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Journal of Alloys and Compounds 234 (1996) 260–263

Journal of ALLOYS AND COMPOUNDS

The study of two-melt phase separation in the Bi–Zn system by the γ attenuation technique

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Received 18 May 1995

Abstract

The shape of the two-melt phase boundary of the Bi–Zn system with miscibility gap has been determined by the γ method. According to our measurements, the coordinates of the critical point are $T_c = 846.5 \pm 2.5$ K, $X_c = 17.0 \pm 1.0$ at.% Bi. In an extended range around T_c the critical exponent β of the coexistence curve equals 0.35 ± 0.02, which agrees closely with non-classical value.

Keywords: Phase diagrams; Phase separations

1. Introduction

The phase diagrams of many binary metallic systems with miscibility gaps have not been investigated in sufficient detail. Application of most of the known phase analysis methods to metallic melts presents difficulties owing to high temperatures, corrosion of the crucibles, and evaporation of the components. Furthermore, these methods are usually laborious as a great quantity of samples (as many as several tens) of different compositions need to be studied. One promising method for investigating the two-melt phase separation which circumvents these difficulties is to measure the attenuation of a narrow beam of γ quanta passing through the sample.

In this article we present a variant of the γ method developed by us to determine the shape of the two-melt coexistence curve and the results of the Bi–Zn system.

2. Experimental details

The measurements were performed with a γ densitometer which has been described in detail elsewhere [1]. ^{137}Cs having a nominal strength of 240 GBq is used for a γ source. The maximum temperature of measurements is limited to 2300 K. The furnace of the γ densitometer has three different heaters which provide a vertical temperature gradient of less than 0.15–0.25 K cm^{-1}. Provision is made in the installation design for vertical movement of the sample with respect to the γ quanta beam. This makes it possible to measure the dependence of the linear attenuation coefficient of radiation on height h.

The law of radiation attenuation for a binary melt with components A and B may be written as

$$\frac{\sigma_A X(h) + \sigma_B[1 - X(h)]}{V[X(h)]} = \frac{1}{l} \ln\left[\frac{J_0}{J(h)}\right] \quad (1)$$

where J_0 and $J(h)$ are the intensities of the radiation after passage through the experimental apparatus with and without the samples respectively, l is the inner diameter of the crucible, $X(h)$ and $V[X](h)]$ are the mole fraction of component A and molar volume of the melt at these site of the beam passage, σ_i (i = A,B) are attenuation sections of the components ($\sigma_i = M_i\mu_i$), M_i are atomic weights and μ_i are mass attenuation coefficients. With knowledge of the concentrate dependence of the molar volume $V(X)$, Eq. (1) enables the determination of the compositions of the two coexisting phases in the liquid systems with a miscibility gap. If the sample concentration is close to the critical concentration, the shape of the coexistence curve may be reconstructed by measurements of the temperature dependence of the attenuation coefficient above and below the two-melt phase boundary, using only a single sample.

SSDI 0925-8388(95)02029-2

The Bi–Zn system with its miscibility gap were studied in order to test the developed procedure experimentally. Bismuth and zinc were 99.99% and 99.9% pure respectively. The sample contained 17.9 at.% Bi, which according to Refs. [2,3] is close to the critical composition. In our experiments the composition change did not exceed 0.03 at.%. The mass attenuation coefficients of Bi and Zn were measured with an error of less than 0.5%. A cylindrical BeO crucible of 40 mm diameter and 70 mm height was used. The internal diameter of the crucible was determined to within 0.1%. Corrections were made to account for the thermal expansion of the BeO and the finite beam diameter. The temperature was measured with a Pt–Pt(10% Rh) thermocouple embedded in the sample in a protective BeO sleeve. Although the absolute temperature uncertainty was ±2.5 K, the relative temperature was accurate to better than ±0.5 K. Before the experiments the furnace was evacuated and filled with pure argon up to 0.1 MPa.

At the first stage in our experiment we determined the molar volume of the melt in the homogeneous region. The sample was heated above the critical temperature (up to 937 K) and was stirred thoroughly with a mechanical mixer. The melt homogeneity was checked by measuring the attenuation coefficient at different heights. The temperature dependence of the molar volume was measured on cooling of the sample. The point of contact with the separation curve was determined from the appearance of a kink in the $J(T)$ dependence.

Measurements in the miscibility gap were carried out on continuous cooling of the sample as well as after holding it for sufficiently long at a constant temperature. It was found that equilibrium in the sample was established when the rate of cooling did not exceed 0.15 K min^{-1} (Fig. 1).

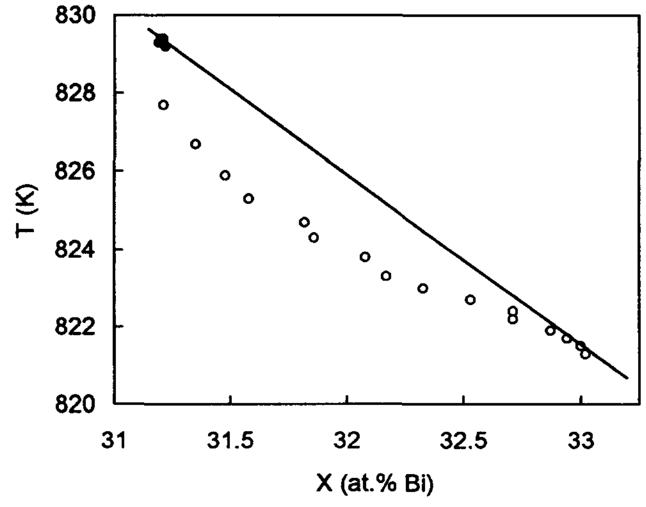

Fig. 1. Part of the Bi-rich branch of the coexistence curve: •, ○, points obtained respectively at constant temperature and on cooling the sample with a rate $v = \Delta T/(100\ \mathrm{s})$, where ΔT is the temperature difference between the neighbouring points; ——, fit of the data obtained at T = constant.

3. Results

The molar volume V (cm^3 mol^{-1}) in the sample of composition $X_0 = 17.9$ at.% Bi is a linear function of the temperature over the whole interval of the complete solubility range (847–937 K):

$$V(X_0, T) = 12.35 + 1.736 \times 10^{-3}(T - 847\ \mathrm{K}) \qquad (2)$$

The values of the molar volume and the volume coefficient of thermal expansion at 873 K are 12.40 ± 0.10 cm^3 mol^{-1} and $(14.0 \pm 0.6) \times 10^{-5}$ K^{-1} respectively. These results agree with data in Ref. [2] within the total experimental error.

As noted above, data on the concentration dependence of the molar volume $V(X)$ are needed to determine the equilibrium compositions of the phases in the system after phase separation. For most liquid binary systems with a miscibility gap, a strong chemical interaction between the atoms of the two components is lacking. The concentration dependence of the excess mixing volume $V_{ex}(X)$ of these systems (in particular, Bi–Zn [2]) is described by a parabola having a maximum at $X = 50$ at.%. The relative value of V_{ex} does not exceed a few per cent, as a rule. In this connection, we used the following relation for the interpolation of the molar volume dependence of the Bi–Zn melts:

$$V(X, T) = V_{\mathrm{Bi}}(T)X + V_{\mathrm{Zn}}(T)(1 - X) + \frac{V_{ex}(X_0, T)X(1 - X)}{X_0(1 - X_0)} \qquad (3)$$

where $V_{ex}(X_0, T) = V(X_0, T) - V_{\mathrm{Bi}}(T)X_0 - V_{\mathrm{Zn}}(T)(1 - X_0)$; $V(X_0, T)$ is the extrapolation of Eq. (2) to the temperature below the point of contact with the separation curve. The temperature dependences of the densities of pure Bi and Zn were taken from Refs. [4,5]. According to our evaluations, the maximum error of $V(X, T)$ does not exceed 1% at $X = 50$ at.% and $T = 680$ K.

The two-melt phase boundary as determined from the measurements and relationships (1), (3) is shown in Fig. 2. We used only averaged data obtained either at constant temperature or at a cooling rate less then 0.15 K min^{-1}. At the monotectic temperature $T_m = 680 \pm 2.5$ K, the Bi-rich and Zn-rich compositions are 61.6 ± 1.5 at.% Bi and 0.95 ± 0.3 at.% Bi respectively. The centres of the two-phase region at the various temperatures appear to fall on a straight line within the limits of the experimental error. The critical point, defined to be the crossing point of the locus of these

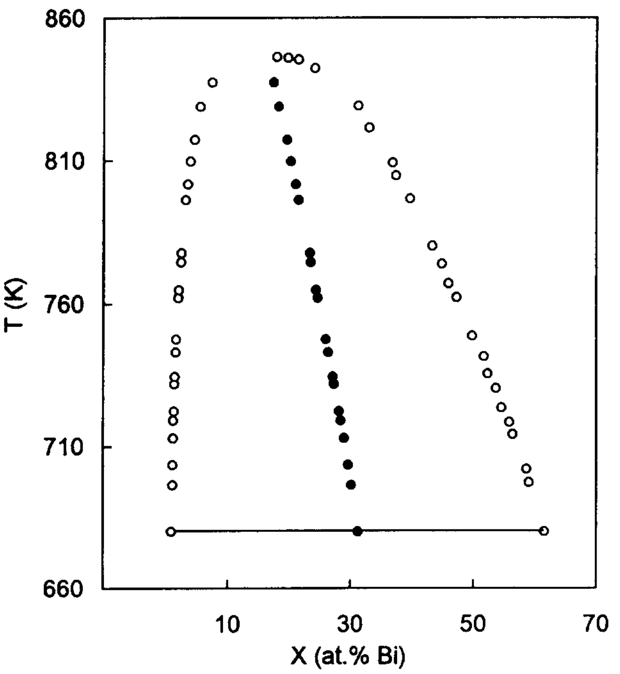

Fig. 2. Two-melt phase boundary for Bi–Zn system: ○, experimental results; •, central points of the two-phase ranges at various temperatures.

central points and the coexistence curve, is $T_C = 846.5 \pm 2.5$ K, $X_C = 17.0 \pm 1.0$ at.% Bi.

4. Discussion

A comparison between our data and the results of other investigations is given in Tables 1 and 2. The positions of the critical point determined in Refs. [2,3] and in our paper are in good agreement. Kleppa's results [6] are the sole exceptions, but they are a rough estimation. The literature data on the composition of the liquid phases in the monotectic points are in a good agreement with our results also. The monotectic temperature presented by Seith et al. [7] and recommended in Ref. [8] is slightly higher than the value measured in our experiments.

Table 1
Coordinates of the critical point in the Bi–Zn system

Ref.	T_C (K)	X_C (at.% Bi)
[6]	≈878	≈15
[3]	849 ± 2	18.5
[2]	853 ± 3	17.8 ± 0.3
Present work	846.5 ± 2.5	17.0 ± 1.0

Table 2
Composition of the liquid phases at the monotectic temperature in the Bi–Zn system

Ref.	T_m (K)	Concentration (at.% Bi)	
		Zn rich	Bi rich
[7]	689	0.6	63.0
Gautier et al. (1896)ᵃ	668	—	—
Arnemann (1910)ᵃ	689	0.3	—
Mathewson et al. (1914)ᵃ	—	0.62	59.6
Present work	680 ± 2.5	0.95 ± 0.3	61.6 ± 1.5

ᵃ The data taken from Ref. [8].

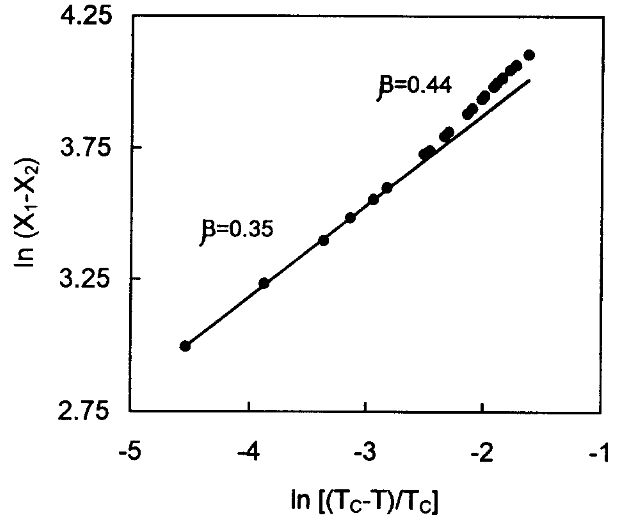

Fig. 3. The dependence of $\ln(X_1 - X_2)$ on $\ln(\tau)$ along the coexistence curve.

According to Ref. [9], the shape of the coexistence curve in the vicinity of a critical point is described by the equation

$$X_1 - X_2 = B\tau^{\beta} \tag{4}$$

where X_1 and X_2 are the concentrations of the phases in equilibrium with each other, β is the critical exponent $\tau = |T_C - T|/T_c$ and B is a constant. The critical exponent can be obtained from a plot of $\ln(X_1 - X_2)$ against $\ln(\tau)$.

A plot revealing this dependence is shown in Fig. 3. Over the temperature range 800 K–T_C (where $\tau < 0.06$) the value of β equals 0.35 ± 0.02. This is close to non-classical value $\beta = 0.31$–0.34 and agrees with $\beta = 0.33 \pm 0.01$ reported in Ref. [2] within the estimated error. However, at temperatures below 800 K the slope of the dependence of $\ln(X_1 - X_2)$ on $\ln(\tau)$ rises sharply and the corresponding β value comes to 0.44 ± 0.02. This is close to the classical value of the critical exponent.

5. Conclusion

A new experimental method for investigating two-melt phase separations using γ radiation has been developed and checked. The major advantage of this method consists in a considerable reduction in the number of samples required and the possibility of studying diversified melts up to 2300 K. The immiscibility region of Bi–Zn melts has been determined. A comparison of the results of our measurements with literature data has been used to demonstrate the reliability of our method. It was established that the shape of the coexistence curve is described by Eq. (4) with a non-classical value of β in an extended region around the critical point up to $\tau = 0.06$.

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