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Abstract

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THE PHENOMENON OF ZONE FORMATION ON ELECTRODES IN THE PROCESS OF ELECTROCRYSTALLIZATION OF METALS

(Presented by Academician A. N. Frumkin, October 4, 1957)

Nobili discovered the phenomenon of the formation of colored rings of lead peroxide on an iron anode during electrolysis of a solution of lead salts under conditions in which a point cathode was placed near the anode ([1]). The distribution of current on the electrode for this case was considered by Riemann ([2]) and Weber ([3]), who showed that the current density gradually decreases with distance from the center and that, correspondingly, a decrease in the thickness of the deposit from the center to the edges of the electrode should be observed. For a thin film, such a distribution of the deposit led to the appearance of Newton interference rings.

Arndt ([4]) attempted to investigate the scattering capacity of electrolytes during the electrodeposition of copper in a cell similar in character to Nobili' s cell. The role of the point electrode was played by an opening in a partition separating the cathodic and anodic spaces. A flat cathode was placed opposite the partition with the opening, at a distance of about 2 mm. Arndt found that copper deposits have a number of concentrically arranged zones differing in the character of light reflection and in crystal size. Arndt explained the formation of such zones on the basis of the concept of preferential growth of crystals in the direction of the lines of force, which under the experimental conditions have different inclinations to the cathode.

Shemyakin and Mikhalev ([5]) attempted to explain this phenomenon, as well as a number of other periodic phenomena, using the de Broglie equation and considering the formation of rings as the result of diffraction of ions.

We have investigated the process of electrodeposition of alloys (Cu—Pb, Cu—Zn, Cu—Bi, Cd—Bi, Cu—Sn), as well as of pure metals (Cu, Ni, Co, Zn, Bi, etc.) and the anodic dissolution of copper under conditions analogous to Arndt' s experiments*. In all cases the formation of sharply expressed concentrically arranged zones** was observed (see Fig. 1). As X-ray diffraction studies showed, alloy deposits in different zones differed from one another in phase composition.

The nonuniformity of the current distribution on the cathode, noted by Riemann, should have led to differences in the values of the potentials at the center and at the periphery of the cathode. We measured the cathode potential in its various sections. Figure 2 presents curves characterizing the change in potential with distance from the center of the cathode.

On the basis of data on the potential interval in which one or another phase was formed, it could be obtained in an ordinary electrolyzer while observing the corresponding electrochemical conditions. Thus, the occurrence of zones during the codeposition of two metals is due to a change in the current density and, accordingly, in the cathode potential in the direction from the center to the periphery of the cathode, with which the change in the composition of the deposit is associated

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* The phenomenon of zone formation was observed in all cases when the area of one of the electrodes was considerably smaller than the area of the other. The shape of the small electrode determines the shape of the zones. Thus, for example, in the case of a round electrode (opening) the zones have the form of rings, while in the case of a slit they are ovals. The cell used in our experiments had an opening in the partition of diameter 2.5 mm; the cathode was located at a distance of 3–10 mm.

** The maximum number of rings is observed in the case when, in the central zone, the limiting current for the most electronegative metal is reached.

Fig. 1. Dependence of the arrangement of different zones on the electrode on the electrochemical conditions of their formation.
A –0.5 N $Cu(ClO_4)_2$, 0.5 N $Bi(ClO_4)_3$, 2 N $HClO_4$; $I = 300$ mA; distance from the opening 4 mm,
–0.05 N $Cu(ClO_4)_2$, 0.5 N $Bi(ClO_4)_3$, 2 N $HClO_4$; $I = 300$ mA; distance from the opening 7 mm,
–0.6 N $Cu(ClO_4)_2$, 0.4 N $Cu(ClO_4)_3$, 2 N $HClO_4$, $I = 300$ mA; distance from the opening 4 mm

from a pure, more noble metal to an alloy containing the maximum possible amount of the electronegative component in the given electrolyte.

On the basis of the material obtained, one may suppose that the transition from one zone to another takes place at strictly definite potentials.

As is seen from Fig. 1, the character of the distribution of the zones depends both on the composition of the electrolyte and on the distribution of current over the electrode surface. Thus, with the aid of this cell it is possible to control the composition of the electrolyte and to choose optimal conditions for the electrodeposition of metals and alloys.

In the electrodeposition of pure metals, the formation of zones is also observed. X-ray (Table 1), optical, and electron-microscopic studies made it possible to establish that in this case the zones differ from one another in the size of the crystals, their orientation, and the character of the faceting.

Fig. 2. Curves of the distribution of potential on the cathode. Composition of the electrolyte: $CuSO_4 \cdot 5H_2O$ 200 g/l, H_2SO_4 50 g/l. 1—10 mA; 2—40 mA; 3—100 mA; 4—200 mA.

On the basis of the data obtained in this way and the results of earlier investigations (under ordinary conditions) of the orientation of crystals in copper and nickel deposits ([6]) and of the character of the faceting of copper crystals ([7]) as a function of the conditions under which they are obtained, one may come to the conclusion that, in the case of deposition of pure metals, the formation of zones is due not to differences in the slope of the lines of force, as Arndt supposed, but to differences in the electrochemical conditions of deposition (current density, overvoltage). The characteristic angles at which the most intense reflection of light is observed are due to the fact that in each zone the crystals are faceted by quite definite faces.

Table 1

Zone	Cu	Ni	Co	Zn
Zone	Orientation of crystals	Orientation of crystals	Orientation of crystals	Orientation of crystals
Center	none	[001]	weak [111]	none
I	none	[001], [011]	strong [111]	[112]
II	[111]	none	medium [111]	none
III	[001], [112]	none	none	—

It is interesting to note that, in the case of nickel deposition, a zone of potentials was clearly established in which pitting occurred. Apparently, in this interval of potentials hydrogen bubbles adhere most firmly to the cathode surface ([8]). Consequently, with the aid of this cell it is possible rapidly to determine the interval of potentials at which pitting is observed.

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