Electrophysical properties of the Cu–Pb subsystem of Bi–Cu–Ga–In–Sn–Pb high-entropy alloys

V. Poverzhuk, Yu. Plevachuk, L. Romaka

Ivan Franko National University of Lviv,
Kyrylo and Mefodiy Str., 8, 79005 Lviv, Ukraine
e-mail: yuriy.plevachuk@lnu.edu.ua

The main problems of research on multicimponent high-entropy alloys (HEA) are related to the high melting temperatures of their constituent elements. Therefore, it is useful to study similar multicomponent alloys conisisting of elements with lower melting points, as well as their subsystems with a smaller number of components. According to the concept of multicomponent HEA, high entropy of mixing can stabilize the formation of solid solutions (simple bcc or fcc crystal structure) during solidification. Stabilization of the solid solution and prevention of the intermetallic phases during solidification is provided by the high entropy of mixing in the solid and liquid states. HEA have increased strength, high hardness, thermal stability in combination with good resistance to oxidation and corrosion. These properties allow to significantly expand the scope of these alloys, which have recently begun to be intensively researched as reflow temperature solders. In this work, the electrical resistivity and thermo-electric power of the binary Cu–Pb alloys, which is a subsystem component of the low-temperature HEA Bi–Cu–Ga–In–Pb–Sn, have been studied in a wide temperature range including solid and liquid states.

Key words: Cu-Pb, high-entropy alloys, electrical resistivity, thermoelectric power, microstructure.

1.   Introduction

The development of the industry requires new structural materials with improved physico-chemical properties and operational characteristics. Industrial alloys with several basic elements are usually thermodynamically unstable, and phase transformations with increasing temperature leads to a deterioration of their performance. Formation of intermetallic compounds causes their brittleness. A new class of materials, known as high-entropy alloys (HEA) with high entropy of mixing, which is achieved by a significant number of components, are gradually replacing the conventional alloys [1]. HEA consist of solid solutions (simple bcc or fcc structure) and have good performance properties

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158   ISSN 1024-588X. Вісник Львівського університету. Серія фізична. 2023. Вип. 60

like high hardness, wear resistance, oxidation resistance, good corrosion and radiation resistance, which allow to significantly expand their scope.

The peculiarity of such alloys is the dominant formation of disordered solid solutions, stable due to high entropy of mixing. HEAs form a single-phase stable solid substitution solution. Stabilization of the solid solution and prevention of the formation of intermetallic phases during solidification is provided by the high entropy of mixing in the solid and liquid states. The majority studies of physicochemical and mechanical characteristics of high-entropy alloys were performed with samples in the solid state. At the same time, data on the structure in the liquid state and its transformation during cooling, as well as the mechanisms and sequences of structural-phase transformations during crystallization are practically absent, although it is in the liquid state that the processes of formation of atomic solutions take place, and, therefore, precisely in this initial case of structure nucleation is the easiest to influence and change its formation in the desired direction.

The main difficulties of conducting experiments in extreme thermodynamic conditions of the liquid state are primarily related to the high melting temperatures of the constituent elements. Therefore, it is common to study similar multicomponent alloys, the elements of which have lower melting points. Information about the properties of such low-temperature systems, as well as their subsystems with a smaller number of components, which can be considered as model systems, is necessary both for the further study of the characteristics of high-temperature alloys and for their industrial production. In addition, the low-temperature HEA have recently begun to be intensively researched as reflow temperature solders with low melting points [2,3].

In this work, the electrical resistivity and thermoelectric power of the Cu–Pb binary alloys of the equiatomic composition and of some chemical compositions deviating from the equiatomic one, were studied experimentally. Cu–Pb is a subsystem of the multicomponent high-entropy Bi–Cu–Ga–In–Pb–Sn alloys, and behavior of its structure-sensitive properties is important because among all physical properties, the thermophysical characteristics of the liquid phase play a prominent role. Measurements of the electrical resistivity and thermoelectric power, as well as of their temperature coefficients provide an easy and inexpensive tool for studying phase transitions with changes of temperature in the alloys and gives reliable information about the structural heterogeneity of the melt.

2.   Experimental details

Synthesis of the polycrystalline samples with stoichiometric compositions $Cu_{60}Pb_{40}$, $Cu_{50}Pb_{50}$, $Cu_{40}Pb_{60}$ was carried out by direct arc melting of the constituent metals (content of the basic component not lower than 99,9 wt.%) in protected argon atmosphere with non-consumable tungsten electrode on a water-cooled copper hearth. To remove some traces of impurity first Ti ingot was melted as a getter. For better homogenization the alloys were re-melted twice. The energy dispersive X-ray spectroscopy (EDS) method (the Tescan Vega-3 LMU SEM, equipped with an X-ray analyzer with energy dispersive spectroscopy) was used to control the chemical composition of the samples and determine the exact content of components in the phases.

Temperature dependence of the electrical resistivity $\rho(\mathrm{T})$ and thermoelectric power $S(T)$ was carried out using two experimental facilities. One of them is adapted for the measurements in the solid state while the second one is adjusted for the liquid samples.

Temperature dependence of the electrical resistivity in the solid state was carried out by the 2-point method in the temperature range from 80 K to 400 K. The samples were prepared in the form of rectangular parallelepipeds with dimensions of $1.0 \times 1.0 \times 5$ mm^3. The thermoelectric power was measured using the potentiometric method relative to copper. Measurements of the voltage drop on the samples were carried out in different directions of the electric current to reduce the influence of "parasitic" effects at the contact points.

The 4-point contact method was used for the measurements in the liquid state in the temperature range between the melting points and 1450 K. An original experimental technique allows simultaneous determination of electrical resistivity and thermoelectric power in a wide temperature range. Cylindrical boron nitride crucibles were used for the molten samples. To keep a constant chemical composition of the melt, the measurements were carried out in neutral atmosphere of argon. To avoid a direct contact between melt and thermocouples, the intermediate graphite electrodes for potential and current measurements were inserted into a wall of the crucible. Each electrode was connected with a WRe-5/20 thermocouple for temperature measurements, while one of two dissimilar conductors of the thermocouple was used for the measurement of $S(T)$. The the electrical resistivity was determined with an uncertainty of about 2% and thermoelectric power with an uncertainty of about $\pm$ 5%. The facility and experimental details were reported in [4].

3. Results and Discussion

The chemical compositions of the alloys were both equiatomic and deviated from the equiatomic concentrations by 10 at.% in the direction of their constituent components. Liquid alloys of noble metals with polyvalent elements are known to show non-linear concentration dependences of their physical properties. For example, they exhibit a considerable exothermic heat of mixing, increase of density, and maximum in diamagnetic susceptibility or electrical resistivity at specific concentrations. It is clear that the peculiar non-monotonous variations of the physical properties with composition of liquid alloys are basically caused by changes in their electronic and/or atomic structure, like those of solids. It seems to be becoming evident that many structural features and physical properties of liquid metals and alloys can be reasonably explained only under the assumption of microheterogeneous structure (see [5] and references therein).

According to the phase diagram Cu–Pb system is of the monotectic type and does not contain binary compounds [6]. The X-ray spectral analysis of the samples in the as-cast state showed that all the investigated alloys mainly contain a mixture of Cu and Pb, which is consistent with the Cu-Pb phase diagram. The equiatomic alloy $Cu_{50}Pb_{50}$ contains a (Cu,Pb) mixture as the main matrix and a minor content of Pb and Cu (Fig. 1 a). The $Cu_{60}Pb_{40}$ alloy contains a significant amount of Cu, a small amount of Pb and a mixture (Cu,Pb) (Fig. 1 b). The $Cu_{40}Pb_{60}$ alloy in addition to the mixture (Cu, Pb), contains Pb and a small amount of Cu (Fig. 1 c).

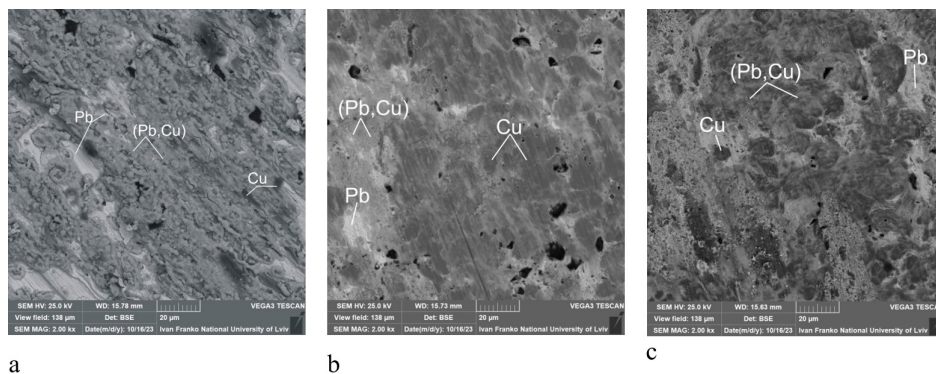*V. Poverzhuk, Yu. Plevachuk, L. Romaka*

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Fig. 1: SEM micrographs of the $Cu_{50}Pb_{50}$ (a), $Cu_{60}Pb_{40}$ (b) and $Cu_{40}Pb_{60}$ (c) alloys.

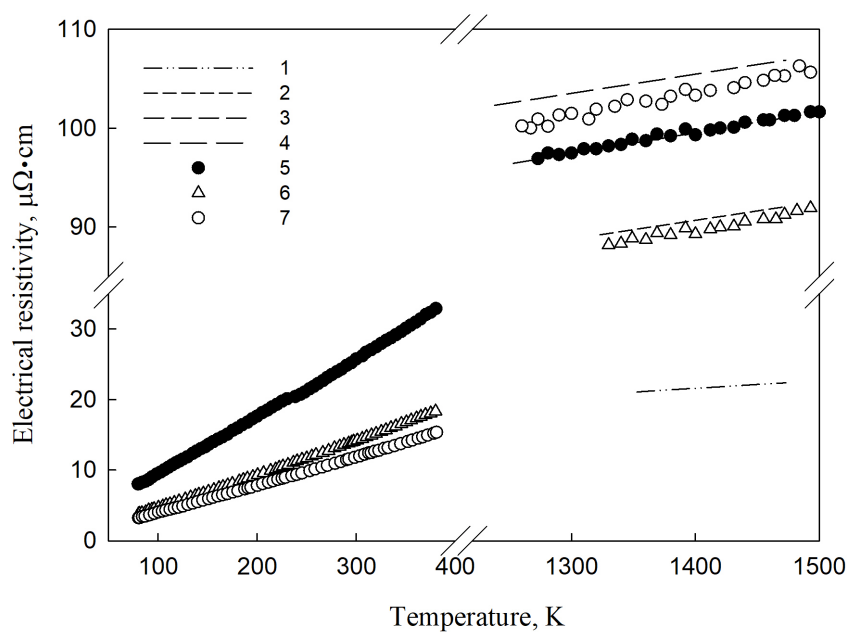Temperature dependence of electrical resistivity is presented in Fig. 2.

Fig. 2: Electrical resistivity vs. temperature of Cu–Pb alloys: 1 – Cu [7]; 2 – $Cu_{60}Pb_{40}$ [7]; 3 – $Cu_{50}Pb_{50}$ [7]; 4 – $Cu_{40}Pb_{60}$ [7]; 5 – $Cu_{50}Pb_{50}$; 6 – $Cu_{60}Pb_{40}$; 7 – $Cu_{40}Pb_{60}$.

As seen from Fig. 1, the alloys of all compositions are characterized by a linear increase in electrical resistivity $\rho(T)$ when heated in the region of low temperature of the solid state between 80 K and 400 K, which indicates a metallic type of conductivity. The resistivity of $Cu_{50}Pb_{50}$ alloy increases faster and the temperature coefficient of resistivity

of this alloy composition is significantly higher.

An increase in the electrical resistivity with temperature for all investigated alloys can be approximated by the following polynomial:

$$\rho = A + BT, \tag{1}$$

where A and B are the fitting coefficients presented in Table 1.

Table 1: Fitting numerical parameters of Eq (1) for Cu-Pb alloys between 80 K and 400 K.

Alloy composition, at.%	A [$\mu\Omega$·cm]	B [$\mu\Omega$·cm·K^{-1}]
$Cu_{40}Pb_{60}$	–0,08	0,0399
$Cu_{50}Pb_{50}$	1,24	0,0818
$Cu_{60}Pb_{40}$	–0,28	0,0483

The electrical resistivity of the molten Cu–Pb alloys were studied in the range between the melting temperatures and 1500 K. The difference between the absolute values of specific electrical resistance of alloys of different compositions remains almost constant in the entire investigated temperature range. It should be noted that this difference increases as the copper content increases. The obtained data are in agreement with results reported in [7] where the nonlinear dependence of resistance on concentration was proved experimentally and theoretically.

The electrical resistivity for all the alloys in the liquid state increases gradually with heating. As seen from Fig. 1, the increase in the electrical resistivity with temperature for all investigated alloys can be approximated by the linear equation:

$$\rho = \rho_0 + \frac{d\rho}{dT}(T - T_{\mathrm{m}}), \tag{2}$$

where ρ_0 is the resistivity at the melting temperature T_m, $\frac{d\rho}{dT}$ is the temperature coefficient of resistivity; ρ_0 and $\frac{d\rho}{dT}$ values are collected in Table 2.

Table 2: Fitting numerical parameters of Eq. (2) for Cu–Pb liquid alloys.

Alloy composition, at.%	ρ_0 [$\mu\Omega$·cm]	$\frac{d\rho}{dT}$ [$\mu\Omega$·cm·K^{-1}]
$Cu_{40}Pb_{60}$	99,78	0,0244
$Cu_{50}Pb_{50}$	96,64	0,0205
$Cu_{60}Pb_{40}$	86,78	0,0213

In contrast to the resistivity behavior in the solid state, dependence of the resistivity on concentration of the investigated melts differs, namely, the lowest resistivity values were observed in the $Cu_{60}Pb_{40}$ melt.

Temperature dependence of thermoelectric power $S(T)$ of Cu–Pb alloys in the temperature range of 80–400 K is complicated (Fig. 3). All the compositions are characterized by small negative S values. Starting from the initial value of -2μV·K^{-1} at 80 K for all compositions, a decrease in absolute values of thermoelectric power with

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a further increase at 150 K for the $Cu_{40}Pb_{60}$ alloy, at 160 K for the $Cu_{60}Pb_{40}$ alloy and at 200 K for the equiatomic $Cu_{50}Pb_{50}$ composition, has been observed with an increase in temperature.
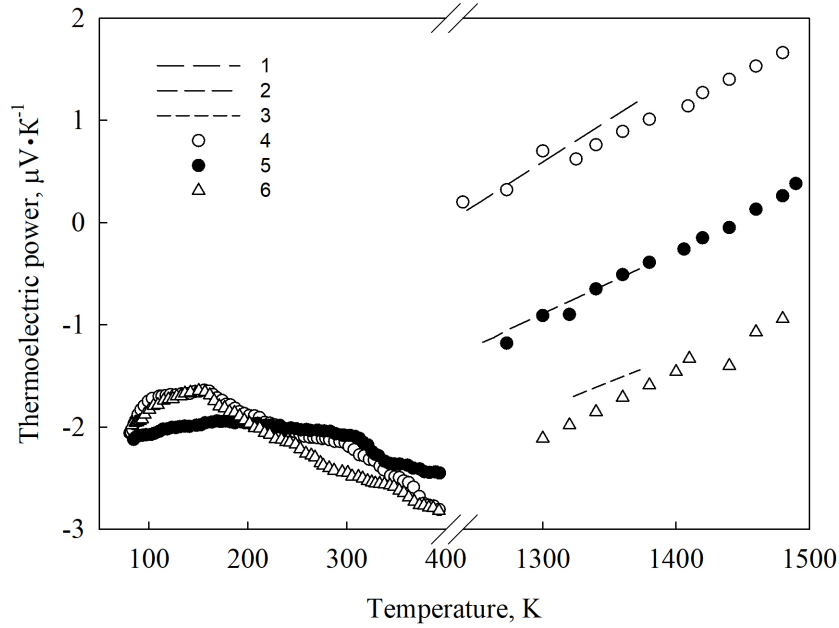

Fig. 3: Thermoelectric power vs. temperature of Cu–Pb alloys: 1 – $Cu_{60}Pb_{40}$ [8]; 2 – $Cu_{50}Pb_{50}$ [8]; 3 – $Cu_{40}Pb_{60}$ [8]; 4 – $Cu_{60}Pb_{40}$; 5 – $Cu_{50}Pb_{50}$; 6 – $Cu_{40}Pb_{60}$.

The thermoelectric power in the temperature range between the melting points and 1500 K of the liquid state is positive for $Cu_{60}Pb_{40}$. With an increase in temperature, a change in the $S(T)$ sign from the negative to the positive one is observed for $Cu_{50}Pb_{50}$, while thermoelectric power of $Cu_{40}Pb_{60}$ remains negative.

The $S(T)$ dependence is nearly linear for all compositions with positive slopes of the curves.

The experimental $S(T)$ data are presented in Fig. 3 together with results reported in [8] for comparison. The increase in the thermoelectric power with temperature for all investigated alloys can be described by the equation

$$S = S_0 + \frac{dS}{dT}(T - T_{\mathrm{m}}), \tag{3}$$

where S_0 is the resistivity at the melting temperature T_m, $\frac{dS}{dT}$ is the temperature coefficient of thermoelectric power; S_0 and $\frac{dS}{dT}$ values are collected in Table 3.

Table 3: Fitting numerical parameters of Eq (1) for Cu-Pb alloys between 80 K and 400 K.

Alloy composition, at.%	S_0 [μV·K^{-1}]	$\frac{dS}{dT}$ [μV·K^{-2}]
$Cu_{40}Pb_{60}$	−2,23	0,0045
$Cu_{50}Pb_{50}$	−1,29	0,0069
$Cu_{60}Pb_{40}$	0,40	0,0051

4.   Conclusions

Studies of the binary Cu–Pb system, which is one of subsystems of the low-temperature multicomponent high-entropy Bi–Cu–Ga–In–Sn–Pb alloys, revealed that even slight deviations of the chemical composition from the equiatomic one lead to noticeable changes in the electrophysical properties like electrical resistivity and thermoelectric power, which are manifested in different temperature ranges both at low temperatures and in the melts. All these features are important and should be considered when manufacturing high-entropy multicomponent alloys with predictable properties. In this context, the data on these characteristics also in the range between the room and melting temperatures are needed, and such studies will be carried out soon using the appropriate experimental equipment.

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Електрофізичні властивості підсистеми Cu–Pb високоентропійного сплаву Bi–Cu–Ga–In–Sn–Pb

В. Повержук, Ю. Плевачук, Л. Ромака

Львівський національний університет імені Івана Франка,
вул. Кирила і Мефодія, 8, 79005 Львів, Україна
e-mail: yuriy.plevachuk@lnu.edu.ua

Основні проблеми у дослідженнях багатокомпонентних високоентропійних сплавів пов'язані з високими температурами плавлення елементів, що входять до їхнього складу. Тому нерідко вивчають подібні багатокомпонентні сплави, що складаються з елементів з нижчими температурами плавлення, а також їхні підсистеми з меншою кількістю компонентів. Відповідно до концепції багатокомпонентного високоентропійного сплаву, висока ентропія змішування може стабілізувати утворення твердих розчинів під час кристалізації (проста ОЦК або ГЦК кристалічна структура). Стабілізація твердого розчину і запобігання утворенню інтерметалічних фаз під час процесу кристалізації забезпечується високою ентропією змішування в твердому і рідкому станах. Такі сплави мають підвищену міцність, високу твердість, термічну стабільність у поєднанні зі стійкістю до окислення та корозії. Ці властивості дозволяють значно розширити сферу їхнього застосування; зокрема, останнім часом такі сплави почали інтенсивно досліджувати як матеріали для низькотемпературних припоїв. Більшість досліджень фізико-хімічних і механічних характеристик високоентропійних сплавів виконано на зразках у твердому стані. Водночас дані про структуру в рідкому стані та її трансформацію під час охолодження, а також про механізми та послідовності структурно-фазових перетворень під час кристалізації практично відсутні, хоча саме в рідкому стані відбуваються процеси утворення атомарних розчинів, і, отже, саме в цьому початковому випадку зародження структури найлегше вплинути і змінити її формування в потрібному напрямі. У пропонованій праці досліджено мікроструктуру, питомий електричний опір і термоЕРС бінарних сплавів системи Cu–Pb, які є складовою підсистеми низькотемпературного високоентропійного сплаву Bi–Cu–Ga–In–Pb–Sn, у широкому діапазоні температур твердого та рідкого станів.

Ключові слова: Cu-Pb, високоентропійні сплави, питомий електричний опір, термоЕРС, мікроструктура.