the anodes into jackets made of a polyvinyl chloride or polypropylene fabric.

The electrolyte should be adjusted with respect to $SnSO_4$, H_2SO_4, and formaldehyde on the basis of chemical analysis data [10]. The Syntanol amount in the electrolyte must be corrected after the amount of electricity of 100 A g^{-1} l^{-1} is passed; 1 g l^{-1} of Syntanol is added to the bath. The consumption of allyl alcohol is 0.02 ml A^{-1} h^{-1}.

CONCLUSIONS

(1) The study of the electrodeposition of tin from a sulfuric acid electrolyte containing organic additives showed that, when Syntanol, formaldehyde, and allyl alcohol are present simultaneously, the current densities at which lustrous coatings are formed vary within 2–10 A dm^{-2}, depending on the $SnSO_4$ concentration in the electrolyte.

(2) Lustrous coatings in tin electrodeposition are formed by the adsorption–diffusion mechanism.

(3) The leveling power of the sulfuric acid electrolyte containing organic additives was studied. It was

found that a tin-plating electrolyte containing Syntanol, formaldehyde, and allyl alcohol has the positive leveling power depending on j_c. It was shown that the degree of luster correlates with the leveling power: the higher the degree of luster, the higher the leveling power.

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