

FORMATION OF A LIQUID METAL DEPOSIT ON A SOLID CATHODE

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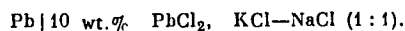
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Various aspects of the formation of electrolytic metal deposits have been the subject of numerous studies. However, most investigations in this field were concerned with electrolysis of aqueous electrolyte solutions, and, in any case, with formation of solid crystalline deposits [1, 2]. Here we present the result of an investigation of the laws governing the formation of liquid metal deposits on solid cathodes during electrolysis of fused chlorides.

It is known that a liquid metal is deposited electrolytically on a solid cathode in the form of individual drops, which generally do not cover the whole cathode surface. The number and size of the drops determine the nature of the deposit, and in particular its degree of subdivision. The latter influences the current efficiency, an important technical characteristic of the process. It is natural, therefore, that the formation of electrolytic deposits of liquid metals is a problem of great practical importance.

EXPERIMENTAL

The investigation procedure was as follows. The electrolyte was fused in a quartz beaker contained in a thick-walled steel cylinder. The beaker was covered by an asbestos lid carrying two porcelain tubes, sealed in by aluminous cement, through which the electrode leads were introduced. The cathode was a steel (St-2) or molybdenum plate, 1.5×1.5 cm in size, with a molybdenum rod as the lead; the anode consisted of the liquid metal under investigation, contained in a quartz tube with a narrow opening (lead, zinc, cadmium) or in a steel crucible (magnesium); the reference electrode was an enclosed lead chloride electrode:



The cell was placed in an electrically heated crucible furnace. The electrolyte temperature was kept constant by means of a thermocouple and an autotransformer.

Direct current was supplied to the electrodes from the UIP-1 stabilized electronic rectifier. The current was measured with the M-104 ammeter, and the cathode potential with the LP-5 tube potentiometer.

The following salts were used in the experiments: KCl and NaCl of c.p. grade, ZnCl_2 , PbCl_2 , and CdCl_2 of analytical grade, and MgCl_2 purified by vacuum distillation. All the salts were remelted and stored in airtight vessels.

The electrolyte, based on KCl-NaCl equimolar mixture, was held for 1 h at 700° after fusion. The electrodes were then immersed in it and kept there for some time without current to allow the cell to return to thermal equilibrium. The holding time was 30 sec for steel cathodes, and 10 min for molybdenum. The reason for this difference is the possibility of corrosion of the steel cathodes. The cathodes were thoroughly polished and degreased before the experiments.

After the current had been switched on, its strength was kept constant for the time required to pass the predetermined quantity of electricity. The cathode was then quickly taken out of the melt, washed in a slow stream of water, and photographed at 20-fold magnification. As the whole cathode surface could not be included in the field of the microscope, several regions were photographed on each cathode, the positions of these regions being the same in all experiments. The number of drops of liquid metal on each

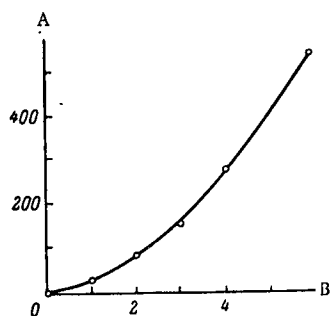


Fig. 1. Effect of current density on the number of drops of cadmium on a steel cathode. $\text{CdCl}_2 = 0.28 \text{ mol. \%}$, $q = 12 \text{ C/cm}^2$. A) Number of drops, n_c (per cm^2); B) current density, i (A/cm^2); the same in Fig. 2.

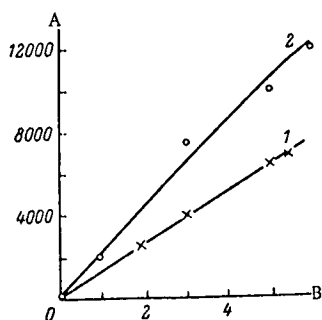


Fig. 2. Effect of current density on the number of drops in the deposit. Curves: 1) Zn, $[\text{ZnCl}_2] = 0.84 \text{ mol. \%}$, $q = 22 \text{ C/cm}^2$, molybdenum cathode; 2) Mg, $[\text{MgCl}_2] = 1.35 \text{ mol. \%}$, $q = 17.8 \text{ C/cm}^2$, steel cathode.

size to the most probable increases. From Figs. 2 and 4 it is possible to calculate the true current density for the electrodeposition, with the assumption that the true working surface of the cathode is equal to the total surface of the growing cadmium drops:

$$S_{\text{true}} = \sum S_{\text{dr.}}$$

It may be assumed in the general case that all the drops are hemispherical, i.e., that $S_{\text{dr}} = 0.5 \pi d^2$. The true current densities for electrodeposition of cadmium calculated with these assumptions are given in the table. It can be easily seen that with a sixfold increase of i_{geom} the value of i_{true} is almost unchanged. In other words, the current density adjusts itself under these conditions.

Effect of Concentration. Figure 4 shows the effect of concentration of the discharging ions on the structure of the deposit. The number of individual drops decreases with increasing CdCl_2 concentration, and at a concentration of 0.665 mol. % most of the cathode becomes covered with a continuous layer of liquid cadmium, i.e., there are no individual drops at all. At lower concentrations separate drops appear and their size decreases so that most of the drops are 0.35–0.55 mm in diameter at 0.28 mol. % CdCl_2 , and 0.15–0.25 mm at 0.16 mol. % CdCl_2 .

The following conclusions can therefore be drawn from the results: 1) the liquid metal deposit on a solid cathode consists of separate drops if the electrolysis time is not too long; 2) under otherwise constant conditions the number of growing drops in the deposit increases and the drop size decreases with

True Current Density in Deposition of Cadmium from 0.28% CdCl_2 Solution in $\text{KCl}-\text{NaCl}$ at 700°

i_{geom} (A/cm^2)	S_{true} (cm^2)	i_{true} (A/cm^2)
0.001	0.080	0.0125
0.002	0.180	0.0111
0.003	0.260	0.0116
0.004	0.310	0.0129
0.006	0.430	0.0139
Average . . .	-	0.0.24

region was then counted and their sizes were determined. The final result for each electrode was averaged over all the regions.

This procedure yielded data characterizing the structure and character of the liquid deposit formed by a given quantity of electricity. Those quantity was chosen so that the deposit consisted of separate and not excessively large drops.

Experiments were carried out on electrodeposition of lead, zinc, cadmium, and magnesium at 700° at current densities below the limiting values. The effects of geometrical current density and concentrations of the discharging ions in the melts on deposit formation were investigated.

Effect of Current Density. It was first of interest to determine the effect of current density on the number of drops of liquid metal formed. The results of investigations of the deposition of cadmium and magnesium on a steel cathode, and of zinc on a molybdenum cathode, are given in Figs. 1 and 2. Figure 3 presents data on the effect of current density on drop size of liquid cadmium deposits. These data show that the total number of n_c of drops in the deposit increases and the most probable drop diameter corresponding to the maximum of the w vs. d curve (Fig. 3) decreases with increase of geometrical current density. At the same time the structure of the deposit becomes more uniform, i.e., the proportion of drops close in

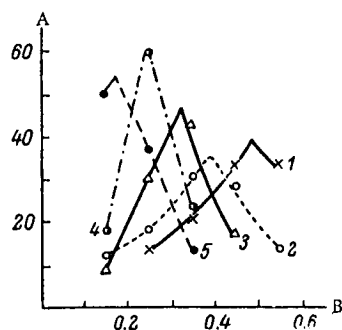


Fig. 3. Proportion of drops (w) of given average diameter d_{av} in cadmium deposits on a steel cathode at $\text{CdCl}_2 = 0.28$ mol. %, $q = 12$ C/cm², and different current densities. Current density (A/cm²): 1) 0.001; 2) 0.002; 3) 0.003; 4) 0.004; 5) 0.006.

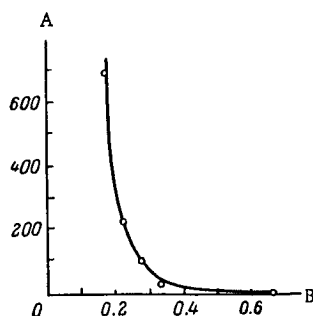


Fig. 4. Effect of CdCl_2 concentration on the number of drops of cadmium on a steel cathode. $i = 0.002$ A/cm², $q = 12$ C/cm², $t = 700^\circ$. A) Number of drops, n_c (per cm²); B) CdCl_2 concentration (mol. %).

increase of geometrical current density; 3) the true current density remains constant over a wide range of geometrical current density (principle of self-regulation of the current density); 4) the number of growing drops in the deposit decreases and the drop size increases with increasing concentration of the discharging ions.

Naturally, these relationships apply when the ions are discharged at a current density considerably lower than the limiting diffusion current density. Near the limiting current density these relationships may temporarily break down because of the nonequilibrium nature of the process.

The above relationships can be explained if it is assumed that the formation of a nucleus of a liquid metal drop on a solid surface requires a certain amount of work. This does not contradict the usual views on the mechanism of formation of a new phase in electrolysis; in particular, it may be associated with passivation of the cathode surface in the electrolyte [1], and it implies, in the final analysis, the existence of a certain (probably very small) potential difference $\tilde{\Delta}\varphi$ between the free (passive) surface of the solid cathode and the growing drops of liquid metal. Because of the potential difference $\tilde{\Delta}\varphi$, the current flows only through the surface of the growing drops and not through the entire surface of the cathode. As polarization in electrolysis of fused salts is almost entirely of concentrational character [3], it is easy to see that under steady electrolysis conditions $\Delta\varphi$ must be somewhat greater than or equal to the concentrational polarization $\Delta\varphi_{\text{conc}}$.

From the well-known relation

$$\Delta\varphi_{\text{conc}} = -\frac{RT}{zF} \ln \left(1 - \frac{i_{\text{true}}}{i_{\text{lim}}} \right), \quad (1)$$

where i_{true} and i_{lim} are the true and limiting current densities, it is easy to obtain

$$\frac{i_{\text{true}}}{i_{\text{lim}}} = 1 - \exp \left(-\frac{zF}{RT} \tilde{\Delta}\varphi \right). \quad (2)$$

As $\tilde{\Delta}\varphi$ remains constant under the given electrolysis conditions (temperature, concentrations of water, oxygen, and other passivating impurities in the melt, etc.), the ratio $i_{\text{true}}/i_{\text{lim}}$ must in the final analysis also remain constant. The value of i_{true} characterizes the total surface of the growing drops, while i_{lim} depends on the electrolyte concentration (C), the diffusion coefficients and transport numbers of the discharging ions (Δ and n), and on the hydrodynamic conditions of electrolysis. We know that in the simplest case

$$i_{\text{lim}} = \frac{zF}{1-n} \cdot \frac{\Delta}{\delta} c, \quad (3)$$

where δ is the thickness of the diffusion layer.

Increase of the geometrical current density leads to increase of $i_{\text{true}}/i_{\text{lim}}$, so that Eq. (2) breaks down and $\Delta\varphi_{\text{conc}}$ becomes greater than $\tilde{\Delta}\varphi$. This leads to appearance of new nuclei and to increase of the total surface of the growing drops until Eq. (2) becomes valid again; i.e., $i_{\text{true}}/i_{\text{lim}}$ must remain constant in a definite range of geometrical current densities.

The ratio $i_{\text{true}}/i_{\text{lim}}$ increases with decreasing concentration of the discharging ions; therefore to satisfy Eq. (2) the true current density must decrease. This is ensured by increase of the number of growing drops. Changes of electrolyte concentration also probably influence $\Delta\varphi$, and therefore the relation between the number of growing drops and concentration is not as simple as the relation between the

number of drops and current density. There is no doubt, however, that the factors governing formation of electrolytic deposits in salt melts are passivation of the cathode surface and concentrational polarization.

SUMMARY

Formation of liquid metal deposits on solid cathodes during electrolysis of fused salts has been investigated. It was shown that increase of current density and decrease of concentration of the discharging ions lead to an increase of the number of drops forming the deposit, and a decrease of their size. These results can be explained on the assumption that the factors governing formation of the deposit are cathodic passivation and concentrational polarization.

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