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X-ray study of the structure of liquid Bi–Tl

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Abstract

The short range order of liquid Bi–Tl alloys was investigated using X-ray scattering. The concentrations of the melts, 10, 12, 14, 16 and 18 at.% Bi, were chosen to correspond to the intermediate phase and the maximum on the liquidus curve in the phase diagram. It is shown that the atomic arrangement is close packed, and similar to that of pure thallium. The influence of the interaction of unlike atoms on the structure is most pronounced at 14 at.% Bi.

Keywords: Structure factor; Bismuth; Thallium; Viscosity

1. Introduction

The purpose of this paper is to investigate the short range order of liquid binary Bi_x–Tl_{1-x} alloys in the range 10–18 at.% Bi. In this region the liquidus curve shows a maximum. In connection with the specific dependence of physical characteristics near the maximum of the liquidus curve, it is interesting to investigate the structure and its concentration and temperature dependences within this region.

2. Experimental

The chemical purity of Bi as well as of Tl was 99.99. The specimens were prepared by melting in an argon atmosphere. The specimen containers were made from pure sintered Al_2O_3 and showed no chemical reactivity with the melts.

For the X-ray diffraction experiments we used a high temperature θ–θ diffractometer with a vertical goniometer. The investigation of melts was carried out with copper radiation ($\lambda_{ka} = 1.54$ Å), which was monochromatized by a graphite crystal. Before taking measurements the liquid surface was cleaned with a special strip, fixed in a feed-through shaft in the chamber wall, in order to provide an oxide-free surface for the X-ray scattering. The intensity was measured from 0.8 to 7.8 $Å^{-1}$ with an accuracy better than ±2%. For the calculation of the Faber Ziman total structure factors the measured data were corrected to account for polarization and incoherent scattering [1]. The investigations were made at temperatures of about 5 K above the corresponding liquidus temperature and higher.

3. Results and discussion

Fig. 1 shows the structure factors $S(q)$ obtained near the liquidus temperatures for different concentrations in the range from 10 to 18 at.% Bi. All these curves have a form which is typical for close packed liquids.

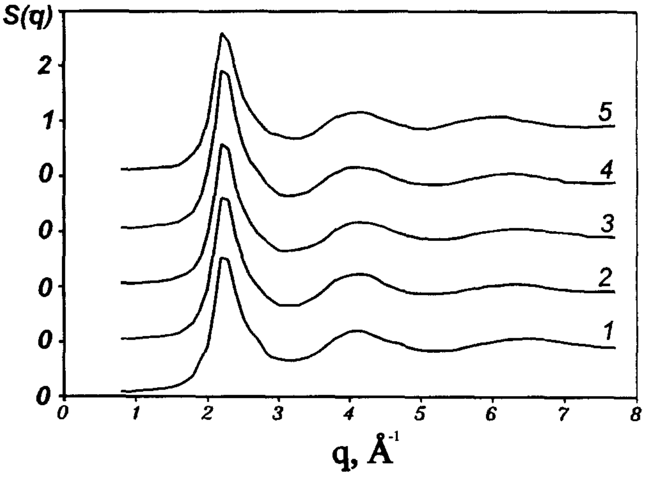

Fig. 1. The structure factors for liquid Bi–Tl alloys: 1, 10; 2, 12; 3, 14; 4, 16; 5, 18 at.% Bi.

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Their maxima show a symmetrical form, with a large height. The right q-side of the main peak does not have a pronounced shoulder located in the same region of the $S(q)$ for liquid pure Bi. Nevertheless, a small trend for its appearance near $q = 2.8\ \text{Å}^{-1}$ can be seen.

The maxima positions of pure liquid Bi and Tl are close to each other, and this shoulder is at the most distinct feature reflecting the differences between the various liquids. The second such type of parameter is the coordination number, which from our measurements is equal to 9 for Bi and 11.5 for Tl. Thus, we deal with melts which consist of components with different packings, and the corresponding chemical bondings are likely to be different too. According to the structural data and measurements of the physical properties [2,3], liquid Bi shows a mixed metallic and covalent bonding. In contrast, liquid Tl belongs to the group of liquids with metallic bonding and a close packed atomic arrangement.

It is seen from Fig. 1 that the experimental structure factors do not change their form significantly with concentration from 10 to 18 at.% Bi. Most sensitive to the addition of Bi are the third maxima. The position of the main peak of $S(q)$ is equal to $2.24\ \text{Å}^{-1}$, and this is close to that of pure Tl. When increasing the temperature from 578 to 603 and 653 K the maxima decrease their height. The position of the main peak is slightly shifted to smaller q values. The third maximum shows a larger shift compared with the first and second maxima. This means that structural changes connected with thermal disordering start to develop on the more remote coordination shell. The same features persist in the temperature dependences of the other concentrations.

The position of the main peak of $S(q)$ is plotted vs. concentration in Fig. 2(a). Increasing the Bi concentration to 18 at.% yields no significant change in the first peak position. A minor increase occurs at 16 at.% Bi, but this is not far outside the accuracy ($\pm 0.01\ \text{Å}^{-1}$) of the measurements. Therefore, this characteristic feature shows that the structure is not dependent on the concentration, and is characterized by a thallium-like atomic arrangement. As the temperature increases the almost constant value of S_1 remains up to 16 at.% and then sharply decreases.

When analysing the ratio of positions of the second and first maxima q_2/q_1 it can be seen that it is close to that of thallium and does not significantly vary within the range from 10 to 16 at.% Bi. With increasing temperature q_2/q_1 also shows a small deviation from the value of 1.84 typical for many simple metals. In Fig. 2(b) the concentration dependence of the distance r_1 of the nearest neighbours, taken from the calculated pair correlation function, is shown. For these alloys r_1 is close to the corresponding value for liquid thallium, but it increases above 14 at.% Bi, and for 18 at.% Bi its value is equal to 3.37 Å. This is very close to the corresponding distance in pure Bi (3.38 Å). In other words, within the range 10–14 at.% Bi the structure is unchanged and characterized by a thallium-like order with a close-packed atomic distribution.

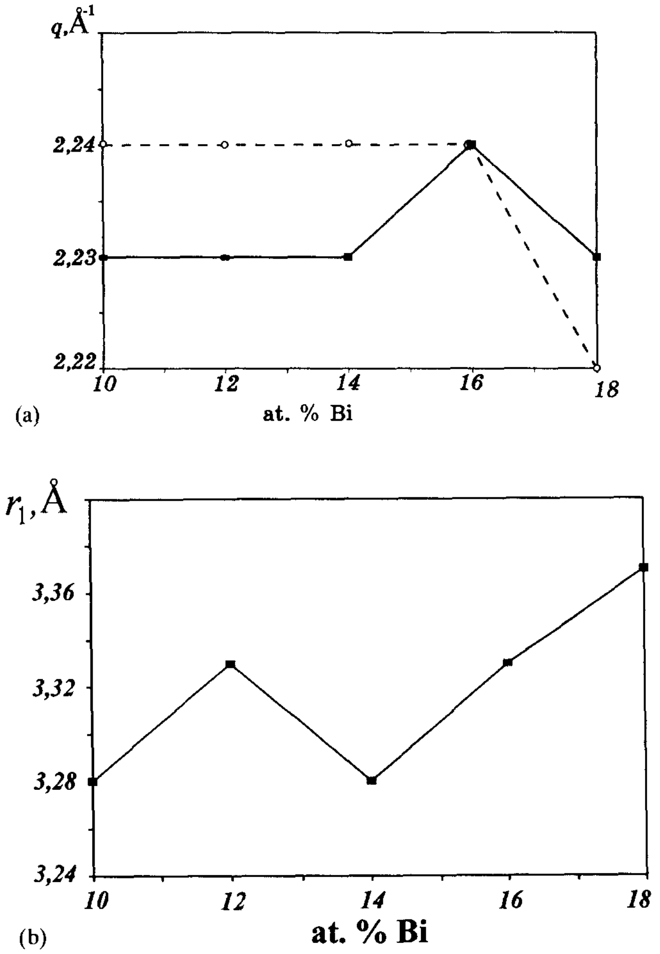

Fig. 2. Concentration dependence for the liquid Bi–Tl alloys of (a) the first maximum position of $S(q)$ at $T_{\text{melting}} + 2$ K (solid line) and $T_{\text{melting}} + 75$ K (dashed line); (b) the first coordination radius r_1 at $T_{\text{melting}} + 2$ K.

When the temperature is at 25 and 75 K above the liquidus curve, the concentration dependences of r_1 show minima at 14 at.% Bi. At this point r_1 is the same as the corresponding value for pure Tl, but near the limits of this concentration range it is close to that for pure Bi. Reduction of r_1 indicates a stronger interaction between atoms of different kinds, but this local reduction is not significant enough to provide changes in short range order and consequently in some physical properties. For example, it was mentioned in Ref. [4] that the concentration dependences of the physical properties do not show extremal points, and according to this alloys exhibiting such behaviour belong to the bertollide phases. The phase diagram in the region of 8–20 at.% Bi shows a flat maximum with a small distance between the solidus and liquidus curves, typical for phases with large homogeneity range.

The area below the first maximum of the atomic distribution function Z_{sym}, which was determined by taking twice the area of the peak in the q-region between the low q-side minimum and the maximum of this peak, is plotted vs. concentration in Fig. 3. This area better corresponds to the measured coordination number than that obtained by taking the area from the low q-side minimum to the high q-side minimum. We have also calculated the coordination number for melts with statistical distribution of atoms, which follows from

$$Z_{st} = X_{Bi}N_{Bi} + X_{Tl}N_{Tl} \qquad (1)$$

where N_{Bi} and N_{Tl} are the coordination numbers of the pure molten components. From our experiments they were equal to 11.6 and 9.0 for Tl and Bi respectively. In Fig. 3 Z_{st} is compared with experimental values in this range of concentration. As is seen from this figure, the experimental values lie below Z_{st} in the region 10–16 at.% Bi and begin to deviate from it in the opposite direction. From this dependence it can be concluded that the energy of interaction of unlike atoms is larger than for atoms of the same kind. This difference in interaction cannot change the principal features of the structure, as derived from the concentration dependence of $S(q)$. Also, it does not significantly affect the other structural parameters. It seems that the dependence of coordination number on concentration is characterized by a minimum at 14 at.% Bi. The local decrease of the atomic packing density is probably connected with a more pronounced fraction of covalent bonding. Such behaviour is not only observed near the liquidus temperature, but also at 75 K and above. Small deviations in Z as well as in r_1 do not mean that significant structural changes occur in this concentration range, but we must note that the maximum interaction of unlike atoms corresponds to 14 at.% Bi, and when compared with the phase diagram presented in Ref. [5] it appears to have slightly shifted from the maximum of the liquidus curve. Results of X-ray diffraction measurements made it possible to conclude that the structure of the intermediate phase investigated does not significantly change when the Bi concentration is less than 16 at.%. Liquid alloys with larger concentration were considered as melts with a more complex structure, consisting of clusters of Bi atoms and microdomains where atoms of different kinds are statistically distributed and only slightly ordered due to the small compound forming ability. This fact, that interaction between unlike atoms is not so strong, may be the main reason why we cannot observe the stoichiometric compounds in this range in the phase diagram; a slight ordering in the liquid state allowing substitution of atoms on the scale of short range order besides other factors is a prerequisite of the wide homogeneity range forming after crystallization.

In order to confirm the structural data we have also measured the viscosity of these liquid alloys. For other concentrations, the viscosity of these melts was already measured earlier [6,7]. It was reported that there was some hysteresis in the temperature dependence of the viscosity. Only after long time thermal treatment was the viscosity upon cooling the same as that upon heating.

In Fig. 4 the concentration dependence of the viscosity is shown. As one can see the viscosity measured upon cooling significantly differs from that obtained upon heating, especially in the range 10–12 at.% Bi. When the composition is above 14 at.% Bi the deviation between the two measurements becomes less.

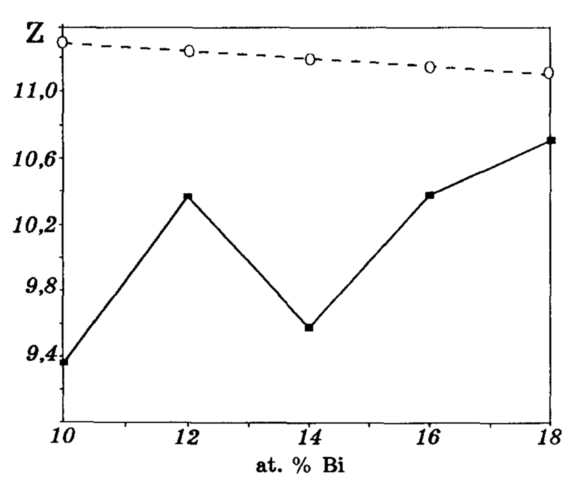

Fig. 3. Concentration dependence of the coordination number for liquid Bi–Tl alloys: experimental data, solid line; calculated data, dashed line.

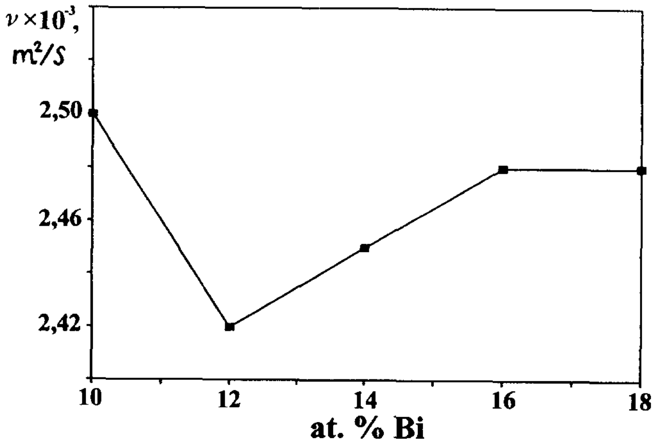

Fig. 4. Viscosity vs. composition at $T_{melting}+2$ K for liquid Bi–Tl alloys.

Taking into account that the accuracy of the viscosity measurements is ±2% and becomes better when investigating a specimen at different temperatures, one may consider the concentration dependence upon cooling as a regular curve on which no singularity is observed. Thus, we can conclude that after long treatment at higher temperatures the liquid alloys corresponding to the intermediate β' phase show the regular transformation of atomic interaction. In the case of heating the measured data show a minimum with a depth larger than the accuracy of the measurements. This minimum is close to the position of the liquidus maximum. It should be noted here that after melting the maximum of the liquidus curve is more closely connected with the chemically ordered structure in the liquid state than after thermal treatment and cooling. Probably heating to higher temperatures leads to the formation of a structure with a more random distribution of atoms. The viscosity reduction observed in the range 10–16 at.% Bi after melting may be caused by the more homogeneous atomic scale structure compared with that formed upon cooling from higher temperatures. A more realistic reason is the change of structure and interatomic interaction upon heating. This change is suggested to be a maximum at about 12 at.% Bi, and becomes less when the concentration deviates from this point. Taking these facts into account, we can conclude that the hysteresis behaviour of the viscosity, which is the result of structural changes, has a dominant influence when the interaction between unlike atoms is the largest. As is seen from Fig. 5, the temperature dependence of $S(q)$ for molten alloys containing 12 at.% Bi shows no significant change. If, however, we focus on the temperature dependence of the second coordination radius r_2, a significant increase with rising temperature is observed, and thus the suggestion of structural change is confirmed by the diffraction data.

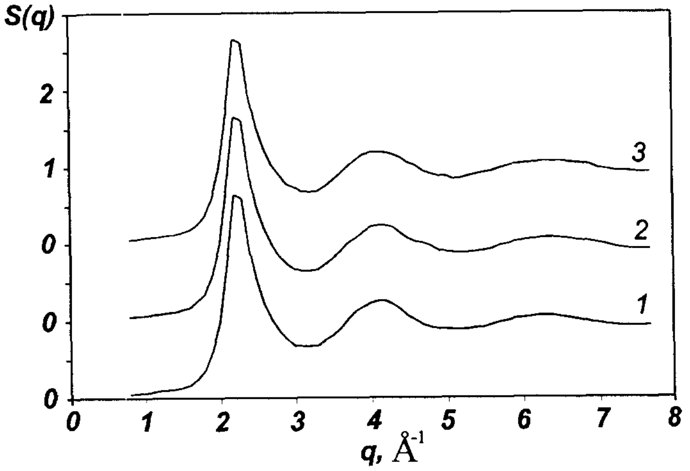

Fig. 5. The structure factors for liquid Bi–Tl alloys containing 12 at.%Bi at different temperatures (1, 578; 2, 603; 3, 653 K).

4. Conclusions

The structure of liquid Bi–Tl alloys, whose concentrations correspond to the intermediate β' phase, shows no significant changes in topology and chemistry, short range order vs. composition. The small reduction of the first coordination radius at about 14 at.% Bi indicates an increase of the interaction between unlike atoms. Hysteresis behaviour of the viscosity is most pronounced within the range 10–14 at.% Bi and is attributed to changes of the interatomic interaction with the temperature varies.

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