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Application of MIVM for phase equilibrium of Sn–Pb–Sb system in vacuum distillation

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ABSTRACT

Based on the molecular interaction volume model (MIVM), the pair-potential energy parameters B_{ji} and B_{ij} of the related binary Sn–Pb, Pb–Sb and Sn–Sb alloy systems were calculated using the infinite dilution activity coefficients ${\gamma_i}^{\infty}$ and ${\gamma_j}^{\infty}$. The activities of components of the Sn–Pb–Sb ternary alloy system were predicted using B_{ji} and B_{ij}. Finally, the vapor–liquid phase equilibrium of the Sn–Pb–Sb alloy system was predicted using only the properties of pure components and the activity coefficients, which indicates that Sn can be separated from Pb and Sb by vacuum distillation thoroughly. A significant advantage of the model lies in its ability to predict the thermodynamic properties of multi-component liquid alloys using only two parameters. Moreover, the MIVM is reliable due to it has certain physical meaning from the viewpoint of statistical thermodynamics.

1. Introduction

A large number of Sn–Pb–Sb alloys will be produced from tin, lead and antimony smelteries every year due to tin, lead and antimony ores usually contain Sn, Pb and Sb at present. In addition, the wasted Sn–Pb alloys recycled from various industries would inevitably contain Sb due to Sb was usually used to produce alloys with Sn and Pb. The separation and recovery of Sn–Pb–Sb alloys, therefore, has become imperative for the refineries of the whole world. There are some serious problems in conventional methods of separation and recycle of nonferrous metals such as evident environment pollution, long flow sheet, high energy consumption, etc. [1]. Vacuum metallurgy has many advantages, such as high metal recovery, short flow sheet and good environmental protection etc., which can eliminate the disadvantages of traditional metallurgical processes. Moreover, it can produce new products to meet the needs of the rapid development of high technology [2]. Over past decades, vacuum metallurgy has been studied and successfully used in refining and separating of various nonferrous crude metals by Dai [3], Ali [4–6] and Wedlock [7] etc., and the area of its application is being extended rapidly.

The thermodynamic properties of multi-component liquid alloys are important for understanding the process metallurgy. In order to obtain the thermodynamic properties of multi-component liquid alloys, the experiments are necessary and reliable. However, the experimental thermodynamic study is very time consuming, and needs not only the excellent instruments but also the financial support continuously. Therefore, model prediction is convenient and economic for obtaining the thermodynamic properties of alloys. The MIVM [8] has been researched and successfully used in predicting thermodynamic properties of binary and multi-component liquid alloy systems in previous work, which indicates that the prediction effect of the MIVM is of better stability and reliability [9–11].

Yang et al. [12] has calculated the phase equilibrium of Pb–Sn system in vacuum distillation by the MIVM, which indicates that the MIVM is reliable and convenient. Nevertheless, their studies focused only on binary alloys. Kong et al. [13] has investigated the application of MIVM for Pb–Sn system in vacuum distillation. However, their studies have not considered the effect of adding Sb into the Pb–Sn system. Moreover, the investigation about the application of MIVM in vacuum distillation of Sn–Pb–Sb ternary alloy has not been reported. The Sn–Pb–Sb ternary alloy, therefore, was selected to demonstrate the utility of MIVM in vacuum distillation in order to provide a rigorous model for predicting the distribution of components of Sn–Pb–Sb alloy in vacuum distillation quantitatively, which will provide an instruction for practical vacuum

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distillation of Sn–Pb–Sb alloy. The purpose of this study, therefore, was to investigate the application of MIVM in predicting the activities and distribution of components of Sn–Pb–Sb ternary alloy in vacuum distillation. The present work will provides an effective and convenient model for the refining and separation of ternary alloys by vacuum distillation.

2. Simple description of MIVM

The MIVM was derived from the statistical thermodynamics, which can be used to predict the thermodynamic properties of multi-component liquid alloy systems using only two infinite dilute activity coefficients γ_i^{∞}, γ_j^{∞}, more details were available in Ref. [8].

The values of B_{ij} and B_{ji} of the related binary alloys Sn–Pb, Pb–Sb and Sn–Sb must be obtained before applying the model into Sn–Pb–Sb ternary liquid alloy, which can be calculated from Eqs. (34–41) in Ref. [8] using the Newton–Raphson methodology if the infinite dilute activity coefficients γ_i^{∞} and γ_j^{∞} are known. The values of γ_i^{∞} and γ_j^{∞} at required temperatures can be calculated as follows.

For a binary mixture *i–j*, the partial molar excess Gibbs energy of component *i* [14] can be expressed as

$$\overline{G}_i^E = \overline{H}_i^E - T\overline{S}_i^E = RT\ln\gamma_i \tag{1}$$

where $\overline{H}_i^E$ and $\overline{S}_i^E$ are the partial molar excess enthalpy and entropy of component *i*, respectively. When $x_i \to 0$, Eq. (1) can be written as

$$\ln\gamma_i^{\infty} = \frac{\overline{H}_i^{E^{\infty}}}{RT} - \frac{\overline{S}_i^{E^{\infty}}}{R} \tag{2}$$

Suppose that the partial molar infinite dilute excess enthalpy $\overline{H}_i^{E^{\infty}}$ and entropy $\overline{S}_i^{E^{\infty}}$ of component *i* are independent of temperature. Then Eq. (2) may be written as

$$\ln\gamma_i^{E\infty} = \frac{a}{T} + b \tag{3}$$

where $a = \overline{H}_i^{E^{\infty}}/R$ and $b = -\overline{S}_i^{E^{\infty}}/R$. Notice that $\overline{H}_i^{E^{\infty}}$ is the partial molar infinite dilute mixing enthalpy of component *i*, viz. $\Delta\overline{H}_i^{M\infty}$. Based on the Eq. (3), the infinite dilute activity coefficient γ_i^{∞} at any temperature can be calculated easily from the values of $\Delta\overline{H}_i^{M\infty}$ and $\overline{S}_i^{E^{\infty}}$ [15]. The predicted values of γ_i^{∞} and γ_j^{∞} are shown in Table 1.

On the other hand, the values of B_{ij} and B_{ji} at the required temperature (T_2) can be obtained from Eq. (6) in Ref. [14] in which the pair-potential energy interaction parameters $(\varepsilon_{ij} - \varepsilon_{jj})/kT$ and $(\varepsilon_{ji} - \varepsilon_{ii})/kT$ may be assumed to be independent of temperature while the values of B_{ij} and B_{ji} are known at a certain temperature (T_1).

The required parameters B_{ij} and B_{ji} of the related Sn–Pb, Pb–Sb and Sn–Sb binary alloys are shown in Table 2.

Table 1
The values of γ_i^{∞} and γ_j^{∞} of the related binary liquid alloys *i–j* at the required temperatures.

Sn–Pb			Pb–Sb			Sn–Sb		
T (K)	γ_i^{∞}	γ_j^{∞}	T (K)	γ_i^{∞}	γ_j^{∞}	T (K)	γ_i^{∞}	γ_j^{∞}
1073	2.165	6.717	1073	0.779	0.776	1073	0.448	0.451
1173	2.051	6.326	1173	0.779	0.775	1173	0.466	0.471
1273	1.959	6.014	1273	0.779	0.774	1273	0.482	0.488
1373	1.883	5.759	1373	0.779	0.774	1373	0.496	0.504
1473	1.820	5.548	1473	0.779	0.773	1473	0.509	0.517
1573	1.768	5.370	1573	0.779	0.773	1573	0.520	0.530

Table 2
The values of B_{ij}, B_{ji}, Z_i and Z_j of the related binary alloys at the required temperatures.

i–j	T (K)	B_{ij}	B_{ji}	Z_i	Z_j
Sn–Pb	1073	0.4955	1.1721	9.44	6.34
	1173	0.4911	1.1848	9.30	6.29
	1273	0.4868	1.1962	9.16	6.21
	1373	0.4828	1.2066	9.03	6.13
	1473	0.4791	1.2157	8.90	6.06
	1573	0.4755	1.2243	8.79	6.00
Pb–Sb	1073	1.0084	1.0377	9.44	6.37
	1173	1.0054	1.0407	9.30	6.10
	1273	1.0022	1.0437	9.16	5.86
	1373	1.0026	1.044	9.03	5.65
	1473	0.9993	1.047	8.90	5.48
	1573	0.9996	1.0473	8.79	5.32
Sn–Sb	1073	1.1117	1.0798	6.38	6.37
	1173	1.1141	1.0721	6.29	6.09
	1273	1.1151	1.0666	6.21	5.86
	1373	1.1182	1.0597	6.13	5.65
	1473	1.1180	1.0566	6.06	5.48
	1573	1.1217	1.0503	6.00	5.32

It is also necessary to determine the coordination numbers *Z* of liquid metals for applying MIVM to Sn–Pb–Sb ternary liquid alloy, and the values of *Z* can be calculated from Eqs. (30–33) in Ref. [8] using the ordinary physical quantities of pure liquid metals [2], as shown in Table 2.

Letting the Sn–Pb–Sb liquid alloy be the 1–2–3 system, the activity coefficient of the component 1 of the system can be written from Eq. (29) in Ref. [8] as

$$\begin{aligned}\ln\gamma_1 = {} & 1 + \ln\left(\frac{V_{m1}}{x_1V_{m1} + x_2V_{m2}B_{21} + x_3V_{m3}B_{31}}\right) - \frac{x_1V_{m1}}{x_1V_{m1} + x_2V_{m2}B_{21} + x_3V_{m3}B_{31}} \\ & - \frac{x_2V_{m1}B_{12}}{x_1V_{m1}B_{12} + x_2V_{m2} + x_3V_{m3}B_{32}} - \frac{x_3V_{m1}B_{13}}{x_1V_{m1}B_{13} + x_2V_{m2}B_{23} + x_3V_{m3}} - \frac{1}{2} \\ & \times\left(\frac{Z_1(x_2B_{21} + x_3B_{31})(x_2B_{21}\ln B_{21} + x_3B_{31}\ln B_{31})}{(x_1 + x_2B_{21} + x_3B_{31})^2}\right) + \frac{Z_2x_2B_{12}[(x_2 + x_3B_{32})\ln B_{12} - x_3B_{32}\ln B_{32}]}{(x_1B_{12} + x_2 + x_3B_{32})^2} \\ & + \frac{Z_3x_3B_{13}[(x_2B_{23} + x_3)\ln B_{13} - x_2B_{23}\ln B_{23}]}{(x_1B_{13} + x_2B_{23} + x_3)^2}\end{aligned} \tag{4}$$

3. Method

3.1. Saturated vapor pressure

The fundamental condition to determine whether the components of multi-component alloys can be separated by vacuum distillation is the differences of the saturated vapor pressure of pure components of alloys. The saturated vapor pressure of pure components can be calculated from the Van Laar equation Ref. [16] expressed as follows

$$lgp^* = AT^{-1} + BlgT + CT + D \tag{5}$$