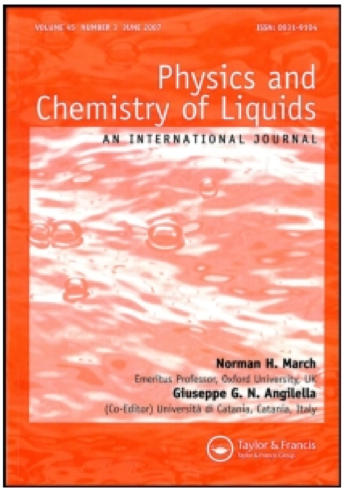

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Quantitative Evaluation of the Structure of Bi-Cu-Melts and Some of Their Properties

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A method for determining the concentration of segregated regions in molten binary alloys is given. The melt consists of a matrix containing both kinds of atoms in statistical distribution and, furthermore, two kinds of inhomogeneities, one kind containing only Cu and the other kind only Bi atoms.

The method is applied to Bi-Cu melts. It is found that nearly all of the inhomogeneities consist of Cu atoms only. The volume concentration of these inhomogeneities within the melt depends on the initial composition of the melt and varies between 10 and 25 volume percent.

From the temperature dependency of the coherent scattering cross section, it follows that the diameter of inhomogeneities remains constant during an increase in temperature of 300°C. The concentration of inhomogeneities, however, is reduced to 50% of the original value. The determination of the derivative of thermodynamic activity with respect to the concentration obtained from scattering experiments shows qualitative agreement with the corresponding values determined directly by thermodynamic measurement.

The mean lifetime of segregated zones can be estimated to be on the order of approximately 10^{-11} sec. Other physical data which were determined with Bi-Cu melts are discussed with regard to the structure of these melts.

1 INTRODUCTION

Starting from the preceding papers Ref.[1,2] in which the scattering of neutrons with different primary energies was studied on molten Bi-Cu alloys for $\kappa > 1.0$ Å^{-1} and $\kappa < 1.5$ Å^{-1}, respectively, a quantitative model for the structure of these melts will be developed in the present work.

Accordingly, as a continuation of Ref.[3], a quantitative method of evaluation is presented which allows calculation of the concentration of segregated regions within these melts from the zero scattering angle intensities. Furthermore, thermodynamic data will be obtained from these intensities.

† Part of the thesis work of W. Zaiss, University of Stuttgart, 1975.

2 DETERMINATION OF THE VOLUME CONCENTRATION OF INHOMOGENEITIES IN SEGREGATED MELTS

The existence of segregated regions or of inhomogeneities in melts is to be understood as follows: at certain points within the melt there appear momentary deviations from the mean concentration (concentration fluctuations). In the following, these regions, each of which contains only atoms of one kind, shall be called "particle".

2.1. Method of evaluation

In Ref.[1] it was shown that molten Bi-Cu alloys show a tendency to segregation which leads to the scattering at small κ-values described in Ref.[2]. This effect can be explained by assuming that the melt contains particles with scattering length density η_p and concentration w_p homogeneously distributed within a matrix with scattering length density η_m and concentration $(1 - w_p)$.

According to Ref.[2], the macroscopic scattering cross section $\frac{d\Sigma}{d\Omega}$ in the direction of the primary beam is

$$\frac{d\Sigma}{d\Omega} = \bar{\rho}_0 \frac{d\sigma(0)}{d\Omega}\bigg|_{COH} = w_p(1 - w_p)(\eta_m - \eta_p)^2 \cdot V_p \tag{1}$$

with ρ_0 = mean number density of the alloy

$\left.\frac{d\sigma(0)}{d\Omega}\right/_{COH}$ = differential scattering cross section for coherent scattering at $\kappa = 0$

w_p = volume concentration of particles

V_p = volume of one particle $= \frac{4\pi}{3} R_p^3$

R_p = radius of one particle

Thus, w_p can be determined from Eq. (1) if the difference $\Delta\eta$ of scattering length density of matrix and of particle is known.

The term

$$(\Delta\eta)^2 = (\eta_m - \eta_p)^2 \tag{2}$$

shall be calculated for a model in the following. Similar considerations were presented in Ref.[3] for the evaluation of small angle X-ray scattering experiments.

The following possibilities exist for the structure of molten alloys with a tendency to segregation:

(a) Particles only of atoms of kind A. Matrix only of atoms of kind B or vice versa.

(b) Particles only of atoms of kind A and particles only of atoms of kind B Matrix of atoms of kinds A and B.

(c) Particles only of atoms of kind B. Matrix of atoms of kinds A and B.
(d) Particles only of atoms of kind A. Matrix of atoms of kinds A and B.

In the following these four possibilities will be treated:
(a) This case corresponds to total segregation and is to be excluded on the basis of the results described in Ref.[1].
(b) This is the most common case, for which the term $(\Delta\eta)^2$ shall now be determined. The following designations will be needed:

w_m = volume fraction of the matrix
w_{A_p}, w_{B_p} = volume fraction of particles consisting of atoms of kind A or B, respectively
w_{A_m}, w_{B_m} = volume fraction of kind A or kind B in the matrix
w_A, w_B = volume fraction of kind A or kind B

In every case, the volume fraction refers to the total melt.

In general, the following relations hold:

$$w_m + w_p = 1 \tag{3}$$

$$w_{A_p} + w_{B_p} = w_p \tag{4}$$

$$w_{A_m} + w_{B_m} = w_m \tag{5}$$

$$w_A + w_B = 1 \tag{6}$$

$$w_{A_p} + w_{A_m} = w_A \tag{7}$$

$$w_{B_p} + w_{B_m} = w_B \tag{8}$$

The scattering length density of the matrix can be calculated using Eq. (9):

$$\eta_m = \frac{1}{w_m}(w_{A_m} \cdot \eta_A + w_{B_m} \cdot \eta_B) \tag{9}$$

with $\eta_A = \rho_A b_A$ and $\eta_B = \rho_B \cdot b_B$, the scattering length densities of the pure elements. ρ_A and ρ_B are the mean number densities of kinds A and B. Particles consisting of atoms of kind A only show a difference $\Delta\eta_A$ in scattering length density compared with that of the matrix η_m:

$$\Delta\eta_A = \eta_A - \eta_m \tag{10}$$

The same holds for kind B

$$\Delta\eta_B = \eta_B - \eta_m \tag{11}$$

For Eqs. (10) and (11) the assumption is made that the scattering length density for one kind of atom is the same within the matrix and within the particles.

The scattered intensity of the single particles is in each case proportional to the squares of $\Delta\eta_A$ or $\Delta\eta_B$. Since these intensities may be added in accordance with the number of particles in dilute systems, the total scattered intensity is proportional to the weighted sum of the squares of scattering length densities:

$$(\Delta\eta)^2 = \frac{1}{w_p}\left[w_{A_p}(\Delta\eta_A)^2 + w_{B_p}(\Delta\eta_B)^2\right] \tag{12}$$

From Eqn. (3) to (9) as well as (10) and (11) it follows together with Eqn. (12):

$$(\Delta\eta)^2 w_p(1 - w_p) = (\eta_A - \eta_B)^2\left[\frac{w_{A_p}}{(1 - w_p)}(w_B - w_{B_p})^2 + \frac{w_{B_p}}{(1 - w_p)}(w_A - w_{A_p})^2\right] \tag{13}$$

Thus, an equation is obtained with three unknowns w_p, w_{A_p}, and w_{B_p}, which can be reduced together with Eq. (4) to two unknowns, w_p and w_{A_p}, for example. Eq. (13) then becomes quadratic in w_p as well as in w_{A_p}. Thus, one variable can be obtained for each case from the other.

For cases (c) and (d), w_p is determined from Eq. (13) to be:

(c) Only particles containing atoms of kind B, i.e. $w_{A_p} = 0$, $w_p = w_{B_p}$.

$$w_p = \frac{1}{1 + (w_A^2/K)} \tag{14}$$

with

$$K = \frac{d\Sigma/d\Omega}{V_p(\eta_A - \eta_B)^2} \tag{15}$$

(d) Only particles containing atoms of kind A, i.e. $w_{B_p} = 0$, $w_p = w_{A_p}$

$$w_p = \frac{1}{1 + (w_B^2/K)} \tag{16}$$

For K see Eq. (15).

2.2 Application of the method of evaluation to molten Bi-Cu alloys

The most common case (b) will be applied to the Bi-Cu melts. This means that the melts consist of a matrix with Cu atoms and Bi atoms in a statistical distribution and two kinds of particles which contain either Cu atoms or Bi atoms. Then, Eq. (13) yields together with Eqs. (1) and (4):

$$K(1 - w_p) = w_{Cu_p}(w_{Bi} - w_p + w_{Cu_p})^2 + (w_p - w_{Cu_p})(w_{Cu} - w_{Cu_p})^2 \tag{17}$$

where K is given by Eq. (15')

$$K = \frac{d\Sigma/d\Omega}{V_p(\eta_{Cu} - \eta_{Bi})^2} \tag{15'}$$

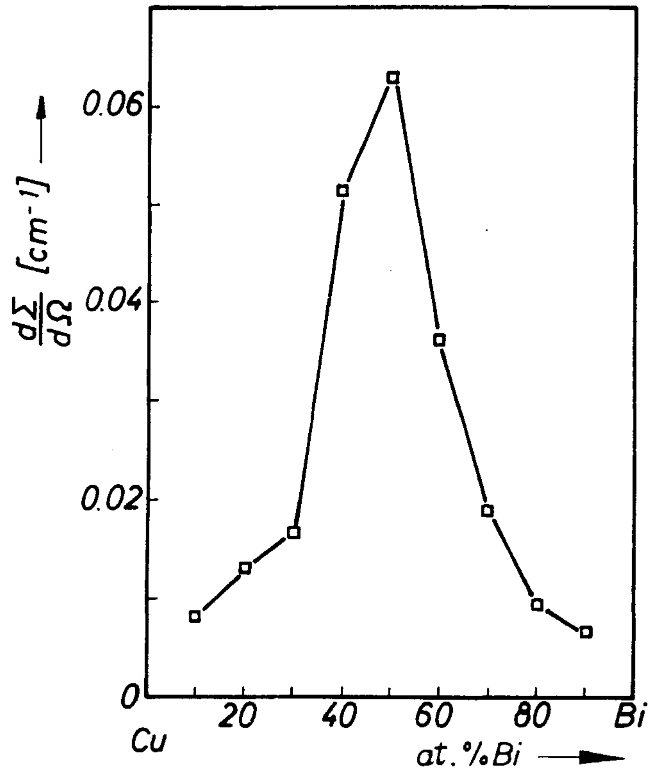

FIGURE 1 Macroscopic scattering cross section from Ref.[2].

In Fig. 1 the macroscopic scattering cross section in the direction of the primary beam $\frac{d\Sigma}{d\Omega}$ is plotted versus the Bi concentration for the data obtained in Ref.[2]. From this plot and from the data for V_p and the values of scattering length densities given in Ref.[3] for an alloy containing 50 at.% Bi, the connection between w_{Cu_p} and w_p was calculated and is plotted in Fig. 2.

The ordinate represents the volume fraction of Cu particles w_{Cu_p}, the abscissa the total particle concentration w_p. A parabolic curve is obtained. The dashed straight line $w_{Cu_p} = w_p$ represents the case in which only particles of Cu atoms exist within a matrix of Cu and Bi atoms (compare case (d)). Apparently, for this case this melt would contain 20.85 vol. % of particles which contain Cu atoms only.

The region of validity of the variable w_p is limited by the two relationships

(18) and (19), respectively:

$$w_{Cu_p} \leq w_p < w_{Cu} \tag{18}$$

$$w_{Bi_p} \leq w_p < w_{Bi} \tag{19}$$

The case of total segregation is excluded by the right hand part of the inequations. The left part leads to the cases (c) and (d).

The two regions of the curve in Fig. 2 which have physical meaning according to conditions (18) and (19) are especially marked. The region defined by the latter condition lies at a particle concentration $w_{Bi_p} = w_p$ of about 70 vol. %. Since the method applied is based on the assumption of a dilute system, the case (c) can thus be excluded.

The region of the function $w_{Cu_p}(w_p)$ described by condition (18) is presented in Fig. 3 for different molten alloys. It is remarkable that the concentration of Cu particles is changed only very slightly with increasing particle concentration w_p and also that the fraction of Bi particles is rather small. As shown in Fig. 3, for a given particle concentration w_p the concentration w_{Cu_p} and also the concentration w_{Bi_p} can be determined immediately using the relationship $w_p = w_{Cu_p} + w_{Bi_p}$.

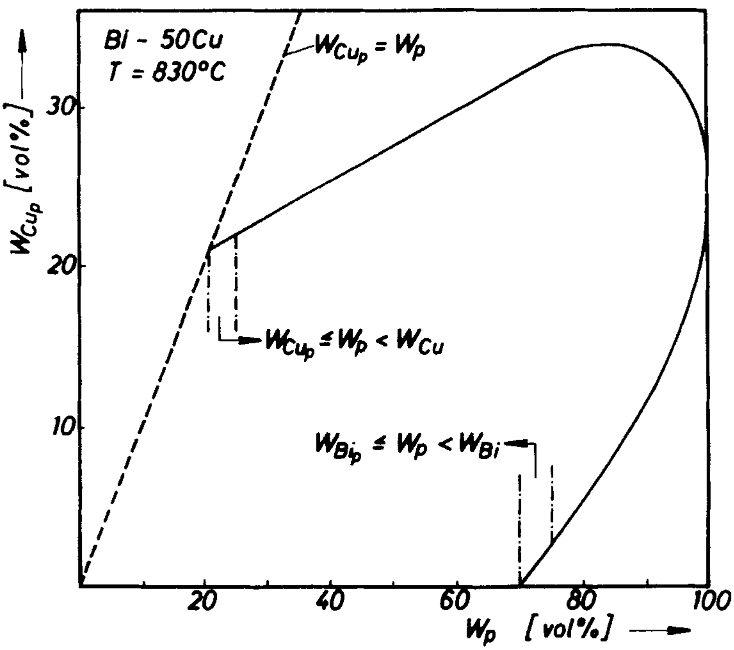

FIGURE 2 Concentration of Cu particles w_{Cu_p} versus total concentration of particles w_p.

In Fig. 4 the concentrations of Bi particles w_{Bi_p} and Cu particles w_{Cu_p} are plotted versus the alloy concentration. Together with Fig. 3, Fig. 4 may be discussed in the following way. In the region defined by condition (18) with an alloy containing 50 at % Cu, for example, w_p increases from 21 to 25 vol.%. Regarding the two possible kinds of particles this means that the Cu particle concentration is between 21 and 22 vol. % and that of Bi particles between 0 and 3%. On the basis of the total number of particles present within the melt this means that approximately 75% are Cu particles with a maximum of 25% being Bi particles. Regarding case (d) – only Cu particles within a Bi-Cu matrix – then of the total amount of Cu within the molten 50 Cu-50 Bi alloy 84 vol. % are within the particles and 16 vol. % within the matrix.

2.3 Temperature dependency of the volume fraction of inhomogeneities

As stated in Ref.[2], the particle diameter is nearly independent of the temperature. Furthermore, it was shown in Ref.[2] that the scattering cross section for zero scattering angle decreases with increasing temperature. This can be

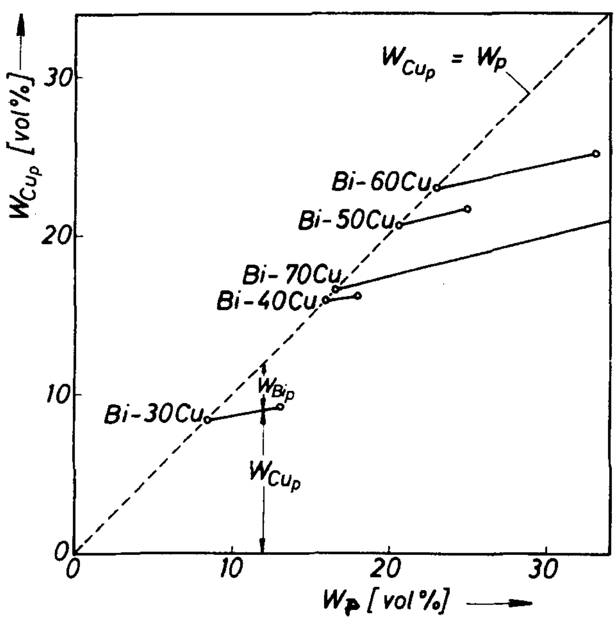

FIGURE 3 Possible concentration of Cu particles in the region $w_{Cu_p} \leq w_p < w_{Cu}$.

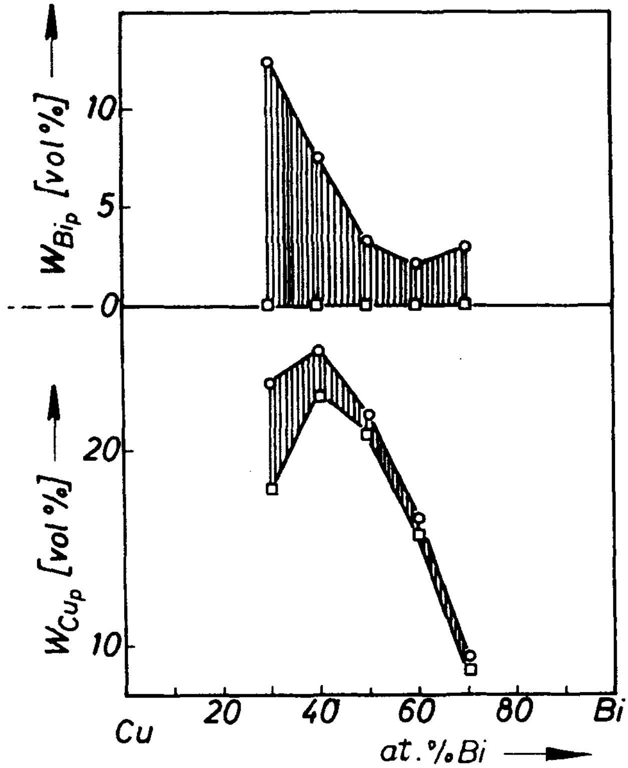

FIGURE 4 Concentration of particles

□ $\begin{cases} w_{Cu_p} = w_p \\ w_{Bi_p} = 0 \end{cases}$ ○ $\begin{Bmatrix} w_{Cu_p} \\ w_{Bi_p} \end{Bmatrix}$ for $w_p = w_{Cu}$

explained by the fact that the volume fraction of particles in the melt decreases. For case (d) – only Cu particles within a Bi-Cu matrix – the concentration w_{Cu_p} for the alloys with 40 and 50 at % Cu, respectively, was calculated for different temperatures using Eq. (16) and is presented in Fig. 5. The temperature dependency can be described in both cases by a linear relationship. Increasing the temperature by 300°C, the particle concentration within the melt is reduced by 50 at %. The decrease in particle concentration is faster for the alloy with 50 at % Bi.

Linear extrapolation of both straight lines in Fig. 5 leads to a value of 1400°C for the temperature where the Cu particles have vanished. This qualitative result is in agreement with the fact deduced in Ref.[2] that at these temperatures the concentration fluctuations are reduced to a large extent.

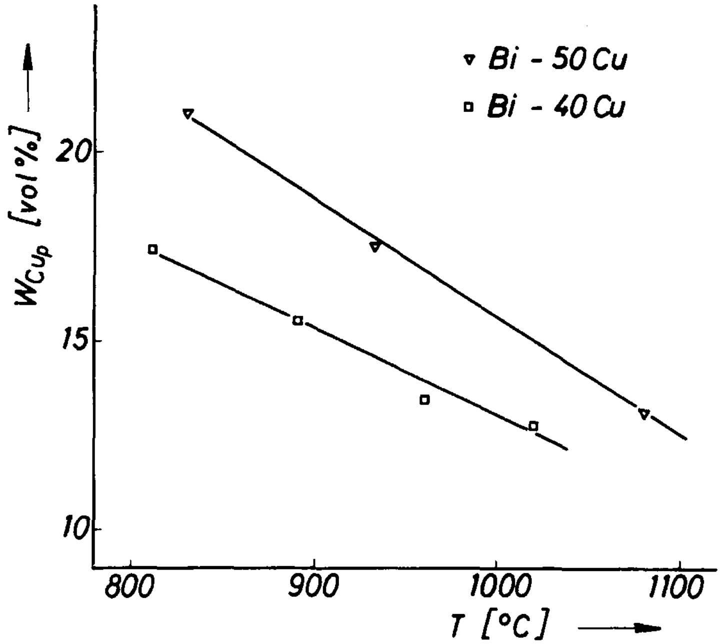

FIGURE 5 Temperature dependency of concentration of Cu particles.

3 DETERMINATION OF THERMODYNAMIC DATA FROM SCATTERING DATA

Having measured the scattering cross section in the direction of the primary beam, these data can be used to derive thermodynamic data, i.e., isothermal compressibility or the derivative of the chemical potential with respect to the concentration of one component[4]. The scattering cross section for neutron scattering is directly related to the derivative of thermodynamic activity a_i with respect to the concentration through the concentration fluctuations. For the macroscopic scattering cross section in the primary-beam direction, it follows from Ref.[4,2] that:

$$\frac{d\Sigma}{d\Omega} = \rho_0 \frac{d\sigma(0)}{d\Omega}\bigg|_{COH} = F\left[\frac{c_1}{a_1}\left(\frac{\partial a_1}{\partial c_1}\right)_{T,P}\right]^{-1} \tag{20}$$

with

$$F = \left(\frac{\rho_0}{\rho_1 \rho_2}\right)^2 c_1 c_2 (\eta_1 - \eta_2)^2$$

and ρ_1, ρ_2 = partial atomic density of component 1 or 2, P = pressure. The

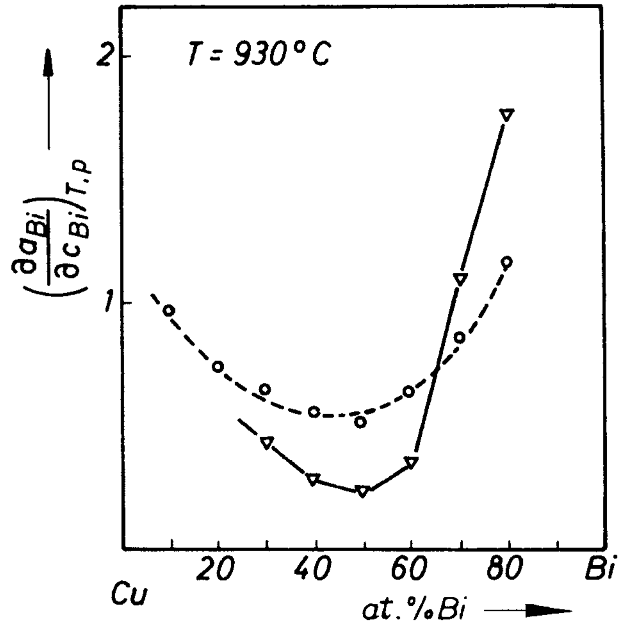

FIGURE 6 Derivative of partial activity of Bi with respect to the concentration.
○ from thermodynamic data in Ref.[7].
△ from scattering data.

term $\left(\frac{\partial a_1}{\partial c_1}\right)_{T,P}$ can be calculated from the results of the scattering experiment described in Ref.[2]. For the Bi-Cu system, the values of partial activities needed for Bi as well as for Cu were taken from Ref.[5] for T = 930 °C at concentrations of zero up to 80 at % Cu. The partial atomic densities for the same temperature were taken from Ref.[6].

The derivative of the activity with respect to the concentration was calculated directly from Eq. (20) on the one hand and determined by graphical differentiation of the partial activity of Bi with respect to the Bi concentration on the other. Figure 6 shows the derivative of the partial activity of Bi with respect to the concentration for T = 930 °C versus the Bi concentration. The curves obtained from both methods show qualitatively the same shape, with a minimum at a concentration of 50 at. % Bi and an increase towards the pure components.

4 LIFETIME OF INHOMOGENEITIES IN SEGREGATED MELTS

In Ref.[2] the shape and magnitude of the particles which exist in molten Bi-Cu alloys were deduced. In this section, some considerations concerning the mean lifetime of these concentration fluctuations shall be presented.

According to Alpert[7], the concentration fluctuations which exist in such binary mixtures decay according to the time law

$$Z(t) \approx \exp\left[-\frac{t}{\tau}\right] \tag{21}$$

From dimensional considerations, Landau and Lifschitz[8] obtained a qualitative estimation for the mean lifetime:

$$\tau \approx \frac{\xi^2}{\overline{D}} \tag{22}$$

τ is the time in which, in a region of dimension ξ, the differences in concentration are eliminated; $\overline{D}$ is the mean diffusion coefficient needed for this purpose. Assuming the following data:

$\overline{D} = 5.10^{-5}$ cm²/sec and $\xi = 3$ Å (according to Ref.[2]) we obtain $\tau = 2.10^{-11}$ sec from eq. (22).

For the Bi-Zn system Egelstaff and Wignall[4] also determined the mean lifetime of concentration fluctuations and obtained for a mean dimension $\xi = 10$ Å $\tau > 5.10^{-11}$ sec, which is in agreement with the mean lifetime obtained during the present work for molten Bi-Cu alloys.

5 COMPARISON OF THE RESULTS OBTAINED FROM SCATTERING DATA WITH OTHER PHYSICAL PROPERTIES OF THE Bi-Cu SYSTEM

Since by scattering neutrons with different primary energy[1,2] it could be shown that inhomogeneities exist in molten Bi-Cu alloys, some further physical properties of these melts shall be discussed in this chapter.

5.1 Density

Gomez *et al.*[6] measured the density of molten Bi-Cu alloys over the whole concentration range. By plotting an isotherm of specific volume versus concentration for the temperature of 1100° C, they obtained negative excess volumes. The maximum deviation amounted to 4.6% with an alloy containing 60 at % Cu. According to Sauerwald[9], systems with negative excess volumes show a tendency to segregation in the molten state.

5.2 Activity

As mentioned above, measurements of the thermodynamic activity were made[5] on molten Bi-Cu alloys at a temperature of 930° C. The activities show positive deviations from Raoult's law, giving a limit of the tendency to segregation in Bi-Cu melts. It should be mentioned in this connection that the heats of mixing in this system are positive and can be up to 1460 cal/(g.atom) (see Ref.[10]).

5.3 Compressibility

From the ultrasonic measurements in Ref.[11] made on molten Bi-Cu alloys, the isothermal compressibility was obtained as a function of the Bi concentration and showed a rather large negative deviation from Raoult's law. This fact was explained by the existence of inhomogeneities consisting mainly of Cu atoms within these melts. Similar conclusions follow from the partial structure factors also calculated for scattering angle zero in Ref.[11]. This is in accordance with the results obtained from scattering experiments at $\kappa = 0$ in Ref.[2].

5.4 Magnetic susceptibility

Takeuchi *et al.*[12] observed a linear relationship between magnetic susceptibility and concentration. The calculation of the magnetic susceptibility of the melts from the diamagnetic susceptibility of monovalent Cu regions and pentavalent Bi ions as well as from the paramagnetic susceptibility of the electron gas is in good accordance with the experiment. Further measurements of the magnetic susceptibility made on molten binary alloys with which scattering experiments in the region of small momentum transfer had also been done are not known from the literature.

Acknowledgements

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