PHYSICAL CHEMISTRY

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON CRYSTALLIZATION OVERVOLTAGE

DURING THE ELECTROLYSIS OF MOLTEN SALTS

(Presented by Academician A. N. Frumkin, 17 XII 1963)

It is known that the exchange currents at the metal–molten salt interface are high, and in the electrolytic deposition and dissolution of metals in these media it is usually only polarization of a concentration character that plays a significant role. However, even at high temperatures the energy difficulties of forming a new phase are not completely removed; therefore in melts there should also be observed polarization associated, for example, with the appearance of crystal nuclei of the electrolytically deposited metal on a substrate of another metal that, under the experimental conditions, does not form an alloy with the first.

We set ourselves the goal of detecting and measuring this kind of crystallization overvoltage. Silver and copper were chosen as the metals to be deposited. The cathode was the end of a platinum or tungsten wire, sealed in glass, 1 mm in diameter.

Fig. 1. Curves η–τ for the deposition of silver on a platinum cathode from an $AgNO_3$ melt at 230° for current densities (mA/cm^2): 1–3.7; 2–2.6; 3–1.7; 4–1.0; 5–0.7. Sinusoidal curve 2000 Hz

The deposition of silver from nitrate and chloride melts and of copper from chloride melts was investigated. The experiments were carried out under galvanostatic conditions. The change in the cathode potential with time at the moment the current pulse was switched on was recorded with an OK-17 M oscillograph, which was somewhat modified for this purpose (the sweep duration was increased and the frequency characteristic of the amplifier was changed). In the intervals between current pulses a potential of +5 mV relative to the reference electrode, which was a wire of the metal being deposited, was applied to the cathode.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

In all the cases investigated* a maximum was observed on the overvoltage–time curves, corresponding to the moment of formation of crystal nuclei on the cathode. For the electrolysis of aqueous solutions, maxima of this kind on switching curves were observed by Samartsev and Evstrop' ev ([1]), Shottky ([2]), and Mutafchiev and Gutsov ([3]).

From the oscillogram shown in Fig. 1 it is evident that, as the polarizing current is increased, the maximum overvoltage increases and at the same time the time required to attain it decreases.

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* In the deposition of silver and copper on a platinum cathode from chloride melts the curves had no maximum, which is probably due to the formation of alloys of these metals with platinum, promoted by the higher electrolysis temperature (380-700°).

The dependence of the maximum overvoltage on the current density (Fig. 2) can be approximately described by an equation similar to the Tafel equation:

$$\eta_{\max} = a + b \lg i,$$

where a and b are constants depending on the experimental conditions. For the deposition of silver on platinum from nitrate melts, a = 100-140 mV, and b = 25-30 mV.

Figure 3 presents a plot of the dependence of the time corresponding to the maximum overvoltage on the current density. Both for the deposition of silver from a melt of pure $AgNO_3$ and for its dilute solutions in $KNO_3 - NaNO_3$, as well as for the deposition of copper and silver from chloride melts, the relation between these quantities over a wide range of current densities is satisfactorily

Fig. 2. Dependence of the maximum overvoltage on current density. 1 – deposition of copper from a $KCl - NaCl - CuCl$ melt (2.44 wt.% Cu) at 700° on a tungsten cathode; 2 –deposition of silver from a $KCl - LiCl - AgCl$ melt (1.5 wt.% Ag) at 380° on a tungsten cathode; 3, 4, 5, 6 –deposition of silver from nitrate melts on a platinum cathode at 250°, with $AgNO_3$ concentrations respectively 5; 1; 2.5; and 100 wt.%.

Fig. 3. Dependence of the time required to reach the maximum overvoltage on current density. Symbols as in Fig. 2.

expressed by the equation:

$$\tau_m i^n = A,$$

Fig. 4

Figure 3: Fig. 4

in which $n = 0.8$-0.9. The value of the constant A for nitrate melts lay in the range from $3 \cdot 10^{-5}$ to $8 \cdot 10^{-5}$.

On the basis of the experimental data, one can calculate the amount of electricity expended on charging the cathode up to the maximum overvoltage:

$$q_m = i\tau_m,$$

and from it estimate the change in the concentration of silver ad-atoms on the platinum surface:

$$\Delta\Gamma \approx \frac{1}{nF}(q_m - C\eta_{\max}),$$

where C is the capacitance of the double layer. Calculations in which $C = 40\ \mu\text{F/cm}^2$ was adopted gave for $\Delta\Gamma$ values of about $1 \cdot 10^{14}$ atoms/cm^2, which is approximately 5% of the number of atoms in a close-packed plane of the (111) crystal lattice of silver. This value is close to that given in the work of Mutafchiev and Gutzow ([3]).

We have established that, along with other experimental conditions, the state of the cathode surface affects the magnitude of the maximum overvoltage. In particular, it was found that the crystallization overvoltage for silver increases if the platinum electrode is subjected to preliminary anodic polarization in a nitrate melt at potentials 1-1.4 V more positive than the equilibrium potential of silver (Fig. 4*a* and *b*). Apparently, this is connected with the formation of thicker oxide layers on the platinum surface ([4]).

Fig. 4. Curves η–τ for the deposition of silver on a platinum cathode ($i = 1.7$ mA/cm^2, $t = 250°$), *a*–$AgNO_3$ concentration 2.5 wt. %, preliminary anodic treatment at 1.4 V; *b*–the same, without treatment; *c*–pure $AgNO_3$.

It is interesting to note that the η–τ curves for dilute solutions of $AgNO_3$ in the KNO_3–$NaNO_3$ melt differ somewhat in shape from the curves for pure molten $AgNO_3$. In the latter case the maximum is sharper, and the drop in overvoltage after it occurs more rapidly (Fig. 4*c*).

This is explained by the difference in the rate of growth of the crystallites formed. If in dilute solutions it is determined by the diffusion toward them of the discharging ions in the electrolyte, then in the pure melt growth is hindered only by the electrical resistance of the electrolyte layer adjacent to the crystallite. Therefore the crystallites that arise grow in the pure melt almost without hindrance, and the cathode potential very rapidly falls to a value at which the formation of crystal nuclei becomes a practically improbable process.

The situation is different when the process is carried out in melts with low concentrations of discharging ions. Then, because of the low diffusion rate, depletion of the electrolyte layer occurs at the surface of the growing crystal, and concentration polarization arises. It prevents the potential of the entire cathode from decreasing, as a result of which the period of nucleus formation is lengthened and their number increases.

It follows from the foregoing that the overvoltage associated with the appearance of crystal nuclei is also characteristic of the electrolysis of molten salts, and that in this process an essential role is played not only by energetic difficulties in the formation of a new phase, but also by the conditions of transport of the discharging ions to the growing crystals.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.