CHRONOPOTENTIOMETRIC MEASUREMENTS IN A FUSED ALUMINIZING ELECTROLYTE

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In electrolytic aluminizing from a $2AlCl_3 \cdot NaCl$ salt melt small quantities of lead and tin ions introduced into the melt by means of the auxiliary anodes lead to an improvement in the coating quality[1].

Chronopotentiometric measurements aimed at calculating the diffusion coefficients of depolarizer ions have been carried out with a view to studying the behavior of these ions in the melt.

The galvanostatic circuit is described in [2]. The P—t curves were recorded on the screen of a type S1-4 oscillograph.

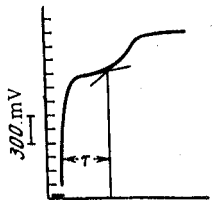

Fig. 1. Curve illustrating the determination of the transition time for Pb^{2+}

The cell consisted of a Perspex test tube having a side arm for passing an inert gas through the melt. The tube was enveloped by aluminum foil and in it were mounted three platinum electrodes: a cathode, an indicator anode, and a reference electrode. The electrode dimensions were selected to suit the requirements of linear diffusion. The electrode surfaces were cleaned with fine (5 μ) emery paper. This is considered an acceptable technique for chronopotentiometric measurements in fused salts since the surface roughnesses produced are very much less than the thickness of the diffusion layer. The electrodes were restored to their original condition by short-circuiting. Since the electrode potential reverted to zero, we considered that the electrodes had been sufficiently restored. A $2AlCl_3 \cdot NaCl$ melt was used as the base electrolyte and was dried by passing dry HCl and argon through it. The HCl drying system contained a vessel filled with dry $AlCl_3$, which is a better drying agent than H_2SO_4 [3], this also serving to prevent extraneous substances from falling into the melt. Lead and tin chlorides purified by conventional methods served as depolarizers. Their concentration in the melt was a mere $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ g-eq/cc.

TABLE 1. Results of Chronopotentiometric Measurements

$I \cdot 10^{-3}$, A	$i \cdot 10^{-2}$, A $\cdot cm^{-2}$	t, sec	$\sqrt{\tau} \cdot 10^{-2}$ A $\cdot cm^{-2} \cdot sec^{1/2}$	1/i	$D \cdot 10^{5}$, $cm^2 \cdot sec^{-1}$
			Pb^{2+}		
5,0	2,0	2,0	2,83	0,50	0,27 *
7,0	2,8	1,0	2,80	0,36	0,27
9,0	3,6	0,6	2,80	0,28	0,27
11,0	4,4	0,4	2,80	0,23	0,27
12,0	4,8	0,3	2,84	0,21	0,27
			Sn^{2+}		
7,0	2,8	4,0	5,60	0,35	0,15
9,0	3,6	2,2	5,35	0,28	0,14
11,0	4,4	1,4	5,20	0,23	0,11
13,0	5,2	1,0	5,20	0,19	0,11
15,0	6,0	0,8	5,35	0,16	0,11
				Mean	0,12

* The diffusion coefficients obtained for Pb^{2+} and Sn^{2+} are in agreement with those obtained by other authors [5].

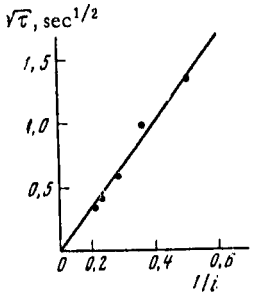

Fig. 2. Relation between $\sqrt{t}$ and 1/i for Pb^{2+} in a $2AlCl_3 \cdot NaCl$ melt, t = 160°.

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The experiments were carried out at 160 ± 3°, this temperature being maintained with the aid of a "Kent" type thermostat and Pt — Pt — Rh thermocouples. The transition time was determined from the P — t curves, as shown in Fig. 1.

The transition time for lead ions was measured at lead ion concentrations in the melt of the order of $1 \cdot 10^{-4}$ g-eq/cc and currents of 5-15 mA, and that for tin ions at tin ion concentrations in the melt of the order of $1\text{-}3 \cdot 10^{-4}$ g-eq/cc and currents of 7-15 mA (see Table 1).

Analysis of the results produced leads to the conclusion that the electrode reaction is diffusion controlled. The product $i\sqrt{t}$ is independent of the polarization current density. The relation between $\sqrt{t}$ and $1/i$ indicates that the kinetics of the electrode process are purely diffusional (Fig. 2), since the graph is a straight line passing through the origin.

The coefficients of diffusion of Pb^{2+} and Sn^{2+} in $2AlCl_3 \cdot NaCl$ are calculated from a formula obtained by solving the Sand equation, namely

$$D = \frac{4 \cdot \tau \cdot I^2}{\overline{u} \cdot n^2 \cdot F^2 \cdot S^2 \cdot C_0},$$

where the symbols have the generally accepted meanings.

From the chronopotentiograms obtained in the presence of Sn^{2+} it is clear that the decomposition potential of the base electrolyte (1.7 V) is not attained, while the limiting potential is 1.3 V. This value corresponds to the second discontinuity on the I — P curve which we obtained with the given electrolyte (Fig. 3). The potentials corresponding to these waves are in agreement with those obtained by the author and his coworkers in [4]. Accordingly, it is reasonable to assume that the transition time value at a potential of 0.8 V applies to the discharge of the divalent tin ions taking part in the electrode process.

We attempted to use chronopotentiometric measurements for electrolyte control, since the electrolyte can change its composition because of hydrolysis and sublimation. It was especially important to control the extent of dehydration of the melt. It follows from Fig. 4 that chronopotentiometric curves plotted with both a moisture containing and a moisture-free electrolyte can be used as a basis for deciding whether the aluminizing electrolyte contains moisture or not. This is important, since moisture impairs coating quality and in some cases even completely prevents the formation of a coating.

The operating stability of the electrolyte was determined by means of prolonged (70 h) aluminizing runs with six $2AlCl_3 \cdot NaCl$ melts using auxiliary lead modifying anodes: at the end of the experiments a sharp drop in current efficiency was observed and the coating quality was impaired. Chemical analysis showed that the electrolyte was appreciably depleted in $AlCl_3$. The P — t curve obtained with platinum electrodes in a working electrolyte indicated that electrolysis occurs at a potential of 1.2 V, i. e. at the lead deposition potential. The same result was obtained on plotting P — t curves on an iron electrode when d_c = 5 A/dm², i. e. under electrolysis conditions. Thus, the decomposition potential of the electrolyte is not attained. The oscillogram also indicated that the electrode was coated with lead, since on switching off the polarizing current the equilibrium potential was that of the lead electrode, namely 1.2 V.

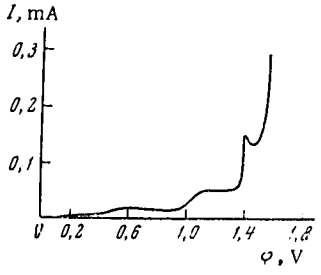

Fig. 3. I — P curve for the electrodeposition of aluminium at a platinum electrode in the presence of Sn^{2+} ions; t° = 200°.

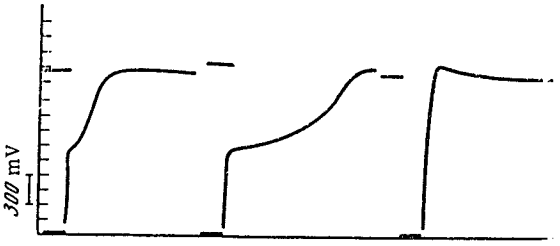

Fig. 4. P — t curves. a) electrolyte containing moisture; b) electrolyte swept with HCl; c) electrolyte swept with argon.

It is known that the coincidence of deposition potentials is a necessary condition for the coprecipitation of metal ions differing in electrochemical properties. In particular, this is attained by raising the concentration of the more negative ions and reducing that of the more positive ions. In our case, as a result of the sublimation of $AlCl_3$ the electrolyte became impoverished in Al ions which led to the coprecipitation of Al and Pb, not at the potential of Al deposition but at the lead deposition potential, which results in impairment of coating quality. Lead has a favorable effect on the electrocrystallization of aluminium only when it is present in the coating in insignificant quantities. High electrolyte lead content leads to impairment of the coating quality. This conclusion is confirmed by analysis of the normal coating and of the dendrites obtained on electrodeposition of Al from an electrolyte impoverished in Al. The lead content of the dense layer of coating was found to be 0.71% by weight, and the lead content of the dendrites 2.42% by weight.

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