Structure Factors of Liquid Cu-Pb Alloys by Neutron Diffraction

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By means of neutron diffraction the structure factors and pair correlation functions of five Cu-Pb alloys, Cu, and Pb in the liquid state have been determined. The nearest neighbour distances have been obtained. The marked effect of small angle scattering with the melt with critical composition (65 at % Cu) is a proof for microsegregation tendency. By comparison with a segregation model for the structure factor the short range order parameter has been derived for melts with 65 and 35 at % Cu, respectively.

Experimental

In the present work pure Cu, pure Pb, and five alloys with different compositions are investigated. The specimen containers were sealed quartz tubes with 10 mm inner diameter and 0.5 mm wall thickness, surrounded by a tube made from 0.1 mm thick Vanadium foil. The height of he specimens was 45 mm. The neutron diffraction experiments were performed at Kernforschungszentrum Karlsruhe (FR 2, Project 14). The heating device was a Vanadium tube furnace in a vacuum vessel heated by direct current supplied by an electronic temperature control unit. The neutron wavelength was 0.103 nm. The scattered intensity was measured in the angle region $5^\circ \leqq 2\theta \leqq 118^\circ$ with 0.25° step scan width. The scan was started four hours after the sample had been heated up to the measuring temperature to assure thermal equilibrium. The average counting rate per position was 6000 counts. For some samples the complete scan was done twice. Thus it could be proofed that no structural change took place during the measuring time.

For correction of the measured data the Paalmann-Pings method [1], and for the normalization the Krogh-Moe method [2] were applied to obtain the structure factors. The multiple scattering correction was done corresponding to [3]. The densities were extrapolated from data given in [4]. The compositions, the densities, and the temperatures of the samples are listed in Table 1. The neutron scattering parameters are listed in Table 2.

Table 1. Compositions, temperatures, and densities of the investigated specimens.

At% Cu	Temperature [°C]	Density [g/cm³]
0	603	10.25
10	960	9.88
35	1050	9.49
65	1050	8.86
80	1170	8.38
85.3	1050	8.36
100	1120	7.90

Table 2. Neutron data for the elements Cu and Pb. b = coherent scattering length; σ_{inc} = incoherent scattering cross section; σ_{a} = absorption cross section.

	b [10^{-12} cm]	σ_{inc} [10^{-24} cm²]	σ_{a} [10^{-24} cm²]
Cu	0.76	0.47	2.12
Pb	0.94	0.0013	0.1

Results

Figure 1 shows the structure factors $S(Q)$ according to the definition:

$$S(Q) = \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(Q)/\langle b^2\rangle \tag{1}$$

where $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(Q)$ = coherent scattering intensity per atom, $\langle b^2\rangle = c_{\mathrm{Cu}} \cdot b_{\mathrm{Cu}}^2 + c_{\mathrm{Pb}} \cdot b_{\mathrm{Pb}}^2$, c = atomic fraction, b = coherent scattering length (10^{-12} cm).

The concentration dependence of the shape of the main peak of $S(Q)$ shows a double peak structure which is typical for binary alloys with microsegregation tendency, that means preference of like nearest neighbours. On alloying more and more Cu to Pb

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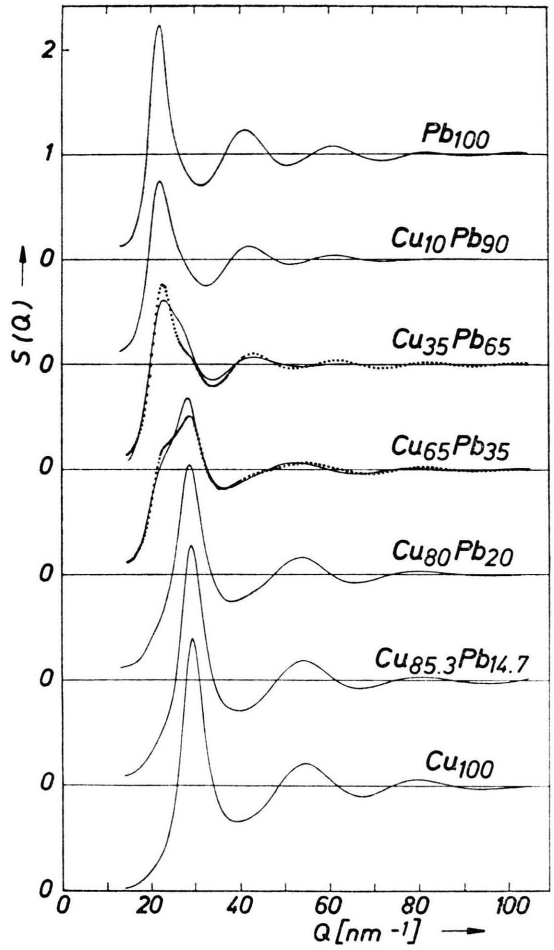

Fig. 1. Cu-Pb system: Structure factors $S(Q)$. —— experimental, ○○○○ segregation model.

up to 35 at% Cu the main maximum stays at the same position as in pure Pb, whereas the influence of Cu yields first a broadening (10 at% Cu) and then a shoulder (35 at% Cu) on the right hand side of the main peak. From 65 at% Cu up to pure Cu the main peak is at the same position as in pure Cu, whereas the Pb contribution is reflected as a shoulder (65 at% Cu) and a small bump (80 at% Cu), respectively, on the left hand side of the main peak. From this behaviour the conclusion can be drawn that within liquid Cu-Pb alloys there is a strong deviation from statistical distribution of Cu and Pb with tendency to maintain the Cu-Cu correlation and the Pb-Pb correlation as in pure Cu and pure Pb, respectively. In the case of statistical distribution of the Cu- and Pb-atoms one would rather expect a gradual shift of the main peak from the Pb side to the Cu side. The position of the main peak Q^1 is shown in Fig. 4 versus the Cu concentration.

Figure 2 shows the diffraction pattern in the low-Q region of an alloy with 65 at% Cu, that means the composition of the critical point in the phase diagram of the Cu-Pb system [6]. It shows a pronounced small angle scattering effect from which the occurence of concentration fluctuations caused by strong preference of like nearest neighbours within the $Cu_{65}Pb_{35}$ melt can be concluded.

Figure 3 shows the pair correlation functions $g(R)$ which have been obtained by Fourier transform of the structure factors according to Eq. (2):

$$g(R) = 1 + \frac{1}{2\pi^2 \varrho_0 R} \cdot \int_0^{Q_M} Q(S(Q)-1)\sin(QR)\,dQ\,, \tag{2}$$

where R = distance from a reference atom, ϱ_0 = mean atomic number density, Q_M = maximum Q value up to which $S(Q)$ has been integrated $\approx 100\,nm^{-1}$.

From the position of the main maximum of $g(R)$ the nearest neighbour distance R^1 was obtained and plotted versus the concentration in Figure 4. Also from this it can be seen that there is no gradual shift from the Pb- to the Cu-side which would correspond to statistical distribution of the Cu- and Pb-atoms. Within Pb-rich alloys the nearest neighbour distance is almost given by the corresponding distance in pure Pb, within Cu-rich alloys it is given by the distance in pure Cu, whereas within the

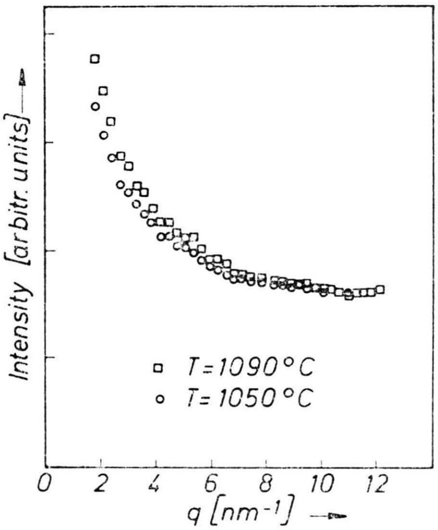

Fig. 2. $Cu_{65}Pb_{35}$: Small angle diffraction pattern [5].

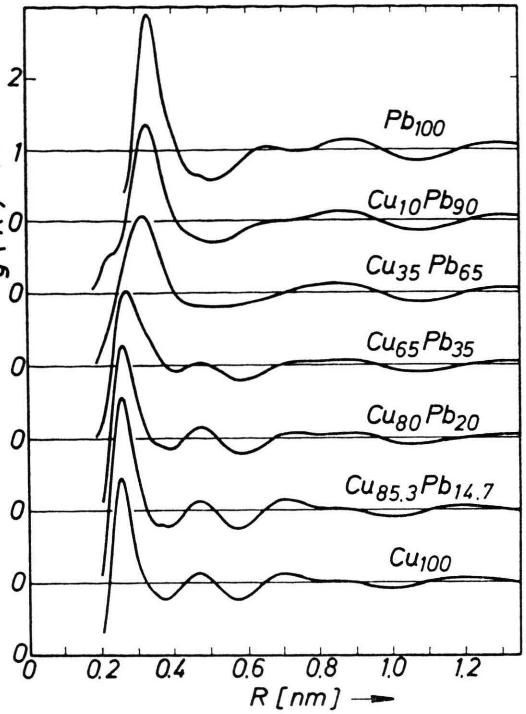

Fig. 3. Cu-Pb system: Pair correlation functions $g(R)$.

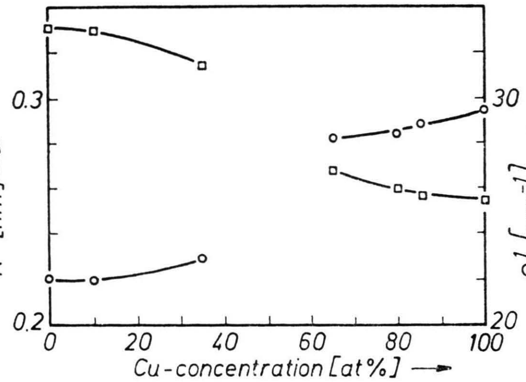

Fig. 4. Cu-Pb system: ○○○ Position Q^1 of the main peak of $S(Q)$, □□□ nearest neighbour distance R^1.

intermediate composition range there seems to occur a jump of the nearest neighbour distance.

Discussion

In the following section a comparison of the measured structure factors of two alloys in the intermediate composition range with a segregation model is made. This model is based on the fact that within Cu-Pb melts there is a marked preference of Cu-Cu and Pb-Pb correlation compared to the Cu-Pb correlation. Within this picture the alloy is treated as if it would consist of three parts:

part 1 = segregated Pb atoms; only Pb-Pb correlation,

part 2 = segregated Cu atoms; only Cu-Cu correlation,

part 3 = statistically distributed Pb and Cu atoms, that means Pb-Pb, Cu-Cu, and Cu-Pb correlation.

Part 1 is now described by the measured structure factor of pure Pb, $S(Q)_{\mathrm{Pb}}$, and part 2 by the structure factor of pure Cu, $S(Q)_{\mathrm{Cu}}$. Part 3 is described by the so called Ashcroft-Langreth structure factor $S(Q)_{\mathrm{HS}}$ [7]. $S(Q)_{\mathrm{HS}}$ is a hard sphere model structure factor which can be calculated for the case of statistical distribution of two kinds of hard sphere atoms with different size. With these three structure factors the total model structure factor is given according to (3)

$$S(Q)_{\mathrm{M}} = (\alpha\, c_{\mathrm{Pb}}\, b_{\mathrm{Pb}}^2\, S(Q)_{\mathrm{Pb}} + \alpha\, c_{\mathrm{Cu}}\, b_{\mathrm{Cu}}^2\, S(Q)_{\mathrm{Cu}} + (1-\alpha)\,\langle b^2\rangle S(Q)_{\mathrm{HS}})/W\,, \qquad (3)$$

$$W = \alpha\, c_{\mathrm{Pb}}\, b_{\mathrm{Pb}}^2 + \alpha\, c_{\mathrm{Cu}}\, b_{\mathrm{Cu}}^2 + (1-\alpha)\,\langle b^2\rangle = \langle b^2\rangle\,.$$

α is the segregation parameter which is a measure for the degree of microsegregation, that means the deviation from statistical atomic distribution.

For the case $\alpha = 1$ one obtains totally segregated Pb- and Cu-melts, whereas for the case $\alpha = 0$ the Pb- and Cu-atoms would be distributed statistically.

Here the value of α is assumed to be equal for Pb as well as for Cu. Therefore the composition of the statistical part 3 is the same as that of the whole melt.

For the calculation of $S(Q)_{\mathrm{HS}}$ we used as hard sphere diameters 0.302 nm for Pb and 0.226 nm for Cu, because these values yield the best fit of the experimental structure factors of molten Pb and molten Cu, respectively, with calculated hard sphere structure factors.

For two concentrations with 65 at% Cu and 35 at% Cu the model structure factors $S_{\mathrm{M}}(Q)$ were calculated which yielded, by varying the parameter α, the best fit to the corresponding experimental structure factor (minimum mean square deviation within the entire Q-range). By this method we obtained for the segregation parameter α:

$\alpha = 0.58$ for $\mathrm{Cu_{65}Pb_{35}}$,

$\alpha = 0.46$ for $\mathrm{Cu_{35}Pb_{65}}$.

This means that the tendency for microsegregation in Cu-Pb melts is stronger in a melt with critical composition (65 at% Cu) than in a melt off this composition (35 at% Cu). The corresponding model curves are shown in Fig. 1 as dotted lines. One can see that this simple model is able to describe the qualitative features of the measured curves, i. e. a maximum at the Q-value where the predominant component has its maximum in the pure liquid state and a shoulder at the Q-value where the minor component has its maximum in the pure liquid state.

In the following it will be shown that the parameter α is identical with the Cowley short range order parameter α^c [8]. In the case of Cu-Pb, α^c is defined according to Eq. (4) by

$$\alpha^c = 1 - \frac{Z_{\mathrm{PbCu}}}{c_{\mathrm{Cu}}\, Z}\,, \tag{4}$$

where

Z_{PbCu} = average number of nearest Cu-neighbours surrounding a central Pb atom,

Z = average total number of nearest neighbours surrounding a central Pb atom or a central Cu atom, respectively.

For the case of preference of like nearest neighbours α^c becomes positive.

Within the picture of the segregation model introduced above the average number Z_{PbCu} of Cu atoms surrounding a Pb atom is a mean value of those numbers which are present in part 1, part 2, and part 3, respectively:

$$Z_{\mathrm{PbCu}} = \alpha\, Z_{\mathrm{PbCu}}^{\mathrm{part\,1}} + \alpha\, Z_{\mathrm{PbCu}}^{\mathrm{part\,2}} + (1-\alpha)\, Z_{\mathrm{PbCu}}^{\mathrm{part\,3}}\,. \tag{5}$$

As there is no Cu-Pb correlation in the segregated parts 1 and 2, the first two terms of (5) are zero. In part 3 the Pb- and the Cu-atoms are distributed statistically, so one can write

$$Z_{\mathrm{PbCu}}^{\mathrm{part\,3}} = c_{\mathrm{Cu}}\, Z^{\mathrm{part\,3}}\,, \tag{6}$$

where

$Z^{\mathrm{part\,3}}$ = average total number of nearest neighbours in part 3.

As the coordination number in molten Cu and in molten Pb are nearly equal, one can set

$$Z^{\mathrm{part\,1}} \approx Z^{\mathrm{part\,2}} \approx Z^{\mathrm{part\,3}} \approx Z$$

and obtains with (5) and (6)

$$Z_{\mathrm{PbCu}} = (1-\alpha) \cdot c_{\mathrm{Cu}} \cdot Z\,. \tag{7}$$

Comparison of (7) with (4) shows that the segregation parameter α introduced in the present study has the same meaning as the Cowley short range order parameter α^c for the case of preference of like nearest neighbours.

Acknowledgement

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