The cluster structure of liquid \((\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x\) alloys

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Abstract. The structure of Cu\(_{0.70}\)Si\(_{0.30}\) eutectic melt and \((\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x\) (x=0.05: 0.10: 0.15) has been studied by means of X-ray diffraction method. The structure factors and pair correlation functions are analysed. It is shown that addition of Pb-atoms to Cu\(_{0.70}\)Si\(_{0.30}\) eutectic melt promotes the increase of inhomogeneities in structure.

1. Introduction

In order to improve the properties of eutectic alloys, that are widely used in different areas of application including electronics, machine building and metallurgy, the different methods are commonly used. One of them which is comparatively new but less motivated from fundamental viewpoint is based on changing of crystallization conditions, i.e. amorphisation from liquid state by quenching, growth of nanocrystals in amorphous matrix and others.

Most of these methods deal with structurally disordered systems (liquid or amorphous) and need the detail information about the precondition for formation of new phase. For example, in order to promote the nucleation process the admixture, that shows a low solubility in major elements of eutectic alloy, is commonly used in order to obtain the nanocrystals in amorphous matrix. Other admixtures (for example Nb-atoms) are used in order to prevent the diffusive processes, that are responsible for the rate of crystallites size increase.

In this work X-ray diffraction method was used in order to study the influence of Pb admixtures on structure of Cu\(_{0.70}\)Si\(_{0.30}\) eutectic melt. Alloys, containing 0, 5, 10 and 15 at.% Pb have been studied at temperatures for 5K above the liquidus curve.

1 Experimental

\((\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x\) alloys with different Pb content (5, 10 and 15 at %) were prepared by arc melting in furnace filled with argon. Samples were placed in chamber of X-ray diffractometer filled with pure helium in order to avoid the oxidation during an experiment. Cu-K\(_\alpha\) radiation, monochromatized with using of LiF crystal, installed in initial beam and Breg-Brentano focusing geometry were used. Scattered intensities were recorded with different angular step, that was less within the region of principal peak and larger at rest values of scattering angles. Experimental results on intensities were corrected on polarization, absorption and incoherent scattering according to [1]. After this procedure
they were normalized and then used for calculation of structure factors (SF) and pair correlation function (PCF). The main structure parameters obtained from these functions were analyzed.

2 Results and discussion

The structure factor for liquid Cu$_{0.70}$Si$_{0.30}$ eutectic alloy in comparison with ones for liquid Cu and Si is shown at figure 1. As it can be seen, the SF for eutectic is more similar to one for liquid copper than for liquid silicon. But it should be noted that the principal peak has a very flat left-hand branch. The reason of such specific profile may be a principal peak of SF for liquid silicon, but if the structural units with silicon-like structure exist in eutectic melt, they should transform a right hand side also because the principal peak for Si is wide and looks like a consisting of two subpeaks. In fact such transformation of right-hand side of SF was not observed. The second feature of SF for eutectic melt is the significantly less height of the main peak in comparison with liquid copper. Hence we have the experimental facts that allow us to conclude that atomic distribution in molten Cu$_{0.70}$Si$_{0.30}$ eutectic melt can not be considered as the microgroups on base of like kind atoms.

Figure 1. The structure factor for liquid Cu$_{0.70}$Si$_{0.30}$ eutectic alloy in comparison with ones for liquid Cu and Si.

On the reason that SF for liquid eutectic is in many respects similar to one of liquid copper, one can suppose that Cu-like atomic arrangement is a dominant in the total structure. Taking into account the tendency to interaction of unlike kind atoms, that follows from equilibrium phase diagram, revealing the chemical components [2] and thermodynamic data (negative enthalpy of mixing [3-7]), we can suppose that some part of Cu and Si atoms forms chemically ordered atomic distribution. In solid state such chemically ordered regions transform into η-phase. On that reason we have investigated this solid alloy at temperature close to melting point and compared the diffraction pattern with structure factor for eutectic melt (figure 2) also.

Figure 2. The diffraction pattern in comparison with the structure factor for liquid Cu$_{0.70}$Si$_{0.30}$ alloy.
The agreement between them can be seen, particularly the intensive peak corresponds to the extended part of the left hand side branch of principal peak.

The existence of preferred interaction between Cu and Si atoms and formation of η-phase like chemical ordering is confirmed by analysis of structure parameters obtained from structure factors and pair correlation functions. Model analysis of most probable interatomic distances $r_1$ and numbers of neighbors $Z$ showed that experimental data are in good agreement with the model ones if suppose the existence of random atomic distribution than in assumption of simple like kind atoms arrangement (Cu-Cu and Si-Si groups).

**Figure 3.** Structure factors for molten $(\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x$ alloys $(1– x=0; 2– x=0.05; 3– x=0.1$ and $4– x=0.15)$

SFs for molten $\text{Cu}_{0.70}\text{Si}_{0.30}$-Pb$_x$ alloys are significantly different from one for liquid eutectic alloy (figure 3). At addition of 5at.% of Pb to eutectic melt, the principal peak height in $S(k)$ decreases that can be attributed to reduction of density in atomic distribution. The most probable reason is a little solubility of Pb atoms in liquid Cu and Si. Consequently, this results the decrease of atomic density. For molten alloys containing 10 and 15 at% Pb the shoulder on left hand side of the principal peak is more pronounced. On the other hand, some structural parameters are in fact unchangeable with Pb-content increase - the principal peak position is the same in entire concentration range. The concentration dependence of the most probable interatomic distances is without significant changes also.

**Figure 4.** Partial structure factors for molten $(\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x$ alloys $(1– x=0.05; 2–x=0.1$ and $3– x=0.15)$
Experimental SFs were used to calculate the partial $S_{ij}(k)$ by means of reverse Monte Carlo method. Some of them are shown at figure 4. As is seen, the $S_{\text{Cu-Cu}}(k)$ function is similar to corresponding SF for liquid copper. Another function $S_{\text{Si-Si}}(k)$ shows a small principal peak, revealing a slight Si-Si correlations. The correlation between Pb atoms is described by $S_{\text{Pb-Pb}}(k)$ which main parameters are close to corresponding ones for liquid lead. These results confirm the above-formulated conclusions about the existence of Pb-clusters in $(\text{Cu}_{0.70}\text{Si}_{0.30})_{1-x}\text{Pb}_x$ melts.

3 Conclusions

Therefore the addition of Pb to Cu$_{0.70}$Si eutectic melt makes its structure more inhomogeneous. At low content of Pb the doped atoms are distributed in matrix of eutectic melt randomly, disturbing atomic distribution of the nearest neighbors. With increase of Pb content the self-associated atomic groups with lead-like structure are aggregated and clusters are formed.

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