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DEPENDENCE OF THE SURFACE STRUCTURE OF ELECTROLYTIC ALLOY DEPOSITS ON THEIR PHASE COMPOSITION

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By the present time, extensive material has been accumulated on the electrodeposition of alloys. It should be noted, however, that the main attention in investigations has been directed toward finding various electrolysis conditions leading to the codeposition of metals. Little attention has been paid to the influence of structural factors and to the nature of the interaction of the components during alloy formation, which to a considerable extent determine the physicochemical properties of the coating.

Meyer and Phillips (^{1}) investigated the influence of various metals, when codeposited with copper in a cyanide solution, on the structure of the deposit formed; in doing so, the authors took into account the nature of the interaction of the components on the basis of equilibrium-diagram data. At the same time, a number of investigations (^{2}) showed that deposits formed during electrocrystallization often differ in their phase composition from the structure expected on the basis of the phase diagrams of these systems. In particular, for alloys of the eutectic type, the possibility was established of forming highly supersaturated solid solutions. The results of the present investigation showed that the formation of a nonequilibrium phase of a supersaturated solid solution is associated with a strong change also in the surface structure of the deposit.

In order to minimize the influence of secondary factors that also affect the surface structure of deposits, metals were selected that made it possible to carry out their joint deposition without adding surfactants or complexing agents to the solution. One of the systems most suitable for this purpose proved to be copper —bismuth.

According to Raub' s data (^{3}), during codeposition of Cu with Bi from perchlorate electrolytes the metals crystallize separately in accordance with the phase diagram. At the same time, proceeding from the concepts developed in our laboratory (^{4}), for this system as well, under certain conditions it was possible to expect the formation of supersaturated solid solutions of bismuth in copper. Indeed, when a solution of $Cu(ClO_4)_2$ 0.6 N, $Bi(ClO_4)_3$ 0.4 N, pH 0.6 (solution I), was used, an alloy was obtained containing a phase of a supersaturated

Figure 1: Surface structure of electrolytic deposits of copper and a copper-bismuth alloy, and of a bismuth deposit. Panels labeled A, B, V, G.

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Figures 2 and 3: Surface structures of copper-bismuth and copper-tin alloy deposits.

Figure 2: Figures 2 and 3: Surface structures of copper-bismuth and copper-tin alloy deposits.

solid solution of bismuth in copper, with a corresponding increase in the copper lattice parameter to a value on the order of 3.635—3.645 Å. The bismuth content in the solid solution increased with current density and, according to X-ray measurements, reached 12 wt. %. With a further increase in current density, the increase in supersaturation led to so considerable a disturbance of the lattice that the lines on the X-ray diffraction pattern disappeared completely. According to chemical analysis, the alloy always contained more bismuth than followed from the data on the increase in the copper lattice parameter; however, no lines other than those of copper were detected on the X-ray diffraction patterns. Raub pointed out a similar phenomenon for the silver—zinc system (^{5}).

Fig. 1. Surface structure of electrolytic deposits of copper and of a copper-bismuth alloy, obtained from a solution containing $Cu(ClO_4)_2$ $0.6N$, $Bi(ClO_4)_3$ $0.4N$, and of a bismuth deposit from a perchloric acid solution. **A** —pure copper, copper parameter $a_{\mathrm{Cu}} = 3.608$ Å; **B** —copper-bismuth alloy, 70% copper, $a_{\mathrm{Cu}} = 3.619$ Å; **V** —copper-bismuth alloy, 50% copper, $a_{\mathrm{Cu}} = 3.635$ Å; **G** —pure bismuth.

Fig. 2. Surface structure of a copper-bismuth alloy deposit obtained from a solution containing $Cu(ClO_4)_2$ $0.2N$, $Bi(ClO_4)_3$ $0.8N$. Alloy composition: copper 70%, bismuth 30%.

Fig. 3. Surface structure of a copper-tin alloy deposit obtained from a sulfuric-acid electrolyte, $a_{\mathrm{Cu}} = 3.700$ Å.

From Fig. 1, which presents electron-microscopic photographs of the surface of alloy deposits with different contents of bismuth, it is seen that, as the supersaturation of the solid solution increases, the surface of the deposit becomes smoother and, at considerable supersaturation, lustrous.

Deposits arising from solutions in which the ratio of the amount of bismuth to the amount of copper was considerably greater than in solution I—namely: $Cu(ClO_4)_2$ 0.2 N, $Bi(ClO_4)_3$ 0.8 N, pH 0.6 (solution II)—were a mixture of pure crystals of copper and bismuth. Fig. 2 gives a photograph of the surface of a deposit of the same composition as that shown in Fig. 1 B, but obtained from solution II.

The dependence of the structure of an alloy deposit on its phase composition is also confirmed by data obtained in the study of copper–tin and tin–lead alloys.

Leiner (^{6}) and Raub (^{7}) pointed to the possibility of the formation of supersaturated solid solutions of tin in copper (up to 14-16%) in obtaining this alloy from cyanide solutions; the latter believed that the formation of supersaturated solid solutions is possible only under conditions in which the discharge potentials of the ions are brought close together by means of complex-forming agents and surface-active substances. The untenability of this point of view was shown in earlier works from our laboratory (^{4}, ^{8}). Indeed, in the electrolysis of a solution containing $CuSO_4 \cdot 5H_2O$ 25 g/l, $SnSO_4$ 75 g/l, H_2SO_4 100 g/l, the joint discharge of the ions begins after the limiting current for copper has been reached. In this case a solid solution arises that is highly supersaturated in comparison with the equilibrium diagram. The value of the lattice parameter of copper reached 3.745 Å, which corresponded to a tin concentration in the solid solution of about 22 wt.% (according to the equilibrium diagram, the solubility of tin in copper at room temperature does not exceed 1% (^{9})).

Fig. 3 gives a photograph of the surface of a copper–tin alloy deposit. The deposit was dense and fine-crystalline, despite the fact that the codeposition of copper with tin took place under conditions of discharge of copper ions in the limiting diffusion-current regime.

According to X-ray diffraction studies, in obtaining a tin–lead alloy from a solution containing $Sn(ClO_4)_2$ 0.8 N, $Pb(ClO_4)_2$ 0.2 N, $HClO_4$ 1N, the formation of supersaturated solid solutions was not observed, which is in agreement with data from earlier investigations (^{10}). The deposit had a coarse-crystalline structure.

On the basis of the investigations carried out, it may be concluded that the formation of supersaturated solid solutions has a substantial influence on the structure of electrodeposited alloys, promoting the occurrence of fine-crystalline deposits. Thus, the occurrence of fine-crystalline and lustrous alloy deposits may be expected in those cases where the electrochemical conditions favor the formation of supersaturated solid solutions, and where there is no dimensional and orientational correspondence between the lattices of the codepositing metals, as a result of which the formation of nuclei of the phase of the more negative metal is hindered (^{11}).

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