Interdiffusion Studies in Liquid Bismuth-Antimony Alloys

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The composition dependence of the interdiffusion coefficient in Bi-Sb melts has been measured in the temperature range from 656 °C to 1010 °C by use of the long-capillary method and electron probe microanalysis. The measured data can be represented as a function of the temperature by an Arrhenius law:

$$D = D_0 \exp(-Q/R\,T).$$

The concentration dependence of the parameters D_0 and Q is given. Analysis of the variation of Q with composition leads to the conclusion that Bi-Sb alloys show more metallic behaviour than unalloyed Bi or unalloyed Sb.

This result is in agreement with the structure of the Bi-Sb melts.

Introduction

Most of the diffusion studies on molten metals done up to now were concerned with the measurement of self-diffusion in melts of unalloyed elements and impurity diffusion in dilute alloys. There exist only a few measurements of the interdiffusion coefficient in binary liquid metal systems over the entire composition range.

In this work the Bi-Sb system was chosen for interdiffusion studies. In a previous work[1] it was shown, by neutron diffraction, that the structure of molten Bi-Sb alloys is more metal-like than that of the unalloyed elements Bi and Sb, which show covalent bonds as well as metallic bond. The objective of the present study was to investigate whether the concentration dependence of the interdiffusion coefficient is correlated to this structural result.

Experimental

The main problem in performing diffusion studies in the molten state is to suppress convection in order to obtain the transport caused by diffusion only. That is why diffusion experiments are done with capillaries containing the melt and there exist two methods which are called the capillary-reservoir method[2] and the long-capillary method[2]. In the first step of this work diffusion runs using both methods were carried out to compare them. The results of these tests showed that for the Bi-Sb system the long-capillary method is superior to the capillary-reservoir method, since only by use of the first method was it possible to suppress the convection. Furthermore only with the long-capillary method the boundary conditions can be produced which are required for the evaluation of the interdiffusion coefficient by the Matano method[3]. The Matano method has the advantage that with a single diffusion specimen the interdiffusion coefficient can be measured over the entire concentration range of the system.

With the long-capillary method as employed here the diffusion process took place in a capillary 60 mm long which was half filled with Bi and half filled with Sb. The capillaries were made of high-purity spectrographic graphite rods with a length of 35 mm and a diameter of 6 mm in which a hole 30 mm long and 1 mm in diameter was drilled. To degas these capillaries, they were annealed for 24 hours at 800 °C in a vacuum of about 10^{-5} torr. This procedure allowed the graphite, because of its porosity, to absorb gases coming out of the molten metal when the capillaries were filled and when diffusion took place. Thus bubbles could be avoided which otherwise would have occured in the diffusion specimen.

The capillaries were filled with Bi and Sb, respectively, using an apparatus, which is described in Reference[4]. Within this apparatus the capillaries were immersed in a Bi melt or a Sb melt, respectively, in vacuum so that their open end was covered by the melt. Argon gas was then admitted into the system to push the liquid metal into the capillaries. Then the capillaries were removed and cooled. The filled capillaries were mounted on a X-ray film and exposed to X-rays. As the metal absorbs the X-rays more than the graphite the shadow of the metal-thread within the capillaries could be seen on the

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developed films, and the capillaries not completely filled thus could be discerned. The long-capillaries were fabricated as shown in Fig. 1 by use of one capillary filled with Bi and one filled with Sb. Both capillaries (r and l) were ground flat at their open end and then turned on a lathe so that the outer diameter of the capillary near the open end was reduced. Then the two parts were joined together by pressing them into a graphite hull (h). The diffusion annealing of these long-capillaries was done with a vertical tube furnace, the tube of which was 150 cm long and 1.7 cm in inner diameter. The temperature was controlled with a chromel-alumel thermocouple. To prevent oxidation of the graphite capillaries, a continuous flow of argon was feed through the tube, which was closed by a flap at the lower end. The samples were fixed on a tungsten wire (0.1 mm diameter) with the Sb-filled part directed upwards and lowered into that region of the furnace where the positive temperature gradient directed upwards was 0.3 grd cm^{-1}. After annealing the specimens were water quenched and then ground parallel to their longitudinal axis until the thread of metal appeared. Then they were polished. Because of the shrinkage during the cooling the metal showed a cavity at the original contact plane of Bi and Sb. This is explained by the fact that the metal solidifies last in that part of the capillary which is surrounded by the hull where the sample is thickest. Solidification and shrinkage begin at the ends of the long-capillary and thus the metal thread is separated in the middle.

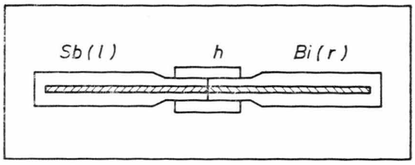

Fig. 1. Long-capillary diffusion specimen.

The concentration profiles of Bi and Sb in the diffusion zone were measured with an electron microprobe (model JXA 3, JEOL, Tokyo). The calibration curves required for these measurements were obtained by means of Bi-Sb standards. For more details of microprobe diffusion analysis see Reference [5]. From the measured densities in the liquid Bi-Sb system[6] it follows that the partial molar volumes of Bi and Sb do not vary significantly with the composition. For that reason the diffusion coefficients can be evaluated from diffusion profiles where the concentrations are plotted as volume fractions. Thus the conversion of the concentrations into moles per volume, which is necessary in general for the application of Fick's second law, can be avoided.

The values of the interdiffusion coefficient were determined using the Matano method[3], where the solution of Fick's second law is given by

$$D(c) = -(1/2\,t)\,(\mathrm{d}x/\mathrm{d}c)\int_0^c x\,\mathrm{d}c\,, \tag{1}$$

where t = diffusion time,
x = diffusion distance,
c = volume fraction of Bi and Sb, respectively.

The evaluation was carried out at those points of the volume fraction-profiles which correspond to atomic fractions of 0.1, 0.2, . . . 0.9. The results are mean values of the values derived from the Bi-profiles and the Sb-profiles. The shrinkage of the metal thread during quenching of the diffusion sample was taken into account by correction of the diffusion distance x by use of the densities at 20 °C and the annealing temperature, respectively. It should be noted that this correction effected a change of about 10 pct of the value of $D(c)$ when the annealing temperature was 1000 °C. At each annealing temperature (656, 702, 755, 803, 1010 °C) five diffusion runs of different duration were performed in order to investigate the time dependence of the process. The run time had to be controlled so that the boundary conditions applying to the Matano method were observed.

Results

Figure 2a shows a diffusion profile of a quenched sample measured by the electron microprobe using a beam diameter of 0.1 mm. The part in the middle of the specimen where the shrinkage cavity occured has been cut out and the profile has been rejoined (dashed line in Figure 2a). Figure 2b shows a section of a diffusion profile obtained from a sample which was not quenched after diffusion. This curve exhibits large concentration fluctuations with an average separation distance of about 0.5 mm. They develop during the cooling and freezing of the liquid by segregation when crossing the two-phase region of the phase diagram of the Bi-Sb system[7]. Using a beam diameter of 2 μ the fluctuations of the concentration within the quenched samples were found to have an average separation distance of about 5 μ. To obtain directly a smoothed diffusion profile the above measurements were carried out with a beam diameter of 0.1 mm. This yielded a curve as shown in Figure 2a.

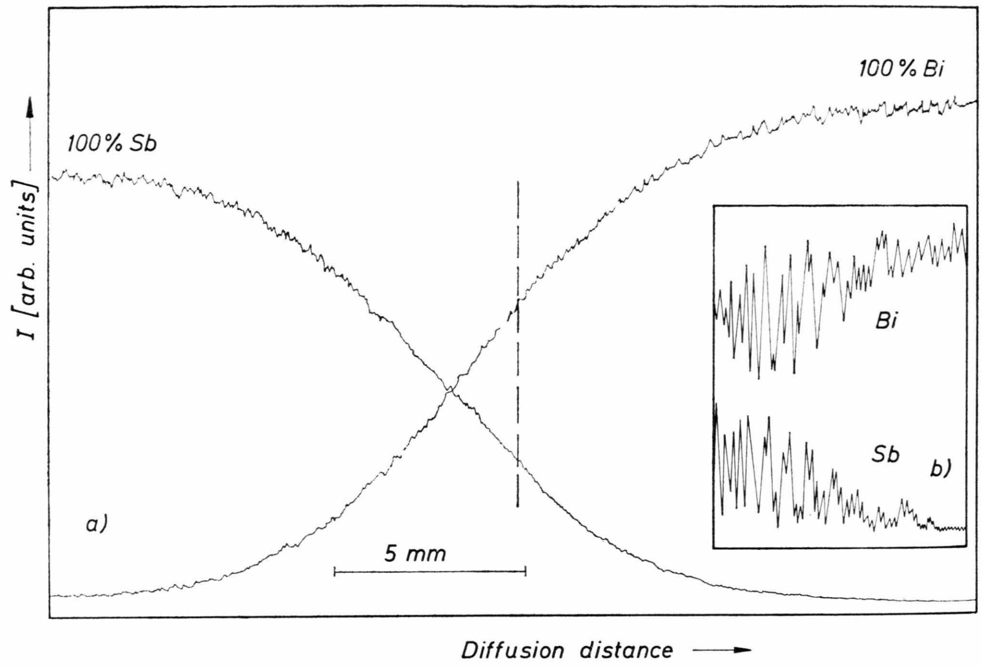

Fig. 2. Bi-Sb system: Diffusion profile of a quenched (a) and an unquenched (b) sample by electron microprobe. I = X-ray intensity from Bi and Sb, respectively.

The time dependence of the growth of the diffusion zone at 755 °C and 1010 °C is shown in Fig. 3, where the distance between the two concentrations 0.1 and 0.2 (volume fractions) is plotted versus the square root of the diffusion time. The result is a linear relationship from which it can be concluded that the process is controlled by volume diffusion [3] and not affected by convection. The fact that the straight lines run through the origin shows that there is no mixture of Bi and Sb caused by the melting at the beginning of the diffusion process.

In Fig. 4 the composition dependence of the interdiffusion coefficient is shown. The data are mean

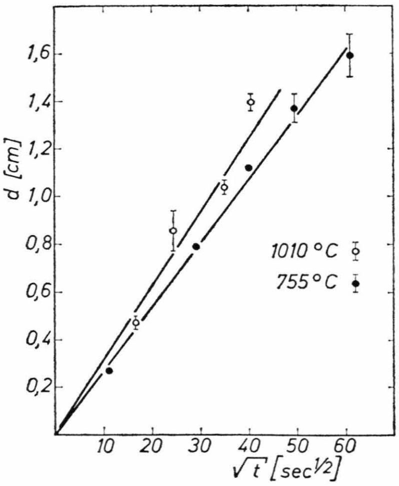

Fig. 3. Bi-Sb system: Growth of the diffusion zone.

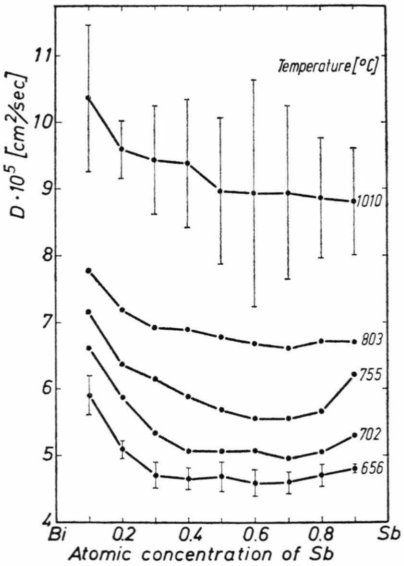

Fig. 4. Bi-Sb system: Interdiffusion coefficients. I Mean square deviation.

values of the values from three up to five samples. The interdiffusion coefficient in the Bi-rich melts is higher than in the Sb-rich melts and exhibits a minimum at least at temperatures below 800 °C. The experimental errors given for 656 °C and 1010 °C in Fig. 4 result from the spread of the single values obtained with the 3 ... 5 samples and are seen to increase with the annealing temperature.

In Fig. 5 the temperature dependence of the interdiffusion coefficient for some selected concentrations is presented by the usual Arrhenius-plot. The experimental points can be well represented by straight lines which are described by the equation

$$D(N_{\mathrm{Sb}}, T) = D_0(N_{\mathrm{Sb}}) \cdot \exp\left[-Q(N_{\mathrm{Sb}})/R\,T\right], \quad (2)$$

where R = gas constant and N = atomic concentration.

The best values for the parameters D_0 and Q and their standard errors were determined by a least squares analysis of the data and plotted versus the composition in Figures 6a, b. This yielded the following results:

1. The so-called activation energy, Q, for the interdiffusion is lower in Bi-rich melts than in Sb-rich melts.

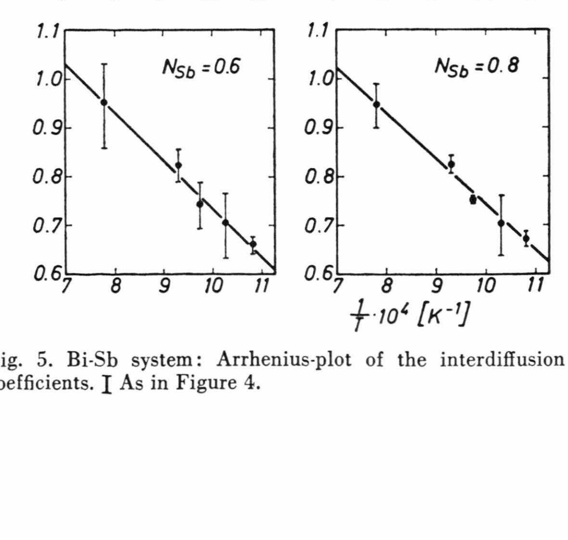

Fig. 5. Bi-Sb system: Arrhenius-plot of the interdiffusion coefficients. I As in Figure 4.

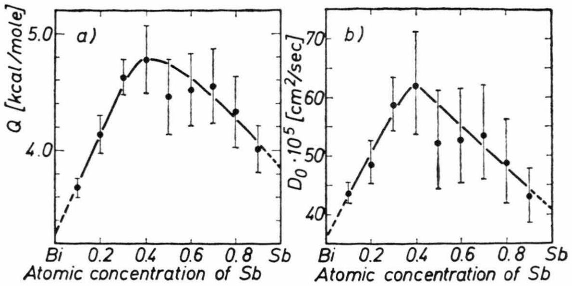

Fig. 6. Bi-Sb system: Parameters for the Arrhenius-type presentation of the interdiffusion coefficient.

2. The activation energy Q as well as D_0 have a marked maximum at the composition where $N_{\mathrm{Sb}} = 0.4$.

Extrapolation of the curves in Figs. 6a and b yielded the values of Q and D_0 for dilute Bi in Sb and dilute Sb in Bi, respectively. With these values the impurity diffusion coefficient of Bi in liquid Sb is given by

$$D_{\mathrm{Bi}}(\mathrm{Sb}) = 4.1 \cdot 10^{-4} \cdot \exp\{-3800 \text{ cal mole}^{-1}/R\,T\} \text{ cm}^2 \text{ sec}^{-1}. \quad (3)$$

The corresponding coefficient for Sb in liquid Bi is given by

$$D_{\mathrm{Sb}}(\mathrm{Bi}) = 3.6 \cdot 10^{-4} \cdot \exp\{-3300 \text{ cal mole}^{-1}/R\,T\} \text{ cm}^2 \text{ sec}^{-1}. \quad (4)$$

Discussion

The variation of the activation energy Q with composition will be discussed first. An empirical rule obtained in the past by diffusion studies shows that the ratio Q/T_{m} and not the value of Q is the proper parameter to distinguish between diffusion in metallic melts and diffusion in melts of semimetals and non-metals (T_{m} = melting temperature). For self-diffusion in pure molten metals it is found that

$$Q/T_{\mathrm{m}} \approx 6.8 \text{ cal mole}^{-1} \text{ grd}^{-1}, \quad (5)$$

where Q = activation energy for self-diffusion [8]. Semi-metals and non-metals show a marked deviation from this relationship. Saxton and Sherby [9] have proposed 5.46 cal mole^{-1} grd^{-1} for semi-metals. Recent measurements [10] yielded an even smaller value of 4.68 cal mole^{-1} grd^{-1} for liquid Sb.

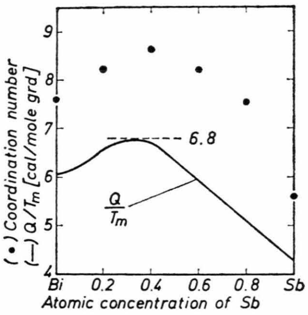

Fig. 7. Bi-Sb system: Coordination number (●) and Q/T_m (——).

For comparison of these findings with the results of the present work the ratio of Q/T_m was calculated by use of the full line in Fig. 6a and the values of T_m from the phase diagram[7] of the Bi-Sb system (T_m being the liquidus temperature).

The full line in Fig. 7 shows the result. Q/T_m has a maximum value of 6.8 cal mole^{-1} grd^{-1} at $N_{Sb} = 0.3 \ldots 0.4$ which is characteristic for normal liquid metals. Approaching the pure components this value decreases especially at the Sb-rich side. From this concentration dependence of Q/T_m it can be concluded that molten Bi-Sb alloys exhibit a more metallic character than the unalloyed elements Bi and Sb. This conclusion is in accordance with structural properties. In a previous study by neutron diffraction[1] the number of nearest neighbours in Bi-Sb melts was determined. This coordination number is also plotted in Fig. 7 and its variation with composition is approximately parallel to Q/T_m having a maximum at $N_{Sb} = 0.4$. At this concentration the number nearly reaches the value of $9 \ldots 10$ atoms which is characteristic for normal liquid metals.

It is pointed out that these considerations have a rather qualitative meaning for two reasons:

1. The value of Q/T_m in Fig. 7 results from interdiffusion measurements, whereas the value 6.8 cal mole^{-1} grd^{-1} used for comparison results from self-diffusion measurements.

2. There is no theoretical evidence that diffusion in liquids is governed by an activated fundamental process which is described by an Arrhenius-law. Following the usual practice the data are displayed in a plot of $\log D$ versus $1/T$ in this work and they are adequately represented by straight lines within the error limits. That is why the description and discussion of the diffusion behaviour in the liquid Bi-Sb system in terms of the parameters D_0 and Q seem to be suitable. The use of Q as an activation energy in the present work has to be understood in this restricted meaning.

Secondly the mobilities m_{Bi} and m_{Sb} of the Bi- and Sb-atoms will be discussed. Using the self-diffusion coefficients D^*_{Bi} and D^*_{Sb} of Bi and Sb they are given by

$$m_{Bi,Sb} = D^*_{Bi,Sb}/k\,T\,, \qquad (6)$$

where k = Boltzmann's constant.

The interdiffusion coefficient is given in terms of the self-diffusion coefficients by the equation of Darken[11]:

$$D = (N_{Bi} \cdot D^*_{Sb} + N_{Sb} \cdot D^*_{Bi}) \cdot (1 + d\ln \gamma_{Bi}/d\ln N_{Bi})\,, \qquad (7)$$

where γ_{Bi} = activity coefficient of Bi.

As the thermodynamic activities in the Bi-Sb system at 927 °C are already known[12] a weighted sum of the mobilities of Bi and Sb can be calculated:

$$N_{Bi} \cdot m_{Sb} + N_{Sb} \cdot m_{Bi} = D/k\,T \cdot (1 + d\ln \gamma_{Bi}/d\ln N_{Bi})\,. \qquad (8)$$

This sum was calculated using the values of D at 927 °C, obtained by interpolation from Fig. 5, and the values of γ_{Bi}, and it is plotted in Figure 8. Figure 8 shows that the mobilities of Bi and Sb in the liquid Bi-Sb system are obviously smallest at the concentration $N_{Sb} = 0.4$ where the number of nearest neighbours (Fig. 7) has a maximum.

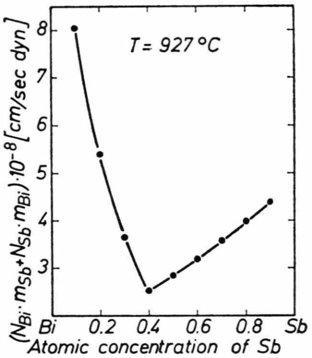

Fig. 8. Bi-Sb system: Mobility-term at 927 °C.

Acknowledgement

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