

Electrocrystallization and Properties of Supersaturated Solid Solutions of Copper

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Abstract. The role of the alloying element in the formation of the structure and properties of electrolytic copper alloys has been determined. The X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) have shown that electrochemical alloying of copper with low-melting metals leads to the formation of supersaturated solid solutions (SSS) on the cathode, crushing of the crystal structure, smoothing of the surface relief, hardening of the deposits obtained, increasing their solderability and corrosive resistance to acidic media.

1. Introduction

Prospects for obtaining electrolytic coatings with improved performance characteristics are associated with the electrodeposition of alloys, whose properties are much wider and more diverse than those of metals. One of the features of the electrocrystallization of alloys is the formation of SSSs arising from the co-deposition of components that in metallurgically produced alloys are practically insoluble in each other or have a limited solubility [1]. In the electrocrystallization of copper, in combination with low-melting metals (Tl, Pb, Bi, Cd), SSSs are sometimes formed, which, due to their high corrosion resistance and appearance, can be used as protective and decorative coatings in various industries.

In this paper, the authors studied the structure and some properties of electrolytic copper alloys with low-melting metals (lead, cadmium and thallium) obtained from EDTA solutions [2]. Data on the structure and properties of Cu-Bi and Cu-Pb alloys, as given in [3, 4], were also used.

2. Materials and methods

The phase structure of deposits was examined by X-ray diffraction 5-7 days after electrolysis with a DRON-2 diffractometer using filtered cobalt radiation. To calculate the parameters of the fcc lattice of copper, the line profiles were recorded (311). The accuracy of determination was $2 \cdot 10^{-4}$ nm. The size of the phase crystallites with the fcc lattice was estimated by the Selyakov-Scherrer method. The surface structure and composition of freshly deposited samples were examined in a scanning electron microscope (JEOL JSM 6380) with an integrated energy dispersive microanalysis system (JED-2300). The thermogravimetric analysis was performed on a Q-1500T (VNR) derivatograph by heating the samples to 600°C at a rate of 20°/min. Techniques for measuring microhardness ($H\mu$), internal stresses (VN), solderability (K), and corrosion resistance ($V\kappa$) of coatings are described in [3].

3. Results and discussion

According to the phase diagrams [4], the solubility of these low-melting metals in copper in the solid state is very small and is less than 1.0%. The difference in the atomic dimensions of the co-deposited



components exceeds the limit obtained by Hume-Rothery for the formation of solid substitutional solutions (15%). However, a voltammetric study [5] showed that at the initial stages of electrocrystallization of binary Cu-Bi, Cu-Pb, Cu-Cd and Cu-Tl systems from EDTA electrolytes, a strong interaction between the components is observed. In the electrocrystallization of copper with bismuth, lead, and thallium, solid solutions are formed with a positive deviation from the ideal solution, and in the electrodeposition of copper with cadmium, a system with a negative deviation from the ideal solution is formed. Obviously, this indicates the formation of deposits of the intermetallic compound Cd_3Cu along with the supersaturated solid solutions of cadmium in copper.

The X-ray diffraction analysis confirmed the results of voltammetric and polarization measurements: when copper is electrodeposited with low-melting metals from EDTA electrolyte, supersaturated solid substitution solutions (SSSs) with a high degree of supersaturation are formed on the cathode (table). As the content of the low-melting component in the SSS increases, the parameter of the metal-solvent lattice increases (Fig. 1), the texture of the latter is dissipated [111], the structure is crushed and the surface relief of the coatings is smoothed out.

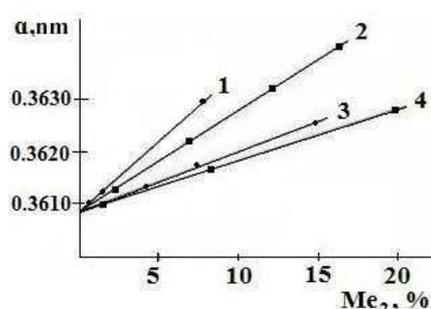


Figure 1. Dependences of the fcc lattice parameter of Cu-Tl (1), Cu-Cd (2), Cu-Bi (3), Cu-Pb (4) alloys on the content of the low-melting component in the deposit

Comparing the experimentally determined lattice parameters with the theoretically calculated by Vegard's law for the proposed copper-based solutions of lead, bismuth and cadmium, it can be concluded that only part of the deposited alloying element enters the copper lattice. The other part is either in the form of dispersed particles of a pure low-melting element, or in the form of oxide and hydroxide compounds of the alloying metal. However, no additional reflexes except for highly diffused lines of solid solutions are observed on the diffractograms of the deposits obtained with small cathode polarizations. Diffuse reflexes on the diffractograms indicate a high dispersion and concentration heterogeneity of the obtained alloys. Diffractograms of the deposits of Cu-Pb, CuBi, and Cu-Cd alloys, obtained at potentials below -0.25; 0.26; -0.51 V, correspondingly, in addition to reflexes of a solid copper-based solution, also contain diffuse reflexes of the phases of pure lead, bismuth and cadmium.

The degree of supersaturation of the resulting solid solutions depends on the conditions of electrocrystallization and is mainly determined by the dispersion of deposits. With the decrease in the size of structural elements (grains or subgrains), the solubility of the alloying component (low-melting metal) in alloys increases. Since the atoms of the alloying component are predominantly localized along the boundaries of grains or subgrains in the SSS, the electrolysis conditions resulting in the grinding of the deposit structure (for example, reduction in the cathode potential) contribute to an increase in the solubility of the low-melting (alloying) component.

In the electrocrystallization of binary alloys with a predominant content of one of the components, the deposits are formed by periodically forming polyatomic layers of the parent metal, on the surface of which nonequilibrium segregation of the atoms of the alloying component occurs [3]. The natural tendency of the resulting deposit to minimize the total free energy promotes the appearance of segregations in defective places of the deposit, mainly along the grain boundaries. The higher the dispersion of the coatings obtained, the greater the extent of the grain boundaries on which the

segregation of the atoms of the alloying component predominantly occurs. A large number of vacancies generated during electrocrystallization also contributes to the formation of solutions [3].

Deposits formed in the presence of small concentrations of thallium ions during large cathodic polarizations are characterized by the presence of two forms of structural elements growth: together with small globular grains, representing a thallium SSS in copper, dendrites of copper with a trunk length of up to 10-15 microns are formed (Fig. 2).

This indicates a change in the mechanism of deposit growth and an increase of the rate of copper deposition on individual crystallization centers. The growth of dendrites is possible under conditions of high diffusion overvoltage due to local depletion of the near-cathode layer by discharging copper ions as a result of catalytic deposition in the neighboring areas of the surface under the influence of thallium adatoms [6-7]. In this case, the type of diffusion of the discharging ions and the nature of the catalytic effect determine the shape and size of the emerging crystallites. Electron-probe analysis of deposits showed that the observed dendrites are a pure copper phase, while the fine-grained deposit phase contains up to 7.5% thallium and represents the SSS of the latter in copper.

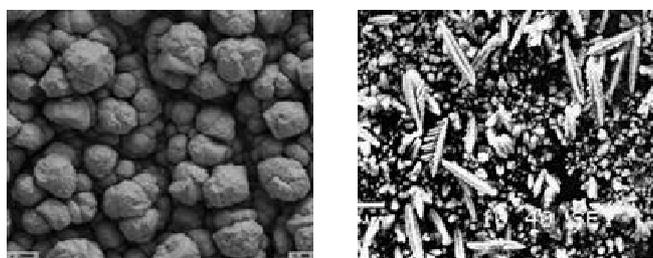


Figure 2. Micrographs of deposits of copper (a) and Cu-1.8% Tl (b) alloy, obtained from EDTA electrolyte

It should be noted that the obtained SSS deposits are metastable systems, the decay of which at room temperature is probably very slow since the radiographs taken after 1.0-1.5 years of storage of the samples showed no changes in the structure of the alloys. Meanwhile, according to the thermography, for each SSS there is a critical temperature, above which it starts to decay. When annealing the SSS on thermograms in the temperature range of 110-160°C, an exothermic effect is observed, which can be interpreted as a corresponding decomposition of a solid solution.

In the investigated alloys, at the initial stages of annealing, an increase in the electrical resistivity is observed (Figure 3), which is usually explained by the formation of clusters of atoms of the dissolved component in the solid solution. The presence of such clusters is also evidenced by the nature of the change in the parameter of the crystal lattice of the solid solution: its values do not change during the entire annealing stage accompanied by an increase in the electrical resistivity (Fig. 3, b). The beginning of the decrease in the lattice parameter coincides with the decrease in the electrical resistivity, when additional reflections belonging to the second phase appear on the diffractograms of the deposits annealed at 120-160°C.

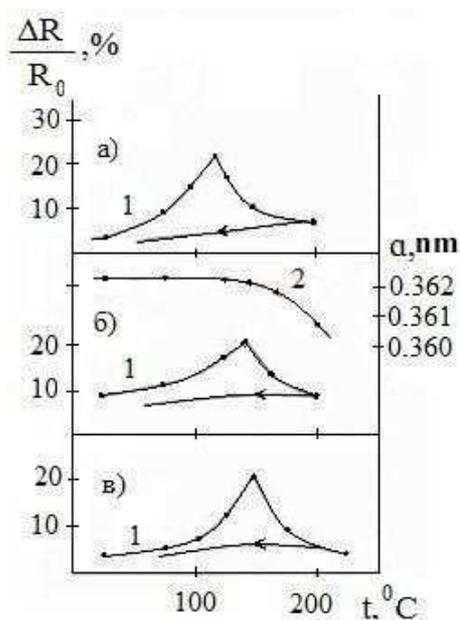


Figure 3. The change in the relative electrical resistivity (1) and the FCC lattice parameter (2) for Cu-14% Bi (a), Cu-7.5% Tl (b) and Cu-16.9% Cd (c) during annealing

Thermal stability of the studied SSS decreases with the decreasing melting temperature of the alloying component (Table). Annealing the SSS for 1 h at 400°C leads to the formation of two-phase mixtures consisting of crystals of pure components (Cu+Me₂).

Table 1. Phase composition, structure and properties of electrolytic copper alloys

Alloy	-E, V	Phases	d, nm	H _μ , MPa	VN, MPa	K _{sol}	VK1
Cu – 1.8%Pb	0.12	Cu(Pb)	120	186	55	72	6.8
Cu – 8.2%Pb	0.18	Cu(Pb)	80	198	43	76	5.0
Cu – 19.2%Pb	0.25	Cu(Pb)	30	201	5	87	3.1
Cu – 28.8%Pb	0.30	Cu(Pb) + Pb	<10	206	-15	88	2.2
Cu – 1.6% Bi	0.22	Cu(Bi)	130	208	62	70	11.1
Cu – 4.7%Bi	0.23	Cu(Bi)	90	222	58	74	10.2
Cu – 7.9%Bi	0.26	Cu(Bi)	35	231	46	81	9.0
Cu – 20.8%Bi	0.31	Cu(Bi) + Bi	15	226	18	85	7.6
Cu – 2.6%Cd	0.33	Cu(Cd)	180	210	85	65	5.8
Cu – 7.2%Cd	0.35	Cu(Cd)	90	216	53	68	5.0
Cu – 12.1%Cd	0.51	Cu(Cd)	65	-	40	73	4.5
Cu – 16.9%Cd	0.60	Cu(Cd) + Cd	25	228	24	78	3.9
Cu – 0.6%Tl	0.50	Cu(Tl)	185	206	80	64	5.6
Cu – 1.8%Tl	0.55	Cu(Tl)	120	215	35	70	5.2
Cu – 7.5%Tl	0.60	Cu(Tl)	50	230	20	82	4.0

Electrochemical alloying of copper deposits with low-melting metals not only leads to a modification of their structure, but also to a change in the properties of coatings. Despite the lower hardness of low-melting metals compared to the hardness of copper, the introduction of their atoms

into its crystal lattice, as a rule, strengthens copper coatings (Table). This is due both to solid-solution hardening, and to an increase in the dispersity and defectiveness of the deposits.

For copper coatings obtained from EDTA electrolytes, the presence of internal tensile stresses (ITSs) is characteristic. When alloying with low-melting metals, ITSs in deposits are usually reduced. The reduction of stresses is obviously related to the fact that low-melting metals with a larger atomic radius than that of copper are included in its lattice, which compensates for deformations related to tensile stresses. An increase in the degree of alloying of Cu-Bi and Cu-Pb alloys can lead to the fact that the researched copper alloys are well soldered, as is evidenced by the appearance of amorphous phases and, accordingly, internal - by the high spreading coefficients (Table 1). Compression stresses are in their composition.

Their solderability after natural aging within 6 months virtually does not differ from the initial one. Corrosion resistance of copper alloys improves with an increase in the content of a low-melting element in them. This is due to higher overvoltage of hydrogen that is observed on the alloying elements than that on copper. In corrosion tests, copper alloys with lead showed the greatest resistance, apparently due to the ability of the latter to passivate in acidic media.

Thus, low-melting metals such as bismuth, lead, cadmium and thallium are effective modifiers of the structure of copper coatings improving their properties.

4. Conclusions

1. Co-electrodeposition of copper with low-melting metals from trilonate solutions crystallizes coatings, which are SSS.
2. The role of a low-melting component in the formation of the structure of electrolytic copper alloys has been revealed. With an increase in the degree of copper alloying, the dispersion and defectiveness of the structure increases, the texture quality degrades and the surface relief of the coatings obtained is smoothed out.
3. Electrolytic alloying of copper with low-melting metals improves the quality and mechanical properties of coatings

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