Measurement and modeling of phase equilibria for Sb-Sn and Bi-Sb-Sn alloys in vacuum distillation

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ABSTRACT

Vapor-liquid equilibria (VLE) and purification of tin from crude Sn containing Bi and Sb has been studied in vacuum distillation. The Sb-Sn and Bi-Sb-Sn systems were investigated in the temperature range from 1000 to 1500 K and at pressure of 5 Pa. Consequently, the content of Sn for the Bi-Sb-Sn system in the liquid phase reached more than 0.99 mol fraction as the temperature higher than 1500 K. It is shown that Bi and Sb can be satisfactorily removed from crude Sn. The VLE data of Sb-Sn and Bi-Sb-Sn alloys were calculated by using Wilson equation and compared with experimental values under vacuum condition. The capability of the equation to predicting the activities of components in whole composition range was also tested. It provides an efficient way to guide the process of vacuum distillation. The experiment results revealed that vacuum distillation is a promising method for the separation and purification of crude metals.

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1. Introduction

The Sn-based alloys were usually used to recycle Sn, which contain Pb, Sb, Bi, Ag, and Cu, etc. Bi-Sb-Sn ternary alloy is common materials in recycling process of tin. Vacuum distillation, which has such advantages as high metal recovery, low impurities in recovered metal, good environmental protection and simple equipment, was widely used for purifying and recycling tin. The evolution of vacuum distillation theory and practice, brought about by its industrial importance, has refined crude tin successfully [1,2]. Vacuum distillation can be used to remove Pb, Sb, Bi, As and other impurities from crude tin [3,4]. The purity of tin is more than 99%, the contents of lead and bismuth in tin can be less than 0.001% by vacuum distillation.

For metallic melts, the effects of separation and purification by vacuum distillation have been investigated [5,6]. In our previously work, the application of vapor-liquid equilibrium (VLE) phase diagram in vacuum distillation was proposed [7,8]. VLE phase diagram can be applied to predict and guide the purification and separation process of alloys in vacuum distillation. With the increasing need for the development of vacuum metallurgy technology, it is highly desirable to accurately calculate the VLE data. For Bi-Sn system, we carried out the experimental investigation in vacuum distillation [9]. Only few experimental data of the Sb-Sn system were reported in literature [10]. No experimental VLE data of Bi-Sb-Sn system have been obtained in previously literature.

This work is focused on separation of Bi and Sb from crude Sn in vacuum distillation. The main objective is to investigate experiment and thermodynamic modeling of VLE data for Sb-Sn and Bi-Sb-Sn systems at pressure of 5 Pa. It provides the basic thermodynamic data for purification of crude Sn by vacuum distillation process. The thermodynamic consistency of the experimental VLE data was checked out by means of the Van Ness test for the binary and ternary systems.

2. Experimental

2.1. Materials

The materials of pure Sn (99.90 wt %), Sb (99.99 wt %) and Bi

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(99.99 wt %) were obtained from Yunnan Tin Group Co., Ltd., China. The specifications of the experimental samples of Sb-Sn and Bi-Sb-Sn alloys are summarized in Table 1.

2.2. Apparatus and experimental procedure

The experiment apparatus of vacuum distillation as shown in Fig. 1. A vertical vacuum furnace was made by Kunming Diboo Technology Co., Ltd. It was heated by induction heating with graphite heater. Fig. 2 is the schematic illustration of the furnace body. In this furnace, the crucible-coil assembly was positioned the center of a water-cooled vacuum chamber which inner diameter 0.22 m, out diameter 0.27 m and 0.2 m depth. The distance between melt surface and condensing surface is 0.1 m. The furnace can be seen as a close system. In order to ensure steady temperature, heating was provided by output current. The pressure was maintained at a desired value by a Rotary oil vacuum pump. Temperature measurements were accomplished using a Pt-100 probes connecting to a digital temperature meter (ANTHONE LU-900M). Pressure was measured with a stand McLeod Gauge. The experimental uncertainties of temperature and pressure are ±5 K and ±2 Pa, respectively.

During experiment, alloy sample was putted into a high purity graphite crucible (99.998 wt % C) with the inner diameter of 0.04 m and a depth of 0.04 m. Then, the crucible was placed inside another crucible-coil with the inner diameter of 0.1 m. The vacuum furnace was heated to the preset temperature as soon as possible. The temperature of chamber was hold at constant after the chamber was evacuated to 5 Pa. Experimental investigations have been carried out in the temperature range between 1000 K and 1550 K.

Due to the surface tension and viscosity of molten metal, boiling may not occur, evaporation process occurs only on the surface of melts. It is very rarely that equilibrium exists within individual or between different phases, as only quasi-stationary states are attained. Equilibrium, therefore, should exist only at the phase boundary [11]. We hypothesized that the distillation processes will approach to a stable level with the extension of time. When the system reaches stable level, a dynamic equilibrium will maintain between liquid metal and vapor on the boundary layer. It will be maintained long enough time to ensure the stability of system during experiment.

The components of distillation product approach to a stable level with the extension of time, which means that the system reaches vapor-liquid equilibrium. After completion of each distillation experiment, the vacuum furnace was cooled to room temperature. The residue was collected in the graphite crucible and the volatile condensed to solid on the stainless steel cold plate which is connecting to the circular cooling water. The samples of the liquid and vapor phases were obtained from residue and volatile, respectively. All the samples under different times were measured.

2.3. Sample analysis

The equilibrium compositions of the vapor and liquid phases were analyzed by an atomic absorption spectrometry and volumetric method with an atomic absorption spectrophotometer

Table 1
Chemical composition of Sn-Sb and Sn-Sb-Bi alloys with different composition.

Sample No.	x_{Sn}	x_{Sb}	x_{Bi}
0#	0.8	0.2	–
1#	0.8	0.1	0.1
2#	0.5	0.25	0.25
3#	0.2	0.25	0.25

(WFX-320 Atomic Absorption Spectrophotometer, supplied by Beijing Rayleigh Analytical Instrument Co., Ltd.) and Potentiometric titration (848 Titrino plus, supplied by Metrohm), respectively. The limit of detection is 0.01 μg/ml. Finally, the experimental uncertainty of the composition measurements was estimated to be within ±0.00001 in mole fraction.

3. Method

3.1. Theory of VLE

The vapor-liquid equilibrium equation can be expressed by the following equation

$$x_i \gamma_i(x_i, T, P) P_i^*(T) = y_i P \tag{1}$$

where x_i and y_i are the mole fraction of species i in the liquid phase and vapor phase, respectively; γ_i is activity coefficient of species i in terms of temperature, pressure and the mole fraction of species i, and $P_i^*(T)$ is saturation pressure of a pure liquid i, respectively. T and P are the temperature and pressure of the system, respectively.

3.2. Wilson equation

The Wilson equation was used as the correlation model in this work [12–14]. For a binary mixture i-j, the respective activity co-efficients of components i and j are:

$$\ln \gamma_i = -\ln(x_i + x_j A_{ij}) + x_j \left(\frac{A_{ij}}{x_i + x_j A_{ij}} - \frac{A_{ji}}{x_j + x_i A_{ji}} \right) \tag{2}$$

$$\ln \gamma_j = -\ln(x_j + x_i A_{ji}) - x_i \left(\frac{A_{ij}}{x_i + x_j A_{ij}} - \frac{A_{ji}}{x_j + x_i A_{ji}} \right) \tag{3}$$

where x_i and x_j are the mole fraction of components i and j. The parameters A_{ij} and A_{ji} are expressed by

$$A_{ij} = \frac{v_j}{v_i} \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \tag{4}$$

$$A_{ji} = \frac{v_i}{v_j} \exp[-(\lambda_{ji} - \lambda_{jj})/RT] \tag{5}$$

where v_i and v_j are the molar volumes of components i and j which are written as a functions of temperature, λ_{ii}, λ_{jj} and $\lambda_{ij}(\lambda_{ij} = \lambda_{ji})$, which are the interaction energies i-i, j-j, and i-j pairs, respectively.

For Wilson equation, $(\lambda_{ji} - \lambda_{ii})$ and $(\lambda_{ij} - \lambda_{jj})$ were considered independent of temperature [15]. Therefore, values of A'_{ji} and A'_{ij} at other temperature T' should be calculated as follows:

$$A'_{ji} = \frac{v'_j}{v'_i} \left(\frac{A_{ji}}{v_j/v_i} \right)^{\frac{T}{T'}} \tag{6}$$

$$A'_{ij} = \frac{v'_i}{v'_j} \left(\frac{A_{ij}}{v_i/v_j} \right)^{\frac{T}{T'}} \tag{7}$$

The values of A_{ij} and A_{ji} can be obtained from Eqs. (2) and (3) using the Newton-Raphson methodology if experimental activity coefficients are known. Substituting the parameters A'_{ij} and A'_{ji} at different temperatures into Eqs. (2) and (3), the activity coefficients γ_i and γ_j can be calculated at correspond temperatures. In this