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Structural disordering in Sn-Pb(Bi) eutectic melts induced by heating

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The structure of liquid $Sn_{0.739}Pb_{0.261}$ and $Sn_{0.57}Bi_{0.43}$ eutectic alloys was studied by means of X-ray diffraction at several temperatures. Structure factors, pair correlation functions and the main structural parameters obtained on their basis were analyzed. We show that the structure of the $Sn_{0.739}Pb_{0.261}$ and $Sn_{0.57}Bi_{0.43}$ eutectic alloys is inhomogeneous and consists of different types of clusters. Upon heating the cluster structure undergoes topological and chemical disordering showing a significant dependence of structural parameters on temperature near the melting point.

Keywords: liquid alloys, chemical bonding in eutectic alloys, chemical short-range order.

INTRODUCTION

Owing to their low melting point and other unique properties, eutectic alloys have been widely used for a long time, e.g. for soldering[1–3]. In contrast to solid solutions, these alloys are less commonly studied due to their unique structure. Theoretical approaches suffer from several problems because of the different sizes of the crystalline grains. Therefore, in order to clarify the physical nature of their properties and their structure--specific behavior, it is necessary to study eutectic alloys using various experimental methods under different thermodynamic conditions.

For the time being, several authors have investigated eutectic alloys, focusing on the solid state[4, 5]. Most of the data available on liquid eutectic melts originate in the measurements of physical properties, whereas diffraction investigations are uncommon[6–10].

The majority of the results on the structure and physical properties of simple eutectic melts confirm the preference towards the interaction of like-kind atoms, which determines the structural features at near-melting temperatures. Moreover, such structure, which is inherently different from a random atomic distribution, persists upon heating, within a certain temperature interval. Certain authors assumed the existence of a "quasi-eutectic" structure[11], which served to interpret diffraction data. Unfortunately, this model was unable to account for the temperature dependence of the structure in such molten alloys. We suppose that liquid alloys which reveal a cluster structure should be more sensitive to temperature, as compared to alloys less prone to clustering.

In this work, we investigated the structure of two Sn--based eutectic alloys – $Sn_{0.739}Pb_{0.261}$ and $Sn_{0.57}Bi_{0.43}$. The binary phase diagrams of these alloys are similar[12] but the substitution of Pb by Bi shifted the eutectic point to the Sn-edge. Such substitution allows the use of $Sn_{0.57}Bi_{0.43}$ as a solder, instead of $Sn_{0.739}Pb_{0.261}$, which is harmful to the environment. The most probable interatomic distances in Pb are 0.05A shorter than in Bi, whereas the number of neighbors is lower in Bi. Only a few eutectic binary systems exhibit near-equiatomic concentration. At present, there are no experimental methods of obtaining the information on the relationship between the concentration of a melt and the content of components in the clusters. However, it is possible to use model methods to find the relation between the content of the melt and the concentration of each component in clusters. We suppose that in the melts of equiatomic concentrations the cluster contents should be similar. In some cases, such as eutectic alloys of a metal with semimetals (Sn, Bi, Sb), one needs to take into account the fact that a fraction of atoms in clusters retain covalent bonds[13]. On the other hand, there are no such clusters in liquid Pb and therefore in alloys with Sn we expect that no Pb atoms will be diluted in Sn-based structural units. Such a cluster structure should be sensitive to temperature, therefore, Sn-Pb(Bi) eutectic melts were studied in this work at two (for Sn-Pb) and three (for Sn-Bi) different temperatures by means of X-ray diffraction.

EXPERIMENTAL

The samples under investigation were prepared from tin, lead and bismuth of high purity (both 99.999%), melted and then cooled in argon atmosphere. The diffraction studies were carried out using a high-temperature diffractometer with a special attachment, which allows investigating the solid and liquid samples at different temperatures (up to 1800 K). Cu-K_α radiation, monochromatized by means of LiF single-crystal as a monochromator and Bragg-Brentano focusing geometry were used. The scattered intensities were recorded as a function of the scattering angle with an angular step of 0.05° within the region of the principal peak and 0.5° for the remaining values of the wave vector. The measurement of the scattered intensity was performed with an accuracy of at least 2%. In order to obtain more accurate scattered intensities, the scan time was set to 100 s. The diffracted intensity was recorded using a NaI(Tl) scintillator detector together with an amplification system. The sample was placed in a round cup of 20 mm in diameter. Intensity curves were corrected for polarization, absorption and incoherent scattering[14] and were subsequently normalized to electron units by the Krogh-Moe method[15]. The obtained intensity curves were used to calculate structure factors (SFs), from which pair correlation functions (PCFs) were calculated. The main structural parameters obtained from SFs and PCFs were subsequently analyzed.

RESULTS AND DISCUSSION

The structure factors for the $Sn_{0.739}Pb_{0.261}$ molten alloy at T = 470K and 570K depend significantly on temperature (Fig. 1). Neither Sn nor Pb revealed such a dramatic change in SFs. The comparison of the SFs for liquid alloys with those of liquid Sn and Pb allowed us to conclude that the structure of the melt is more similar to the structure of tin. However, the shoulder characteristic of SFs of liquid tin is not as pronounced for SFs of eutectic melts. Therefore, we suppose that a certain proportion of the Pb atoms, which are diluted in Sn, changed the structure of tin in such a way that some covalent bonds were broken and transformed into metallic bonding.

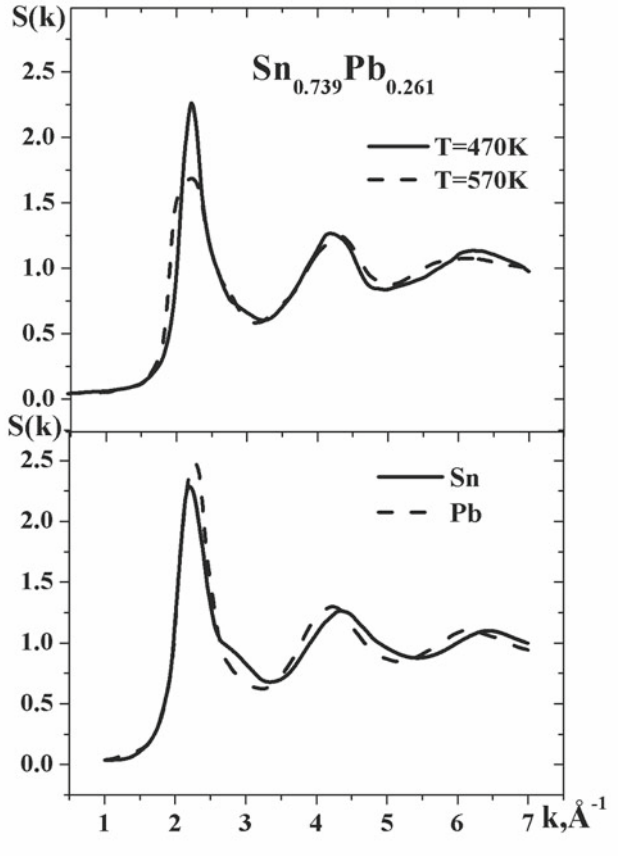

Figure 1. Structure factors for the $Sn_{0.739}Pb_{0.261}$ molten alloy

By comparing structural parameters obtained from the SFs and PCFs (Table 1) with those obtained for liquid pure Sn and Pb (at their melting points) we can conclude that the formation of a mixture of Sn-Sn and Pb-Pb clusters is accompanied by an increase in the most probable interatomic distance and by a decrease in the coordination number Z. This conclusion is confirmed by comparing the predictions of the model structure factor with the experimental one (Fig. 2). Calculation of the model SFs under the assumption of additive scattering from both the Sn and Pb regions can be easily performed using SFs of liquid tin and lead:

$$S(k) = C_{Sn} K_{Sn}^2 S_{Sn}(k) + C_{Pb} K_{Pb}^2 S_{Pb}(k),$$

where C_{Sn}, C_{Pb} are the fractions of tin and lead; K_{Sn}, K_{Pb} are their scattering abilities, respectively.

One can observe that liquid Sn-Pb eutectic alloy distends its structure in comparison with the structure of its components. The free volume which appears in the molten eutectic is necessary for the mobility of clusters in case of changes of thermodynamic conditions. These clusters are not as densely packed as in highly ordered materials (simple liquid metals, liquefied inert gases).

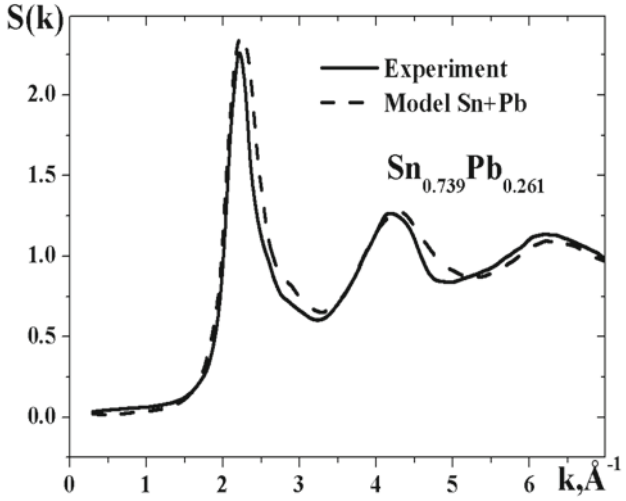

Figure 2. Experimental structure factor compared with SFs calculated according to the "quasi-eutectic" model

Clusters change their structural parameters upon heating, which explains the shape of the SF at the higher temperature (T = 570K). Overheating by 100K was accompanied by a reduction in the height of the principal peak (Fig. 1). The most probable interatomic distances r_1 increased slightly and so did the coordination number. Such behavior could be attributed to the rearrangement of atoms in the clusters with an increase in atomic density, similar to the effect which occurs in liquid tin after melting. We presume that the distance between the clusters increased as well. The structural parameters (r_1, Z) were interpreted within the framework of the self-associated and random atomic distribution models. By comparing the experimental data (Table 1) with the results of calculations (r_1^{sa} = 3.3A, Z^{sa} = 9.3, r_1^{rd} = 3.7A, Z^{rd} = 21.5), we conclude that the self-associated atomic distribution model leads to better agreement with the experimental data. Therefore at overheating of 100K above the liquidus temperature the alloy still retains its inhomogeneous structure.

In the case of the $Sn_{0.57}Bi_{0.43}$ eutectic melt, the contents of Sn and Bi are almost identical, in contrast to the Sn-Pb eutectic. This may be a consequence of similar values of structural parameters for Sn and Bi. The structure factors of both Sn and Bi reveal a shoulder on the right-hand side of the principal peak (Fig. 3).

Table 1. The main structural parameters of the $Sn_{0.739}Pb_{0.261}$ molten alloy

T, K	k_1, A^{-1}	k_2, A^{-1}	$S(k_1)$	Δk	r_1, A	r_2, A	Z
470	2.22	4.18	2.36	0.47	3.30	6.26	8.3
570	2.21	4.30	1.68	0.83	3.34	6.19	9.0
Sn	2.21	4.33	2.28	0.57	3.23	6.3	10.9
Pb	2.28	4.23	2.48	0.55	3.33	6.4	10.9

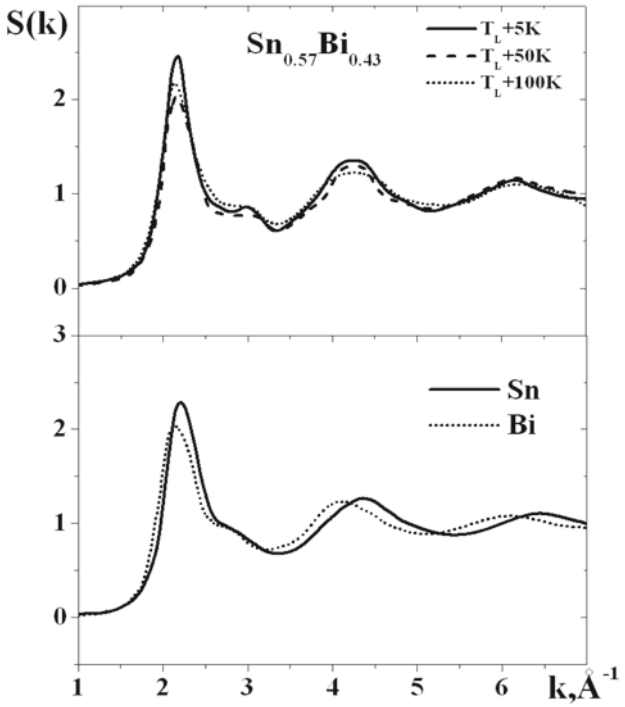

Figure 3. UV spectrum showing a probable formation of intermediate complex in oxidation of aromatic anil by MMPP

The comparison of the structural parameters of the liquid eutectic with those of liquid Sn and Bi confirmed the existence of Sn- and Bi-based clusters. Upon heating, the structure of the clusters became more stable, yielding the same value of the most probable interatomic distance (Table 2). A similar tendency was observed for the coordination number. Hence, the atomic distribution in Sn- and Bi-based clusters is similar for both kinds of clusters and therefore, we suppose that these clusters transform into another type of clusters, with unlike neighbouring atoms, without a significant change of their structural parameters.

The structural changes occurring with a change in temperature are related to the temperature dependence of the parameters, which can be determined from the SFs and PCFs. Our major focus was the analysis of the principal peak position k_1 of the SF, the most probable interatomic distances r_1 and the coordination number Z. However, the analysis of the structural data for liquid metals showed that the height of the principal peak $S(k_1)$ depends on temperature.

In accordance with the hard-sphere model[13], this parameter was considered to be a measure of packing density. Figure 4 shows significant differences between the temperature dependence of $S(k_1)$ for the liquid components of alloys (Sn, Bi, Pb) and those of eutectic melts.

For the $Sn_{0.739}Pb_{0.261}$ eutectic melt, the decrease in $S(k_1)$ is very abrupt, whereas for liquid Sn and Pb, it is smooth. Such behavior confirms the existence of clusters which during their destruction upon heating need more

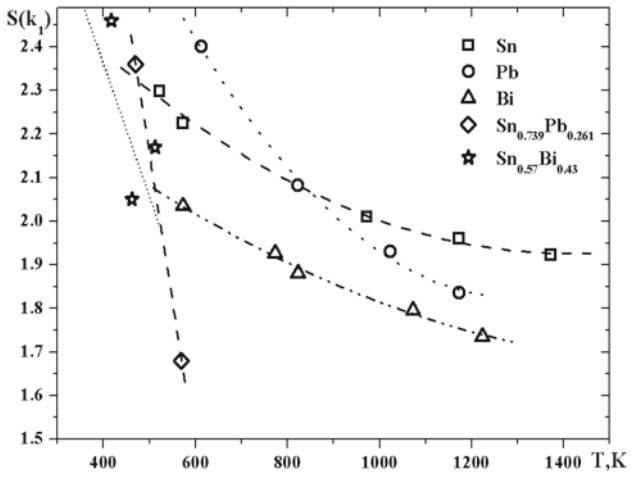

Figure 4. Comparison of the temperature dependence of $S(k_1)$ for liquid Sn, Bi and Pb with that of eutectic melts

free volume, which, in turn, results in a lowering of the packing density. In contrast, for the $Sn_{0.57}Bi_{0.43}$ eutectic melt, the corresponding dependence is not so dramatic as for the $Sn_{0.739}Pb_{0.261}$ liquid alloy, indicating that the structure of clusters is less inhomogeneous.

The values of metallic radii of Sn, Pb, Bi are r_{Sn}=1.58 A, r_{Pb}=1.74A and r_{Bi}=1.82A. Thus, the difference of these radii, which is a measure of solubility, is greater for Sn-Bi than for Sn-Pb. This is in disagreement with the results of our diffraction studies. In order to work around the inconsistency, we assumed that the similarity of the short-range order was a more significant factor than the atomic size difference.

On the other hand, our results were consistent with the thermodynamic data. In particular, the enthalpy of mixing for both systems is positive, resulting in a preferred tendency to like-atom interactions. The value of the enthalpy of mixing is larger for the Sn-Pb binary alloy[11, 16, 17].

CONCLUSIONS

The atomic distribution of liquid eutectic alloys Sn-Pb and Sn-Bi was inhomogeneous in the temperature range from T_{melt}+5K to T_{melt}+100K. The main structural units were Sn- and Pb-based clusters. A certain fraction of Pb atoms, which are diluted in Sn, changed the structure of tin in such a way that some covalent bonds were broken and transformed into metallic bonds.

The eutectic Sn-Bi melt contains Sn- and Bi-based clusters. The obtained results allowed us to suppose that these clusters transform upon heating into another type of clusters, with unlike neighbouring atoms, without a significant change of their structural parameters.

Table 2. The main structure parameters for the $Sn_{0.57}Bi_{0.43}$ molten alloy

T, K	k_1, A^{-1}	k_2, A^{-1}	$S(k_1)$	Δk	r_1, A	r_2, A	Z
417	2.17	4.25	2.46	0.45	3.32	6.37	9.1
462	2.15	4.26	2.05	0.5	3.3	6.36	8.7
512	2.14	4.27	2.17	0.58	3.3	6.32	8.7
Sn	2.21	4.33	2.28	0.57	3.23	6.3	10.9
Bi	2.13	4.12	2.03	0.68	3.38	6.6	8.8

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