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Application of molecular interaction volume model for predicting the Ca activity coefficients in Si–Ca binary and Si–Ca–Pb ternary alloys

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ABSTRACT

In this paper, the activity coefficients of calcium in Si–Ca binary and Si–Ca–Pb ternary alloys were each calculated by the molecular interaction volume model (MIVM). The value of the infinite dilution activity coefficient of calcium was determined to be 0.000863 in the Si–Ca binary alloy at 1723 K. The activities of silicon and lead in the Si–Pb binary alloy and of calcium and lead in the Ca–Pb binary alloy were calculated by the Kuo-chih Chou's method using phase diagrams, whose effectiveness was verified. In comparison with the experimental data, all errors predicted by the MIVM were between ±0.22 to ±29.7% and the standard deviations were between $\pm 2.26 \times 10^{-7}$ to ±0.073. Such predicted values are actually small and in good agreement with the experimental data, which indicates that the MIVM is reliable to predict the activities or activity coefficients of Si–Ca binary and Si–Ca–Pb ternary alloys.

1. Introduction

The calcium impurity in solar grade silicon shortens the lifetime of the excited carriers in a silicon solar cell and disturbs electricity generation. The calcium content in metallurgical grade silicon has been predominant in current national standard. Accordingly, the removal of calcium from silicon is a major issue during the silicon purification process. The removal of calcium from silicon is accomplished by selective oxidation followed by the interoxide reaction between the formed calcium oxide and silicon dioxide to form calcium silicate [1]. The technology to produce multicrystalline silicon *via* the metallurgical route involves several processes to remove the calcium impurity, including hydrometallurgy [2], vacuum refining [3,4], and direct solidification [5–7]. The use of this method may decrease the content of calcium in the molten silicon. Researchers at home and abroad have done an ample amount of work for the reduction of calcium impurity content and have obtained satisfactory removal effect.

Activity is an important thermodynamic parameter. The lack of thermodynamic property of calcium in molten silicon has been one of the main obstacles, which has impeded further progress of the metallurgical route. Meanwhile, the experimental studies of thermodynamic properties are expensive, time consuming and difficult to conduct. Accordingly, theoretical prediction is suitable to obtain the thermodynamic parameters [8–10]. The foremost advantage of molecular interaction volume model (MIVM) lies in its ability to predict the thermodynamic properties of liquid alloys using only two binary infinite activity coefficients. Actually, Tao [11] showed that his model can be used to predict the properties of a multicomponent system in the premise of nearly ideal alloys.

In the current study, the Si–Ca binary and Si–Ca–Pb ternary alloys were selected as the research objects. First, the activity coefficients of calcium in the Si–Ca binary alloy are calculated by the MIVM. Second, the activities of the Si–Pb and Ca–Pb binary alloys

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are calculated by the Kuo-chih Chou's model [12–14]. Third, the activity coefficients of the Si–Ca–Pb ternary alloy are calculated by the MIVM. Finally, the results are compared with the experimental data to verify the reliability of this model.

2. Application of the MIVM in the Si–Ca binary alloy

The MIVM developed by Tao [15] is a fluid-based model, and it is derived from statistical thermodynamics. A model of the molar excess Gibbs energy can be expressed as follow [15].

$$G_m^E = RT\left(\sum_{i=1}^{c} x_i \ln\frac{V_{mi}}{\sum_{j=1}^{c} x_j V_{mj} B_{ji}} - \frac{1}{2}\sum_{i=1}^{c} Z_i x_i \left(\frac{\sum_{j=1}^{c} x_j B_{ji} \ln B_{ji}}{\sum_{j=1}^{c} x_j B_{ji}}\right)\right) \quad (1)$$

Where R is the mole gas constant; x_i and x_j are the molar fraction of component i and j; Z_i and Z_j are the nearest atoms or first coordination number of i and j respectively; the coordination number of Z_i and Z_j have been previously reported [16]. V_{mi} and V_{mj} are molar volume of the pure metals.The input parameters of Z is temperature dependent, but the properties do not vary much with temperature [15,17]. Additionally, B_{ij} and B_{ji} are pair-potential energy parameters between i and j which can be defined as:

$$B_{ij} = \exp\left[-\left(\varepsilon_{ij} - \varepsilon_{jj}\right)/kT\right] \quad (2)$$

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

Where k is the Boltzmann constant; T is the absolute temperature; ε_{ii}, ε_{jj} and ε_{ij} are the i-i, j-j, and i-j pair-potential energies, respectively.

In a i-j binary alloy, the expression of the activity coefficients γ_i and γ_j can be expressed as follow.

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

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

When x_i or x_j approaches to zero, the infinite dilution activity coefficients γ_i^0 and γ_j^0 can be derived from the Eq. (4) and Eq. (5).

$$\ln\gamma_i^0 = 1 - \ln\left(\frac{V_{mj}B_{ji}}{V_{mi}}\right) - \frac{V_{mi}B_{ij}}{V_{mj}} - \frac{1}{2}\left(Z_i \ln B_{ji} + Z_j B_{ij} \ln B_{ij}\right) \quad (6)$$

$$\ln\gamma_j^0 = 1 - \ln\left(\frac{V_{mi}B_{ij}}{V_{mj}}\right) - \frac{V_{mj}B_{ji}}{V_{mi}} - \frac{1}{2}\left(Z_j \ln B_{ij} + Z_i B_{ji} \ln B_{ji}\right) \quad (7)$$

For predicting the activities of the components in the silicon-based melts, the relative parameters of the pure components are necessary, and are shown in Table 1 [16,17].

The values of B_{ji} and B_{ij} can be obtained by the Newton-Raphson methodology [15]. In order to get the values of the binary parameters at various temperatures, assuming the pair-potential parameters are independent of temperature, the following equations can be applied.

$$\theta_{ij} = -\frac{\varepsilon_{ij} - \varepsilon_{jj}}{k} \quad (8)$$

$$\theta_{ji} = -\frac{\varepsilon_{ji} - \varepsilon_{ii}}{k} \quad (9)$$

Then the values of B_{ji} and B_{ij} in the i-j binary alloy can be obtained at some temperatures. For instance, the binary parameters needed in the binary system at 1700 K are listed in Table 2 [18].

The activity coefficients of calcium in dilute concentration have been calculated in the Si–Ca binary alloy based on Eq. (4), and the relationship between x_{Ca} and $\ln\gamma_{Ca}$ in the Si–Ca binary alloy at 1723 K is shown in Fig. 1. According to the results, Ca shows a negative deviational behavior from the ideal solution. The value of the infinite dilution activity coefficient of calcium was determined to be 0.000863 at 1723 K.

A comparison of our results to those from other investigations revealed the consistency between them. Tuset JKr [19] and Oliveira et al. [1] obtained the calcium activity coefficients based on the alpha function and chemical equilibrium of liquid silicon with slags, while Sudavtsova et al. [20] measured the enthalpies of mixing liquid silicon and calcium by calorimetry at 1773 K. The activity coefficients of calcium determined in the present work agree well with the results of Tuset JKr, Oliveira et al., and Sudavtsova et al., particularly since they are in the same order of magnitude. In addition, the present calculation results are relatively close to the data calculated using the reported activity coefficients data. For instance, the infinite dilution activity coefficient of calcium was 0.000982 at 1723 K [21].

3. Using phase diagrams to calculate the activities in the Si–Pb binary alloy and the Ca–Pb binary alloy

Kuo-chih Chou [12] developed the method to calculate the activity and activity coefficient from the binary phase diagram using Richardson's assumption, this method was used to calculate the Ca–Pb and Si–Pb binary alloys activities. The binary alloy phase diagram was obtained from a previous report [22].

For the Si–Pb binary alloy, the following equations were used to calculate the component 1, 2 activities in the left-hand side of the eutectic point [13].

Table 1
Some physical parameters of 3 elements [16,17].

Metal	T/K	V_m (cm^3/mol)	Z
Si	1687	$11.1[1 + 1.4 \times 10^{-4}(T - 1687)]$	7.9
Pb	1073	$19.42[1 + 1.24 \times 10^{-4}(T - 874)]$	10.5
Ca	1073	$29.5[1 + 1.6 \times 10^{-4}(T - 1385)]$	10.3

Table 2
Values of γ^0_1, γ^0_2, B_{21}, B_{12}, θ_{21} and θ_{12} of liquid 1–2 binary alloy [18].

System 1–2	T/K	γ^0_1	γ^0_2	B_{21}	B_{12}	θ_{21}	θ_{12}
Si–Ca	1700	0.002	0.001	1.48	1.44	666.47	619.89