Influence of non-stationary electrolysis modes on the properties of copper-tin alloy coatings

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Abstract. Interrelation of operational properties of copper-tin alloy coatings (microhardness, solderability, transient resistance, corrosion resistance), and the modes of stationary and non-stationary electrolysis, allowing to form the coatings with a given set of properties, is revealed. The results of corrosion tests that determine the field of application of the copper-tin alloy are obtained.

1. Introduction
Physical and mechanical properties of coatings, such as microhardness, adhesive power with the base, transient electric resistance, solderability, and corrosion resistance are important characteristic features of the quality of galvanic deposits determining the field of application of the coating under certain operating conditions [1]. Copper-tin alloy is used as a protective (for steel parts used in fresh water at temperatures up to 100°C), antifriction, decorative coating, and also as a solder and underlayer coating when coated with chromium [1-3].

In the electronic industry, POS-61 alloy (tin-lead solder) is used as a coating for printed circuit boards. However, according to the European Union Directive on environmental safety RoHS, which since mid-2006 limits the lead content (not more than 0.01%) in each homogeneous material of new electronic equipment [4], works aimed at replacing lead-containing coatings by lead free ones [5] are actual. Considering good solderability of the copper-tin alloy, as well as the stability of this property under atmospheric conditions, coatings with a high tin content (more than 30%) can be recommended as an alternative to POS-61.

For coatings of parts of radio electronic equipment, an important property is the magnitude of the transient electric resistance, as well as its stability during operation.

The review [6] notes that over the past 20 years, there have been a series of developments on the bronze coating, including nanostructured coating, environmentally friendly baths (such as those based on methanesulfonic acid), and more promising coatings, including multilayer and composite materials. An increased attention is paid to non-aqueous baths, such as ionic liquid electrolytes of room temperature. The technology of obtaining deposits with controlled morphology, composition and structure of deposits has been improved by new electrolytes, additives and pulse electrolysis. The variety of applications for copper-tin alloy coatings has expanded to lithium batteries with a new layer structure. The electrochemical aspects of bronze deposition are illustrated by data from the authors’ laboratories and other sites, where the use of electrolytes based on methanesulfonic acid due to its universality and lack of environmental impact is emphasized. A wide range of coating compositions, color and surface structures are possible using suitable additives, and control of electrolyte mixing and electrodeposition...
conditions. This review focuses on electrochemical voltammetric methods, as well as morphological studies using scanning electron microscopy. Thematic sections that require further research and development are identified.

In [7], the mechanism for deposition of coatings by tin-copper alloy obtained by electrodeposition by pulse current was investigated. The tin-copper alloy coatings obtained by pulse current electrodeposition actually consisted of two layers: a solid solution of tin in copper and an intermetallic compound Cu$_6$Sn$_5$. In addition, it was found that pulse electrodeposition of the alloy contributes to an increase in the copper content. Based on the results of the study, the authors put forward a theory that explains the increase in the copper content by the metal substitution reaction that occurs during the “relaxation” period of electrodeposition by pulse current. In [8], the effect of current and deposition potential, the concentration of copper ions, the concentration of tin ions, and the concentration of surfactant on the composition of the deposited tin-copper alloy was studied. Tin-copper alloys were deposited from the bath with methanesulfonic acid containing a perfluorinated cationic surface-active agent. Electrodeposition was performed using a rotating disk, a rotating cylinder, and a rotating cylinder in the Hull cell. The presence of surface-active agent has led to a shift in the copper deposition potential compared with the tin deposition potential. Thus, both “normal” deposition (Cu is deposited at a more positive potential than Sn), and “anomalous” deposition (Sn is deposited with a more positive potential than Cu) may occur. The authors carried out the electrodeposition of tin-copper alloys in a wide range of operating modes of electrolysis to obtain the color of the coating surface from golden yellow to light brown. In this case, bronze coatings of golden color can be obtained, containing 70-80% Cu and 20-30% Sn. When an alloy with a predominance of tin was deposited, the copper content in the alloy was in the range of 3-9% along the length of the rotating cylindrical cathode in the Hull cell.

The studies of the corrosion behavior of the tin-copper alloy coating were conducted. The appearance of corrosion in conditions of high temperature and humidity may cause the growth of tin whiskers. In [9], the relationship between the corrosion of various tin-copper alloys (0-5% copper), and the growth of whiskers was investigated. Alloys deposited as a coating on a copper base were stored at high temperature and humidity (85°C/85% relative humidity). It was found that tin-copper alloys demonstrate differences in the growth trends of whiskers. To find the relationship between the behavior of whiskers and the corrosion resistance of the alloys, polarization studies were performed. The corrosion behavior of the layers through the cross-section using a focused ion beam was also studied. A series of tests showed that the probability of the appearance of whiskers of different alloys depends on three various factors: the corrosion resistance of the coating, the rate of expansion of corrosion products, and the rate of metal/alloy recrystallization.

In [10], corrosion caused by high temperature and humidity on coatings of pure tin and tin-copper alloy was described. A new phenomenon concerning the appearance of whiskers of copper oxide on a tin-copper alloy deposited on copper substrates (copper content of 1-5% was stored at 105°C/100% relative humidity) was observed. The whiskers of copper oxide have showed similar growth properties of tin whiskers. The authors have developed a model for understanding the development of whiskers of copper oxide. Localized corrosion of the tin coating reaches the intermetallic layer Cu$_6$Sn$_5$, and copper oxide accumulates as a result of Cu$_6$Sn$_5$ corrosion. Expanding SnO$_x$ contracts and squeezes copper oxide in the form of whiskers.

There is information in [11] about the possibility of controlling the operational properties of metal coatings using non-stationary modes (in particular, when the cathode vibration and the imposition of a magnetic field on the electrolyte).

Thus, to study the effect of different electrolysis modes (vibration of the cathode and the imposition of an alternating magnetic field on the electrolyte) on the physical and mechanical, electrical, and corrosion properties of the copper-tin alloy coatings is relevant. The results of the study will allow to create a technology to form coatings of copper-tin alloy of a given composition with a given set of operational properties.
2. Materials and methods
The microhardness of the coatings was measured using a PMT-3 microhardness tester; a four-sided diamond pyramid of the indenter with an apex angle of 136° was inserted perpendicular to the coating layer with a load of 0.1 to 1 Н. The following formula was used in the calculations:

\[ H = \frac{1.854P}{d^2}, \]

where \( P \) is the load on the diamond pyramid, Н; \( d \) is the length of the diagonal of the print, m; \( H \) is the number of hardness, Pа.

To eliminate the influence of the substrate, the sample was coated with a thickness of 8 ... 12 mkm.

Transient resistance \( (R_t) \) is a complex function of various surface properties (electrical, mechanical, and measurement conditions). The theory of transient resistance is based on the fact that the contact of real bodies with a rough surface occurs on separate “contact spots”, the number of which depends on the sample roughness, and the magnitude of the mechanical load on the contact [12, 13]. The “electrical” component of the transient resistance includes the electrical characteristics of the surface (the presence of corrosion products on the surface and their electrical conductivity, type of conductivity, size of the exclusion area). The study of the transient electric resistance of copper-tin alloy coatings was carried out indirectly by measuring the voltage drop on the contact pair at different load (GOST 24606.3-82):

\[ R_t = \frac{\Delta E}{I}, \]

where \( R_t \) is the transient electric resistance, Ohm; \( \Delta E \) is the voltage drop at the contact, В; \( I \) is the current in the circuit, А.

The reference contact was a gold-plated spherical contact with a spherical rounding diameter of 1.5 mm. When measuring, the load on the contact pair changed from 0.5 to 2.0 Н, and the current in the contact circuit was 10 mA.

Since an important indicator for the coatings with copper-tin alloy is their ability to solder, the method for determining this indicator is a necessary condition for determining their quality. Determining the ability of the coating to solder allows making timely adjustments to the technological process of the coating deposition, and thereby affecting the quality of the connection of parts by the soldering method [14].

The spreading coefficient value is taken as an indicator of solderability \( (K_{spr}) \) (GOST 9.302-88, GOST 20.57.406–81, GOST 28235–89).

\[ K_{spr} = \frac{D - H}{D} \times 100\%, \]

where \( D \) is the diameter of a hypothetical solder droplet; \( H \) is the solder droplet height.

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\[ D = \frac{\sqrt[3]{1.9m}}{\rho} \]

where \( m \) is the solder mass; \( \rho \) is the solder density.

During the experiment, POS-61 solder (61% of Sn, 39% of Pb, melting point is 190ºС), and active flux of the F-38H grade [19] were used.

To estimate solderability by the value of the spreading coefficient, the following scale was used (table 1).

| Solder spreading coefficient, % | Solderability | Solder spreading coefficient, % | Solderability |
|-------------------------------|--------------|-------------------------------|--------------|
| up to 60                      | bad          | 70 – 80                       | satisfactory |
| 60 – 70                       | insufficient | 80 – 90                       | good         |
| 90 or more                    |              |                               | very good    |
The main characteristic of protective coatings is their corrosion resistance. One of the main objectives of the deposition of protective coatings is to increase the corrosion durability. The protective properties and corrosion resistance of the copper-tin alloy coatings were evaluated according to the results of climatic tests in a humidity chamber. The tests in the humidity chamber were carried out at a relative humidity of 93±3% and a temperature of 40±2 °C (GOST 9.905-82).

The adhesion strength of the galvanic coating by copper-tin alloy with the base was determined by the method of bending and scratches [1].

The bending method is recommended for coatings on parts made of a material with a thickness or diameter of less than 3 mm. The sample is bent at an angle of 90° in both directions until fracture. There should not be breakaway of the coating in the place of fracture; the cracking of the coating is not taken into account [1].

The scratch method is recommended for coatings with a thickness of less than 10 mkm. At least three parallel scratches are applied to the surface of the coating with a tip with a distance of 2–3 mm between them, and at least three scratches perpendicular to them. The scratches are applied in one direction to the base metal. After testing, there should be no breakaway of the coating between the lines and in the grid of squares [1].

To assess the corrosion resistance of galvanic coatings with a copper-tin alloy, climatic tests in a humidity chamber were carried out. Climatic tests in a humidity chamber at a relative humidity of 93±3% and a temperature of 40±2°C were carried out for 28 days, and the evaluation of the corrosion resistance of the coatings was carried out by “corrosion resistance score” ($K_D$) (GOST 27597-88). Steel samples of 20×30 mm galvanic coated by copper-tin alloys were subjected to corrosion testing. At the same time, for the comparative assessment of the corrosion resistance of copper-tin alloy coatings, samples coated with copper were placed in a humidity chamber (GOST 9.308-85).

3. Results
The dependence of the microhardness of the copper-tin alloy coatings on the alloy composition has a maximum corresponding to the tin content in the alloy of 20-25% (Fig. 1). The microhardness of coatings varies from 0.78 hPa for pure copper to 0.55 hPa for an alloy with a tin content of 45%. The maximum of microhardness of 1.75 hPa corresponds to an alloy with a tin content of 23%, which exceeds the microhardness of pure copper by more than two times. The dependence of microhardness on the composition of the galvanic sediment is similar to the dependence of a metallurgical alloy [1].

![Figure 1. Dependence of microhardness of the copper-tin alloy coating on the composition: 1 – casting alloys, 2 – coatings obtained in the stationary mode, 3 – coatings obtained by applying an alternating magnetic field, 4 – coatings obtained by cathode vibration.](image)

The microhardness of sediments obtained in non-stationary modes of electrolysis, such as cathode vibration and application of an alternating magnetic field on the electrolyte is approximately 0.2-0.3 hPa is lower than when using the stationary mode. However, their microhardness is close to the microhardness of a copper-tin alloy obtained by casting. This is due to the difference in the structure of the alloy obtained in different modes of electrolysis. In the stationary mode, an alloy with a fine-
crystalline structure is deposited; under the cathode vibration, the crystals are larger, and when the alternating magnetic field is applied on the electrolyte, the crystals are stretched along the magnetic field lines.

The research of the copper-tin alloy solderability has showed that the spreading coefficient value depends on the concentration of tin in the alloy \((C_{Sn})\) and this dependence can be described in the range of tin content in the alloy from 0 to 45% by the following equations with a correlation coefficient in the range from 0.9641 to 0.9866:

\[
K_{spr} = 97.378e^{10^{-4}C_{Sn}}
\]

for the coating obtained by cathode vibration;

\[
K_{spr} = 97.322e^{210^{-4}C_{Sn}}
\]

for the coating obtained by applying an alternating magnetic field on the electrolyte;

\[
K_{spr} = 97.035e^{310^{-4}C_{Sn}}
\]

for the coating obtained in the stationary mode.

Thus, for an alloy containing 45% of tin, the solder spreading coefficient is 98.3%. This corresponds to a very good solderability (according to the solderability criteria table). The solderability of these samples after climatic tests in the humidity chamber and the salt fog chamber does not practically differ from the initial values.

A regular growth of solderability with increasing tin content allows using an alloy with a tin content of 40–45% as a finishing coating for printed circuit boards.

The copper-tin alloy with a tin content of 17–22% is characterized by a low and stable in time value of the transient electric resistance (Table 2 and Table 3). The components of the copper and tin alloy do not have such characteristics. Freshly deposited coating by copper has a low value of transient electric resistance (Table 2), but it increases dramatically over time (Table 3) due to the formation of corrosion products on the metal surface.

| Contact load, H | 0 | 0.055 | 0.045 | 0.049 | 0.067 | 0.082 | 0.093 | 0.1 | 0.108 | 0.111 | 0.12 |
|----------------|---|-------|-------|-------|-------|-------|-------|----|-------|-------|-----|
| Tin content in the alloy, % | 19 | 0.045 | 0.032 | 0.0357 | 0.052 | 0.062 | 0.071 | 0.078 | 0.087 | 0.09 | 0.099 |
|                | 20 | 0.037 | 0.025 | 0.027 | 0.04 | 0.048 | 0.055 | 0.059 | 0.066 | 0.068 | 0.075 |

Table 2. Transient electric resistance of the copper-tin alloy coating depending on the composition of the alloy and contact load.

| Tin content in the alloy, % | 0 | 4 | 8 | 12 |
|-----------------------------|---|---|---|----|
| 0                           | 0.037 | 0.077 | 0.105 | 0.12 |
| 20                          | 0.027 | 0.035 | 0.04 | 0.043 |
| 25                          | 0.041 | 0.054 | 0.064 | 0.071 |
| 30                          | 0.055 | 0.072 | 0.087 | 0.1  |

Table 3. Transient electric resistance of the copper-tin alloy coating depending on time in the humidity chamber and the composition of the alloy.

As is known, the resistivity of copper is 0.017 Ohm-mm²/m, and that of tin is 0.143 Ohm-mm²/m. A significant increase in the electric resistivity of the copper-tin alloy is natural, since usually the electric resistance of the alloys is higher than of pure metals [16].

Table 2 shows the values of the transient electric resistance of copper, as well as of copper-tin alloy coatings, depending on tin content in the alloy at different contact loads. As can be seen, the smallest transient resistance is characterized by a copper-tin alloy with a tin content of 20%. Alloys with tin
content of more than 25% have a higher transient electric resistance than copper. A high tin coating is initially characterized by increased values of the electrical transient resistivity, which in principle excludes its use as a material for switching electrical contacts.

The transient resistance value and its change in time are determined by the state of the surface and corrosion resistance [12]. The operation reliability of radio electronic equipment depends largely on the service life of detachable electrical low-current contacts.

After corrosion tests in the humidity chamber, measurements of transient electric resistance (Table 3) showed that a copper-tin alloy of different composition has a fairly stable value of transient resistance for a short period of time. At the same time, the transient resistance of copper increased by 2-3 times.

The stability of the low transient electric resistance of the copper-tin alloy is due to its increased corrosion resistance.

Thus, the measured values of transient electric resistances of copper-tin alloys show the possibility of their use for electrical low-current contacts operating under these conditions, as well as to reduce the consumption of precious metals, and increase the reliability and durability of radio electronic equipment.

During the tests, the copper coating acquired a dark color, completely having lost luster. The corrosion behavior of a copper-tin alloy with tin content of 20% is more similar to copper in appearance. The coatings by alloys with tin content from 20% to 30% have faded, and pitting has appeared on their surface. It should be noted that darkening and losses of luster are not so significant compared with copper, and at the end of the tests, a partial luster is observed on the sample. The copper-tin alloy coatings with tin content of 30% to 40% have practically not been subjected to corrosion damage and retain a brilliant appearance, and only partially covered with colors of tinge. The electrolysis modes, such as vibration and the imposition of an alternating magnetic field on the electrolyte, have virtually no effect on corrosion resistance, but to a greater extent effect the composition of the alloy. Both the cathode vibration and an alternating magnetic field contribute to an increase in tin content of the alloy.

The corrosion resistance score $K_D$ for copper-tin alloys was from 5 to 9, while for the copper coating it was 3. The corrosion resistance score $K_D$ from 5 to 10 corresponds to the successful completion of the corrosion test.

Based on the analysis of the results of corrosion tests, it can be concluded that the galvanic coatings of the copper-tin alloy have high corrosion resistance due to the formation of a dense corrosion film on their surface that protects the material from further corrosion damage.

4. Conclusion

Thus, non-stationary modes of electrolysis, such as cathode vibration and the imposition of an alternating magnetic field on the electrolyte, contribute to the formation of galvanic coatings of a copper-tin alloy with a wide range of tin content in the alloy, thereby having a significant impact on their properties.

It was found that cathode vibration and the imposition of an alternating magnetic field on the electrolyte lead to the formation of coatings with a copper-tin alloy, which have a low and stable transient resistance, good solderability, and high corrosion resistance. This allows using these coatings for low-current contacts, as well as soldering coatings for the production of printed circuit boards.

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