Structure of Molten Bi-Zn-Alloys by Means of Neutron Diffraction

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Z. Naturforsch. **38a,** 395–398 (1983); received December 15, 1982

Neutron diffraction experiments were performed with five molten Bi-Zn-alloys and the two molten elements Bi and Zn. The total structure factors and the pair correlation functions are given. The concentration dependence of the experimental nearest neighbour distances and the experimental coordination numbers is in accordance with the segregation behaviour prevailing in these melts.

1. Introduction

The constitution diagram [1] of the Bi-Zn-system as shown in Fig. 1 is very similar to that of the Al-In-system. The molten alloys of the latter system were investigated by means of X-ray wide-angle [2] and small-angle [3] scattering. Since up to now only diffraction experiments with one Bi-Zn-melt containing 30 at.-% Bi are known [4], it seemed interesting to investigate this system by means of neutron diffraction. The present paper may be seen in context with the experimental work on melts from the Sn-Zn-system [5] which show small angle scattering, thus indicating a segregation tendency which is also in agreement with the inflection point of the corresponding liquidus line. In the case of Bi-Zn a "two melt"-region exists, which should reflect a more pronounced segregation tendency.

2. Theoretical Outline

The coherently scattered intensity is described according to [6] as well as the structure factors and the pair-correlation functions. To obtain the coherently scattered intensity all the necessary corrections were applied to the measured intensity according to [5].

3. Experiments

Seven different specimens were prepared for the neutron diffraction experiments. As initial substances, Bi (99.995% (Sodipro)) and Zn (99.98% (Sodipro)) were used. The components were melted under vacuum and sealed into quartz tubes of 8 mm inner diameter and a wall thickness of 0.5 mm. The concentrations are indicated in Fig. 1, the temperature of investigation was 650 °C for all melts. To obtain thoroughly mixing of the two components, the melts were heat treated at 800 °C for 30 min before each investigation. All specimens showed a bright surface after the measurement, so that the results are not influenced by oxide layers. Neutrons with the wavelength of $\lambda = 0.691$ Å were used in the D4-instrument of ILL, Grenoble. As furnace a cylindrical tube made from vanadium foil was used. The scattered neutron intensity was recorded in the region $2° \leqq 2\theta \leqq 83°$ corresponding to $0.3\ \text{Å}^{-1} \leqq Q \leqq 12\ \text{Å}^{-1}$ in steps of $\Delta 2\theta = 0.3°$ using pulse preset, the statistical error being less than 1%.

The coherent scattering lengths as taken from [7] are: $b_{\text{Zn}} = 0.57 \cdot 10^{-12}$ cm and $b_{\text{Bi}} = 0.852 \cdot 10^{-12}$ cm. The mean number densities for 650 °C as taken from [8] are:

$$\varrho_{0,\text{Zn}} = 0.0582\ \text{atoms/Å}^3 \quad \text{and}$$
$$\varrho_{0,\text{Bi}} = 0.0276\ \text{atoms/Å}^3.$$

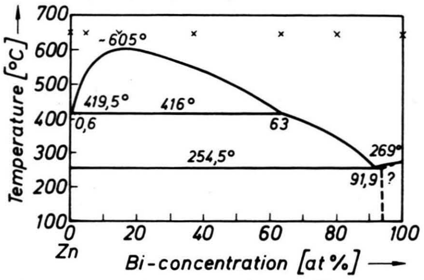

Fig. 1. Bi-Zn-System: Phase diagram according to [1]. (× = melts investigated during the present work).

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4. Results and Discussion

Figure 2 shows the total structure factors for seven melts from the Bi-Zn system. Starting from pure Bi, the position of the main maximum shows a small shift from 2.1 Å^{-1} (100% Bi) via 2.13 Å^{-1} (80% Bi), 2.20 Å^{-1} (63% Bi) to 2.30 Å^{-1} (37% Bi). More remarkable is the decrease of the intensity of the main peak. Starting from pure Zn, the position of the main maximum remains constant at 2.87 Å^{-1}. The intensity of the main peak of Bi decreases also very strongly which leads to a non resolved double peak for the structure factors with melts from 37 up to 80 at.-% Bi.

The structure factor of the pure Bi melt shows on the right hand side the shoulder well known for molten Bi. In [9] for the Bi-Zn-melt with critical composition ($c_{\mathrm{Bi}} = 0.178$) small angle scattering was observed at the temperature of 646 °C using neutrons with the wavelength 5.3 Å. Also from thermodynamical data a rise of the total structure factors $S(Q)$ towards $Q = 0$ at least for the Bi-concentrations between 5 and 37 at.-% is to be expected. Nevertheless, it was not possible during the present work to detect small angle scattering with the experimental arrangement used.

Thus, the further discussion will be merely concerned with the wide angle region of $S(Q)$. Using

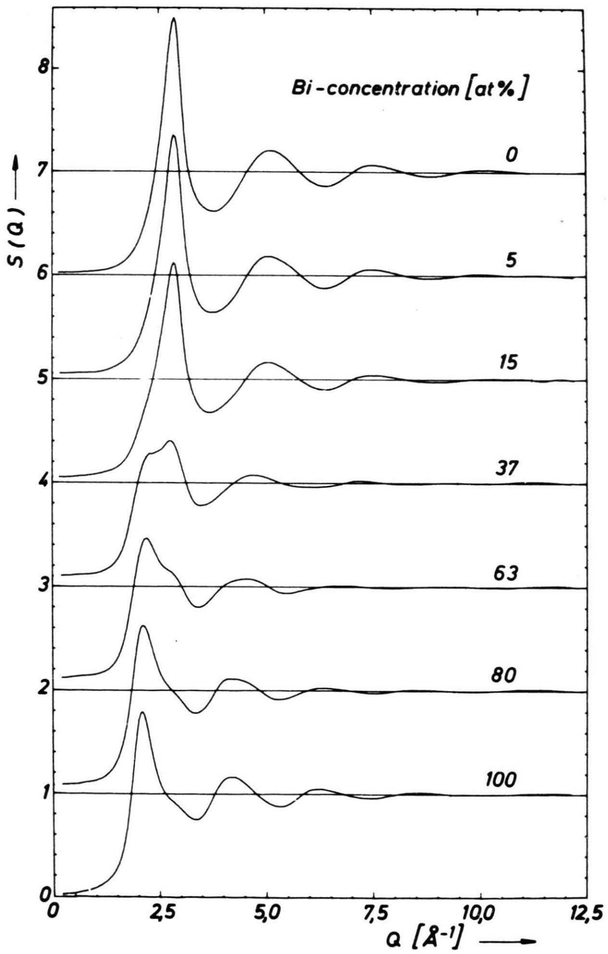

Fig. 2. Bi-Zn-system: Structure factors for 650 °C.

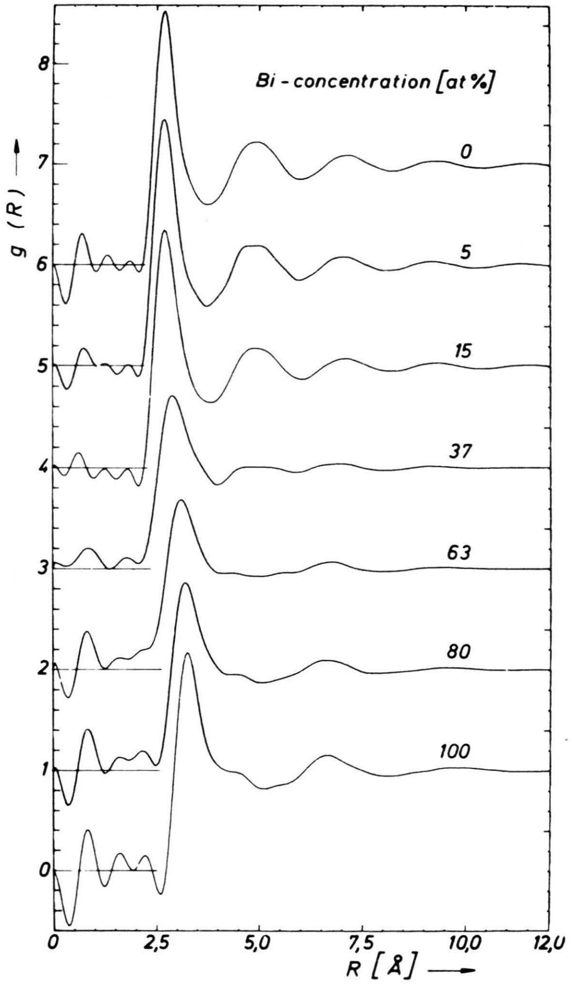

Fig. 3. Bi-Zn-system: Pair correlation functions for 650 °C.

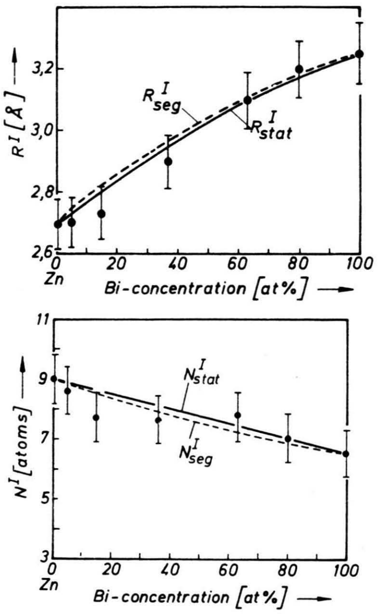

Fig. 4. Bi-Zn-system: a) Experimental nearest neighbour distance R^I, b) Experimental coordination number N^I.

the integration lengths of 11.2, 12.2, 11.25, 9.5, 9.7, 9.4, and 9.3 Å^{-1}, respectively, for the melts with Bi-concentrations of 0, 5, 15, 37, 63, 80, and 100 at.-%, respectively, the pair correlation functions $g(R)$ of Fig. 3 were obtained.

The position of the main maximum shifts continuously from the value of pure Zn (2.70 Å) to that of pure Bi (3.25 Å). In the case of the melts with 37 at.-% and 63 at.-% Bi, the oscillations beyond the main maximum are strongly damped. This feature has to be explained by the mutual extinction of the oscillations belonging to the distance correlations between the larger Bi atoms and the smaller Zn atoms, respectively, whereas the contribution of the Bi-Zn-pairs is small due to the segregation tendency. In Fig. 4, upper part, the nearest neighbour distance R^I is plotted versus the concentration.

The solid line shows the run expected for statistical distribution of both kinds of atoms as calculated according to (1):

$$R^\mathrm{I}_\mathrm{stat} = \frac{c_\mathrm{Bi}\, b_\mathrm{Bi}\, R^\mathrm{I}_\mathrm{BiBi} + c_\mathrm{Zn}\, b_\mathrm{Zn}\, R^\mathrm{I}_\mathrm{ZnZn}}{c_\mathrm{Bi}\, b_\mathrm{Bi} + c_\mathrm{Zn}\, b_\mathrm{Zn}}\,. \tag{1}$$

The dashed line corresponds to total segregation and is calculated according to (2) (see [10]):

$$R^\mathrm{I}_\mathrm{seg} = \frac{c_\mathrm{Bi}\, b^2_\mathrm{Bi}\, N^\mathrm{I}_\mathrm{Bi}\, R^\mathrm{I}_\mathrm{BiBi} + c_\mathrm{Zn}\, b^2_\mathrm{Zn}\, N^\mathrm{I}_\mathrm{Zn}\, R^\mathrm{I}_\mathrm{ZnZn}}{c_\mathrm{Bi}\, b^2_\mathrm{Bi}\, N^\mathrm{I}_\mathrm{Bi} + c_\mathrm{Zn}\, b^2_\mathrm{Zn}\, N^\mathrm{I}_\mathrm{Zn}} \tag{2}$$

with

$c_\mathrm{Bi}, c_\mathrm{Zn}$ = concentration of component Bi, Zn in atomic fractions;
$R^\mathrm{I}_\mathrm{BiBi}, R^\mathrm{I}_\mathrm{ZnZn}$ = nearest neighbour distance of pure element Bi, Zn;
$N^\mathrm{I}_\mathrm{Bi}, N^\mathrm{I}_\mathrm{Zn}$ = experimental coordination number of pure element Bi, Zn.

Table 1. Melts with segregation tendency. Main maximum position Q^I of $S(Q)$.

Shape of main peak of the molten alloys	System	Element	Q^I [Å^{-1}]	ΔQ^I [Å^{-1}]	ΔQ_rel [%]
Double peak	Bi-Cu	Cu	2.93	0.78	36
		Bi	2.15		
	Bi-Zn	Zn	2.91	0.76	35
		Bi	2.15		
	Cu-Pb	Cu	2.93	0.73	33
		Pb	2.20		
	Cu-Sb	Cu	2.93	0.68	30
		Sb	2.25		
	Sn-Zn	Zn	2.91	0.64	28
		Sn	2.27		
Single peak	Al-In	Al	2.64	0.18	7
		$Al_{0.7}In_{0.3}$	2.46		
	Al-Sn	Al	2.64	0.36	16
		$Al_{0.7}Sn_{0.3}$	2.28		
	AuCs-Cs	$Au_{0.5}Cs_{0.5}$	1.99	0.66	50
		Cs	1.33		
	Cd-Ga	Cd	2.56	0.05	2
		Ga	2.51		

Regarding the error bars, which correspond to the uncertainty in the R^{I}-determination of ± 3%, the concentration behaviour of the nearest neighbour distance R^{I} is not in contradiction with the segregation tendency of the Bi-Zn-melts.

The same stands for the concentration dependence of the total coordination number N^{I} which is shown in the lower part of Figure 4. The solid line between the value for molten Bi (6.6 atoms) and that for molten Zn (9 atoms) shows the run expected for statistical distribution of both kinds of atoms and is obtained as a straight line connecting $N^{\mathrm{I}}_{\mathrm{Zn}}$ and $N^{\mathrm{I}}_{\mathrm{Bi}}$. The dashed line corresponds to total segregation and is calculated according to Eq. (3) (see [10]):

$$N^{\mathrm{I}}_{\mathrm{seg}} = \frac{c_{\mathrm{Bi}}\, b^2_{\mathrm{Bi}}\, N^{\mathrm{I}}_{\mathrm{Bi}} + c_{\mathrm{Zn}}\, b^2_{\mathrm{Zn}}\, N^{\mathrm{I}}_{\mathrm{Zn}}}{(c_{\mathrm{Bi}}\, b_{\mathrm{Bi}} + c_{\mathrm{Zn}}\, b_{\mathrm{Zn}})^2}\,. \tag{3}$$

The structure factors of the melts Bi-Cu [11], Sn-Zn [5], Cu-Pb [12], and Cu-Sb [13] which belong also to the segregation type show a similar concentration dependence. In each case the position of the main maximum of the pure elements remains unchanged when they are alloyed with the second component but shows decreasing intensity with increasing concentration of the second component. This behaviour leads to a double headed main maximum at mean concentrations which is characteristic for these melts.

There is however another group of melts with segregation tendency, namely from the Al-In- [2], Al-Sn- [14], Au-Cs- [15] and Cd-Ga-systems [16] for which the position of the main maximum of the structure factor shifts continuously from the position obtained with element A to that obtained with element B. Table 1 shows a compilation of the Q^{I}-values of the molten components together with their absolute and relative differences. With the exception of the AuCs-Cs-system one learns that for $\Delta Q_{\mathrm{rel}} > 20\%$ the maximum of $S(Q)$ shows a double peak structure whereas for smaller differences only a single peak is observed.

Acknowledgement

Thanks are due to ILL, Grenoble for the allocation of beam time at the high flux reactor.

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