UDC 546.56.86.22.15

NATURE OF EUTECTIC CRYSTALLIZATION IN THE $Fe_{0,67}Sb_{0,33}$ – Pb SYSTEM AND THE POSSIBILITIES OF APPLICATION OF THE DETECTED HOMOGENEOUS PHASES IN SOLID-STATE ELECTRONICS

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Received 06.10.2023
Accepted 29.12.2023

Abstract: *From the phase diagram it is clear that the $Fe_{0,67}Sb_{0,33}$ – Pb system is quasi-binary and has a eutectic type of phase formation. The solid solution region with a boundary of ~4 mol% Pb at 300K was discovered in the system. Based on the temperature dependence of the contact resistance of the eutectic $Fe_{0,67}Sb_{0,33}$ and the solid solution alloy $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$, it was established that the contact resistance of these materials varies within $8\cdot10^{-4} \div 5\cdot10^{-4}$ om·sm^2, which makes them promising for use as switching layers in thermoelectric converters. It has been determined that the solid solution with the specified composition is also suitable for the manufacture of low-resistance thermistors.*

Keywords: *eutectic crystallization, solid solution, switching material, thermistor.*
DOI: 10.32737/2221-8688-2024-1-68-75

Introduction

As is known, iron and its intermetallic compounds, obtained by its interaction with various materials, are widely used as magnets and mind tools. Besides, in solid-state electronics, antimony–chalcogen iron complexes are applied as semiconductors with various functional properties [1-6]. The field of application of pure lead, which is another component of the system, is wide (X-ray protection, battery plates, ammunition production, etc.), its alloys with antimony are a material used in the manufacture of publishing elements and industrial pumps. Lead chalcogenides and alloys with complex composition obtained on their basis are promising for energy converters in terms of photo and thermoelectric properties [7-10]. In [11], the phase diagram of the Fe-Sb binary system was analyzed and it was noted that the system produced a continuous compound containing FeSb and another peritectic compound with the formula $FeSb_2$. The composition $Fe_{0,67}Sb_{0,33}$ corresponds to eutectic and melts at 996°C [12].

It should be noted that studies of some cross sections in the ternary system Fe – Sb – Pb were carried out in [13-15]; however, the results of these studies did not provide enough information to fully elucidate the physicochemical interaction occurring in the system. For example, in the [13] it has been shown that a large area of the triangle covers the foliation formed by the primary components. But no exact border of this territory has been defined. In addition, there are other misunderstandings in the triangle. Therefore, taking into account the need to study additional sections in the Fe – Sb – Pb triangle, we explored the $Fe_{0,67}Sb_{0,33}$ – Pb section and carried out a number of studies to expand the areas of application of the obtained alloys. The $Fe_{0,67}Sb_{0,33}$ – Pb system has not been studied so far.

Experimental section

$Fe_{0,67}Sb_{0,33}$ eutectic, which is the initial component of $Fe_{0,67}Sb_{0,33}$ – Pb system, was synthesized from high-purity Fe and Sb elements. The components $Fe_{0,67}Sb_{0,33}$ and Pb were synthesized by alloying at a pressure of 0,133Pa using the ampoule method. Alloys of the $Fe_{0,67}Sb_{0,33}$ – Pb system were subjected to heat treatment at a temperature of 250^0C for 240 hours to homogenize them. Equilibrium alloys were studied by methods of physicochemical analysis: differential thermal analysis (DTA), X-ray diffraction (XRD), microstructural analysis (MSA), as well as by measuring density and micro-hardness.

Differential thermal analysis was carried out by means of a Pt/Pt-Rh thermocouple on a low-frequency temperature recorder TERMOSCAN-5. Also, X-ray phase analysis of the alloys was carried out on a D2 PHASER diffractometer. CuK_{α} and a Ni filter were used as irradiators. Also, microstructure analysis was carried out using a MIM-8 brand microscope. Solutions of NHO_3 + H_2O = 2:1 were used as dyes to identify phase boundaries in the samples. Pb - rich alloys were etched with NaOH alkali. Microhardness was measured using a PMT-3 metallographic microscope. Density was determined by the pycnometric method, where toluene was used as a filling solution. The methods used mainly in physicochemical analysis [16]. Alloys of the $Fe_{0,67}Sb_{0,33}$ – Pb system were gray alloys obtained in compact form. It was established that alloys containing 0-60 mol% were resistant to air and organic solvents. Alloys with a 60-100 mol% Pb content were gradually covered with an oxide film. Samples rich in $Fe_{0,67}Sb_{0,33}$ are highly soluble in solid nitric acid. Pb - rich alloys gradually dissolve in alkalis NaOH and KOH. During the thermal analysis of alloys, it was found that two endothermic effects are formed in thermograms. The presence of two thermal effects in thermograms indicates the two-phase nature of alloys (with the exception of α solid solution compositions).

The value of the contact resistance of the solid solution alloy $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ of the eutectic composition $Fe_{0,67}Sb_{0,33}$ was measured within the temperature range 100÷450 K according to the method given in [17].

Results and discussion

The microstructure analysis of $Fe_{0,67}Sb_{0,33}$ – Pb system alloys shows that they are two-phase. Around $Fe_{0,67}Sb_{0,33}$ there is only a single-phase field.

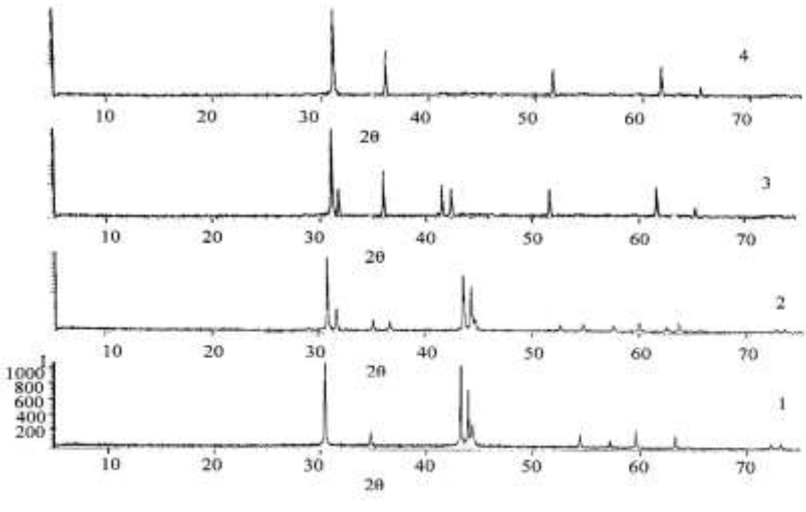

Fig. 1. X-ray diffractograms of alloys of the $Fe_{0,67}Sb_{0,33}$ – Pb system (1 – $Fe_{0,67}Sb_{0,33}$; 2 – 20; 3 – 60; 4 – 100 mol% Pb)

Thus, X-ray phase analysis fully confirms the accuracy of DTA and MSA analyses. Based on the results of physicochemical analysis, the phase diagram of the $Fe_{0,67}Sb_{0,33}$ – Pb system was constructed (Fig. 2). The system is quasi-binary and has a eutectic phase diagram. In the system at room temperature, a 4 mol% solid solution region is formed based on $Fe_{0,67}Sb_{0,33}$, while a solid solution region is not detected based on Pb.

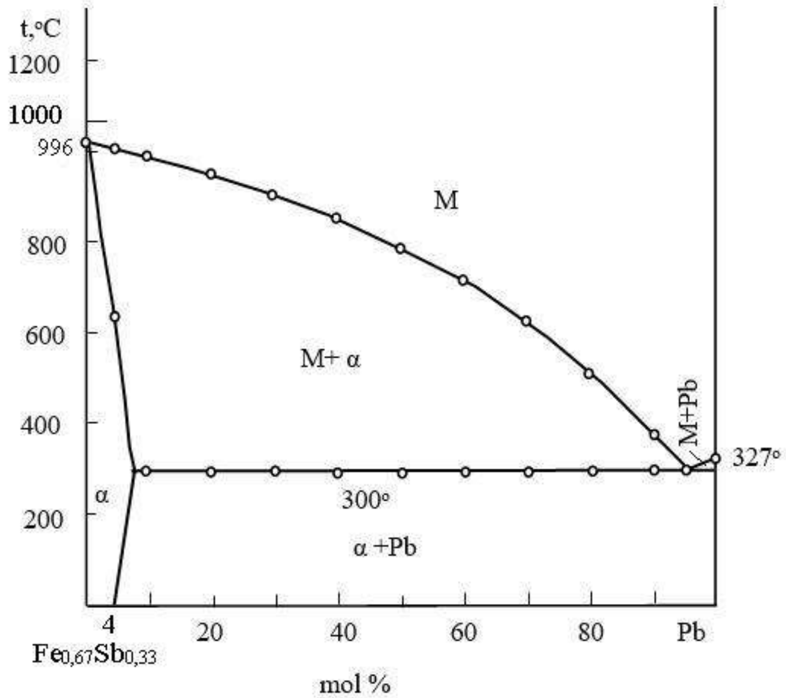

Fig. 2. Phase diagram of the $Fe_{0,67}Sb_{0,33}$ – Pb system

The liquidus of the $Fe_{0,67}Sb_{0,33}$ – Pb system consists of liquidus alloys of the solid solution - α and the element Pb, formed on the basis of the $Fe_{0,67}Sb_{0,33}$ eutectic. Crystallization of the solid solution - α from the liquid occurs in the concentration range of 0-95 mol% Pb. The joint crystallization of the solid solution - α and Pb ends with the formation of a double eutectic, which also has a content of 95 mol% Pb and a temperature of 300^{0}C. In the eutectic crystallization system, the formation of crystalline centers of the $Fe_{0,67}Sb_{0,33}$ phase in a liquid alloy with a composition corresponding to the eutectic point is more likely than in the Pb-rich phase. During the crystallization of eutectic alloys, pseudo-primary crystals of the $Fe_{0,67}Sb_{0,33}$ phase are first separated under conditions of light super-cooling (~3-5^{0}C). After a short period of time, crystals of the second phase are formed. As shown in [18], the fact that the eutectic phases have an even number of intergrowths is not considered to be a stable characteristic of the system, since its state can be changed by introducing appropriate additives into the system. The composition of the studied alloys and the values of other measured parameters are given in Table 1. In the compositions of solid solutions, an increase in microhardness is observed, which indicates that the detected solid solutions belong to the substituting type.

It is known that eutectic alloys belong to the class of composite materials. They have potentially superior properties due to many features and are widely used for ohmic contacts in electronic devices [19]. For this reason, intensive scientific and applied work is currently being carried out to obtain eutectic alloys of a new composition and study their properties.

In particular, the use of eutectic compounds as inter-element switching materials in thermoelectric energy converters creates effective conditions for obtaining high-quality results [20].

Table 1. Results of measurements of compositions, thermal effects, densities and microhardness of alloys of the $Fe_{0,67}Sb_{0,33}$ – Pb system

Composition, mol%		Thermal effects, ^{0}C	Pycnoetic density, g/m^3	Microhardness of phases, MPa	
$Fe_{0,67}Sb_{0,33}$	Pb			Phases rich in $Fe_{0,67}Sb_{0,33}$	Phases rich in Pb
				P=0,15 N	P=0,01 N
100	0.0	996	7.42	3400	–
95	5.0	640,993	7.69	3500	–
90	10	300,990	7.81	3300	–
80	20	300,960	8.21	3300	–
70	30	300,910	8.59	3300	–
60	40	300,860	8.99	3300	–
50	50	300,790	9.38	3300	–
40	60	300,720	9.77	3300	350
30	70	300,630	10.16	3300	350
20	80	300,515	10.55	–	350
10	90	300,380	10.94	–	350
5,0	95	300	11.14	–	350
0,0	100	327	11.34	–	350

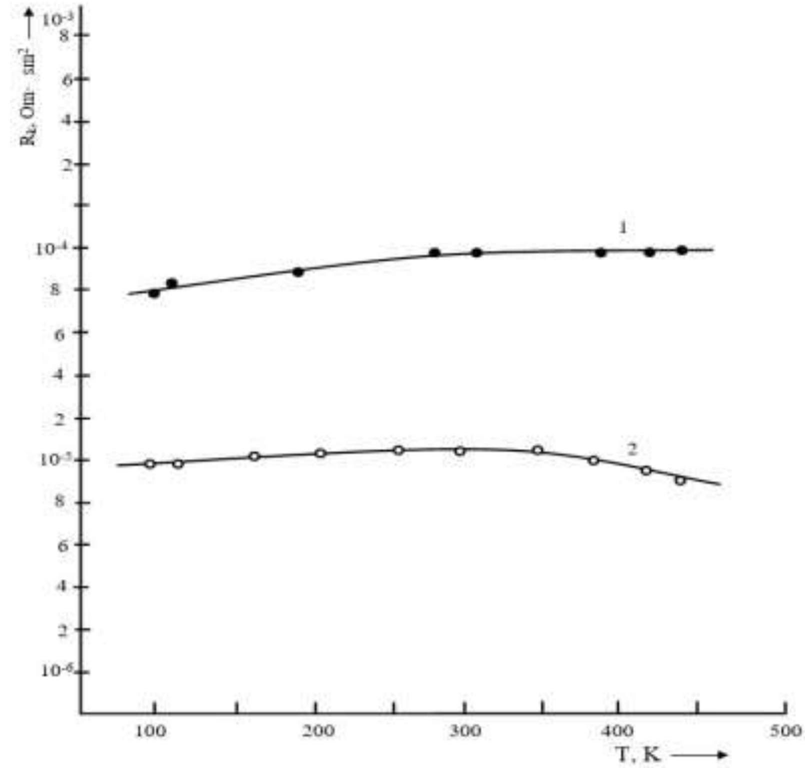

Fig. 3. Temperature dependences of the contact resistance of the eutectic composition $Fe_{0,67}Sb_{0,33}$ (1) and the solid solution alloy $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ (2).

Taking these into account, the temperature dependences of some electrophysical parameters of the eutectic alloy containing crystals of $Fe_{0,67}Sb_{0,33}$ and solid solutions $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ were studied, and based on the results obtained, the extent of their application in device manufacturing was clarified. The temperature dependences of the contact resistance values of the $Fe_{0,67}Sb_{0,33}$ eutectic and the solid solution$(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ in thin squareshaped samples shown in the experimental part are shown in Fig.3.

In both samples, the amount of R_K shows a linear increase up to room temperature. A linear increase in resistance with increasing temperature in contact materials is considered normal [21]. The dependence curves decrease after passing the maximum, that is, the resistance decreases in absolute value. In considering that eutectic compositions with metallic properties have found a wide range of applications as a switching layer in thermal generators with alternative energy sources, then there is no doubt that the synthesized eutectic $Fe_{0,67}Sb_{0,33}$ and solid solution $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ are promising for thermo-elements. On the other hand, the efficient operation of thermoelectric energy converters and the presence of stable parameters depend on the efficiency of the material used in the generator and the transition resistance between the contact material and the semiconductor crystal.

This dependence is characterized by the formula $Z = \alpha^2 / æ\left(\rho + \frac{R_K}{\ell}\right)$. Here, Z - is the thermoelectric efficiency of the semiconductor material of the thermocouple, α - is the coefficient of thermoelectric motive force (thermo EMF) in the thermocouple material, æ - is the thermal conductivity of the material, ρ - is the specific resistance of the thermocouple material, and ℓ - is the length of the thermocouple arm, that is, its height. The quantities in parentheses in the denominator of the formula only characterize the switching material, and their role in the thermoelectric efficiency is great.

To achieve the ohmic nature of the contact, in the metal-semiconductor contact (here the eutectic composition is like a metal, and any branch of the thermocouple is like a semiconductor) the output work of the metal must be smaller than the output work of the semiconductor material. Otherwise, as the difference in output work rises, the height of the barrier fence will also rise linearly, that is, a Schottky barrier will appear in the contact and the contact will perform the task of a Schottky diode. However, due to the influence of surface phenomena in the metal-semiconductor contact, this factor may be disrupted and become ineffective. For this reason, the choice of contact materials based on output characteristics provides no positive result when choosing ohmic contacts. Taking into account the above, it is necessary to develop technologies for producing semiconductor alloys with heavily doped regions that provide favorable volumetric metal-semiconductor contact. In other words, the contact like this should form a structure of the $n^+ – n$ or $p^+ – p$. For such a heavily alloyed region, a solid solution alloy containing $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ can be used, since it is known from the literature that solid solution alloys belong to the class of highly alloyed materials. For this reason, the $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ solid solution alloy is capable of creating good compatibility with the semiconductor arm of a thermocouple in addition to being a quality ohmic contact [19].

The synthesized eutectic composition $Fe_{0,67}Sb_{0,33}$ and the solid solution alloy $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ may have another area of application. As can be seen from Fig.3, the resistance decreases at temperatures above 300 K in both samples. This feature allows these materials to be used in the manufacture of thermistors. Thus, comparing the parameters of thermistors in the literature, it is known that the resistive indicators of the synthesized composition $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ are competitive with thin-film metal-ceramic thermistors and low-resistance wire thermistors with high dissipative capacity specified in [22].

Conclusion

- The nature of the physicochemical interaction of the eutectic alloy $Fe_{0,67}Sb_{0,33}$ with metallic lead was clarified and the state diagram of the $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ system was established for the first time. The mechanism of eutectic crystallization in the system was described;
- From the temperature dependence of the contact resistance of the solid solution alloy $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$, discovered on the basis of the $Fe_{0,67}Sb_{0,33}$ eutectic, it was established that this composition is not only a high-quality

switching material for thermocouples, but is also promising for production of low-ohm thermistors.

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$Fe_{0,67}Sb_{0,33}$ – Pb SİSTEMİNDƏ EVTEKTİK KRİSTALLAŞMANIN TƏBİƏTİ VƏ AŞKAR EDİLƏN HOMOGEN FAZALARIN BƏRK CİSİM ELEKTRONİKASINDA TƏTBİQ İMKANLARI

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Xülasə: Qurulan hal diaqramından məlum olmuşdur ki, $Fe_{0,67}Sb_{0,33}$ – Pb sistemi kvazibinar olub evtektik tipli fazaəmələgəlmə təibətinə malikdir. Sistemdə sərhəddi 300K-də ~4 mol%Pb olan bərk məhlul sahəsi aşkar edilib. $Fe_{0,67}Sb_{0,33}$ evtektikısının və onun əsasında alınan $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ bərk məhlul ərintisinin kontakt müqavimətinin temperatur asılılığından müəyyən edilmişdir ki, bu materialların kontakt müqaviməti $8\cdot10^{-4}\div5\cdot10^{-4}$ Om·sm^2 qiymətləri araısnda dəyişir ki, bu da onları termoelektrik çeviricilərində kommutasiya təbəqəsi kimi istifadə edilməsi üçün perspektivli edir. Göstərilən tərkibli bərk məhlul tərkibinin aşağı omlu termorezistorların hazırlanması üçün də yararlı olduğu müəyyənləşdirilmişdir.

Açar sözlər: Evtektik kristallaşma, bərk məhlul, kommutasiya materialı, termorezistor

ПРИРОДА ЭВТЕКТИЧЕСКОЙ КРИСТАЛЛИЗАЦИИ В СИСТЕМЕ $Fe_{0,67}Sb_{0,33}$ – Pb И ВОЗМОЖНОСТИ ПРИМЕНЕНИЯ ОБНАРУЖЕННЫХ ОДНОРОДНЫХ ФАЗ В ТВЕРДОТЕЛЬНОЙ ЭЛЕКТРОНИКЕ

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Аннотация: Из построенной фазовой диаграммы системы $Fe_{0,67}Sb_{0,33}$ – Pb следует, что она является квазибинарной и имеет эвтектический тип фазообразования. В системе обнаружена область твердого раствора с границей ~4 мол% Pb при 300 K. На основе температурной зависимости контактного сопротивления эвтектики $Fe_{0,67}Sb_{0,33}$ и твердорастворного сплава $(Fe_{0,67}Sb_{0,33})_{0,99}Pb_{0,01}$ установлено, что контактное сопротивление этих материалов изменяется в пределах $8\cdot10^{-4}\div5\cdot10^{-4}$ ом·см^2, что делает их перспективными для использования в термоэлектрических преобразователях. Определено, что твердый раствор указанного состава пригоден также для изготовления низкоомных терморезисторов.

Ключевые слова: эвтектическая кристаллизация, твердый раствор, переключающий материал, термистор.