This change in the properties during heat treatment is apparently due to a change in the structure and phase composition of the coatings. Regardless of the boron content, for all the specimens thermographic analysis gives a curve with two maxima: the first, which is diffuse, at 300°, the second, sharper maximum at 440-460°C.

Using x-ray analysis* we established that after heat treatment for 1 to 5 h at 300°C all the coatings were amorphous to x rays. They became x-ray crystalline only after heat treatment at 500°C, when they consisted of α-Fe and the borides Fe_2B and FeB. However, there is no relation between the boron content of the coatings and the type of boride formed. No other boron-containing compounds were observed. Clearly, all the boron present in the coatings is converted at a high temperature to boride.

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*The x-ray analysis of the coatings was performed by our colleague at the Institute, R. Yushkenas.

ELECTRODEPOSITION OF BRASSES FROM PYROPHOSPHATE ELECTROLYTES

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UDC 621.357.7:669.55'5

Pyrophosphate electrolytes are the most promising of cyanide-free brass plating electrolytes. A number of authors have investigated the influence of organic and inorganic additives on the composition of the alloy and its deposition rate [1-3], and established the marked influence of pH on the properties of the deposits. We have investigated the influence of pH on the deposition kinetics and phase composition of the alloy obtained from a pyrophosphate brass plating electrolyte.

We selected an electrolyte of the composition (g/liter) $K_4P_2O_7$ 300, $ZnSO_4 \cdot 7H_2O$ 60, the $CuSO_4 \cdot 5H_2O$ concentration being varied from 2 to 12. The electrolyte was prepared in distilled water from reagents of analytical reagent grade; the pH was varied from 7.5 to 9.5 by adding sulfuric and citric acids.

Coatings 6-10 μm thick were deposited onto a nickel substrate from different electrolytes at a current density of 75-100 A/m^2. The phase composition was investigated on a stationary DRON-2 x-ray diffractometer with a GP-4 attachment and a KSP-4 recording device, using the characteristic radiation of a copper anode K_α and selectively absorbing nickel filters. The current yield of the alloy was determined gravimetrically. The cathodic polarization was measured in a standard cell by means of a P-5848 potentiostat by the galvanostatic method.

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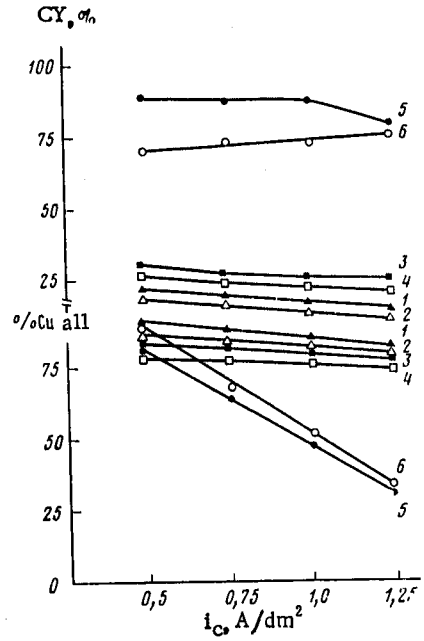

Fig. 1

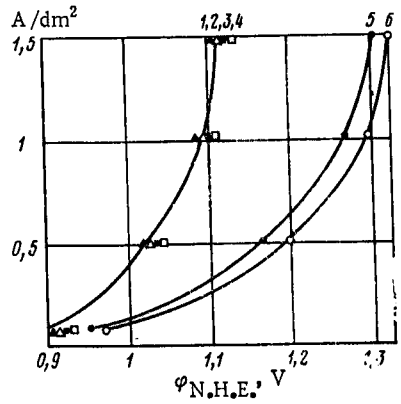

Fig. 2

Fig. 1. Current density vs composition (a) and current yield (b) of copper—zinc alloy: 1, 3, 5) with citric acid; 2, 4, 6) with sulfuric acid. Value of pH: 1, 2) 7.5; 3, 4) 8.0; 5, 6) 9.5.

Fig. 2. Current density and pH vs electrodeposition potential of copper—zinc alloy: 1, 3, 5) with citric acid; 2, 4, 6) with sulfuric acid. Value of pH: 1, 2) 7.5; 3, 4) 8.0; 5, 6) 9.5.

It was established (Fig. 1) that at pH 8.0 and 7.5, with an increase in the current density from 50 to 125 A/m^2, the copper content of the alloy is almost unchanged, but decreases markedly at pH 9.5.

In return the current yield of the alloy (Fig. 1) at pH 9.5 was 70-90%, whereas at pH 7.5 and 8 it was less than 30%. In the presence of citric acid the current yield of the alloy is somewhat higher; this is attributable to its inhibiting effect on hydrogen evolution. Note also that with an increase in the current density the current yield shows little change.

The polarization curves (Fig. 2) obtained at pH 7.5 and 8.0 with sulfuric and citric acid practically merge. At pH 9.5 the polarization sharply increases; the increase is greater in the presence of citric acid.

The results of the polarization measurements can be explained as follows. Under concentration polarization conditions, an important part is played by mixing of the electrolyte by the bubbles of the evolving hydrogen. As is known, with an increase in the zinc content

TABLE 1

Copper content of electrolyte, g/liter	Method of changing the pH	pH	i_c, A/m^2	Copper content of deposit, mass %	Lattice parameters a, Å	Color of deposit
2	Citric acid	7,5	100	72	3,66	Yellow
4		8,0	100	80	3,63	»
12		9,5	100	50	3,63	Reddish gray
			75	65	3,61	»
2	Sulfuric acid	7,5	100	73	3,68	Yellow
4		8,0	100	80	3,65	»
12		9,5	100	52	3,61	Reddish gray
			75	69	3,61	»

of brass, at pH 9.5 (Fig. 2) the hydrogen evolution overvoltage increases, the amount of hydrogen evolved decreases, and the current yield increases.

It was visually established that at pH 9.5 and a copper content of 75 ± 5% the deposits are reddish gray, while at pH 7.5 and 8.0 they are yellow.

It will be seen from Table 1 that at pH 7.5 the deposits from electrolytes with citric and sulfuric acids have lattice parameters for indices (111) close to yellow metallurgical brasses (a = 3.68-3.70 Å) with an α phase. At pH 9.5 the deposits of brass with a copper content of 75% had lattice parameters approximating to those of pure copper (a = 3.60-3.62 Å).

Thus it was established that the change in the external appearance of electrolytic brasses in relation to the pH is due to a change in the phase composition. The decorative appearance and phase composition of the electrolytic deposits correspond to metallurgical brasses only in the pH range 7.5-8.0. We did not obtain good yellow brass deposits in the more alkaline region.

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THE ROLE OF AMINOETHERS IN THE PRODUCTION OF LUSTROUS METAL COATINGS

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Organic substances are added to the electrolytic baths in order to produce lustrous copper coatings not requiring polishing [1-7]. The most effective brighteners are thiourea and its derivatives [3, 8-10], but coatings obtained with them are very brittle and easily peel off the substrates, and the feasible range of current densities is narrow [8].

We have investigated aminoethers (Table 1) as brighteners; they have been investigated by us previously as hydrogen absorption inhibitors (the plasticity retention is 93-100%).

The basic composition of the electrolyte (in grams/liter) was: $CuSO_4 \cdot 5H_2O$, 125; $NH_2—CH_2—CH_2—NH_2$ (ethylenediamine, base), 50%, 240; H_2SO_4, 60; pH 7.3-7.8. The reagents were of analytical grade. The electrolyte was purified for 6-8 h.

The luster of the deposits was measured with an FB-2 photoelectric luster meter relative to uviol glass, the luster of which is 65 rel. units. The range 50-90 rel. units corresponds to a lustrous surface, and 90-100 rel. units to a specular surface. The porosity of the coatings was determined according to GOST 3247-46; the throwing power was determined by the remote and near cathode method:

$$TP = \frac{l_r' l_n - m_{c_r} / m_c}{l_r / l_n} \cdot 100\%,$$

where l_r and l_n are the distances from the anode to the remote and near cathodes, and m_{cr} and m_c are the masses of metal actually separating on the cathodes.

The cathode was a plate of steel 20 measuring 40 × 40 × 3 mm. The coatings were examined under the microscope. The cathode potential was measured by a compensation method relative

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