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# Composite Multicomponent of Gallium Pastes–Solders

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*Contact interaction of copper-zinc and copper-silver alloys is investigated with eutectics melts of the system Ga-Zn as composite components of gallium pastes – solders have been revealed. Interaction products have been determined depending on the structure and temperature of contacting components. Structures of developed new low temperature solders have been approved on the basis of gallium.*

*Keywords: gallium, pastes – solders, brass, copper-silver alloys, interaction, eutectic.*

## Introduction

The low temperature of fusion and high moistening ability of gallium gave the bases to use it as a base component for creation of pastes – solders (metal glues or cements).

In a basis the fluxless soldering of diverse materials lays interaction of powder and other disperse materials with gallium melt. Interaction products of gallium with metals (Cu, Ag, Ni, Mn and etc) have the temperature of fusion much more (up to 900 °C), than clean gallium so making the soldering at the temperature, for example 50 °C, it is possible to receive permanent joints which can work at temperatures more than 250 °C or even higher.

Fusible diffusion hardening gallium pastes – solders, possessing unique properties [1-4], have also essential lacks: high cost, duration of hardening processes, the small impact strength, limited time of safety of technological properties after preparation and a number of other restrictions of their application.

For increase of technological opportunities and operational characteristics of gallium pastes – solders the additional researches directed on the search of new structures and structures of initial solid and liquid phases of solders with the purpose of elimination of available lacks and creation of new competitive technologies of connection of diverse materials of the type metal – ceramics, metal – glass, metal – graphite, etc, are necessary.

In recent years scientific and practical interest to this subject has essentially increased [5-7], the convertible and irreversible processes occuring at heating and cooling of basic components of gallium

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pastes – solders and determining their physicomechanical properties are thoroughly studied. There are technological recesses for their effective application [8-11].

Doubtless practical interest as main initial hard components of these solders are powders of copper alloys with zinc in the field of solid solutions and eutectic Cu-Ag as presence of atoms of zinc and silver in corresponding structures accelerates the process of jet diffusion [1, 8, 9]. And as a liquid basis it is possible to use fusible eutectic alloys of gallium with zinc, tin, indium which have the temperature of fusion less than 25°C. Varying components and structures of solid and liquid phases, it is possible to find an optimal composite structure of solders with the minimal contents of gallium and silver, and as well modes of the soldering in each concrete case of diverse materials connection, beginning with room temperature.

The purpose of the present work is kinetics study , the mechanism and products of interaction of components of gallium pastes – solders, including with the maximal content of zinc and the minimal contents of gallium and silver.

## Materials and methods

For research of contact interactions were used standard single-phase brasses Л63 and Л68 with the content of zinc of 37 % and 32 % on weight accordingly (the rest is copper) in the form of plates, powders and chip materials, eutectic alloys of gallium (GOST 12797-77) with mark zinc ЧДА at the contents of zinc up to 20 % on weight and powders of solder ПСр 72 in accordance with GOST 19738-74.

Dispersivity of gallium pastes – solders fillers were changed from 100 nanometers up to 200 microns.

Junction quality, the form and the sizes of the formed phases have been investigated in optical microscope AXIO-Observer. Z1m, Carl Zeiss. For definition of element composion of phases EDX the spectrometer Oxford Instruments of scanning electronic microscope JEOL JSM 7001F of the shared Center by instrument base of the Siberian federal university has been used. Scanning of samples junction was carried out at an accelerating voltage 20 *кВ*, on a line with a step from 1 micron and less.

The phase structure of interaction products of alloys with gallium melts was determined on x-ray diffractometer D8 Advance. Experiment parameters are: Bragg-Brentano geometry, an initial corner of scanning 20°, final – 90°, the step of scanning 0,007°, the time of scanning 0,1 s/step. At this the data on the phase structure, received by us earlier [1], and as well known structures of double alloys [10] were taken into account.

## Results

In the first stage the research of interaction products of pure copper plates with liquid gallium through its interlayer with thickness no more than 0.3 mm at temperatures from 30°C to 200°C has been carried out. It has been found, that as a result of jet diffusion at the temperature of 150°C the intermetallic $CuGa_2$ is formed (Fig. 1), that corresponds to the data [2, 3, 5]. This intermediate phase contains the maximal content of gallium and has the minimal temperature of fusion 254°C.

In an interval of temperatures of 150-200°C it is formed not only intermetallic $CuGa_2$, but also thin layers of a firm solution of gallium in copper, and also intermetallic $Cu_9Ga_4$ (Fig. 2). The chemical composition of intermetallic $CuGa_2$ (the junction middle) corresponds to 64 % of gallium by mass, and

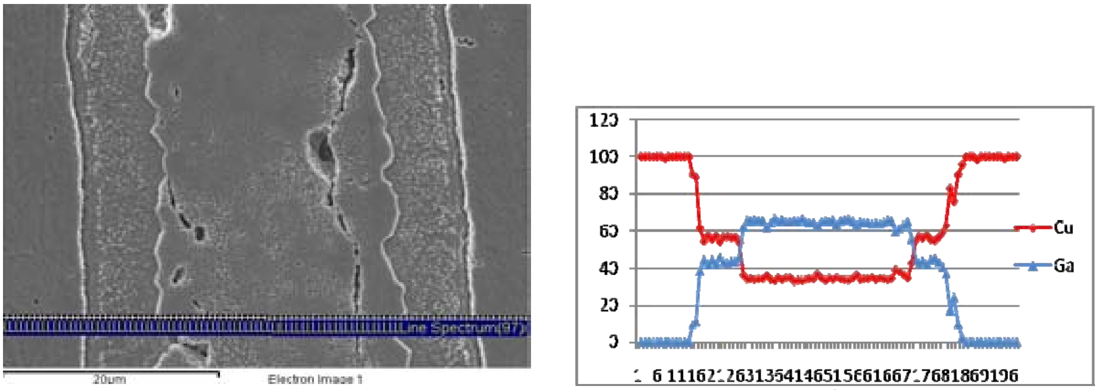


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Fig. 1. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on junction of copper plates with gallium after isothermal exposure at 150 °C for 120 hours.

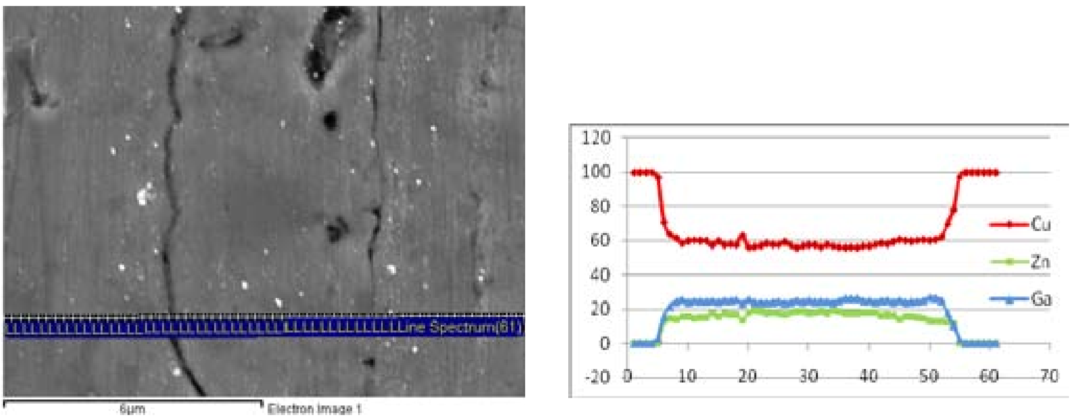


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Fig. 2. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on junction of copper plates with gallium after isothermal exposure at 200 °C for 120 hours.

intermetallic $Cu_9Ga_4$ (on junction edges) – 42 % of gallium by mass. Comparing the obtained data with a known diagram Cu-Ga [13], it is possible to be convinced, that in our case the formed intermetallic $Cu_9Ga_4$ is a phase **γ**, to be exact, a phase **$\gamma_3$** with the maximal gallium contents.

At copper plates contacting through a melt interlayer Ga-Zn (Zn – 5 % by mass) at the temperatures 150 °C is found out not only intermetallic $CuGa_2$, but also very thin layer intermetallic $Cu_9Ga_4$ (a phase **$\gamma_3$)** on junction edges (Fig. 3). The additive in to gallium melt of atoms of zinc starts to promote displacement of chemical reaction of gallium with copper in area of formation intermetallic with the big content of copper and the greater temperature of fusion of 468 °C.

Further, at copper plates contacting through a melt interlayer Ga-Zn (Zn – 10 % by mass) at the same temperatures a mixture of crystals of the phase $Cu_9Ga_4$ is formed and fine crystals of zinc, the intermetallic $CuGa_2$ has not been found (Fig. 4). In this case in comparison with previous one the

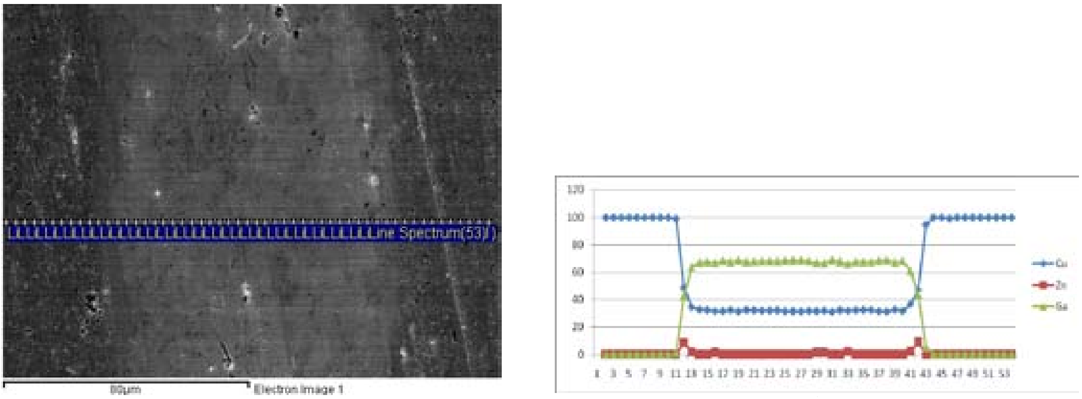


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Fig. 3. Microstructure, a line of scanning *(a)* and concentration curves *(b)* distribution of elements on junction of copper plates by the alloy Ga-Zn with the zinc content of 5 % after isothermal exposure at 150 °C for 120 hours.

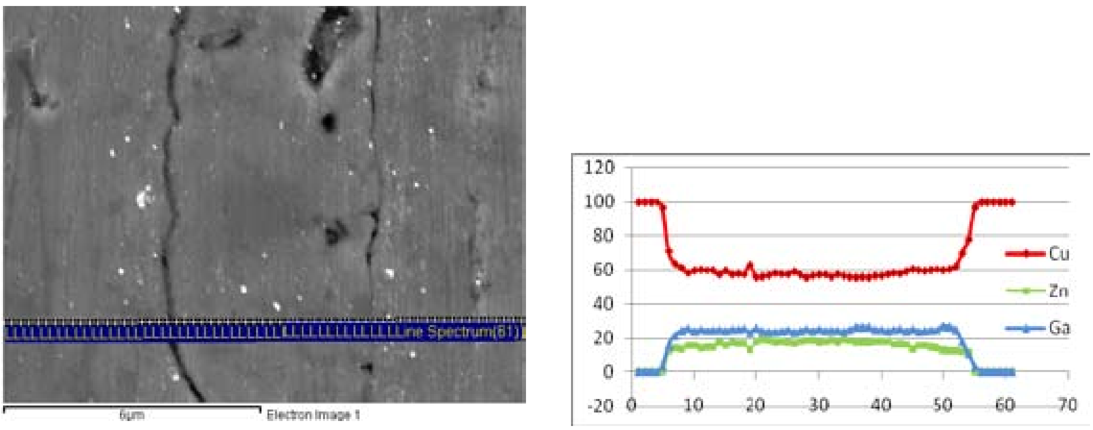


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Fig. 4. Microstructure, a line of scanning *(a)* and concentration curves *(b)* distribution of elements on junction of copper plates by the alloy Ga-Zn with the zinc content of 10 % after isothermal exposure at 200 °C for 120 hours.

crystal structure of intermetallic $Cu_9Ga_4$ corresponds to the phase $\gamma_1$ (32 % of gallium by mass, and the rest is copper) [13]. The zinc contents on junction (about 18 %) is almost twice more of initial one, that it is possible to explain by pressing out atoms of zinc in to the depth of soldered seam in process of growth of new phases from two sides.

At contacting brasses plates Л63 through liquid gallium at temperature 150 °C (Fig. 5) the phase layer $\gamma$ essentially is extended in comparison with contacting conditions, shown in Fig. 3. The increased zinc content on the junction edges on the bounetary of brass interface and formed new intermediate phases is also observed.

After contacting of brass plates Л63 through the melt interlayer Ga-Zn (Zn – 10 % by mass) at the same temperatures 150 °C intermetallic $Cu_9Ga_4$ is also absent. The phase $\gamma_1$ (32 % of gallium by

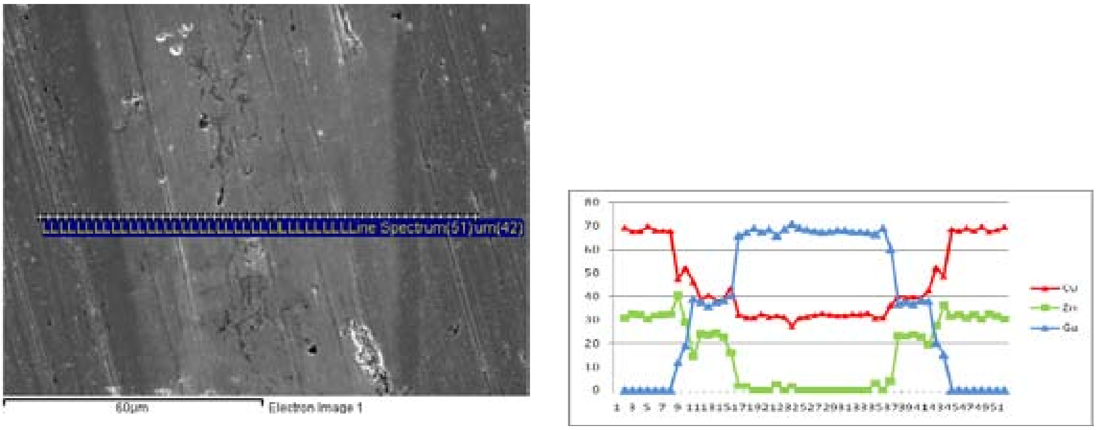


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Fig. 5. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on plates junction of brasses Л68 of gallium after isothermal exposure at 150 °C for 120 hours.

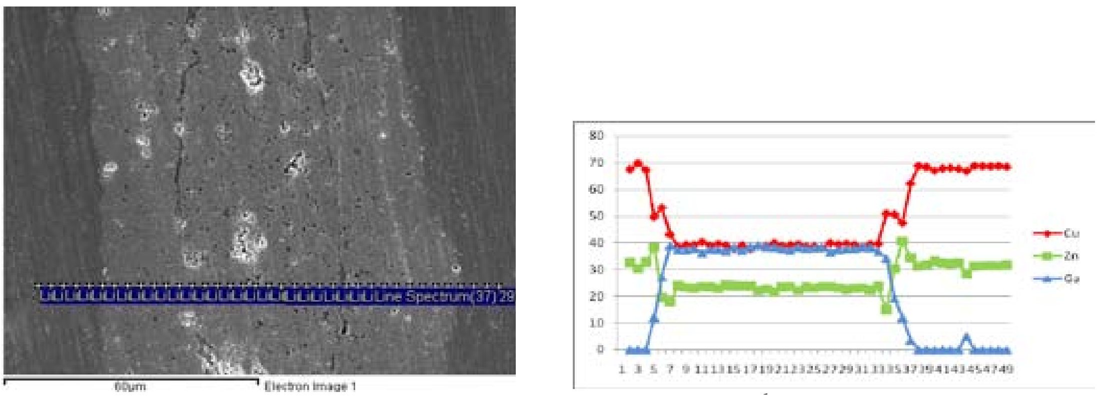


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Fig. 6. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on plates junction of brasses Л63 through the melt interlayer Ga-Zn (Zn – 10 % by mass) alloy Ga-Zn at 200 °C for 120 hours.

mass, and the rest is copper) with the maximal contents of gallium and thin layers of a firm solution of gallium in copper on junction edges prevails (Fig. 6).

After contacting of single-phase brasses plates Л63 and Л68 through the melt interlayer Ga-Zn (Zn – 10 % by mass) at temperatures 200 °C are present, by structure, a solid solution of gallium and zinc in copper, phase versions **γ** and zinc crystals, at this the maximal content of zinc on junction edges reaches 52 % by mass (Fig.7), and is not decreased below 20 % in the middle of the seam.

Results of x-ray phase analysis of interaction products of brasses with the Ga-Zn melt after contacting at the temperature 150°C have confirmed the presence of the following formed phases: a solid solution of gallium in copper, the intermetallic $CuGa_2$ and $Cu_9Ga_4$, and a firm solution of gallium in zinc as well (Fig. 8).

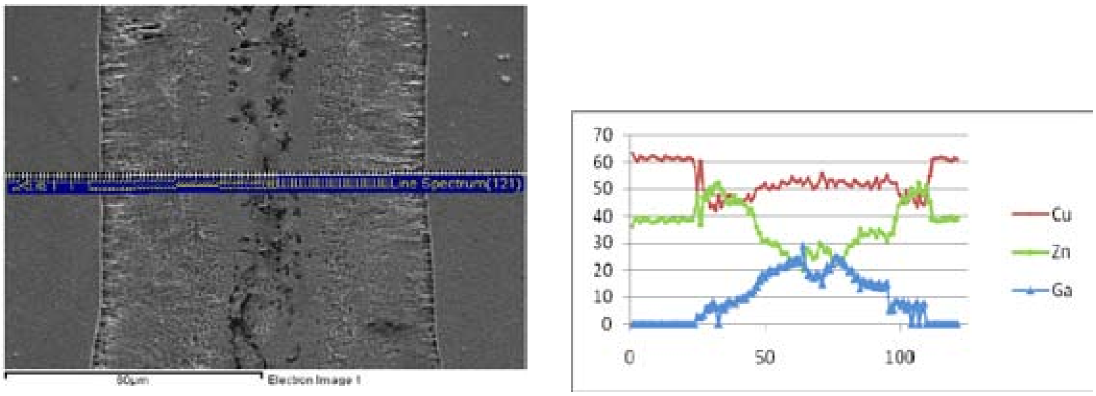


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Fig. 7. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on plates junction of brasses Л63 alloy Ga-Zn with the zinc contents of 10 % after isothermal exposure at 200 °C for 120 hours.

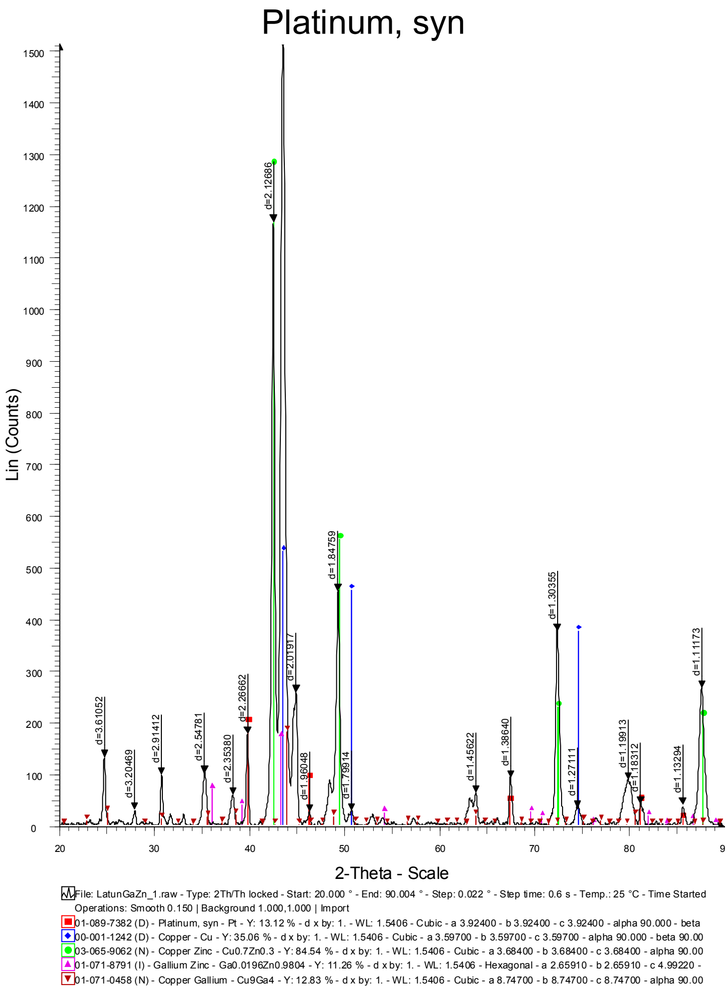


Fig. 8. Diffractogram of interaction products of brasses Л68 with the melt Ga-Zn (Zn – 10 %) after contacting at the temperature 150°C for 120 hours.

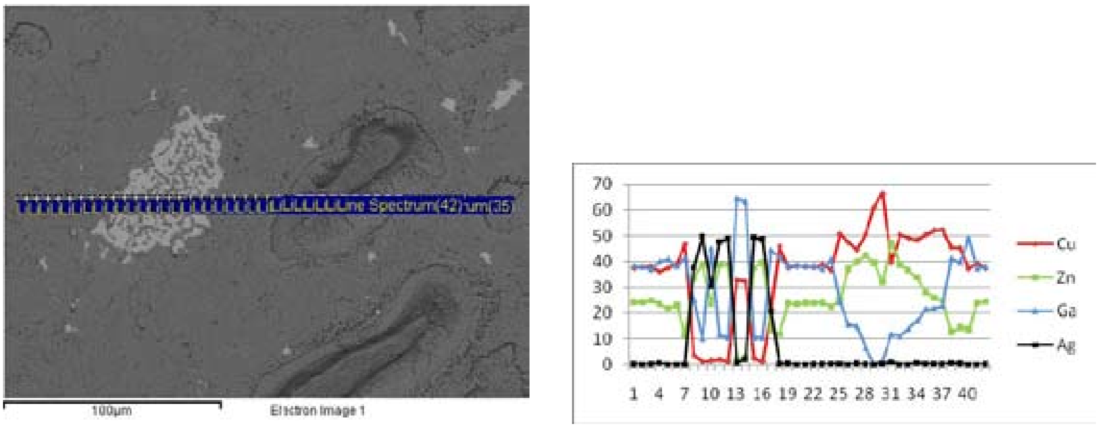


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Fig. 9. Microstructure, a line of scanning *(a)* and concentration curves *(b)* elements distributions on hardened paste at 150°C with the content: brass chip Л63 of 45 % by mass, eutectic Cu-Ag 10 % and alloy Cu-Zn of 45 %, in which zinc is of 10 % on by mass

At transition to powder and chip compositions (gallium pastes – solders) the element and phase structure of interaction products of brasses and copper – silver alloy with gallium and alloys of gallium with zinc essentially is not changed (Fig. 9). As a result of jet diffusion the brass particles are surrounded if go from the center of a particle, with a layer of a solid solution of zinc and gallium in copper, further follow versions of a phase **γ.** The zinc content in a composition is not reduced less than 10-20 % by mass along the whole length of a line of scanning, including interaction products of a eutectic particle Cu-Ag with the melt Ga-Zn. It is seen from the left part (Fig. 9 *b*) of concentration curves of elements distribution on the hardened paste, where silver atoms are present. Besides having at preparation of paste the equal sizes of particles of a brass and eutectic Cu-Ag it is visible in Fig. 9, that speed of interaction of gallium with an eutectic alloy is much higher in comparison with interaction of gallium with brass. Eutectic particles have completely reacted with gallium, and brass particles in the middle have kept the initial structure under all other equal conditions of reaction.

Thus zinc atoms presence in initial brasses and liquid gallium displaces the chemical reaction of gallium with copper into the area of intermetallic formation with higher copper content: the intermetallic $Cu_9Ga_4$ at the temperature less than 150°C is formed; according to the Cu-Ga diagram [13] the intermetallic $CuGa_2$ is to be formed at the temperature 254°C.

Thus zinc atoms presence in the initial solid phase (brass) and in initial liquid phase (an alloy of gallium with zinc) as a result of contact interaction of these diverse phases gives a mixture of fragile crystals of the intermetallic $Cu_9Ga_4$ and relatively plastic, strong and enough “refractory” zinc with fusion temperature more 400°C. And crystals of zinc surround crystals of fragile intermetallic (it is distinctly visible in Fig. 7), that means destruction of fragile intermetallic skeleton which is present at hardening of known pastes – solders at the use of a powder of copper or bronze as the initial solid component at them.

The addition of disperse particles of a copper-silver alloy in to the structure of gallium pastes – solders appreciably accelerates the process of their hardening due to the greater speed of jet diffusion of gallium in heterogeneous structure eutectic Cu-Ag [1].

The offered model of structure of hardened gallium pastes – solders has been realized in developed and approved solder by us [9] and will be improved further.

## Conclusions

1. Presence of zinc atoms in the initial powder of a single-phase brass and in the gallium melt accelerates and displaces chemical reaction of gallium with copper in area of intermetallic formation with the bigger copper content: in zinc contents pastes – solders on the basis of gallium the intermetallic $Cu_9Ga_4$ is formed at temperatures less 200°C.

2. Pastes – solders on the basis of an alloy of gallium with zinc, incorporating two fillers as solid particles of brass and eutectic Cu-Ag, harden faster and have the structure which does not contain a fragile intermetallic skeleton.

3. Composite multicomponet gallium pastes – solders, possessing more technological and higher operational properties, are perspective for diffusion soldering of diverse materials.

*The work is executed within the framework of the federal target program.*

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# Многокомпонентные композиционные галлиевые пасты-припои

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*Исследовано контактное взаимодействие медно-цинковых и медно-серебряных сплавов с эвтектическими расплавами системы Ga-Zn как композиционными составляющими галлиевых паст-припоев. Определены продукты взаимодействия в зависимости от состава и температуры контактирующих компонентов. Апробированы составы разработанных новых низкотемпературных припоев на основе галлия.*

*Ключевые слова: галлий, пасты-припои, латунь, медно-серебряные сплавы, взаимодействие, эвтектика.*