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INFLUENCE OF ANTIMONY ON STRUCTURE AND MECHANICAL PROPERTIES OF PRE-EUTECTIC COPPER-PHOSPHORUS ALLOYS

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The results of investigations of pre-eutectic alloys of Cu–P–Sb system are presented. The melting temperature range was determined using high-temperature differential thermal analysis. It was found that antimony alloying of copper-phosphorus pre-eutectic alloy provides a decrease in the solidus and liquidus temperature. On the basis of experimental and literature data, the surfaces of liquidus and solidus of ternary alloys were constructed. Using micro-X-ray spectral analysis, the chemical composition and a number of structural components of Cu–6.29P–1.97Sb alloy were determined. The influence of antimony on technological and mechanical properties, as well as morphology of cast ternary pre-eutectic copper-phosphorus alloys is shown. 10 Ref., 2 Tables, 6 Figures.

Keywords: copper-phosphorus pre-eutectic alloys, antimony, temperature of solidus and liquidus, microstructure, ultimate tensile strength

Copper-based alloys are widely used in modern mechanical engineering. They differ by chemical composition, physical and mechanical properties. Brazing is often applied for joining them that allows preserving the initial base metal structure and provides the specified mechanical characteristics. Alloys of copper-silver system are often used as brazing filler metals. They are characterized by an acceptable melting temperature range, sufficient ductility and strength [1]. The disadvantages of silver brazing filler metals include their high cost that increases the final price of the products. Economic inexpediency of application of such brazing filler metals often promotes wider application of less-expensive brazing filler metals based on copper-phosphorus system. At present brazing filler metals on copper-phosphorus base of eutectic and pre-eutectic composition are more promising substitutes of silver-containing brazing filler metals [1-4]. They have comparatively low melting temperature [5] and good physico-technological properties (Figure 1, *a*, *b*).

Phosphorus is a good deoxidizer for copper (residual oxygen content is close to zero). Formation of copper phosphides results in increase of binary alloy hardness. Phosphorus essentially reduces the melting temperature, improves the fluidity and wear resistance

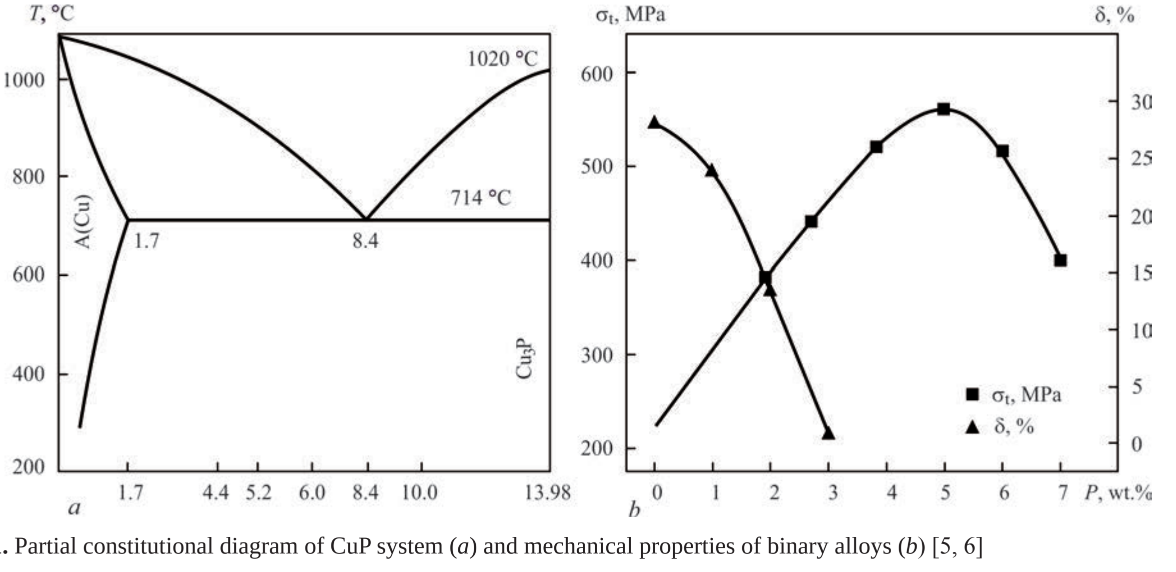

Figure 1. Partial constitutional diagram of CuP system (*a*) and mechanical properties of binary alloys (*b*) [5, 6]

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of the brazing filler metal. However, alloys of eutectic composition are extremely brittle (Figure 1, *b*). In order to preserve the high ductility properties and lower the melting temperature of brazing filler metals of copper-phosphorus system, containing 3–6 wt.% phosphorus, additional alloying by other elements, such as silver, zinc, tin and antimony is used [4].

The experience of the last decades showed that in most of the cases such brazing filler metals can be used for brazing the most nonferrous metals and alloys. Antimony is one of the elements reducing the melting temperature of alloys of copper-phosphorus system. It can be assumed that antimony, being in the same group of periodic table with phosphorus, can have a positive impact on melting temperature and phase composition of the filler metal of ternary Cu–P–Sb system.

This work presents the results of investigation of the influence of antimony as one of the depressants of copper-phosphorus filler metals, on the solidus and liquidus temperature, structure and mechanical properties of pre-eutectic alloys of copper-phosphorus system.

Materials and methods of investigations. Experimental brazing filler metals were melted in a graphite crucible in the laboratory resistance furnace. Phosphorus copper MF10 with 10.18 % wt.% phosphorus, copper M1, and antimony Sb00 were used as the charge. Phosphorus concentration was varied in the range from 3 to 6 %, that of antimony — from 2 to 6 %. After component melting, the alloy was soaked up to complete dissolution of the component elements. Cast billets were used for chemical analysis and conducting metallographic investigations of experimental filler metals.

Melting temperature of experimental alloys was determined, using a unit for high-temperature differential thermal analysis in a helium atmosphere.

Metallographic investigations were conducted using optical (Neophot 32) and scanning electron microscopy (TescanMira 3 LMU). Chemical element distribution was determined by the method of local X-ray microanalysis, using energy-dispersive spectrometer Oxford Instrument X-max 80 mm^2 with application of INCA program package. Locality of X-ray microscopic measurements did not exceed 1 μm, microstructure filming was conducted in back-scattered (BSE) electrons that allows studying the microsections without chemical etching.

Mechanical testing was conducted with application of experimental brazing filler metals in the cast state. Obtained ingots were used to make M12-6K samples to GOST1497–73.

Investigation results and their analysis. Binary Cu–P, Cu–Sb systems are already well studied, and the constitutional diagrams are given in publications [5]. These are diagrams of eutectic type. The eutectics form between solid solutions and chemical compounds. This leads to the assumption that the ternary system also has an eutectic component. Phosphorus and antimony have a considerable influence on the melting temperature of copper alloys. At the temperature of 200 °C up to 2 wt.% antimony dissolves in copper. Therefore, alloying of copper alloys by antimony in this concentration range should not cause formation of additional phases. Binary diagrams have steep liquidus lines near eutectic transformation points [5].

In phosphorus-antimony binary system no compounds of antimony with silver were found, but at cooling below 612 °C the saturated melt decomposes into the solid and gaseous phases [7]. In the solid state, phosphorus and antinomy do not impair the mechanical properties of copper [8, 9].

Known is the positive influence of antimony and phosphorus on surface tension of antimony and its melting temperature [9]. Addition of these elements

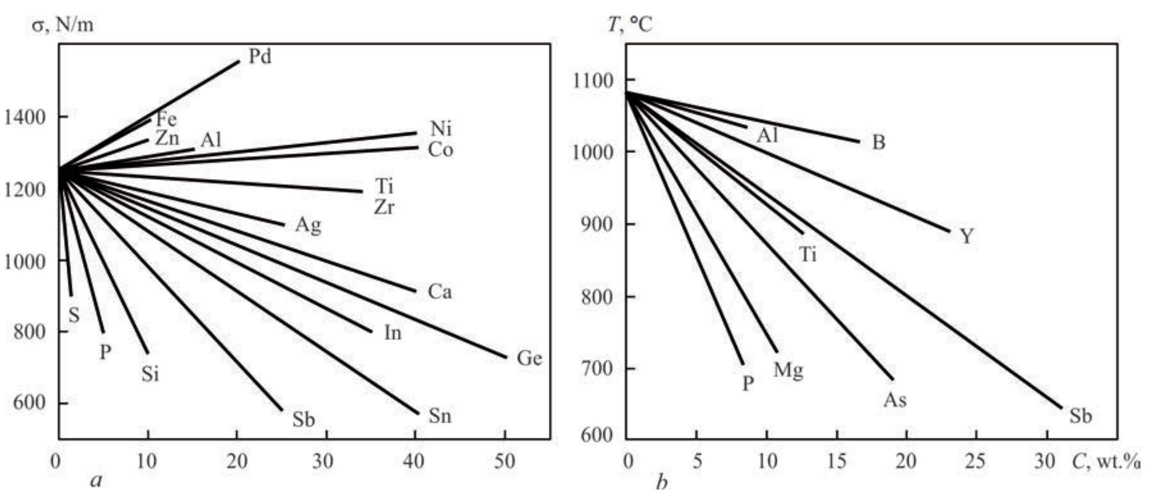

Figure 2. Influence of chemical elements of the composition C on surface tension (*a*) and copper melting temperature (*b*) [8, 9]

to copper reduces the surface tension (Figure 2, *a*) and lowers the melting temperature (Figure 2, *b*).

High-temperature differential thermal analysis of the studied alloys showed that when adding antimony to the pre-eutectic alloy of copper-phosphorus system, a lowering of solidus and liquidus temperature is observed (Table 1).

So, increase of the amount of antimony from 1.5 to 5.64 wt.% at phosphorus content > 5.0 wt.% leads to lowering of solidus temperature from 655 to 620 °C. Liquidus temperature here also decreases from 680 to 660 °C. In fact, increase of phosphorus and antimony content leads to a significant lowering of solidus temperature and certain lowering of liquidus temperature, compared to previous alloys.

Liquidus (Figure 3, *a*) and solidus (Figure 3, *b*) surfaces of experimental alloys were plotted, proceeding from the obtained results of high-temperature differential thermal analysis, published data of constitutional diagrams of binary alloys with application of mathematical methods of data processing.

Table 1. Physico-technological properties of experimental alloys of Cu–P system alloyed by antimony

Alloy number	Element content, wt.%			Melting temperature, °C			Spreading area, mm^2
	Cu	Sb	P	T_S	T_L	ΔT	
1	Base	5.87	3.61	625	665	45	218.75
2		4.96	4.37	620	690	70	364.6
3		3.87	5.2	685	700	15	364.6
4		4.97	3.31	650	715	65	218.75
5		2.97	4.14	690	780	90	218.75
6		3.70	3.0	640	710	70	291.6
7		3.75	4.44	630	700	70	291.6
8		1.50	5.05	655	680	25	364.6
9		2.97	5.2	655	670	15	364.6
10		5.64	6.78	620	660	40	372.4

These surfaces allow reducing the number of experiments at selection of specific chemical composition of the brazing filler metal, which the most completely corresponds to the specified requirements and specified temperature ranges of solidification. They correlate well with the results obtained using the regression models [10].

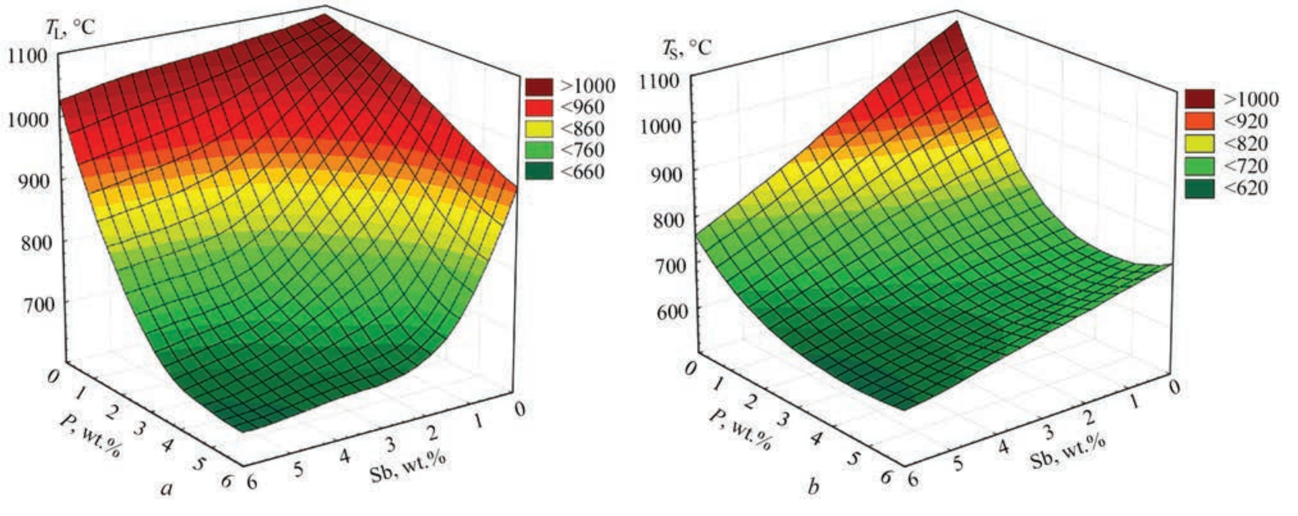

Figure 3. Liquidus (*a*) and solidus (*b*) surfaces of alloys based on Cu–P–Sb system

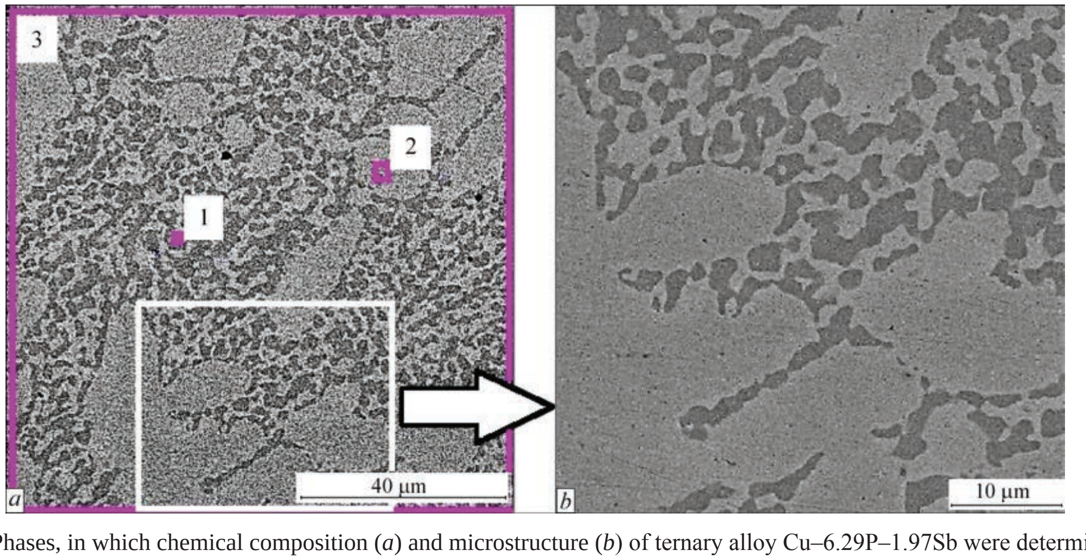

Figure 4. Phases, in which chemical composition (*a*) and microstructure (*b*) of ternary alloy Cu–6.29P–1.97Sb were determined

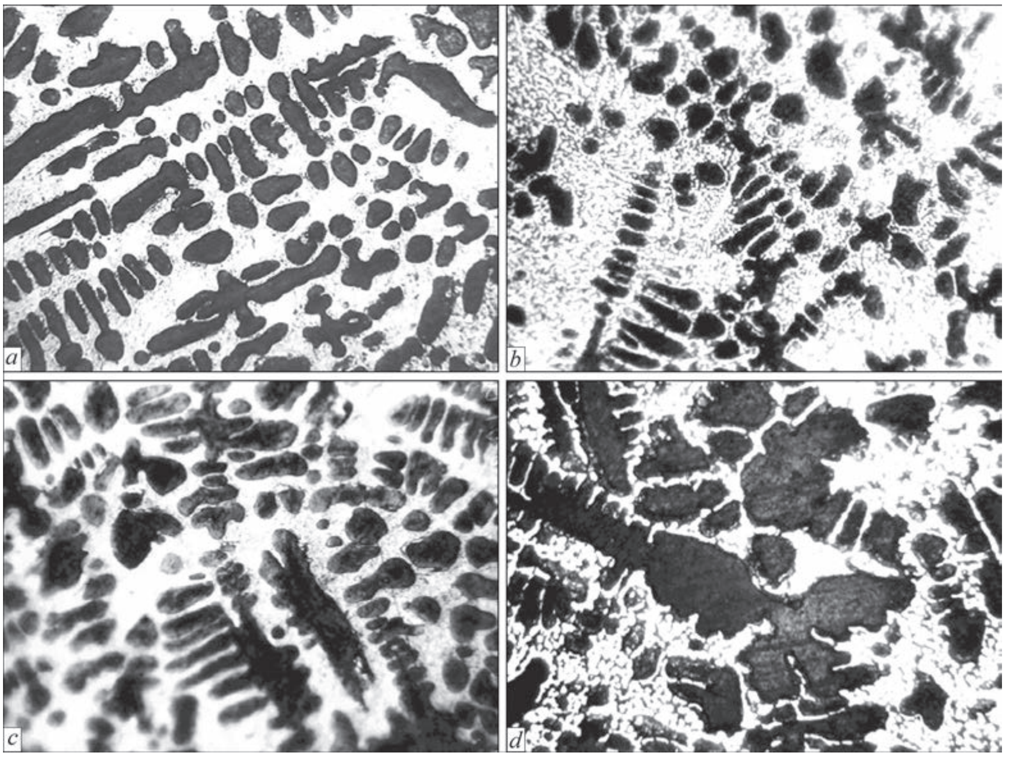

Figure 5. Microstructure of Cu–P–Sb alloy at different content of antimony: *a* — 0; *b* — 3; *c* — 4; *d* — 5 % and constant content of phosphorus of 5 w.% (×500, optical microscope)

Investigations of spreading over copper of copper-phosphorus filler metals alloyed with antimony, showed that simultaneous increase of phosphorus and antimony concentration leads to enlargement of the spreading area (see Table 1). A pre-eutectic alloy, containing more than 5 % antimony and more than 6 % phosphorus, is characterized by maximum spreading area.

Results of X-ray microanalysis showed that the microstructure of the cast alloys with 2 % antimony, is formed by the following phases: primary dendrites of α-solid solution of phosphorus and antimony in copper; copper phosphide (Cu_3, P) in the form of dark inclusions and rod-like eutectic, that consists of the solid solution and phosphide of copper (α-Cu + Cu_3P), which precipitates in interdendritic regions (Figure 4, Table 2).

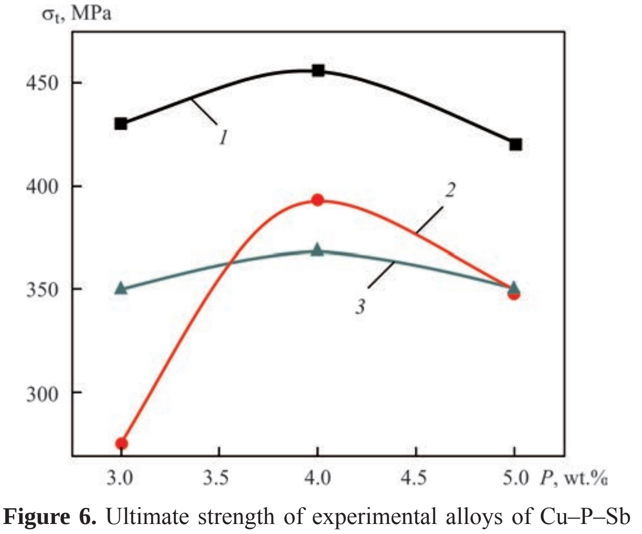

Figure 6. Ultimate strength of experimental alloys of Cu–P–Sb system, depending on the degree of phosphorus and antimony alloying: *1* — Sb = 3; *2* — 4; *3* — 5 %

Antimony concentration in copper phosphide exceeds its concentration in the solid solution (see Table 2).

Optical microscopy studies of the structure revealed that the alloys of copper-phosphorus system at a constant phosphorus content (5 %) retain the morphological features with increase of antimony concentration, but increase of the fraction of copper-based solid solution α-Cu and of the dendrite dimensions is observed, which is characteristic for pre-eutectic alloys (Figure 5).

Mechanical testing of brazing filler metals at room temperature showed that at 4 wt.% concentration of phosphorus maximum values of ultimate tensile strength (σ_t) of ternary Cu–P–Sb alloys with 3, 4 and 5 wt.% antimony are observed. It should be noted that further increase of the amount of antimony in the pre-eutectic copper-phosphorus alloy with up to 5 %

Table 2. Chemical composition of structural components of Cu–6.29P–1.97Sb, wt.% ternary alloy

Spectrum number	P	Cu	Sb
1	13.87	84.93	1.20
2	0.92	98.54	0.54
3	6.29	91.74	1.97

phosphorus, leads to lowering of ultimate strength (Figure 6).

Obtained investigation results show that acceptable strength characteristics are found in pre-eutectic copper-phosphorus alloys, where antimony concentration does not exceed 3 wt.%. In its turn, lowering of the content of phosphorus (≤ 3 wt.%) and antimony (≤ 2 wt.%) promotes considerable increase of brazing temperature and deterioration of filler metal spreading.

Brazing filler metals of Cu–P–Sb system have been successfully tested in brazing of a number of products and individual assemblies from copper and its alloys in electrical engineering industry, as well as dissimilar metals, in particular, copper alloy with 29NK precision alloy. These filler metals provide good service properties of brazed structures from corrosion-resistant copper-nickel alloys (German silver) that are used in marine shipbuilding.

Conclusions

Pre-eutectic alloys of copper-phosphorus-antimony system were studied. High-temperature differential thermal analysis showed that increase in the amount of antimony from 1.5 to 5.64 wt.% at phosphorus content > 5.0 wt.% leads to lowering of the solidus and liquidus temperature from 655 to 620 °C, respectively. Liquidus and solidus temperatures of pre-eutectic alloys of Cu–P–Sb system were plotted, proceeding from the experimental and literature data.

Local X-ray microanalysis showed that the main structural components of pre-eutectic alloys of copper-phosphorus-antimony system are primary dendrites of copper-phosphorus-antimony solid solution. Rod-like eutectic formed by copper phosphide and copper-based solid solution precipitates in interdendritic regions.

At constant concentration of phosphorus of 4 wt.% maximum tensile strength is observed in cast copper alloys doped by antimony in the amount from 3 to 5 wt.%. At further increase of the amount of antimony, a decrease in strength is found in pre-eutectic copper-phosphorus alloy with up to 5 % phosphorus, so its concentration should be limited.

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