

Investigation of Powders to Make Lead-Free Paste for High-Temperature Soldering of Copper Alloys

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Abstract

Investigation of a series of fine powders of the copper alloy with the addition of 15 mass % tin, 4 mass % nickel and 5 mass % phosphorus was carried out by means of X-ray photoelectron spectroscopy. It was shown that the chemical composition of subsurface layers of powder particles of the solder depends on preparation procedure and affects the quality of soldering.

INTRODUCTION

High-temperature soldering using various solid copper and silver based solders is traditionally used in manufacturing fuel, hydraulic, cryogenic, vacuum devices, and in power electronics hardware made of copper and copper alloys in order to connect various structural elements. High technological characteristics of soldered connections (increased thermal conductivity, high plasticity, strength, corrosion stability *etc.*) are achieved with the use of silver-containing solders [1]. However, the use of silver in the composition of solders increases their cost substantially. From this point of view, development of alternative methods of soldering using less expensive components becomes urgent.

One of the possible versions of making the soldering technology cheaper is to develop soldering pastes based on copper-phosphorus alloys. These pastes include fine powdered solder, a fluxing composition based on liquid volatile organic ingredients, and special additives in some cases. Undoubted advantage of soldering pastes over solid alloys is the possibility to solder difficultly accessible sites with narrow

clearance. Moreover, soldering paste is applied onto a species before soldering, which is technologically more convenient for mass production and allows one to measure out the necessary amounts of solder more precisely. It should be noted that the alloys of copper with phosphorus are distinguished by high fluidity, corrosion stability and relatively low melting point. Copper-phosphorus solders also possess self-fluxing properties, which allows one to solder copper and some its alloys without using fluxes [1]. The soldering properties of a copper-phosphorus alloy may be improved by adding supplementary components. For instance, the introduction of nickel into a copper-phosphorus alloy improves its corrosion stability; lead or tin decrease the melting point and increase the plasticity of the alloy. However, according to ecological requirements, the introduction of lead into the alloy is undesirable. Starting from June 2006, a planned transition from to lead-free soldering technology occurs in the countries of the European Union. As practice shows, the high quality of soldering is achieved with the use of copper-phosphorus alloy with nickel and tin added.

In the present work, we report on the investigation of a series of fine powders of

the copper alloy with the addition of 15 mass % tin, 4 mass % nickel and 4–5 % phosphorus by means of X-ray photoelectron spectroscopy (XPES). The possibilities of the use of XPES in the development of powder solders are demonstrated. It is shown that the chemical composition of subsurface layers of powder particles of the solder depends on preparation method and has a strong effect on soldering quality.

EXPERIMENTAL

The powders of copper alloy with 15 mass % tin, 4 mass % nickel, 4–5 mass % phosphorus were prepared using two procedures: by grinding in a ball mill and by spraying of the melt with a gas jet. The spraying set-up is an injector to supply a gas under a plate on which a falling stream of the alloy heated to a temperature of 800 °C [2, 3]. The melt spreads over the plate and gets sprayed by the gas at a pressure of 4–5 MPa at a moment when it flows down the plate in a layer of 0.1–0.3 mm. The advantage of this procedure is that it allows obtaining fine solder particles of spherical shape with low impurity content. The commercial fraction of the required size was separated with the Fritsch device. Particle size was determined with Fritsch 38 Analisette analyser.

Investigation of the chemical composition of subsurface region of the particles was carried out with VG ESCALAB HP electron spectrometer using AlK_{α} radiation ($h\nu = 1486.6$ eV). The scale of bond energies was calibrated preliminarily on the basis of the positions of peaks $Au4f_{7/2}$ (84 eV) and $Cu2p_{3/2}$ (932.67 eV) in the spectra of gold and copper foil, respectively. The relative content of the elements in the analysis zone (the depth of analysis being 2–3 nm) was determined on the basis of the integral intensities of XPES signals taking into account the coefficients of atomic sensitivity [4]. In order to increase the depth of analysis, layer-by-layer etching procedure was applied. Ion etching of the samples was carried out with an argon gun VG AG-21 (beam energy: 3 keV, current density: ~ 20 μA). The rate of layer removal was ~ 1 nm/min [4, 5]. The reference sample was OKS-600 powder of the commercial

CuSnPNi solid solder (BrazeTec, Hanau, Germany, U.S. Pat. 5378294).

RESULTS AND DISCUSSION

The quality of soldering is essentially dependent both on the chemical composition and on the degree of oxidation or pollution of the surface of powder solder particles. The oxygen content of the solder is considered to be not higher than 0.5 %. It should be stressed that the important parameter is not only the bulk oxygen content but also its amount in a thin subsurface layer which reacts at the very beginning of soldering process with the flux and the metal of details to be soldered because the use of oxidized solder leads to the formation of a junction of poor quality. The negative effect is also caused on the properties of soldering paste by carbon deposits, which are often formed on the surface of powder particles of solid solders. Developing soldering pastes one should also take into account the fact that the elemental composition of the surface of powder particles can substantially differ from the bulk composition, which is a result of segregation processes and affects the soldering quality. From this point of view, when developing the technology of powder solders, one should obtain a detailed information about the chemical composition of the surface of solder particles.

The soldering paste prepared on the basis of the sieved fraction <40 μm of the fine copper alloy powder obtained by grinding in a ball mill (sample 1) possessed unsatisfactory soldering properties. The surface of a spot of the flowed solder has become coated with a black CuO film and was characterized by the low fusion coefficient. As a rule, such behaviour is characteristic of powder solders containing a large amount of oxygen. At the same time, analysis of the powders of different lots of powder solder showed that the bulk concentration of oxygen is 60 to 3000 ppm. Therefore, it may be assumed that the main part of oxygen is localized in the subsurface layer in the form of an oxide film. Indeed, according to XPES data, the surface of solder powder particles is oxidized. The overall photoelectron spectra of samples 1 and OKS-600 are shown

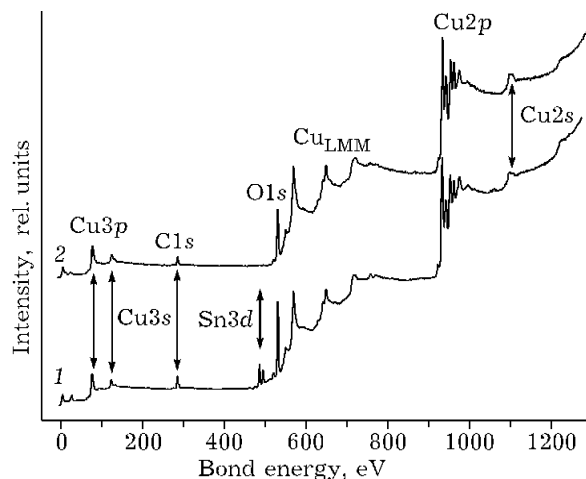


Fig. 1. Overall X-ray photoelectron spectra of the surface of solder powder particles of sample 1 (1) and the reference sample OKS-600 (2).

in Fig. 1. The most intensive lines are determined by electron photoemission from copper levels Cu3p, Cu3s, Cu2p, Cu2s. Three clearly exhibited lines in the region 570, 650 and 720 eV correspond to the Auger spectrum of Cu_{LMM}. The lines in the region of 285 and 530 eV are determined by electron photoemission from the levels C1s and O1s, respectively. Relative atomic concentrations of the elements in the subsurface region of powder particles of the alloys under investigation are shown in Table 1.

When melt spraying with air flow was used (sample 2, sieved fraction <40 μm), the concentration of oxygen in the subsurface region of the powder alloy increases (see Table 1). Moreover, in comparison with the reference sample, the surface is enriched with carbon, tin and phosphorus. Nickel concentration on the surface is below the sensitivity limit of XPES. Carbon is localized mainly on the surface, and

its concentration decreases sharply just after several minutes of ion etching (see Table 1). The position of C1s line ($E_b \sim 285$ eV) corresponds to carbon atoms included in hydrocarbon fragments. Phosphorus is present on the surface mainly in the form of phosphates (atomic ratio [O]/[P] ~ 3.2). The P2s spectra of the initial surface exhibit two lines near 187.1 and 190.6 eV (Fig. 2). The first line corresponds to phosphorus atoms incorporated in CuSnPNi alloy, while the second, a more intensive one, corresponds to phosphate groups [4]. After ion etching, the concentration of phosphate groups decreases substantially; only one line is observed in P2s spectra around 187.1 eV. It should be noted that metal phosphides possess fluxing properties, while the presence of phosphates on the surface worsens soldering properties of solders.

In order to decrease the oxygen content of the subsurface region, a lot of solder powder was prepared on the basis of the fraction <40 μm of a copper alloy sprayed in nitrogen jet (sample 3). Spraying of CuSnPNi alloy in nitrogen flow leads to a decrease in the content of phosphorus and tin on the surface of solder particle, and this is an evidence of the fact that the segregation of these elements occurs at a high rate in the presence of oxygen at high temperature. The main part of phosphorus on the surface of this sample is also localized on the surface in the oxidized state (PO_4^{3-}). Spraying in nitrogen flow causes a decrease in the surface concentration of carbon. It should be noted that the amount of carbon correlates with the surface concentration of tin (see Table 1). It may be assumed that an increase in the surface concentration of tin leads to a higher carbon content of the surface due

TABLE 1

Relative atomic concentrations of elements in the subsurface region of solder powder particles, determined by means of XPES

Sample No.	[Sn]/[Cu]	[Ni]/[Cu]	[O]/[Cu]	[O]/[Cu+Sn]	[P]/[Cu]	[C]/[Cu]
1	0.14	0.03	2.4	2.1	0.097	1.7
2	1.1 (0.19)	0.00 (0.13)	12 (0.36)	5.6 (0.30)	3.7 (0.40)	9.3 (0.87)
3	0.81 (0.30)	0.00 (0.16)	5.5 (0.33)	3.1 (0.25)	1.1 (0.34)	5.3 (1.0)
OKS-600	0.002 (0.095)	0.02 (0.03)	1.7 (1.3)	1.6 (1.1)	0.005 (0.093)	1.0 (0.80)

Note. Atomic ratios determined after ion etching for 2 min are shown in parentheses.

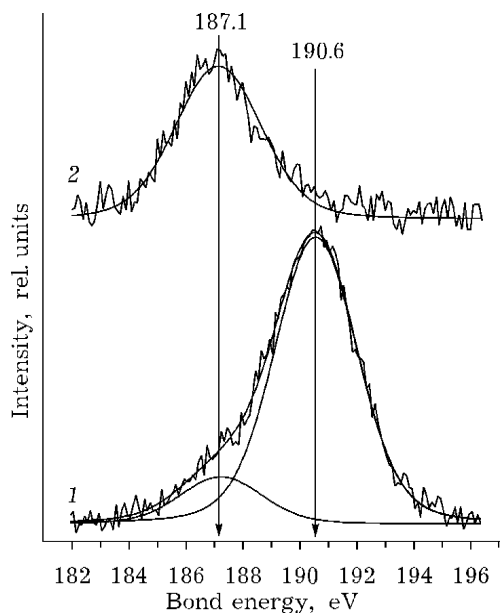


Fig. 2. P2s spectra of the surface of solder powder particles of sample 2 recorded before (1) and after ion etching for 9 min (2).

to the catalytic conversion of hydrocarbons and CO, which are usually present in small amounts in the atmosphere [6, 7].

Figure 3 shows $\text{Cu}2p_{3/2}$ spectra of the investigated samples. According to the literature data [4, 8–11], for copper in the metal state and for Cu_2O oxide, the position of $\text{Cu}2p_{3/2}$ line is 932.4–932.7 eV. Copper in Cu^{2+} state is characterized by a larger bond strength (933.4–934.1 eV) [8–11]. Moreover, a characteristic shake-up satellite is observed in $\text{Cu}2p_{3/2}$ spectrum of copper (II) compounds around 942 eV; its relative intensity depicts the amount of copper in Cu^{2+} state. Thus, for the stoichiometric oxide CuO , the integral intensity of the shake-up satellite is ~50 % of the intensity of the main line of $\text{Cu}2p_{3/2}$ [8]. Therefore, the subsurface region of the OKS-600 sample contains copper mainly in the oxidized Cu^{2+} state (see Fig. 3, a). In this case, the position of $\text{Sn}3d_{5/2}$ line is ~486 eV, which corresponds to tin in the metal state (see Fig. 3, b). Quite contrary, for sample 2, the position of $\text{Sn}3d_{5/2}$ line is ~487 eV (tin in the oxidized state). It may be assumed that in the case of tin segregation a layer of tin oxide is formed on the surface; it prevents copper oxidation. Indeed, a narrower $\text{Cu}2p_{3/2}$ peak and low intensity of the shake-up satellite in the spectrum of sample 2 provide evi-

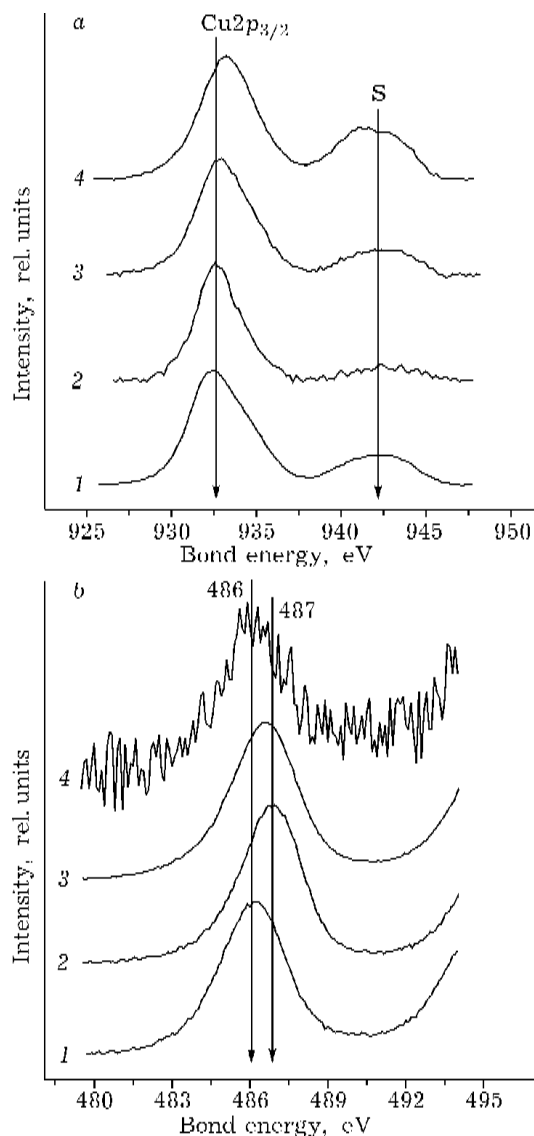


Fig. 3. $\text{Cu}2p_{3/2}$ (a) and $\text{Sn}3d_{5/2}$ (b) spectra of the initial surface of particles in the powder solder, samples 1 (1), 2 (2), 3 (3), OKS-600 (4). S is the line of the shake-up satellite.

dence of the predominance of metal copper in the subsurface region. In the spectra of samples 1 and 3, $\text{Cu}2p_{3/2}$ line is wider and has an asymmetric shape, which is an evidence of the presence of copper both as a metal and in the oxidized state in the subsurface region (see Fig. 3). Phosphorus is also oxidized on the surface forming metal phosphates. After ion etching within several minutes, the spectra of $\text{Cu}2p$, $\text{Ni}2p$ and $\text{Sn}3d$ correspond to the metal state.

So, the data obtained provide evidence that an oxide layer 1–2 nm thick is formed on the surface of powder solder particles, which pre-

TABLE 2

Estimations comparing the oxidized state of different fractions of sample 3

Fraction size, μm	Calculation			XPES	
	Content of the class, mass %	Layer mass, mg	Fraction mass, mg	[O]/[Cu]* in fraction, %	Distribution of oxygen over fractions, %
4	6.0	3.E-04	6.E-02	1.E-02/1.E-04	41.2
7	1.0	3.E-05	1.E-02	8.E-03/8.E-05	23.5
12	7.0	1.E-04	7.E-02	5.E-03/5.E-05	13.7
20	39.0	4.E-04	4.E-01	3.E-03/3.E-05	8.2
30	30.0	2.E-04	3.E-01	2.E-03/2.E-05	5.5
40	16.0	7.E-05	2.E-01	1.E-03/1.E-05	4.1
45	1.0	4.E-06	1.E-02	1.E-03/1.E-05	3.7

*The first value shows XPES data before ion etching, the second one – after etching.

vents further oxidation of the metal [12]. An exception is sample 1 which was prepared by grinding in a ball mill. In this case, oxidation occurs at a larger depth. After ion etching for 12 min, that is, after removal of the upper layer about 12 nm thick, the atomic ratio [O]/[Cu] is ~ 0.6 . It is most probable that grinding in a ball mill destroys the structure of particles. Oxygen diffusion along grain boundaries causes oxidation at a large depth.

Assuming the spherical shape of particles and the presence of only a thin oxidized layer on the surface, we carried out quantitative estimations of oxygen content for different fractions of solder particles and compared the results with the data obtained in layer-by-layer analysis. The results of calculations of the relative oxygen content depending on particle size for sample 3 are shown in Table 2. One can see that the major part of oxygen ($\sim 65\%$) is present on the surface of the fine fraction ($5\text{--}7\ \mu\text{m}$) of powder that accounts for 6% of total volume. This is connected with the fact that the smaller-sized particles possess larger specific surface. Therefore, in order to obtain a high-grade powder for soldering pastes, one should separate and remove this fraction.

Powder calibration by isolating the fraction with particle size less than $10\ \mu\text{m}$ allowed us to decrease the content of oxidized forms in solder powder substantially. The technology of production of such a calibrated powder provided the possibility to organize the production of soldering paste MON-15-4 at the Novosibirsk

Tin Plant. The paste is intended for soldering copper and brass parts. The pastes made of calibrated powder possess stable spreadability without the formation of a black thin coating and provide tightness and strength of the soldered parts.

CONCLUSION

The investigation showed that the chemical composition of the subsurface layers of powdered solder depends on the preparation procedure and has a strong effect on the quality of soldering. It was revealed that the degree of surface oxidation of powder solder particles decreases substantially for spraying in nitrogen in comparison with spraying in the air. The major part ($\sim 65\%$) of oxygen is present in the fine fraction ($5\text{--}7\ \mu\text{m}$) of the powder. Separation of this fraction improves substantially the quality of the powder solder.

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