

## STRUCTURE OF TIN-BASED ALLOYS

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### ABSTRACT

Short range order of  $\text{Cu}_x\text{Sn}_{1-x}$  liquid alloys, containing 0; 2.5; 5; 7.5; 10 and 12.5 at.% Cu has been studied by means of x-ray scattering method. The structure factors and binary correlation functions are analyzed. It is shown that Sn-enriched liquid alloys can be considered as atomic solutions, where Cu-atoms substitute tin-ones. Structural inhomogeneities of liquid tin persist with increasing of copper content.

### INTRODUCTION

Tin - based alloys are widely used due to their low melting temperature and the ability to form the eutectic alloys. These alloys have a practical using as solder materials. During last few years significant interest has been focused on the studying of eutectics for Pb-free solders. Tin - based alloys are promising for solders and Sn-Cu is one of them.

The aim of this work was to study the structure of tin-enriched liquid alloys in order to determine the departure from random atomic distribution and ideal solution model. The phase diagram of Cu-Sn system shows the existence of chemically ordered phases which belong to electronic kind compounds. Enthalpy of mixing is negative over all concentration range and its minimum point lies at 22 at.% of Sn. At 3 at % Cu and  $T=500\text{K}$  the eutectic point is observed. Thus, tin enriched alloys show the high sensitivity of phase formation process to composition. It is of interest to study what is solubility of copper in liquid tin and what are the structural changes upon adding of Cu-atoms to tin.

### EXPERIMENTAL

X-ray scattering method was used to obtain experimental structure factor (SF). Bragg-Brentano focusing geometry was used [1]. The intensity curves as a functions of scattered angles were corrected on absorption factor, incoherent intensity and then normalized to electron units [2]. The monochromatization of x-ray radiation was carried out by LiF crystal installed in initial beam. All experiments on diffraction were carried out in chamber filled with helium of high purity in order to avoid the oxidation of sample surface. The scattered intensity values were recorded with  $10^\circ$  step in the region of first peak and  $30^\circ$  in the rest region. The temperature of sample

was measured and stabilised with accuracy  $\pm 2\text{K}$ . Samples were synthesised from tin and copper of high purity (99.999% Sn, 99.99% Cu).

## RESULTS AND DISCUSSION

The x-ray diffraction studies were carried out for Sn-Cu liquid alloys containing 0; 2.5; 5; 7.5; 10 and 12.5 at.% of Cu at the temperatures close to liquidus line. Solutions within this concentration region are commonly considered as a diluted solutions. On this reason it is possible to suppose that soluted atom interacts only with atom of matrix. In our case only Cu-Cu and Cu-Sn interactions are possible.

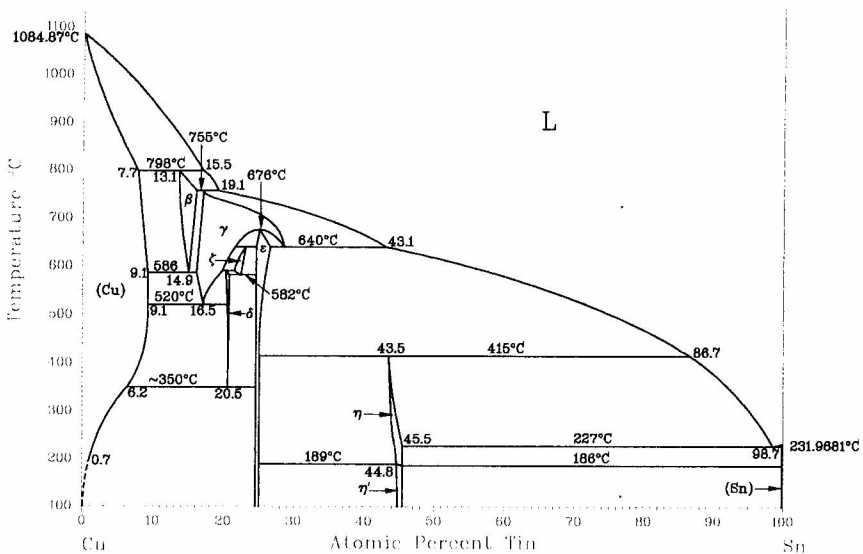


Figure 1. Cu-Sn phase diagram

Phase diagram of Cu-Sn system in region of such concentrations is characterized by existence of eutectic point at 98.7 at.% Cu. Melting temperature of eutectic phase equals to 500K. Chemically ordered  $\eta$ -phase ( $\text{Cu}_6\text{Sn}_5$ ) and pure tin are component of eutectic in solid state. The solubility of copper in tin is very small, whereas the solubility of tin in copper is about 9 at. % at higher temperatures ( $\sim 860\text{K}$ ) (Fig.1.) Such situation is in disagreement with values of ionic radii of components ( $r_{\text{Sn}}=1,45\text{\AA}$ ;  $r_{\text{Cu}}=1,35\text{\AA}$ ) [3] As it can be seen the ionic radius of copper is somewhat higher than one of tin. This fact allows to suppose that solubility of copper in tin should be higher than solubility in opposite part of phase diagram. This discrepancy disappears if take into account the difference between crystalline structures of tin and copper. This difference exists also upon melting and it is of interest to study whether features of solubility, noted above are pronounced in liquid state.

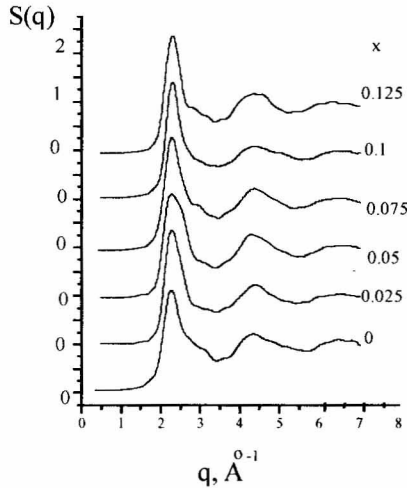


Figure 2. Structure factors for  $\text{Cu}_x\text{Sn}_{1-x}$  liquid alloys ( $T=T_L+5\text{K}$ )

The structure factors for  $\text{Cu}_x\text{Sn}_{1-x}$  liquid alloys are shown in Fig.2. As it can be seen the profiles of SF in many respects are similar to ones of liquid tin. The shoulder on right hand side of principal peak in SF is pronounced for all curves up to 12.5 at.% of Cu. The position of main maximum shows the shift to large  $q$  values within concentration range 0-10 at. % Cu. Second maximum position shows no significant changes, but some anomalous behavior near 10 at.% concentration point is observed. Concentration dependence of second to first maximum position ratio is somewhat higher than for typical liquid metals (1.86). This structural characteristic is almost the same as in liquid tin. This fact confirms the dominant influence of Sn-like atomic arrangement on atomic topology of  $\text{Sn}_{1-x}\text{Cu}_x$  liquid alloys.

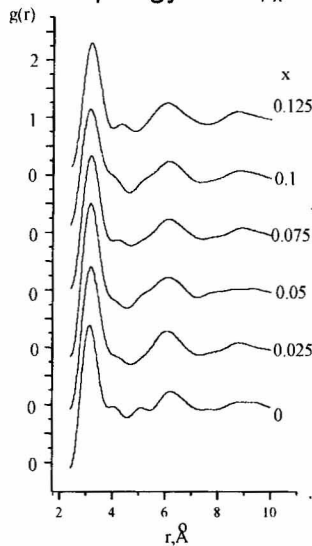


Figure 3. Binary correlation functions for  $\text{Cu}_x\text{Sn}_{1-x}$  liquid alloys ( $T=T_L+5\text{K}$ )

Using Fourier transformation of structure factors, binary correlation functions  $g(r)$  were calculated (Fig.3.). Tin- like structure of liquid alloys is also displayed in main parameters of these functions. Fig.4. represents the concentration dependence of most probable distance to nearest atoms. Almost linear dependence of this parameter is observed.

Some transformation of shoulder may be a result of structural changes in structural units where interaction between atoms is partly covalent. Analyzing the position of the first peak in binary correlation function  $g(r)$  it can be observed the reducing of this parameter, which represents the mean interatomic distance. First addition of Cu-atoms does not significantly changes the atomic distribution of tin. These atoms occupy free volume in structure of tin and as result some reducing of interatomic distance occurs. Such defects are caused by existence of structural inhomogeneities in liquid tin. As follows from diffraction studies [4,5] and our data structure of liquid tin can be described by model which suppose the existence of structural units of two kinds: densely packed atomic groups where atoms interact via partly covalent bonds and close packed ones with metallic bonds. Coexistence of these structural units requires the formation of free volume dynamical regions.

At the same time some parts of Cu-atoms substitute tin ones. On this reason the reducing of  $r_1$  with adding of Cu-atoms is not so rapid as the model of random atoms distribution predicts. Thus, the concentration interval of alloys, studied in the work can be considered as range of dilute solution of copper in tin with Sn-like topology of atomic distribution due to tendency to persist the covalent bonds upon melting.

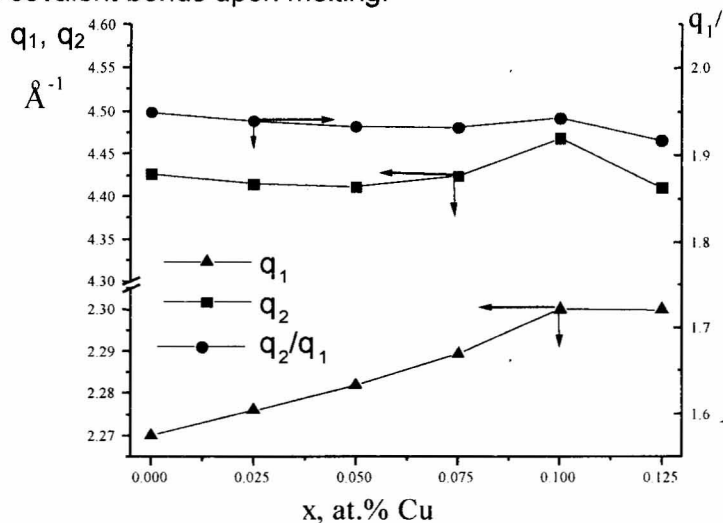


Figure 4. Concentration dependence of structure parameters of  $S(q)$   
 $q_1$  – first maximum position,  
 $q_2$  – second maximum position,  
 $q_2/q_1$  – second to first maximum position ratio.

## CONCLUSIONS

Analyzing the structural parameters obtained from structure factors and binary correlation function it is possible to conclude the existence of two mechanism of dilute solution formation: substituting of tin atoms by copper ones and occupying of free volume in structure of tin by of less size Cu atoms.

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