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# The structure of liquid solder $Sn_{0.97}Cu_{0.03}$

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The structure of liquid solder $Sn_{0.97}Cu_{0.03}$ has been studied by means of x-ray scattering method. The analysis of structure factors allowed to conclude that atomic distribution in this melt is inhomogeneous. Beside Sn-based structural unit the local groups where Cu-atoms are soluted in tin also exist. It is shown that vibrational treatment of melt significantly transforms the structure upon solidification.

## 1. INTRODUCTION

The environment protection requires the using of new lead free soldering materials. Sn-based alloys where lead is substituted by another element are of great practical interest now. In order to satisfy the needed working parameters of solder it should have the definite composition, which determines the main physical properties such as electroconductivity , viscosity, surface tension, elastic and other coefficients. The main characteristic of solder is its structure which shows changes upon solidification and is responsible for temperature dependencies of physical properties.

Most of solder alloys have a compositions close to eutectic points in equilibrium phase diagram. On this reason the alloying of new solder materials is connected with the studying of eutectic metallic systems structure.

## 2. THEORETICAL BACKGROUNDS

The structure of binary eutectic alloys in liquid state has been studied by means of X-ray and neutron diffraction method.[1-3] It was shown that atomic distribution near liquidus line temperatures is inhomogeneous and like kind atom groups are main structural units. When

temperature increases atomic distribution shows the tendency to formation of structure with random atomic distribution. In some works liquid eutectic alloy is considered as a liquid atomic solution and the specific structure in solid state is a product of eutectic crystallization. [4-5]

One of an important parameter of inhomogeneous structure is the size of structural units, which can not be determined exactly at present time. Some results for it derived from small angle neutron diffraction, model estimation yield the values, which lie in the range from about 100 to 1000 nm . The measuring of physical properties at different concentration points evidently indicates the deviation from liner dependence, which has a extremal value for eutectic composition [5]. Thermodynamic data show the positive deviation from the values which are observed for ideal solutions.

The degree of such deviation is dependent mainly on atomic radius and electronegativity difference. Some eutectics alloys show the easy amorphysation by means of rapid quenching of melt. Thus there are facts which allow to consider the high sensitivity of eutectic systems alloys to temperature and composition. On other hand these alloys prefer to arrange their atomic distribution on the base of like kind atom groups.

$Sn_xCu_{1-x}$ alloys have been studied in liquid state by means of X-ray and neutron diffraction methods. The physical properties (density, viscosity, surface tension and other) were measured too [5,6]. Although the much experimental data about structure of liquid Sn-Cu alloys were obtained, the main attention was paid to the features of atomic ordering in molten chemical compounds and to deriving of partial structure factors.

The aim of this paper was to study the structure of eutectic $Sn_{0.97}Cu_{0.03}$ liquid alloy.

## 3. EXPERIMENTAL

For the investigation solder alloy produced by « AMASAN » (ISO 3677: BSn97Cu3 230÷ 250 was prepared). X-ray diffraction method was used. The sample was placed into vacuum chamber filled with He during experiment in order to protect the oxidation of surface. The angular dependence of scattering by sample intensity was recorded automatically within range of wave vector $0.1 \div 0.7 nm^{-1}$. X-ray beam was monochromatized by reflection from LiF crystal's plane.

## 4. RESULTS AND DISCUSION

Angular dependence of scattered intensity was corrected on absoption and incoherent scattering [7] and used to calculate the structure factors. *Fig.1* represent graphically the structure factor obtained at the temperature 5K above of melting point. It can be seen that main three peaks and shoulder indicate the tin like structure in the liquid alloy. Analyzing the maxima positions of liquid alloy in comparison to ones of liquid tin, it is possible to see some discrepancies. At first the main peak for solder shifts slightly to larger K-values than for tin and second one to opposite direction. At second the principal peak height of structure factor for solder is higher than for tin.

Using Fourier transformation of structure factor the radial distribution function of atoms $G(R)$ was derived. The main peak's position as a most probable distance form initial to nearest neighbor atoms is obtained to be 0.330 nm what is somewhat shorter (0.335 nm) than for liquid tin. The square under first peak of this function determined the number of nearest neighbors. This quantity equals to 9.6 and is larger than for tin (9.1).

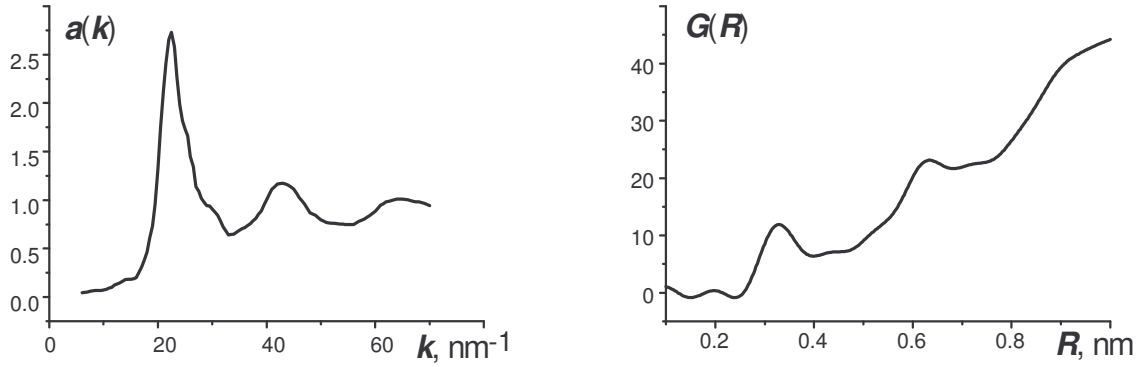


Figure 1. The structure factor (a) and radial distribution of atom function (b) for molten Sn0.97Cu0.03 alloy.

Taking into account the changes in structural parameters analyzed above we can conclude that presence of 3 at.% of copper in alloy leads to some changes in atomic distribution of tin. These are more significant that in assumption of ideal liquid solution. Using the values of first maxima positions in structure factor of liquid Sn and Cu we have estimated the shift in this case ($2.3*10^{-3}nm^{-1}$). Some other dopes which exist in solder cannot significantly increase this value due to less value of first maximum position in structure factor. For Ni dope only it is lager ($0.31nm^{-1}$) than for copper.

Thus, the structure of Sn-based solder shows the deviation from ideal solution, which, as we suggest, is caused by existence of inhomogenous atomic distribution. Structural inhomogeneities are also widely used for the description of structure in liquid semiconductors and semimetals. The main precursor of such atomic distribution is the shoulder on the right hand side of main peak. It is pronounced in structure factors of investigated solder as well as for liquid tin.

The higher first peak in structure factor of solder in comparison to one of tin is the evidence of more densed packing of atoms in first melt. This fact is confirmed by values of squares under first peak in function of radial distribution of atoms. Atomic radius of Cu-atoms is less then Sn-ones and last occupy the vacant sites in structure of liquid tin. The number of vacancies is sufficient for it due to inhomogenecous atomic distribution. Hence, the formation of more metallic liquid upon adding of Cu atoms significantly changes the main properties of this solder.

Another reason of inhomogeneties which are revealed in liquid alloy, is the forming of chemically ordered clusters whose atomic arrangement is close to structure of solid intermetallic compounds. In case of Sn-Cu eutectic as follows from phase diagram this compound is $Cu_6Sn_5$. Consequently there are possibility to form the regions, where the main properties of solder can be different and in many cases worse than needed.

In order to reduce the inhomogeneties it is possible to overheat the melt but in many practical cases of soldering this procedure is impossible. Another way for it is to break the structural units with using of external energy. In this paper we propose do it by means of vibrational treatment of melt. The producing of low frequency vibration and introducing them into liquid alloy was realized according to the scheme described in [8]. Upon vibration treatment melt was picked out and rapidly cooled. The metallographic studies of samples upon different regimes of vibrational treatment show the changes in microstructure (*Fig.2*). It can be seen that formation of dendrite like structure is more pronounced when the time of treatment becomes longer. Thus it is possible to make the structure of melt more

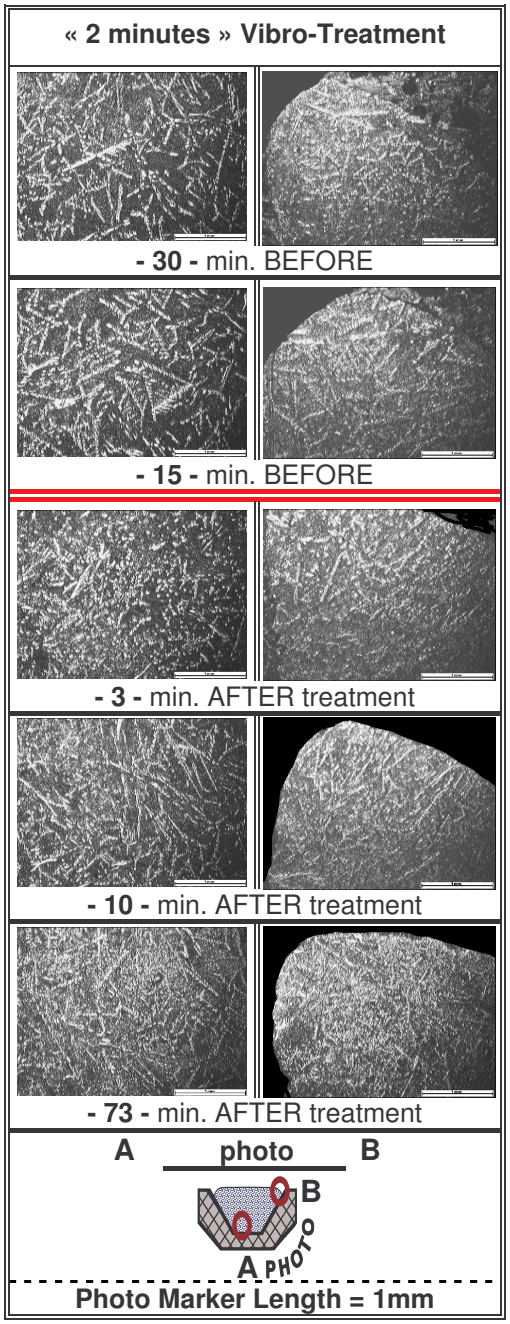


Figure 2. The structural changes caused by 50Hz vibrational treatment upon solidification.

homogeneous with using of vibrational treatment method but new metastable structural state transforms via formation of more large units. According to this fact the melt should be in liquid state a little period of time before solidification.

## 5. CONCLUSIONS

Short range order of liquid $Sn_{0.97}Cu_{0.03}$ solder is characterized by existence of inhomogeneities in atomic arrangement. Main structure units are atomic groupes on the base of Sn structure.

Cu atoms are sotuted in some part of Sn atoms and another part of tin atoms form self like atomic distribution. Inhomogeneous structural state can be transformed by means of mechenical vibrational treatment.

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