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Application of molecular interaction volume model in vacuum distillation of Pb-based alloys

HongWei Yang [a,b,c,*], Bin Yang [a], BaoQiang Xu [a,b], DaChun Liu [a,b], DongPing Tao [b]

[a] National Engineering Laboratory of Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, PR China
[b] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, PR China
[c] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China

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ABSTRACT

A method is presented for calculating the separation coefficients of Pb–Au and Pb–Sn alloys in vacuum distillation based on molecular interaction volume model (MIVM). A significant advantage of the model lies in its ability to predict the thermodynamic properties of liquid alloys using only binary infinite activity coefficients. The calculated results of Pb–Ag, Pb–Au, Pb–Sb, Pb–Sn and Sb–Sn show good agreement with experimental data in literature. It shows that the prediction effect of the proposed method is of better stability and reliability because the MIVM has a good physical basis.

1. Introduction

There are some serious problems in conventional producing methods of nonferrous metals such as environment pollution, high energy consumption, too much employees, low economic profits etc. Vacuum metallurgy can eliminate the disadvantages of traditional metallurgical processes, expand machining range, and produce new products to meet the needs of the development of high technology. Vacuum distillation has been studied and used in separation of various elements from nonferrous alloys and the area of its application is being extended rapidly [1–3]. Over past decades, refining and separation of various impurities from nonferrous crude metals by vacuum distillation have been studied by Dai and coworkers, especially Pb-based alloy systems [4–7]. Generally, the thermodynamic properties of alloys are important to estimate the separation degree and the products' composition quantitatively. The experimental thermodynamic study of a system is very time consuming since a great number of measurements are necessary. Therefore, theoretical predicting is a significant and effective approach to obtain thermodynamic properties of alloys, especially for multicomponent ones.

In our previous paper, the molecular interaction volume model (MIVM) was obtained from a physical basis [8]. It is a two-parameter model, which is able to predict the thermodynamic properties in a multicomponent solution system using only the ordinary physical quantities of pure liquid metals and the related binary infinite dilute activity coefficients. The prediction effect of MIVM is of better stability and safety through our previous work [9–11].

In the present work, the MIVM has been applied to calculate the activities of components of Pb–Ag, Pb–Au, Pb–Sb, Pb–Sn and Sb–Sn alloys. The predicted values are compared with experimental data to verify the reliability of the method. The separation coefficients of Pb–Au and Pb–Sn alloys were calculated in vacuum distillation based on the MIVM.

2. Method

2.1. Separation coefficient in vacuum distillation

The reason of refining of crude metals or separation of alloys by vacuum distillation is the composition difference between distillated gas product and liquid phase. For example, at the part of rich lead (crude lead, >90% Pb) in Pb–Sn alloy, lead is selectively volatilized during distillation, and at the part of rich tin (crude tin,

* Corresponding author. National Engineering Laboratory of Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, PR China.
E-mail address: hongweiyy@yahoo.com.cn (H. Yang).

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Table 1
Vapor pressure of the components at different temperature [12].

T/K	1073	1173	1273	1373	1473	1573
P^*_{Ag}/pa	6.70×10^{-3}	8.71×10^{-2}	0.75	4.68	22.70	89.78
P^*_{Au}/pa	2.99×10^{-7}	9.29×10^{-6}	1.67×10^{-4}	1.97×10^{-3}	1.65×10^{-2}	1.05×10^{-1}
P^*_{Pb}/pa	7.24	42.25	185.82	655.13	1.94×10^{3}	4.97×10^{3}
P^*_{Sb}/pa	273.92	899.38	2.45×10^{3}	5.76×10^{3}	1.21×10^{4}	2.31×10^{4}
P^*_{Sn}/pa	8.11×10^{-5}	1.38×10^{-3}	1.51×10^{-2}	1.16×10^{-1}	6.79×10^{-1}	3.17

>90% Sn), antimony is preferentially volatilized into gas phase. A concept β i.e. separation coefficient was introduced from theoretical derivation for i–j binary alloy, that is

$$\beta = \frac{\gamma_i}{\gamma_j} \bullet \frac{p_i^*}{p_j^*} \tag{1}$$

Where γ_i and γ_j are activities coefficient of i and j components, respectively; p_i^* and p_j^* are saturated vapor pressure of i and j components, respectively. The vapor pressures of pure Pb, Au and Sn at the different temperature are shown in Table 1.

When $\beta > 1$ or $\beta < 1$, the separation of alloys could happen, but when $\beta = 1$ it could not. Therefore, the separation coefficient β can be used to estimate whether the components may be separated via vacuum distillation for all alloys.

2.2. Molecular interaction volume model

According to MIVM [8], the molar excess Gibbs energy G_m^E of the multicomponent can be expressed as:

$$\frac{G_m^E}{RT} = \sum_{i=1}^{n} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{n} x_j V_{mj} B_{ji}} - \frac{1}{2} \sum_{i=1}^{n} Z_i x_i \left(\frac{\sum_{j=1}^{n} x_j B_{ji} \ln B_{ji}}{\sum_{k=1}^{n} x_k B_{ki}} \right) = -\frac{S_m^E}{R} + \frac{H_m^E}{RT} \tag{2}$$

where Z_i is the nearest molecule or first coordination number; V_{mi} and V_{mj} are the molar volumes of i and j, respectively; x_i, x_j and x_k the molar fractions; and the pair-potential energy interaction parameters B_{ij} and B_{ji} are defined as, respectively,

$$B_{ij} = \exp\left[-(\varepsilon_{ij} - \varepsilon_{jj})/kT\right] \quad B_{ji} = \exp\left[-(\varepsilon_{ji} - \varepsilon_{ii})/kT\right] \tag{3}$$

where ε_{ii}, ε_{jj} and ε_{ij} are the i–i, j–j, and i–j pair-potential energies, $\varepsilon_{ij} = \varepsilon_{ji}$, k the Boltzmann constant, and T the absolute temperature. For a binary mixture i–j, the activity coefficients of component i and j are, respectively

$$\ln\gamma_i = \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}}\right) + x_j \left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) - \frac{x_j^2}{2}\left(\frac{Z_i B_{ji}^2 \ln B_{ji}}{(x_i + x_j B_{ji})^2} + \frac{Z_j B_{ij} \ln B_{ij}}{(x_j + x_i B_{ij})^2}\right) \tag{4}$$

$$\ln\gamma_j = \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) - x_i \left(\frac{V_{mj} B_{ji}}{x_i V_{mi} + x_j V_{mj} B_{ji}} - \frac{V_{mi} B_{ij}}{x_j V_{mj} + x_i V_{mi} B_{ij}}\right) - \frac{x_i^2}{2}\left(\frac{Z_j B_{ij}^2 \ln B_{ij}}{(x_j + x_i B_{ij})^2} + \frac{Z_i B_{ji} \ln B_{ji}}{(x_i + x_j B_{ji})^2}\right) \tag{5}$$

when x_i or x_j approaches zero, the infinite dilution activity coefficients γ_i^∞ and γ_j^∞, respectively, are derived from Eqs. (4) and (5):

$$\ln\gamma_i^\infty = 1 - \ln\left(\frac{V_{mj} B_{ji}}{V_{mi}}\right) - \frac{V_{mi} B_{ij}}{V_{mj}} - \frac{1}{2}\left(Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}\right) \tag{6}$$

$$\ln\gamma_j^\infty = 1 - \ln\left(\frac{V_{mi} B_{ij}}{V_{mj}}\right) - \frac{V_{mj} B_{ji}}{V_{mi}} - \frac{1}{2}\left(Z_i \ln B_{ij} + Z_i B_{ji} \ln B_{ij}\right) \tag{7}$$

In order to determine the required binary parameters B_{ij} and B_{ji}, the infinite dilution activity coefficients of the binary liquid alloys and the related parameters of their components must be obtained. The related parameters of pure metals [12,13] are shown in Table 2. The coordination number Z_i of liquid metals can be estimated by the equation [14].

$$Z_i = \frac{4\sqrt{2\pi}}{3}\left(\frac{r_{mi}^3 - r_{0i}^3}{r_{mi} - r_{0i}}\right)\rho_i r_{mi} \exp\left(\frac{\Delta H_{mi}(T_{mi} - T)}{Z_c R T T_{mi}}\right) \tag{8}$$

where N_i is the molecular number and V_i is the molar volume, $\rho_i = N_i/V_i$ is the molecular number density; ΔH_{mi} and T_{mi} are the melting enthalpy and the melting temperature, respectively; $Z_c = 12$ is a close-packed coordination, T the liquid metal temperature and R the gas constant; r_{0i} and r_{mi} are the beginning and first peak values of radial distance in a radial distribution function near its melting point, respectively. The r_{0i} may be fitted as a proportion of atomic covalent diameter, d_{covi}, which implies that a covalent bond length formed by sharing the outermost valence electrons with other element atoms approaches the closest distance between adjacent atoms; and the r_{mi} is approximate to the atomic diameter observably, σ_i, namely,

$$r_{0i} = 0.918 d_{covi}, \; r_{mi} = \sigma_i \tag{9}$$

The infinite dilution activity coefficients of binary liquid alloys [15] and the required binary parameters B_{ij} and B_{ji} are shown in Table 3, respectively.

Table 2
The related parameters of the components [12,13].

i	V_{mi} cm^3/mol	ΔH_{mi} kJ/mol	σ_i 10^{-8} cm	r_{0i} 10^{-8} cm
Ag	11.6 [1 + 0.98 × 10^{-4}(T-1234)]	11.09	2.88	2.46
Au	11.3 [1 + 0.69 × 10^{-4}(T-1336)]	12.76	2.88	2.46
Pb	19.4 [1 + 1.24 × 10^{-4}(T-600)]	4.81	3.50	2.70
Sb	18.8 [1 + 1.30 × 10^{-4}(T-904)]	39.75	2.80	2.40
Sn	17.0 [1 + 0.87 × 10^{-4}(T-505)]	7.20	3.26	2.59

Table 3
The values of γ_i^∞, γ_j^∞, B_{ij} and B_{ji} of the binary alloys i–j at the required temperatures [15].

i–j	T/K	γ_i^∞	γ_j^∞	B_{ij}	B_{ji}	Z_i	Z_j
Pb–Ag	1300	1.101	1.530	0.5974	1.4450	8.91	10.61
Pb–Au	1400	0.174	0.397	1.5808	0.4558	8.99	10.90
Pb–Sb	905	0.731	0.842	0.6317	1.3410	9.71	6.97
Pb–Sn	1050	2.057	1.710	1.1131	0.8052	9.60	8.81
Sb–Sn	970	0.458	0.556	1.6276	0.5680	6.71	6.48