PHYSICAL CHEMISTRY

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Abstract

Full Text

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INVESTIGATION OF THE STRUCTURE OF LIQUID Bi–Sn ALLOYS

The properties of liquid alloys are determined mainly by the strength of intermolecular bonds and by the mutual arrangement of molecules governed by it. It is therefore important to establish experimentally the structure of liquid alloys and to find at least a qualitative connection between the structure of an alloy and its properties.

If a liquid consists of several kinds of atoms, then the radial distribution curve can be calculated from the following equation (^{1}):

$$4\pi r^2 \rho(r) = 4\pi r^2 \sum_{a=1}^{p} m_a k_a \rho_a(r) =$$

$$= 4\pi r^2 \left(\sum_{a=1}^{p} m_a k_a^2 \right)^2 V_m^{-1} + \sum_{a=1}^{p} m_a k_a^2 \frac{2r}{\pi} \int_0^\infty S \left(\frac{I_n}{\sum_{a=1}^{p} m_a f_a^2(S)} - 1 \right) \sin rs \, ds. \quad (1)$$

For the investigation of the Bi–Sn system we had at our disposal an EM-4 electron-diffraction instrument, which had to be adapted for operation at high temperatures. For this purpose a special specimen holder was made (Fig. 1). The heating element was a strip of tantalum sheet, which, by means of special clamps 1 and porcelain insulators 2, was attached to a metal base 3. This device was inserted into the stage of the electron-diffraction instrument and could perform all the necessary movements. Current was supplied to the heater through clamps 1, which were connected by flexible leads 4 to the side socket available on the EM-4 electron-diffraction instrument.

Fig. 1. Specimen holder

The method of free metal films proposed by A. I. Bublik and B. Ya. Pines (2) did not give encouraging results. The best results were achieved when the film of free metal was strengthened with the thinnest layers of quartz.

The specimens were prepared as follows: a thin layer of polystyrene was deposited on a slide, and then, on a VUP-4 apparatus, quartz, a layer of metal, and again a layer of quartz were successively evaporated. The evaporation was calculated so that the thickness of the quartz layer did not exceed $1 \div 2 \cdot 10^{-7}$ cm, and that of the metal layer $30 \div 40 \cdot 10^{-7}$ cm. The films were separated by dissolving the polystyrene in a mixture of benzene with dichloroethane.

The photographs were taken at $t = 290^{\circ}$. From the photographs obtained, the curve of the experimental intensity for the given alloy was constructed in the usual way (3). Since the Bi and Sn atoms are sufficiently heavy, the correction for

We neglected incoherent scattering. The intensity curves were normalized by comparing the areas under the curves $I(S)S^2$ and

$$\left(\sum_{a=1}^{p} f_a^2(S) m_a \right) S^2.$$

Here

$$\sum_{a=1}^{p} f_a^2(S) m_a = C_1 f_1^2 + C_2 f_2^2,$$

where C_1 and C_2 are the concentrations of the corresponding components in atomic fractions.

The intensity curves obtained are shown in Fig. 2. The positions of the diffraction maxima are given in Table 1.

Let us first consider the pure metals. The positions of the intensity maxima for Sn agree well with the data of K. Gamertsfelder (4) and A. I. Bublik (8). The structure of liquid Bi apparently changes strongly with temperature. Comparing our data with those of Hendus (6) ($t = 390^{\circ}$), we see that the positions of the first maxima almost coincide (2.05 units of S in Hendus); instead of our second shoulder and third maximum, Hendus has a small shoulder maximum at $S = 3.05$, which apparently was formed owing to the influence of the first two. The positions of the remaining maxima changed only slightly.

Table 1

Figure 2

Figure 2: Figure 2

Alloy composition (wt %)	Position of maxima ($S = 4\pi \sin\vartheta/\lambda$)	Position of maxima ($S = 4\pi \sin\vartheta/\lambda$)	Position of maxima ($S = 4\pi \sin\vartheta/\lambda$)	Position of maxima ($S = 4\pi \sin\vartheta/\lambda$)	Position of maxima ($S = 4\pi \sin\vartheta/\lambda$)
Alloy composition (wt %)	1	2	3	4	5
Sn_{pure}	2.22	–	2.90	4.25	6.15
80 Sn–20 Bi	2.14	–	2.57	4.07	5.10
60 Sn–40 Bi	2.12	–	–	4.05	5.85
40 Sn–60 Bi	2.10	–	3.05	3.95	6.05
20 Sn–80 Bi	2.08	–	–	3.75	5.19
Bi_{pure}	1.98	2.22	3.14	3.80	5.05

Comparing the intensity curves of the intermediate alloys with one another, we observe a gradual transition from the type of pure Sn to the type of pure Bi, without the formation of additional maxima.

The values obtained for the normalized intensity were used to calculate the radial distribution function by formula (1).

The integral in formula (1) was computed on an electronic computer; the values of r were taken at intervals of 0.05 Å.

To determine the mean number of atoms per unit volume, published data on the densities of liquid Bi–Sn alloys (^{7}) were used. The radial distribution curves calculated in this way are shown in Fig. 3.

Fig. 2. Normalized intensity curves of liquid Bi–Sn alloys.
a –alloy Sn 80%–Bi 20%;
b –Sn 60%–Bi 40%;
v –Sn 20%–Bi 80%;
g –eutectic (Sn 41%–Bi 59%).

It is convenient to divide the discussion of the curves obtained into three stages.

1. **Pure Bi and Sn** (Fig. 3). The position of the first maximum on the radial distribution curve of Sn_{pure} (3.25 Å) agrees well with the published

Fig. 3. Radial distribution curves of liquid Bi–Sn alloys. The designations are the same as in Fig. 2.

Figure 3: Fig. 3. Radial distribution curves of liquid Bi–Sn alloys. The designations are the same as in Fig. 2.

data for this temperature (4). The same applies to the number of nearest neighbors—10.

The data of different authors on the radius of the first coordination sphere of liquid Bi differ considerably. Thus, Hendus (6) found at 390° that the radius of the first coordination sphere is 3.32 Å, while A. I. Bublik and A. G. Buntar (8) determined this quantity as 4.15 Å at 400° and 3.85 Å at 300°.

The value we obtained, 3.85 Å, agrees well with the data of the latter authors. The number of nearest neighbors is 7.02 (7-8 according to Hendus' s data).

2. **Alloy of eutectic composition** (Fig. 3). The first maximum (from 2.95 Å to 4.65 Å) of the radial distribution curve is the result of the superposition of three maxima: a large maximum

Fig. 3. Radial distribution curves of liquid Bi—Sn alloys.
The designations are the same as in Fig. 2

at 3.30 Å, a smaller maximum at 4.15 Å, and a small maximum at 3.75 Å.

The position of the first maximum agrees well with the value of the smallest distance between atoms in liquid Sn (3.25-3.35 Å). As for the distance of 4.15 Å, according to A. I. Bublik and A. G. Buntar', it can exist in liquid Bi, although at a higher temperature (400°). The value 3.75 Å is close to the arithmetic mean of r_1 and r_2 (3.72-3.75 Å). It is therefore natural to assume that it represents the distance between unlike atoms (the Bi—Sn distance and vice versa). Under the radial distribution curve, areas were separated out corresponding to all three maxima, from which the numbers of nearest neighbors were calculated.

The calculations showed that around a given Sn atom, at a distance of 3.35 Å, there are 7.8 Sn atoms; in addition, somewhat farther away (3.85 Å) there are another 2.1 Bi atoms. Thus, the total coordination number, 9.9, is equal to the coordination number of pure tin.

If, however, Bi is at the center of the coordination sphere, then around it are grouped 2 Sn atoms (r = 3.85 Å) and 5.2 Bi atoms (r = 4.15 Å). The total coordination number, 7.2, is close to the coordination number of pure bismuth (7). Such incorporation of Sn atoms into the coordination sphere of Bi evidently leads to its expansion, characteristic of higher temperatures.

In the case described, there is a clearly expressed tendency toward microheterogeneity. Bi and Sn atoms tend to surround themselves with like atoms. Atoms of the other kind are expelled from the coordination spheres and form, as it were, secondary, additional spheres. However, complete microheterogeneity, as, for example, in the eutectic alloys Bi—Pb (9) or Pb—Sn (10), is not obtained.

3. **Alloys of compositions intermediate between the eutectic and the pure components.** Here the maxima do not

are separated, and their positions do not coincide with the positions of the maxima of the pure components.

Such patterns may arise either because of the presence of a certain ordering in the distribution of atoms or, conversely, in the case of complete miscibility of the components, when atoms of both kinds enter the environment of a given atom. However, the first assumption has no basis, since no compounds of Bi with Sn exist.

Let us consider the second case. A peak on the radial-distribution curve of a binary alloy may arise, generally speaking, as the result of the superposition of all four conceivable environments, i.e., environments of the type a—a, a—b, b—a, b—b. If we assign to each environment its own radial-distribution function, then we may write:

$$S_{\max} = 4\pi \int_{r_1}^{r_2} \rho_{\exp}(r) r^2 dr =$$

$$= 4\pi \int_{r_1}^{r_2} \left[C_a k_a^2 \rho_{aa}(r) + C_a k_a k_b \rho_{ba}(r) + C_b k_a k_b \rho_{ba}(r) + C_b k_b^2 \rho_{bb}(r)\right] r^2 dr. \quad (2)$$

In a real alloy, atoms of both kinds will enter the environment of a given atom; moreover, in the case of complete miscibility the probability of such entry will be proportional to the concentration of the corresponding component, so that $\rho_{aa} = C_a \rho^0_{aa}$, $\rho_{ab} = C_b \rho^0_{ab}$, $\rho_{ba} = C_a \rho^0_{ba}$, $\rho_{bb} = C_b \rho^0_{bb}$. Therefore we may write:

$$S_{\max} = 4\pi \int_{r_1}^{r_2} \rho_{\exp}(r) r^2 dr =$$

$$= 4\pi \int_{r_1}^{r} \left[C_a^2 k_a^2 \rho^0_{aa}(r) + C_a C_b k_a k_b \rho^0_{ab}(r) + C_a C_b k_a k_b \rho^0_{ba}(r) + C_b^2 k_b^2 \rho^0_{bb}\right]^2 dr. \quad (3)$$

For the case of complete miscibility one may set

$$\rho^0_{aa}(r) = \rho^0_{ab}(r) = \rho^0_{ba}(r) = \rho^0_{bb}(r) = \rho^0_{cp}(r). \quad (4)$$

Then formula (3) is transformed as follows:

$$S_{\max} = 4\pi \int_{r_1}^{r_2} \left[C_a^2 k_a^2 + 2C_a C_b k_a k_b + C_b^2 k_b^2\right] \rho_{cp}(r) r^2 dr; \tag{5}$$

since, by virtue of normalization, $4\pi \int_{r_1}^{r_2} \rho(r) r^2 dr = n$, it follows that

$$S_{\max} = (C_a^2 k_a^2 + 2C_a C_b k_a k_b + C_b^2 k_b^2)\, n. \tag{6}$$

Calculating the coordination numbers from this formula, we obtain the following results. Alloy No. 1: $n_{\text{tot}} = 12.4$, of which Sn ~ 10 atoms, Bi ~ 2 atoms. Alloy No. 2: $n_{\text{tot}} = 10.1$, of which Sn ~ 6 atoms, Bi ~ 4 atoms. Alloy No. 4: $n_{\text{tot}} = 10.2$, of which Sn ~ 3 atoms, Bi ~ 7 atoms.

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