ELECTROCHEMICAL BEHAVIOR OF ALLOYS WITH AN AMORPHOUS STRUCTURE

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The electrochemical behavior of both amorphous and crystalline copper—bismuth alloys (30-35% wt. copper) was studied, these alloys having been produced by the electrodeposition method [1, 2] — a simple and reliable method for producing alloys with an amorphous structure [3].

Electrodeposition was effected from solutions 0.5 N $Cu(ClO_4)_2$, 0.5N $Bi(ClO_4)_3$, and 1.0N $HClO_4$ at room temperature, with a current density of 20 mA/cm^2 through vertical copper rods 3 mm in diameter and with a cathode surface 4 cm^2 in area. The structure of the plating, approximately 20 μ thick, was x-ray analyzed. In order to produce systems with a phase-equilibrium constitution of the crystal structure, some specimens were also heat treated in vacuum at 200°C for 10-15 min.

The equilibrium potential of amorphous copper—bismuth electrodes in a 1.0N $Bi(ClO_4)_3$ + 1.0N $HClO_4$ solution was approximately 30 mV more negative than the potential of pure bismuth. The potential of heated specimens was stable and close to the potential of pure bismuth. In this way, on the basis of their equilibrium potentials, one would expect alloys with an amorphous structure to be more corrosively active.

However, with a short circuit between two Cu—Bi electrodes, one heat treated and one not, a current flows through an NaCl or $Bi(ClO_4)_3$ solution in a direction which indicates that the alloy specimen which has not been heat treated is less corrosion-resistant.

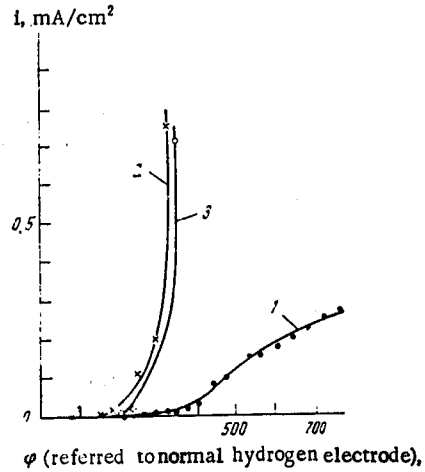

Fig. 1

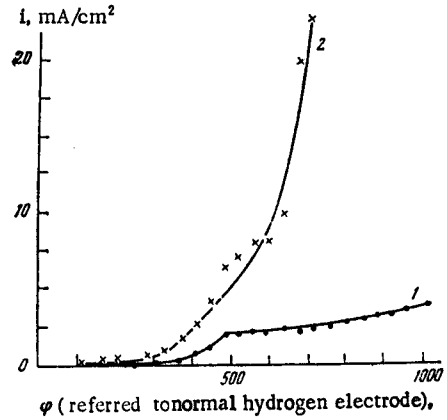

Fig. 2

Fig. 1. Rate of anodic dissolution of copper—bismuth alloys in a 0.1N Na_2SO_4 solution: 1) amorphous alloy, 2) crystalline alloy, 3) copper.

Fig. 2. Rate of anodic dissolution of copper—bismuth alloys in a 0.1N NaCl solution: 1) amorphous alloy, 2) crystalline alloy.

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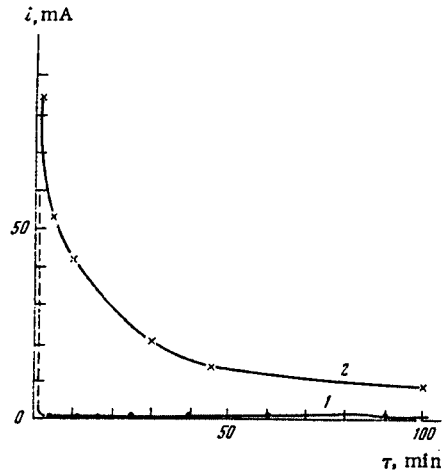

Fig. 3. Anode current i (mA) as a function of time τ (min), during dissolution of copper—bismuth alloys in 0.1N Na_2SO_4 at φ = +1050 mV: 1) amorphous alloy, 2) crystalline alloy.

With the aid of a model 1P-410B potentiostat, the alloy specimens were polarized in 0.1N Na_2SO_4 and 0.1N NaCl solutions, whereupon they were held at various potential levels for 3-5 min in each case.

According to Figs. 1 and 2, in both solutions the density of the anode current is high across specimens with a phase-equilibrium structure, but the dissolution curve for the heat treated alloy in Na_2SO_4 comes close to the respective curve for pure copper. The curve for pure bismuth under these conditions almost coincides with the axis of abscissas, which indicates a passive state of its surface. After anode treatment, the heat treated specimens, unlike those not heat treated ones, changed color from pink to brown and often peeled off the substrate.

The decrease in the anode current with time, under a constant polarization potential (Fig. 3) confirms the validity of our data pertaining to the dissolution current in amorphous and phase-equilibrium alloys. The differences are analogous at other potential levels.

Thus, under the given test conditions, galvanically produced phase-equilibrium alloys of copper and bismuth have been found less corrosion-resistant than such alloys with a nonequilibrium fluidlike structure.

Although the amorphous alloys under consideration here are chemically similar to the CuBi compound [3], the nature of the chemical bond between their components should not differ substantially from the chemical bond in crystals [4].

Although the standard electrode potentials of copper (0.34 V) and bismuth (0.28 V) are close, the tendency of bismuth to passivation causes the potential difference between both alloy components to change so as to make the copper anodic (Fig. 3), while ionization of the latter will result in a dissolution process [5]. The surface layer of the amorphous alloy becomes richer in bismuth and acquires the electrochemical properties of the latter [6], i.e., becomes passivated. Passivation must, in this case, be facilitated by a surface profile which is smoother than that of phase-equilibrium alloys and devoid of grain boundaries [7]. One may also assume that the amount of the passivated component increases faster on the surface of an amorphous alloy than on the surface of a crystalline alloy and thus approaches the stability limit when the alloy is amorphous [8].

The presence of copper crystals and grain boundaries in crystalline two-phase systems facilitates the access of an electrolytic solution to the corroding component (copper) and results in a localization of the anodic process at the "copper segments" as well as at the bismuth-enriched surface layer. However, the passivation of phase-equilibrium alloys proceeds much slower than that of amorphous alloys.

Similar studies of the behavior of iron-phosphorus alloys have not revealed a significant difference in the dissolution rate between amorphous and crystalline specimens. In some cases amorphous alloys were even more corrosively active. This disparity between the behavior of copper—bismuth and iron phosphorus alloys should be attributed to the possibility of slight anodic oxidation of both components in an iron—phosphorus alloy.

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