J. Min. Metall. Sect. B-Metall. 54 (2) B (2018) 243 - 249

Journal of Mining and Metallurgy,
Section B: Metallurgy

ISOBARIC (VAPOUR + LIQUID) EQUILIBRIA OF BINARY Pb-Sn AND Sb-Sn SYSTEM AT 2Pa

J. Gao[a,c], J. Xu[a,c], B. Yang[a,b], L. Kong[a,c,*], B. Xu[a,b,*], Y. You[a,c]

[a] National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, PR China
[b] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization in Yunnan Province, Kunming, PR China
[c] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, PR China

(Received 22 March 2018; accepted 23 May 2018)

Abstract

A new experimental method for determining vapor-liquid equilibrium (VLE) of binary alloys was designed in this study. The VLE data of Pb-Sn and Sb-Sn alloys were determined by using this new method. The experimental data passed the thermodynamic consistency test (Van Ness test), and the $y_{(MAD)}$ *was 0.4066 and 0.6667, respectively, indicating that the experimental method is correct and reliable. The activity coefficient of Pb-Sn and Sb-Sn alloys was calculated by using the molecular interaction volume model (MIVM). The maximum average relative deviation Si and maximum average standard deviation Si* are ±1.34% and ±0.009, respectively, which indicates that the calculation of the activity coefficient of the Pb-Sn and Sb-Sn alloys by MIVM is reliable. The VLE data of Pb-Sn and Sb-Sn alloys were calculated based on the VLE theory and MIVM, and the calculated results agreed well with the experimental VLE data. The VLE phase diagrams of Pb-Sn and Sb-Sn alloys were also established in this study. The VLE phase diagrams offer a valid and intuitive way to analyze the product compositions' dependence of temperature and pressure during the process of vacuum distillation. This will have immense significance in guiding the actual production of vacuum metallurgy.*

Keywords: *New experimental method; VLE; Pb-Sn, Sb-Sn alloys; MIVM; Thermodynamic consistency test*

1. Introduction

At present, there are many methods for determining vapor-liquid equilibria: 1) circulation method [1-2], 2) static method [3], 3) flow method [4], and 4) saturated vapor pressure method [5], which are mature and widely used in the field of chemical engineering. These methods, however, cannot be used to determine the VLE data of an alloy system due to the high temperature (e.g. 1173 K) required for determining the VLE data of alloys and the strong cohesiveness of components of alloys. Vacuum distillation is the only method that is currently used to determine the VLE of alloy systems, and has been employed to determine the VLE of binary lead-tin [6], lead-antimony [7], tin-antimony [8], lead-copper [9] and lead-silver [10] binary alloys by the National Engineering Laboratory for Vacuum Metallurgy of Kunming University of Science and Technology. The errors between the calculated results and experimental VLE data determined by vacuum distillation, however, are very large. For example, in the binary lead-antimony system, the mole fraction of vapor composition determined by vacuum distillation is 0.45 bigger than the calculated data, and the liquid phase points seriously deviated from the liquidus as well [7]. In fact, vacuum distillation is not a strict vapor-liquid equilibrium, as the vapor phase continuously condenses on the condenser during distillation. Therefore, this study proposed a brand new experimental method to determine the vapor-liquid equilibrium of alloys based on the definition of vapor-liquid phase equilibrium. New VLE data of Pb-Sn and Sb-Sn alloys were determined using this new method. A comparison between the calculated results of MIVM and the experimental VLE data was also carried out in this study.

2. Experiment Materials and Methods

2.1. Materials used and Alloy preparation

Granulated metallic Pb (99.999 mass pct), granulated metallic Sn (99.99 mass pct), and Sb polycrystalline lumps (99.99 mass pct) were supplied

---

**Corresponding author:kkmust@126.com; kmxbq@126.com*

DOI:10.2298/JMMB180322012G

by Leshan Kai Yada Photoelectric Technology Co., Ltd., China. The information about Pb-Sn and Sb-Sn alloys used in this study is given in Table 1 and Table 2. For the alloy preparation process, refer [7].

Table 1. *Information of Pb-Sn alloys used in this study*

no.	Total mass (g)	x_{Pb}	x_{Sn}
1	100	0.9	0.1
2		0.6	0.4
3		0.3	0.7

Table 2. *Information of Sb-Sn alloys used in this study*

no.	Total mass (g)	x_{Sb}	x_{Sn}
1	100	0.7	0.3
2		0.4	0.6
3		0.1	0.9

2.2. Apparatus and procedure

The VLE measurements were carried out in a steel crucible (Fig. 1, 66 mm ID × 80 mm OD × 110 mm Ht, capillary tube length is 600 mm), equipped with a vacuum pump (2XZ-4Z, China), a heating control system, a resistance furnace and a cooling system. The pressure was measured with a vacuum gauge with an uncertainty of ± 2Pa.

The temperature was measured with a thermocouple with an uncertainty of ± 2 K.

In a typical test, the prepared 100 g Pb-Sn alloy (or Sb-Sn alloy) was placed in a stainless steel crucible, and the crucible, in which a capillary had been previously inserted,was welded. The corrugated pipe was connected, in turn with the capillary, a vacuum gauge, and a vacuum pump, and the connection port was sealed with vacuum grease to ensure complete sealing. Then, the system was evacuated to 2 Pa with a rotary vacuum pump. Finally, the steel crucible was placed in an electric resistance furnace.

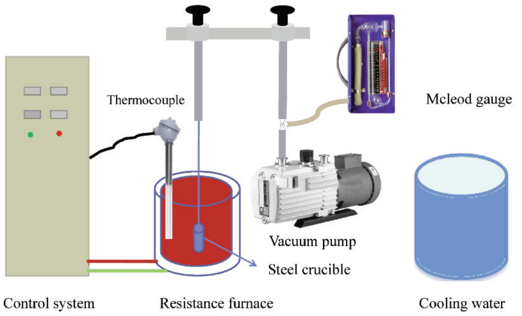


Figure 1*. Schematic diagram of the experiment equipment*

Then, the temperature at which the alloy components began to evaporate was calculated based on the vapor-liquid equilibrium theory, and the experiment was carried out at this temperature. If there is no vapor phase component at this temperature, it means that the component with higher vapor pressure in the alloy does not evaporate at this temperature. Then, the temperature was increased at a temperature gradient of 5 K until the gas phase could be collected on the crucible wall, and this temperature was considered as the bubble point temperature of the alloy. Then, the experiment was conducted at this temperature until the system reached equilibrium.

According to the VLE theory [7], when the system reaches equilibrium, the vapor phase and liquid phase are in a dynamic equilibrium state, and the change in holding time will not affect the equilibrium state (i.e., the composition of the vapor and liquid phase). When the composition of the vapor phase and the liquid phase is no longer changing, the holding time is considered to be the equilibrium time. At the bubble point temperature, at least four experiments were carried out for each alloy in order to obtain the equilibrium time. The equilibrium time for each alloy is shown in Tables 3 and 4.

At the end of each experiment, the steel crucible was removed from the furnace, and placed directly in the water to quench. The residues and volatiles were then collected from the bottom and the sidewall of the crucible, respectively. The above steps were repeated with another component alloy to get new VLE data.

2.3. Content Analysis

The contents of both Pb and Sb in the volatiles (vapor phase) and residues (liquid phase) were determined by titration. The EDTA titration for Pb contents were carried out in the acetic acid media, and the xylene orange was taken as the indicator (the color was changed from amaranth to luminous yellow at the endpoint). The EDTA standard solution was standardized with Pb (Ⅱ) standard solutions prepared from pure metal (99.999 mass pct). The Sb contents were titrated by cerium (Ⅳ) sulphate at 353 K, and the detailed analysis is available in reference [8]. For both Pb and Sb content of each sample, at least five analyses were conducted for obtaining a mean value of mass fraction, and the corresponding repeatability was better than 0.0005. The various uncertainty sources (e.g., repeatability, purity of reagent, uncertainty of volumetric and weights equipment, etc.) were combined by using the root sum of the squares in order to obtain a combined standard uncertainty of the content analysis. In this work, the combined standard uncertainty was estimated to be within ± 0.003 in mole fraction.

As the calculation principle and procedure for combined standard uncertainty has been reported in detail previously [11], the calculation procedure is only briefly outlined here. The procedure comprises the following five steps: (1) Specifying the measurand; (2) Identifying all relevant uncertainty sources; (3) Quantifying each uncertainty component; (4) Each quantified component is expressed as a relative standard deviation; and (5) All uncertainty components are combined by using the root sum of the squares. For example, in the measurement of a measurand y ($y = p / (q \times r \times ...)$), which has n sources of uncertainty for which the n standard uncertainties u(p), u(q), u(r)…, have been determined, then the combined standard uncertainty u_c(y) for the measurement is given by:

$$u_c\left(y\right) = y\sqrt{\left(\frac{u\left(p\right)}{p}\right)^2 + \left(\frac{u\left(q\right)}{q}\right)^2 + ...} \qquad (1)$$

where $u(p)/p$ and $u(q)/q$ are the uncertainties in the parameters, expressed as relative standard deviations.

The Sn contents in the volatiles and residues were obtained by solving the equation of mass balance accounting for the VLE, respectively.

3. Results and discussion

3.1. Experimental data

The new VLE data for the binary Pb-Sn and Sb-Sn alloy were determined using the new method, and are listed in Table 3 and Table 4, respectively. Where T is the equilibrium temperature (K), t is the equilibrium time (h), and x_1 and y_1 represent the mole fraction of Pb and Sb in the liquid and vapor phase, respectively. It can be seen from Table 3 that under the condition where system pressure was 2 Pa and temperature range was from 1057 to 1227 K, Pb-Sn alloy can be completely separated, and the vapor phase is composed of lead. When the system pressure is fixed, an increase in temperature is not conducive to the separation and purification of the alloy.

Table 3. *Experimental VLE data for temperature T, liquid-phase mole fraction x_i, and vapor-phase mole fraction y_i, for the Pb (1) + Sn (2) binary system, measured at 2 Pa*[a]

no.	T /K	P /Pa	t /h	$x_{1\text{exp}}$	$y_{1\text{exp}}$	$y_{1\text{cal}}$	$y_{(\text{MAD})}$
1	1057	2	5	0.8720	0.9971	0.9999	0.4066
2	1138		4	0.5288	0.9956	0.9999	
3	1227		3	0.2136	0.9948	0.9999	

[a] u (x) = u (y) = ± 0.003

Table 4. *Experimental VLE data for temperature T, liquid-phase mole fraction x_i, and vapor-phase mole fraction y_i, for the Sb (1) + Sn (2) binary system, measured at 2 Pa*[a]

no.	T /K	P /Pa	t /h	$x_{1\text{exp}}$	$y_{1\text{exp}}$	$y_{1\text{cal}}$	$y_{(\text{MAD})}$
1	1038	2	4	0.6085	0.9920	0.9999	0.6667
2	1093		3	0.3656	0.9897	0.9999	
3	1183		2	0.0812	0.9980	0.9999	

[a] u (x) = u (y) = ± 0.003

3.2. Thermodynamic consistency test (Van Ness test)

The thermodynamic consistency test is a method for checking the reliability of the VLE data. Based on a derivative of the Gibbs-Duhem equation [12-14], a number of thermodynamic consistency tests can be obtained. The activity coefficients of the components in the mixture are linked by Gibbs-Duhem equations. In this study, Van Ness test [15-18] was used to test the thermodynamic consistency of the VLE data determined by the new method, and it can be expressed as follows:

$$y_{(MAD)} = \frac{1}{n}\sum_{i=1}^{n} 100\left|y_i^{\exp} - y_i^{cal}\right| \qquad (2)$$

where $y_{(MAD)}$ is the absolute deviation; n is the number of experimental points; y_i^{exp} is the experimental data; and y_i^{cal} is the calculated results of the MIVM.

According to the Van Ness test, if the absolute deviation $y_{(MAD)}$ is less than 1, the experimental data is proved to be reliable. As can be seen in Table 3 and Table 4, the absolute deviation is 0.4066 and 0.6667, respectively, which indicates that the VLE data obtained by this new method is reliable. The deviation comes mainly from the following aspects:

1) The experiments were carried out under high temperature and low pressure.
2) A certain deviation comes from chemical analysis.
3) Vapor phase components cannot be completely collected.

3.3. Activity coefficient prediction

Molecular interaction volume model (MIVM) [19-22] is a very successful thermodynamic model, which was used to predict the thermodynamic properties in a multi-component solution system using only the ordinary physical quantities of pure liquid metals and the related binary infinite dilute activity coefficient. The value of the infinite activity coefficient used in this paper is listed in Table 5.

Table 5. *Value of γ_ι^∞ andγ_φ^∞ [23]B_{ij} and B_{ji}, Z_i and Z_j of the binary alloys i-j*

i-j	T (K)	γ_i^∞	γ_j^∞	B_{ij}	B_{ji}	Z_i	Z_j
Pb-Sn	1050	2.195	6.816	0.5198	1.2204	9.478	6.402
Sb-Sn	905	0.411	0.411	1.077	1.076	6.5512	6.9698

According to the MIVM, the activity coefficients of components of a binary mixture *i-j* can be expressed as:

$$\ln\gamma_i = \ln\left(\frac{V_{mi}}{x_iV_{mi}+x_jV_{mj}B_{ji}}\right)+x_j\left(\frac{V_{mj}B_{ji}}{x_iV_{mi}+x_jV_{mj}B_{ji}}-\frac{V_{mi}B_{ij}}{x_jV_{mj}+x_iV_{mi}B_{ij}}\right)$$
$$-\frac{x_j^2}{2}\left(\frac{Z_iB_{ji}^2\ln B_{ji}}{(x_i+x_jB_{ji})^2}+\frac{Z_jB_{ij}\ln B_{ij}}{(x_j+x_iB_{ij})^2}\right) \quad (3)$$

$$\ln\gamma_j = \ln\left(\frac{V_{mj}}{x_jV_{mj}+x_iV_{mi}B_{ij}}\right)-x_i\left(\frac{V_{mj}B_{ji}}{x_iV_{mi}+x_jV_{mj}B_{ji}}-\frac{V_{mi}B_{ij}}{x_jV_{mj}+x_iV_{mi}B_{ij}}\right)$$
$$-\frac{x_i^2}{2}\left(\frac{Z_jB_{ij}^2\ln B_{ij}}{(x_j+x_iB_{ij})^2}+\frac{Z_iB_{ji}\ln B_{ji}}{(x_i+x_jB_{ji})^2}\right) \quad (4)$$

where x_i and x_j are the mole fractions, V_{mi} and V_{mj} the molar volumes of the components *i* and *j* in liquid phase, respectively, *R* is the universal gas constant, and *T* is the absolute temperature. First, the infinite activity coefficient in Table 5 was plugged into formula 3 and 4. The *B* parameter can be obtained by the Newton iteration method. Then, the *B* parameter and coordination number are plugged into equations (3) and (4), and the activity coefficient can be calculated. The calculation procedure for B_{ij}, B_{ji} and coordination number Z_i and Z_j are available for reference [24]. The calculated activities and the experimental data of Pb-Sn alloy at 1050 K, Sb-Sn alloy at 905 K are shown in Table 6 and Table 7, respectively.

Table 6. *Calculated activities and the experimental data [23] of Pb-Sn alloy at 1050 K*

x_{Pb}	$\gamma_{\text{Pb,exp}}$	$\gamma_{\text{Pb,cal}}$	x_{Sn}	$\gamma_{\text{Sn,exp}}$	$\gamma_{\text{Sn,cal}}$
0.1	2.043	2.080	0.9	1.004	1.003
0.2	1.899	1.950	0.8	1.017	1.015
0.3	1.764	1.810	0.7	1.042	1.040
0.4	1.641	1.663	0.6	1.084	1.090
0.5	1.514	1.514	0.5	1.156	1.178
0.6	1.382	1.368	0.4	1.293	1.335
0.7	1.246	1.234	0.3	1.571	1.620
0.8	1.124	1.119	0.2	2.151	2.180
0.9	1.035	1.034	0.1	3.458	3.420

3.4. Deviation calculation

In order to verify the reliability of the MIVM, the average relative deviation S_i and the average standard deviation S_i^* are introduced as follows:

$$S_i = \pm\frac{100}{n}\sum_{i=1}^{n}\left|\frac{\gamma_{i,\exp}-\gamma_{i,cal}}{\gamma_{i,\exp}}\right| \quad (5)$$

Table 7. *Calculated activities and experimental data [23] of Sb-Sn alloy at 905 K*

x_{Sb}	$\gamma_{\text{Sb,,exp}}$	γ_{Sncal}	x_{Sn}	$\gamma_{\text{Sn,exp}}$	$\gamma_{\text{Sn,cal}}$
0.9	0.991	0.991	0.1	0.486	0.487
0.8	0.965	0.965	0.2	0.566	0.567
0.7	0.923	0.923	0.3	0.647	0.648
0.6	0.867	0.868	0.4	0.726	0.727
0.5	0.800	0.801	0.5	0.800	0.801
0.4	0.726	0.727	0.6	0.867	0.868
0.3	0.647	0.648	0.7	0.923	0.923
0.2	0.566	0.567	0.8	0.965	0.965
0.1	0.486	0.487	0.9	0.991	0.991

$$S_i^* = \pm\left[\frac{1}{n}\sum_{i=1}^{n}\left[\gamma_{i,\exp}-\gamma_{i,cal}\right]^2\right]^{\frac{1}{2}} \quad (6)$$

where *n* is the number of experimental data, $\gamma_{i,exp}$ and $\gamma_{i,cal}$ are the experimental values and calculated values of the activity coefficients of component *i*, respectively. The average relative deviation S_i and the average standard deviation S_i^* for Pb-Sn and Sb-Sn alloy were calculated from Eqs. (3) and (4), respectively, as shown in Table 8.

Table 8. *Average relative deviation S_i and average standard deviation S_i^* of Pb-Sn and Sb-Sn alloy*

Pb-Sn	S_{Pb}	S_{Pb}^*	S_{Sn}	S_{Sn}^*
	±1.23%	±0.008	±1.34%	±0.009
Sb-Sn	S_{Sb}	S_{Sb}^*	S_{Sn}	S_{Sn}^*
	±0.09%	±0.0006	±0.09%	±0.0006

It can be seen from Table 8 that the maximum average relative deviation and the maximum average standard deviation are ± 1.34% and ± 0.009, respectively, which indicates that the calculation of the activity coefficient of the Pb-Sn and Sb-Sn alloy by MIVM is reliable.

3.5. VLE prediction by MIVM

The fugacity of each component in the vapor and liquid phase is equal when the system reaches equilibrium. As the liquid phase is not an ideal solution, in order to make the VLE calculation method suitable for the non-ideal solution, the γ was introduced based on Raoul's law for the low pressure (p = 2 Pa) system in this study. Hence, the equation for VLE can be expressed as follows [25]:

$$y_ip = x_i\gamma_ip_i^{\text{sat}} \quad (i=1,2,\ldots,N) \quad (7)$$

where p_i^{sat} is the saturated vapor pressure of pure component i at temperature T; p is the system pressure; x_i and y_i are the mole fraction of component i in the liquid phase and vapor phase, respectively; and γ_i is the activity coefficient of component i in the liquid phase.

For a binary alloy system *i-j,*

$$x_i + x_j = 1 \qquad y_i + y_j = 1 \tag{8}$$

$$p = p_i^{sat}\gamma_i x_i + p_j^{sat}\gamma_j x_j = p_i^{sat}\gamma_i x_i + p_j^{sat}\gamma_j(1-x_i) \tag{9}$$

By connecting equations (8) and (9), x_i and y_i can be obtained as follows:

$$x_i = \frac{p - p_j^{sat}\gamma_j}{p_i^{sat}\gamma_i - p_j^{sat}\gamma_j} \tag{10}$$

$$y_i = \frac{p_i^{sat}\gamma_i}{p} x_i \tag{11}$$

The VLE calculation in this case is an iterative procedure of estimating a temperature and calculating the partial pressure of the components from the vapor pressures of the pure components and the activity coefficients at given temperature, until the system pressure p fixed by γ_i is equal to the value that is set. Then, the T, x_i and y_i are output. Fig. 2 shows the flowchart for calculating VLE for the Pb-Sn, Sb-Sn alloy system.

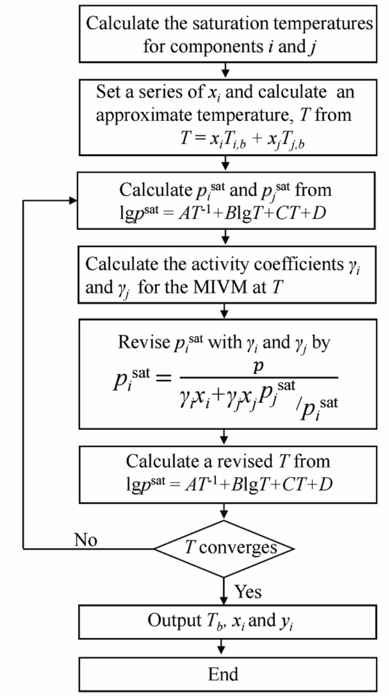


Figure 2*. Flowchart for calculating VLE of Pb-Sn, Sb-Sn binary alloy system*

The steps required to calculate the VLE are as follows:

1. Calculate the saturation temperatures for components i and j from $\lg p^{sat} = AT^{-1} + B\lg T + CT + D$. The value of *A, B, C, D* is shown in Table 9.

2. Set a series of x_i and calculate an approximate temperature, T from $T = \sum_{i=1}^{c} x_i T_{i,b}$ and note that $\sum_{i=1}^{c} x_i = 1$

3. Calculate p_i^{sat} and p_j^{sat} from the equation: $\lg p^{sat} = AT^{-1} + B\lg T + CT + D$.

4. Calculate the activity coefficients γ_i and γ_j from equations (3) and (4).

5. Calculate y_i from equation (11).

If the absolute difference of p is less than the tolerance value, then output T_b, x_i and y_i, otherwise estimate a new value for T and go to step 3 until the system pressure p is equal to the total pressure that is set (e.g., 2 Pa).

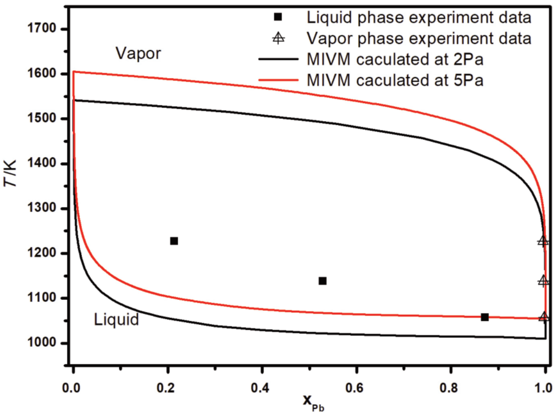
Table 9. *Evaporation constant of the elements in Pb-Sn and Sb-Sn alloy [26]*

Element	*A*	*B*	*C*	*D*	*T* /K
Pb	-10130	-0.985	0	13.28	601-2022
Sn	-15500	0	0	10.355	505-2875
Sb	-6500	0	0	8.495	904-1860

Based on the procedure shown in Fig. 2, the VLE data can be calculated. The calculated VLE data for Pb-Sn and Sb-Sn alloys were also listed in Tables 3 and 4. It can be seen from Tables 3 and 4 that the calculated VLE data, especially the vapor phase data agree well with the experimental results, which indicates that the calculation of VLE data of Pb-Sn and Sb-Sn alloys by MIVM is reliable.

In order to compare experimental results and calculated VLE data more intuitively, the *T-x* phase diagram of Pb-Sn and Sb-Sn binary alloy system were established by using the calculated VLE data, as shown in Fig. 3.

It can be seen from Fig. 3 that the calculated VLE data of Pb-Sn and Sb-Sn binary alloy systems by this



(a)

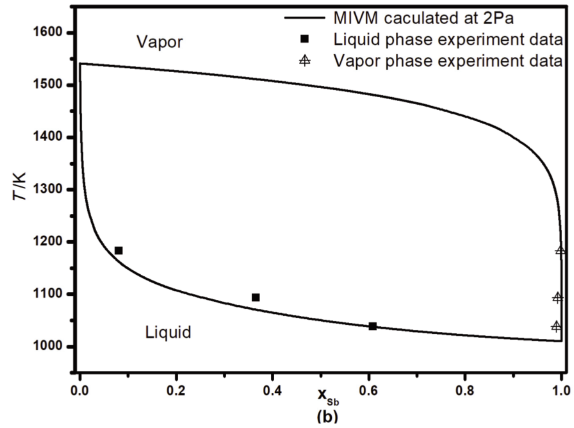


***Figure 3**. VLE phase diagram of alloy system: (a) Pb-Sn, (b) Sb-Sn; ■ liquid phase point, △ vapor phase point*

method, agree with the experimental data. In other words, the VLE phase diagrams obtained by this method are available for predicting and analyzing the process of vacuum distillation of Pb-Sn and Sb-Sn alloys. However, there is still little deviation between the experimental data and calculated results. The reasons for the higher liquid phase data than the liquidus are attributed to the following aspects: (1) The MIVM adopted during calculations can bring certain errors; (2) The saturated vapor pressure of pure metals adopted during calculations will also bring certain errors.

The tendency of vapor composition in Fig. 3 apparently shows that Sn has a worse evaporation ability than Pb and Sb in this binary system, which indicates that Sn will enrich in the liquid phase, while Pb and Sb will do so in the vapor phase in the vacuum distillation process. The vapor-liquid equilibrium phase diagram of the alloy can predict the final product of the vacuum distillation and guide the setting of important parameters such as temperature and vacuum degree during vacuum distillation. For example, the increase in pressure leads to a rise in the temperature required for vacuum distillation to separate alloys. Hence, the system pressure should be reduced as far as possible when vacuum distillation is used to separate Pb-Sn, Sb-Sn alloys.

4. Conclusions

A brand new experimental method to determine VLE data of alloys was proposed in this study. New VLE data of Pb-Sn and Sb-Sn binary alloys were determined at 2 Pa by using this new experimental method, which passed the thermodynamic consistency test (Van Ness test). This indicates that this new method and the VLE data are reliable. The activity coefficients of Pb-Sn and Sb-Sn alloy was calculated using the MIVM, and the maximum average relative deviation S_i and maximum average standard deviation S_i^* are ±1.34% and ±0.009, respectively, which indicates that the calculation of the activity coefficient of the Pb-Sn and Sb-Sn alloy system by MIVM is reliable.

The VLE data of Pb-Sn and Sb-Sn binary alloy system was also calculated based on the MIVM and VLE theory, and the calculated data are highly consistent with the experimental data. This study provides a useful method for experimental determination of VLE data of an alloy system, which is of great significance not only for the verification of calculated VLE data of alloy systems, but also for the efficient separation and purification of alloys by vacuum methods.

Acknowledgement

The authors are grateful for the financial support from the General Program of Natural Science Foundation of China (NSFC) under Grant No. 51474116, the Union Program of NSFC-Yunnan Province under Grant No. U1502271, the High-level Talent Platform Construction Program of Kunming University of Science and Technology under Grant No. KKKP201752023, and the National Key Research and Development Program of China under Grant No. 2016YFC0400400.

References

[1] J. Gao, K. Zhang, D.M. Xu, L.Z. Zhang, N.N. Chen, C.L. Li, J. Chem. Eng. Data, 62 (7) (2017) 1948-1954.

[2] L.Z. Zhang, D.M. Xu, J. Gao, L.W. Zhao, Z.S. Zhang, C.L. Li, J. Chem. Thermodyn., 102 (2016) 155-163.

[3] F. Rivollet, A. Chapoy, C. Coquelet, D. Richon, Fluid Phase Equilibr., 218 (1) (2004) 95-101.

[4] M. Rogalski, K. Rybakiewicz, S. Malanowski, Ber. Bunsenges. Phys. Chem., 82 (1977) 1070-1073.

[5] M.M. Abbott, Fluid Phase Equilibr., 29 (1986) 193-207.

[6] L.X. Kong, B. Yang, Y.F. Li, B.Q. Xu, D.C. Liu, G.B. Jia, Metall. Mater. Trans. B, 43 (2012) 1649-1656.

[7] J.J. Xu, L.X. Kong, B.Q. Xu, B. Yang, Y.J. You, S. Xu, Y.Z. Zhou, Y.F. Li, D.C. Liu, Metall. Mater. Trans. A, 47 (9) (2016) 4494-4501.

[8] L.X. Kong, J.J. Xu, B.Q. Xu, S. Xu, B. Yang, Y.Z. Zhou, YF. Li, D.C. Liu, Fluid Phase Equilibr., 415 (2016) 176-183.

[9] C. Zhang, W.L. Jiang, B. Yang, D.C. Liu, B.Q. Xu, H.W. Yang, Fluid Phase Equilibr., 405 (2015) 68-72.

[10] H.W. Yang, C. Zhang, B. Yang, B.Q. Xu, D.C. Liu, Vacuum, 119 (2015) 179-184.

[11] A.L. Rodomonte, A. Montinaro, M. Bartolomei, J. Pharmaceut. Biomed., 42 (2006) 56-63.

[12] L.S. Darken, J. Am. Chem. Soc., 72 (7) (1950) 2909-2914.

[13] M. Sacchetti, J. Chem. Educ., 78 (2) (2001) 260-263.

[14] J.P.E. Grolier, J.M.D. Río. J. Solution Chem., 44 (5) (2015) 987-1003.

[15] H. Li, S.Q. Xia, M. Wu, P.S. Ma, J. Chem. Thermodyn., 87 (2015) 141-146.

[16] P.L. Jackson, R.A. Wilsak, Fluid Phase Equilibr., 103 (2) (1995) 155-197.

[17] C.B. Nan, H. Xiong, B.Q. Xu, B. Yang, D.C. Liu, H.W. Yang, Fluid Phase Equilibr., 442 (2017) 62-67.

[18] C.B. Nan, H.W. Yang, B. Yang, D.C. Liu, H. Xiong, Vacuum, 135 (2017) 109-114.

[19] D.P. Tao, Thermochim. Acta, 363 (1-2) (2000) 105-113.

[20] L.X. Kong, B. Yang, B.Q. Xu, Y.F. Li, Y.S. Hu, D.C. Liu, Metall. Mater. Trans. A, 46 (3) (2015) 1205-1213.

[21] B. Yang, L.X. Kong, B.Q. Xu, D.C. Liu, Y.N. Dai, Trans. Nonferrous Met. Soc. China, 25 (4) (2015) 1315-1324.

[22] A.X. Wang, Y.F. Li, B. Yang, B.Q. Xu, L.X. Kong, D.C. Liu, Vacuum, 109 (2014) 127-134.

[23] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected Values of Thermodynamic Properties of Binary Alloys, ASM, Metals Park, Ohio, 1973, p. 916.

[24] D.P. Tao, Metall. Mater. Trans. B, 45 (1) (2014) 142-149.

[25] F.A.A. Al-Rub, R. Datta, Chem. Eng. J., 81 (1-3) (2001) 83-89.

[26] Y.N. Dai, B. Yang, Vacuum Metallurgy of Nonferrous Metals, Metallurgical Industry Press, Beijing, 2000, p. 180 (in Chinese).

IZOBARIČNI (PARA+TEČNOST) RAVNOTEŽNI NAPON BINARNOG Pb-Sn I Sb-Sn SISTEMA PRI PRITISKU OD 2Pa

J. Gao[a,c], J. Xu[a,c], B. Yang[a,b], L. Kong[a,c,*], B. Xu[a,b,*], Y. You[a,c]

[a] Nacionalna tehnička laboratorija za vakuum metalurgiju, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, NR Kina

[b] Glavna laboratorija za vakuum metalurgiju za obojene metale, Junan provincija, Kunming, NR Kina

[c] Glavna državna laboratorija za složene resurse obojenih metala i njihovu upotrebu, Junan provincija, Kunming, NR Kina

Apstrakt

U ovom radu je osmišljen novi eksperimentalni metod za utvrđivanje ravnoteže para- tečnost kod binarnih legura. Ravnoteža para- tečnost kod Pb-Sn i Sb-Sn legura je određen pomoću ove nove metode. Eksperimentalni podaci su u skladu sa termodinamičkim testom konzistencije (Van Nesov test), i dobijeno je da je $y_{(MAD)}$ *0,4066 i 0,6667, što ukazuje da eksperimentalni metod tačan i pouzdan. Koeficijent delovanja za Pb-Sn i Sb-Sn legure je izračunat pomoću modela molekulskih interakcija (MIVM). Dobijeno je da maksimalno prosečno relativno odstupanje* S_i *iznosi ±1.34%, a maksimalno prosečno standardno odstupanje* S_i^* *iznosi ±0.009, što ukazuje da je izračunavanje koeficijenta delovanja kod Pb-Sn i Sb-Sn legura pomoću MIVM pouzdano. Podaci o ravnotežnom naponu pare tečnosti kod Pb-Sn i Sb-Sn legura su dobijeni na osnovu teorije o ravnotežnom naponu pare tečnosti i modela molekulskih interakcija (MIVM), a dobijeni rezultati se slažu sa svim eksperimentalnim podacima. U ovom radu su predstavljeni i fazni dijagrami Pb-Sn i Sb-Sn legura. Ovi fazni dijagrami pružaju prihvatljiv i intuitivni način da se analizira kako temperatura i pritisak utiču na sastav proizvoda tokom vakuumske destilacije. Ovo će imati veliki uticaj na stvarnu proizvodnju vakuumske metalurgije.*

Ključne reči: *Novi eksperimentalni metod; Ravnotežni napon pare tečnosti; Pb-Sn i Sb-Sn legure; Model molekulskih interakcija (MIVM); Termodinamički test konzistencije*