ISSN 2616-8685 .JOURNAL OF PHYSICS AND ELECTRONICS Vol. 26(2), 2018
DOI 10.15421/331820

PHASE AND STRUCTURAL TRANSFORMATIONS IN COPPER AND ITS ALLOYS UNDER THE ELECTROLYTIC DISCHARGE

L.I. Fedorenkova*

Oles Honchar Dnipro National University, Dnipro, Ukraine
**e-mail: Luba.Fed@gmail.com*

Copper and its alloy were treated in an electrolytic plasma formed in the boron-containing electrolyte under the action of discharge in order to obtain a diffusion coating with enhanced hardening characteristics and the structural changes in the surface layer of the metal that occur in this case were studied. As a result of processing in electrolytic plasma, characterized by high heating and cooling rates, a diffusion layer was formed on the surface of copper and an alloy based on it (brass). The layer contains nanosized inclusions of copper borides, ternary compounds Cu-B-H, Cu-B-O concentrated mainly along grain and phase boundaries and providing hardening of the metal surface. The action of the discharge provides structural and phase transformations in the metal, the deformation of the grains - elongation in the direction of the driving force (electric transfer) at a depth of 100 μm and the creation of metastable states in the surface layers. Moving vacancies and compressing atoms in the direction of the force create conditions for the rapid movement of boron atoms. With increase in current density and time of treating, the size of nanostructures decreases. Their size is of the order of 6-16 nm. Obtaining wear-resistant coatings on copper and its alloys, which include phases containing copper and boron, increases the strength characteristics of copper and its alloys by 1.5-2 times.

Keywords: electrolytic plasma, microhardness, cooling rates**,** diffusion layer, nanosized inclusions, copper borides**,** hardening.

Received 12.11.2018; Received in revised form 15.12.2018; Accepted 21.12.2018

1. Introduction

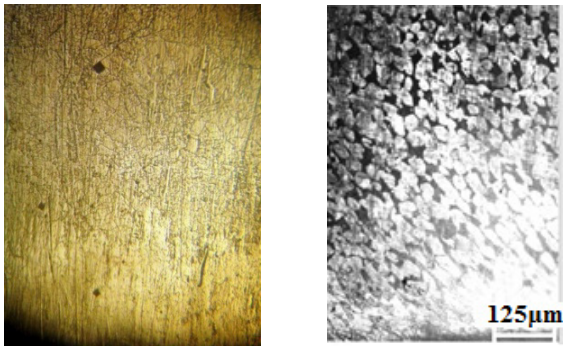
Copper and its alloys are widely used in engineering as structural materials. However, in conditions of elevated temperatures, corrosion and wear, copper alloys have insufficient resistance. To develop protective layers that increase resistance of copper alloys of gas and chemical corrosion, erosion and cavitation wear, various methods of diffusion saturation of copper and its alloys are used [1, 2]. In this work, copper and an alloy based on it were treated in an electrolytic plasma formed in the boron-containing electrolyte under the action of discharge in order to obtain a diffusion coating with enhanced hardening characteristics and increased durability and also to study the structural changes in the surface layer of the metal that occur in this case.

2. Materials and methods

Diffusion saturation of copper and an alloy based on it (brass) was carried out in the electrolytic plasma formed during discharge in an aqueous electrolyte solution containing boron in the electrolysis regime: U = 60-70 V, j = 0.7-2.5 A/cm^2, t = 20 min. The treated samples were investigated using X-ray diffraction analysis with a DRON-2 diffractometer using copper radiation lines, metallographic analysis using Neophot-21 microscope and PMT-3 microhardness tester with a load of 50 g, and layer-by-layer spectral analysis.

3. Results and discussion

As a result of electrolytic plasma treatment characterized by high heating and cooling rates of 10^5 K/s [3], the microstructure of diffusion layer is shown in Fig. 1 was formed on the surface of copper and its alloy (brass). A structureless layer with microhardness on average twice as high as that of the basic metal was formed on the copper surface (Fig. 1, a). Under the action of discharges when the current density reaches 2 A/cm^2, in the surface layer of brass there is a deformation of the grains – along the direction of the driving force action (electric transfer) at a depth of 100 μm (Fig. 1, b).



a) × 250 **b) × 100**

Fig. 1 The microstructure of the diffusion layer on the surface of: a) copper, b) brass after electrolytic plasma treatment in regimes: a) *U* = 65V; *j* = 0.8-1.8A/cm^2; *t* = 15 min; b) *U* = 70V; *j* = 2 A/cm^2; *t* = 10 min.

Under the action of discharges when the current density reaches 2 A/cm^2, in the surface layer of brass there is a deformation of the grains – along the direction of the driving force action (electric transfer) at a depth of 100 µm (Fig. 1, b).

High heating and cooling rates (10^5 K/s) contribute to the formation of areas in the surface layer, in which the process of α and β phases separation in brass does not have time to occur, a structureless zone is formed (Fig. 1). These areas can be quasi-amorphous structures, resulting from a strong distortion of the basic metal lattice enriched with boron, hydrogen, and oxygen. The microhardness of the layer exceeds the microhardness of the base by 3-5 times.

The diffusion layer on copper and brass is represented by the compounds listed in Table 1. In addition, the boron distribution over copper sample depth is presented here, depending on the regime of treating.

Table 1

Results of X-ray diffraction, metallographic and layer-by-layer spectral analysis depending on treating mode in electrolytic plasma

Treated regime	Depth of layer, µm	The density of blackening boron lines, rel. units	Microhardness, GPa	X-ray results
Cu1, *j*=0.9-1.8A/cm^2, *U*=65V, *t*=15min	10	0.65	1.78±0.08	CuB_{24}, $Cu_2B_{10}H_{10}$, $Cu_3B_2O_6$,
	100	0	1.21±0.06,	
	200	0.52	0.96±0.06	
Cu2, *j*=0.7-1.1A/cm^2, *U*=60V, *t*=40min	10	1.3	1.92±0.10	CuB_{24}, CuB_3H_8, CuB_2O_4,
	100	0.6	1.15±0.11	
	200	0	0.88±0.06	
Copper-based alloy (brass) *j*=2.5A/cm^2, *U*=70V, *t*=10min			4.12, 2.40, 0.70	α – light phase – 1.07 GPa; β – dark phase – 1.60-2.86 GPa

Among the phases that are suitable for identification, copper boride and Cu-B-H ternary compounds, as well as Cu-H hydride, whose lines are present only on the X-ray pictures of a copper alloy (brass), should be highlighted. They are absent in technically pure copper. Crystal lattice distortions, deformation of the grains and phase structure in the surface layer of the treated metals and alloys, uneven distribution of microcrystalline structures formed in the layer during saturation and in metastable state make it difficult to

identify diffraction responses on the sciagram. This explains some variety of phases suitable for identification. The broadening of the diffraction maximum is observed on sciagrams, obtained when shooting in copper radiation the samples of copper alloy treated in electrolytic plasma in the mode: U = 70 V; j = 2-5 A/cm^2; t = 10-4 min. The coherent scattering region calculated by the Selyakov–Scherer formula has a size of the order of 6-16 nm. With increasing current density and time of treating, the size of nanostructures decreases. At the same time the finely dispersed borides inclusions are formed in the diffusion layer.

The results of the layer-by-layer spectral analysis (Table 1) show the dependence of the boron distribution on the treatment mode in the electrolyte plasma. With prolonged (about 40 min.) treatment in electrolyte plasma, the boron concentration decreases gradually from the surface into the depth of the metal. With greater current density and shorter time of treating, the boron concentration is distributed like a shock wave, where in the course of the wave the boron is missing.

The calculation of the boron distribution from the layer-by-layer spectral analysis results gives the dependence shown in Fig. 2, where the depth of boron diffusion is determined by the mode of treating.

Jump-shaped boron distribution at a higher current density speaks in favor of the diffusion process model, according to which diffusion is divided into fast and slow stages. The fast diffusion stage includes vacancy and crowding diffusion mechanisms. Vacancies moving and compressing atoms in the direction of the force create conditions for the rapid movement of boron atoms. With longer time of treating, boron diffusion from the environment of saturation is significantly reduced, but the boron movement inside the metal for taking places with a minimum of energy is increased. Boron has a limited solubility in copper, which at eutectic temperature of 1333 K is 0.09 %, and does not react with copper even at very high temperatures [4]. However, under these conditions, in the oxidation environment absence, boron reacts with copper to form double and ternary compounds (Table 1). Under the conditions of electrolytic plasma, copper borides are formed mainly as microcrystalline inclusions, irregularly distributed over the depth of the layer.

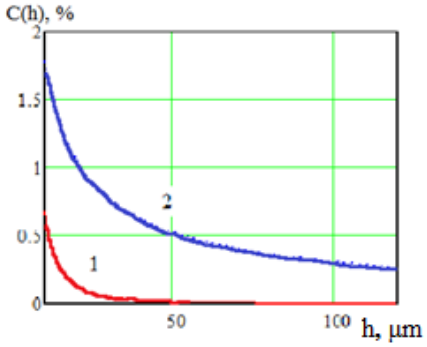


Fig. 2. Distribution of boron concentration over the depth of the copper sample treated in modes: 1 – j = 0.9 -1.8 A/cm^2, U = 65 V, t = 15min; 2 – j = 0.7-1.1 A/cm^2, U = 60 V, t = 40 min.

According to the calculations of the temperature distribution over the sample depth, the maximum temperature falls on the volume with a diameter of 1-1.2 μm [3]. Outside this size range, the temperature decreases sharply and, according to experimental data [3], on average on the metal surface depending on the treated conditions ranges from 373 K to 600 K. Under these conditions, the diffusion coefficient depends on temperature, which was determined by the formula

$$D = D_o e^{-\frac{Q}{RT}} \quad (1)$$

where D_0 is a preexponential factor directly related to the number of particles involved in the jump to overcome the barrier height, cm^2/s; Q is activation energy, J/mol; T is absolute temperature at which diffusion occurs, K; R = 8.31 J/(K·mol) is the universal gas constant. According to Frenkel-Brown [5, 6] there is a connection $D_0 = \frac{a^2}{6\tau_0}$ where a is a lattice period, Å; τ_0 = 1/ν is average time of one oscillation, s; ν is maximum frequency of the atom oscillation, 1/s. As a result of the calculations, we received D_0 =0.00852 cm^2/s for copper. To determine the activation energy, the Brown theory was used; according to it heat of loosening $Q = 3b^2 RT_{melt}$ where T_{melt} is metal melting point, K; b is a constant close to one. Considering this, equation (1) takes the form

$$D = D_o e^{-\frac{3b^2 T_{melt}}{T}} \quad (2)$$

Basing on the data, the diffusion coefficient of boron in copper under the action of local temperature (10^5 K) has a magnitude of order 10^{-2} cm^2/s. Under the average temperature (200-600 K) the diffusion coefficient of boron in copper is of the order of 10^{-6} cm^2/s.

Thus, under the conditions of copper treatment in electrolyte plasma, the diffusion process acceleration is observed with copper borides and ternary compounds Cu-B-H, Cu-B-O formation in the diffusion layer. They strengthen the surface by 1.5-2 times, depending on the mode of treating and the copper alloy composition.

4. Conclusions

For the first time the strengthening diffusion layer is obtained on the surface of copper and brass as a result of treating by electrolytic plasma formed in a boron-containing aqueous electrolyte solution. The diffusion layer includes nanosized finely dispersed copper borides, ternary compounds concentrated mainly along the grain and phase boundaries and providing hardening of the metal surface. The discharge action provides structural changes and the creation of metastable states in the surface layers of the saturated metal. Obtaining wear-resistant coatings on copper and its alloys, which include phases containing copper and boron, increases the strength characteristics of copper and its alloys by 1.5-2 times.

References

1. **Zemskov, G.V.** Mnogokomponentnoye diffuzionnoye nasyshcheniye metallov i splavov / G.V. Zemskov, R.A. Kogan. – M.: Metallurgiya, 1978. – P. 167-208.
2. **Radyuk, A.G.** Formirovaniye diffuzionnyh sloyov na poverhnosti medi i yeyo splavov / A.G. Radyuk, A.E. Titlyanov, A.E. Ukraintsev // Tsvetnyye metally. – 2007. – No. 5. – P. 95-97.
3. **Fedorenkova, L.I.** Temperaturnoe vozdeystviye elektrolitnoy plazmy na strukturu poverhnosti metalla // Fizika i tehnika vysokih davleniy. – 2014. – Vol. 24, No. 1. – P. 136-144.
4. **Vol, L.E.** Stroyeniye i svoystva dvoynyh metallicheskih sistem. – M.: Fizmatgiz, 1962. – T. 1. – P. 701-703.
5. **Merer, Kh.** Diffuziya v tverdyh telah. M.: Izd-vo inostrannoy literatury, 2011. – 536 p.
6. **Bokshtain, B.S.** Diffuziya v metallah. M.: Metallurgiya, 1978. – 248 p.