Fluctuations in medium-range structure of Bi-based metallic liquid alloys

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Abstract. Liquid structure of Bi50Zn50, which is situated at around the Bi-rich end of miscibility gap in Bi-Zn system, has been investigated by neutron and x-ray diffraction experiments and following analysis using reverse Monte Carlo (RMC) structural modelling. Among the partial correlations calculated from the structural model obtained by RMC, the Zn-Zn partial has a large temperature variation. It is found that there are medium-range fluctuations in Zn distribution which have a scale of 10 Å.

1. Introduction

Structural fluctuations in liquid metallic alloys consisting of polyvalent metals have been drawn attentions in liquid metal physics. Especially Bi-based liquid alloys still stimulate researchers on temperature variation of physical properties such as viscosity, sound velocity, thermodynamics and so on because some of them observed peculiar behaviour of the properties but the others claim their ways to treat liquid sample during measurements. These controversial situations may be related to large structural fluctuations existing even in miscible region [1]. We aim at revealing such structural fluctuations by diffraction measurements and following analysis using reverse Monte Carlo (RMC) structural modelling. Bi-Zn system has a miscibility gap with a critical composition of Bi18Zn82 ranging from 0 to 60 at. % Zn [2]. Earlier structural study on liquid Bi-Zn system by neutron diffraction measurements just above the coexistence curve of miscibility gap show that there are large differences in the profile of the total structure factor, $S(Q)$, between the Zn and Bi sides from the critical composition [3]. To know from microscopic viewpoint what fluctuations evolve by approaching to the two-phase region with decreasing temperature is of fundamental importance to understand a leading factor which induces phase separation in metallic liquid alloys. In this study as a first stage of our research to understand structural fluctuations in Bi-based liquid alloys, we focus on liquid Bi50Zn50 which is situated near at the Bi-rich end of miscibility gap, because reduction of partial structures is easy and under competition in extending local ordering between the constituents predominance of one type of fluctuations can be expected.

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2. Experiments

2.1. Neutron diffraction
Neutron diffraction measurements for Bi$_{50}$Zn$_{50}$ were carried out using the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan [4]. HERMES has a movable multi-detector system with 150 × 3 He detectors in each 1° interval in scattering angle. In our experiment, two angle-sets were applied to cover the scattering angle from 7.0 to 156.5° with 0.5° interval. The sample of Bi$_{50}$Zn$_{50}$ alloy was obtained by mixing pure elements of Bi and Zn in an evacuated silica tube at 800 °C and then quenched to prevent macroscopic phase separation. The sample sealed under vacuum in a cylindrical fused silica cell with dimension of 8 mm in an inner diameter and 0.5 mm in a wall thickness was located in a furnace chamber filled by He gas. The incident neutron beam was 1.125 Å in wave length which was provided by a Ge(5 5 1) monochromator. After subtraction of the contributions of the cell and the furnace background from the scattering intensity taking into account of neutron absorption by the sample and the cell, structure factors, $S_N(Q)$, of neutron diffraction were obtained over a momentum-transfer range from $Q = 0.65$ to 10.85 Å$^{-1}$ at 520, 750 and 850 °C.

2.2. X-ray diffraction
X-ray diffraction measurements for Bi$_{50}$Zn$_{50}$ were performed with a two axis diffractometer installed at BL08W in SPring-8, Sayo-gun, Hyogo, Japan [5]. Incident X-ray was 182.6 keV in energy and 0.0679 Å in wavelength. The Bi$_{50}$Zn$_{50}$ sample was shaped into a disk with 0.7 mm thickness to optimize x-ray transmission and located into a gap of quartz plates which were made from a couple of glass tube with one-end closed and polished down to 0.3mm thickness. The sample in the cell was set in a furnace chamber filled up by He gas. High temperatures from 520 to 850 °C were achieved by a nickel chrome resistance wire set in the chamber. Structure factors, $S_X(Q)$, of x-ray diffraction were obtained from $Q = 0.70$ to 24.00 Å$^{-1}$ in a momentum transfer space at 520, 600, 750 and 850 °C. For the sake of comparison, pure liquid Bi was also measured at 500 °C by using BL08W and pure liquid Zn was done at 470 °C using BL04B2 [6].

3. Results
The total structure factors of liquid Bi$_{50}$Zn$_{50}$ obtained by neutron and x-ray diffraction measurements are compared in figure 1. In $S_N(Q)$ at 520 °C, the first peak is located at 2.0 Å$^{-1}$ accompanied by a shoulder at a higher $Q$ side. This characteristic shoulder structure was observed in the earlier
work [3]. In $S^X(Q)$, the ratio of the intensity of the shoulder to the first peak is smaller than that in $S^N(Q)$. It is interesting to notice that the oscillations beyond $3.5\,\text{Å}^{-1}$ are not coincide well between $S^N(Q)$ and $S^X(Q)$. With increasing temperature, the first peak remains at $2.0\,\text{Å}^{-1}$ and the shoulder structure becomes smaller and even broader. At 850 °C, the differences between $S^N(Q)$ and $S^X(Q)$ are small compared with those at a lower temperature. The differences between $S^N(Q)$ and $S^X(Q)$ originate from the difference in the scattering abilities of x-ray and neutron beams between Bi and Zn atoms. For neutron diffraction, the coherent scattering length of Bi is 1.5 times larger than that of Zn (Bi: 8.532 fm, Zn: 5.680 fm). On the other hand, the number of electrons in the Bi atom is more than twice of Zn atoms (Bi: 83, Zn: 30). As a result, Bi-Bi correlations are emphasized in x-ray diffraction while Zn-Zn correlations are more detectable in neutron diffraction, as tabulated in table 1.

| Table 1. Weighting factors of partial structures of Bi-Bi, Bi-Zn and Zn-Zn for x-rays and neutron diffraction spectra of Bi$_{50}$Zn$_{50}$. |
|-----------------|-----------------|-----------------|
|                 | Neutron         | X-ray\((Q = 0)\) |
| Bi-Bi           | 0.360           | 0.539           |
| Bi-Zn           | 0.480           | 0.390           |
| Zn-Zn           | 0.16            | 0.07            |

Total pair distribution functions, $g^N(r)$ and $g^X(r)$, by neutron and x-ray diffractions were derived by a conventional Fourier transformation from $S^N(Q)$ and $S^X(Q)$, respectively as shown in figure 2. There are significant differences in the first peak position and profile between $g^N(r)$ and $g^X(r)$. The first peak in $g^X(r)$ at 520 °C is located at $3.3\,\text{Å}$ and slightly shifts to a shorter $r$ direction with increasing temperature. Although that in $g^X(r)$ is settled at $3.1\,\text{Å}$ at every temperature, slightly shorter than that in $g^N(r)$, the profile changes significantly from an asymmetric shape with a shoulder at a shorter $r$ side at the lowest temperature to a rather symmetric shape at the highest temperature. Taking into account the weighting factors of the partial structure shown in table 1, the shoulder structure locate at the larger $r$ side of the first peak in $g^N(r)$ is reasonably attributed to Zn-related partials while the peak at $3.3\,\text{Å}$ in $g^X(r)$ is assigned as Bi-Bi partial. The second peaks observed in a $r$ region between 6 to 8 Å shifts the peak position to a shorter $r$ direction with increasing temperature, regardless of thermal expansion [2].

4. Reverse Monte Carlo structural modelling

To approach more detailed partial structures and medium-range fluctuations in the atomic distribution of liquid Bi$_{50}$Zn$_{50}$, the reverse Monte Carlo (RMC) structural modelling [7, 8] was applied to $S^N(Q)$ and $S^X(Q)$ simultaneously. The RMC program creates an atomic configuration model in three-dimensional space reproducing the experimental structure factor and the pair correlation function. In
our modeling procedure, 5000 particles (Bi: 2500, Zn: 2500) were distributed at random in a cubic box as the initial configuration. The cube sizes were selected to give the proper number density [2] at each temperature and periodic boundary condition was applied to the simulation box. In addition, the particles are subject to a physical restriction of the cutoff distance of 2.0 Å which represents minimum distance between particles. The results of the RMC applied to x-ray and neutron diffraction data of liquid Bi$_{50}$Zn$_{50}$ are shown also in figure 1 as diagonal crosses(×) for x-ray and plus marks(+) for neutron. The neutron- and x-ray-weighted total structure factors calculated by the structural model obtained by the RMC procedure reproduce well simultaneously the experimental data of $S^N(Q)$ and $S^X(Q)$.

Partial pair distribution functions, $g_{\alpha\beta}(r)$ ($\alpha, \beta =$ Bi, Zn), calculated from the atomic configuration of the RMC model are shown in figure 3. As expected from the difference between $S^N(Q)$ and $S^X(Q)$, Zn-related partials are distributed in a shorter distance than Bi-Bi correlation. The large temperature dependence of the asymmetrical shape of the first peak in $g_{\text{Zn-Zn}}(r)$ is mainly attributed to the Zn-Zn partial correlation since $g_{\text{Zn-Zn}}(r)$ exhibits a large temperature dependence in the height of the first peak located at 2.7 Å from 4.0 at 520 °C to 2.4 at 850 °C. The Bi-Bi partial correlation shows an interesting distribution that the first peak located at 3.3 Å has a tail at a longer side decreasing gradually up to about 6 Å. The first peak of $g_{\text{Bi-Zn}}(r)$ is situated at an intermediate atomic distance between $g_{\text{Zn-Zn}}(r)$ and $g_{\text{Bi-Bi}}(r)$. The second peaks are diverged among three partials, i.e., 4 - 6 Å for $g_{\text{Zn-Zn}}(r)$, 5 - 7 Å for $g_{\text{Bi-Bi}}(r)$, and 6 - 8 Å for $g_{\text{Bi-Zn}}(r)$. The spikes seen at 2 Å in all partials are spurious by the cut off length set at 2 Å for all partial pairs.

![Figure 3](image1.png)

**Figure 3.** Partial pair distribution functions of liquid Bi$_{50}$Zn$_{50}$ obtained by reverse Monte Carlo structural modelling. Dotted blue line: Bi-Bi correlation, broken green lines: Bi-Zn correlation and solid red line: Zn-Zn correlation. As references, the pair distribution functions of pure liquid Bi and Zn are shown in the lower.

![Figure 4](image2.png)

**Figure 4.** Temperature dependence of Zn-Zn partial structure factors, $S_{\text{Zn-Zn}}(Q)$, of liquid Bi$_{50}$Zn$_{50}$ obtained by reverse Monte Carlo. Solid red line: 850 °C, broken green lines: 750 °C and dotted blue lines: 520 °C. For the sake of comparison, the structure factor of pure liquid Zn on 470 °C is depicted as black full thick line.
5. Discussion

In general, liquid alloys with miscibility gap exhibit concentration fluctuations even in much higher temperatures far from two-phase region and then increases them by approaching the coexistence curve with decreasing temperature. The present composition of Bi$_{50}$Zn$_{50}$ is far from the critical composition for the miscibility gap of around Bi$_{18}$Zn$_{82}$ in liquid Bi-Zn system, but still situated in the two-phase region. Among three partials in our RMC results, only $g_{Zn-Zn}(r)$ shows a large temperature variation. The position of the first peak in $g_{Zn-Zn}(r)$ is almost coincident with the first neighbour distribution of pure liquid Zn. However, the oscillations beyond the first neighbour in $g_{Zn-Zn}(r)$ are suppressed compared with those of pure liquid Zn where the second, the third and the fourth peaks clearly distinguished at around 4.7, 7.8 and 9.0 Å.

The corresponding partial structure factors, $S_{Zn-Zn}(Q)$, of liquid Bi$_{50}$Zn$_{50}$ are shown in figure 4 together with the structure factor of pure liquid Zn, $S_{Zn}(Q)$, at 470°C obtained by x-ray scattering. $S_{Zn}(Q)$ has a prominent but asymmetrical first peak at 2.95 Å. First peaks of $S_{Zn-Zn}(Q)$ of liquid Bi$_{50}$Zn$_{50}$ are located at a slightly lower $Q$ than that of $S_{Zn}(Q)$, accompanied by a hump at a lower $Q$ side which is remarkable at the highest temperature. There is a significant prepeak at 0.75 Å$^{-1}$ in $S_{Zn-Zn}(Q)$ of liquid Bi$_{50}$Zn$_{50}$, which originates from medium-range structural fluctuations. Zn distribution is extracted from the three-dimensional structural model of liquid Bi$_{50}$Zn$_{50}$ created by RMC as shown in figure 5. To visualize fluctuations in Zn distribution, sticks are attached to atomic pairs locating within 3.6 Å which corresponds to the first neighbouring shell. The medium-range structural fluctuations of the scale of about 10 Å can be seen in the Zn distribution.

6. Summery

Neutron and x-ray diffraction measurements of liquid Bi$_{50}$Zn$_{50}$ were performed at 520, 600, 750 and 850 °C which are all above the coexistence curve of the miscibility gap (only x-ray for 600°C). The results of RMC structural modelling simultaneously applied to the neutron and x-ray experimental data reveal that, among three partials of Zn-Zn, Bi-Zn and Zn-Zn which all contribute to the first neighbouring shell, Zn-Zn partial correlation has shortest atomic distance and exhibits a large temperature variation. The medium-range structural fluctuations of the scale of about 10 Å in Zn distribution cause the prepeak at 0.7 Å$^{-1}$ in $S_{Zn-Zn}(Q)$.

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