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Calculation of Liquid–Solid Interfacial Free Energy in Pb–Cu Binary Immiscible System

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Abstract: Based on the solid–liquid interfacial free energy theory of the complex Warren binary & pseudo-binary system and through the simplification of it by taking Pb–Cu binary system as an example, the physical model for it in binary immiscible system can be obtained. Next, its thermodynamic formula is derived to obtain a theoretical formula that only contains two parameters, and comparisons are made with regard to γ_{SL} calculated values and experimental values of MPE (multiphase equilibrium method) under several kinds of temperatures. As manifested in the outcomes, the improved physical model and theoretical formula will become not only easy to understand but also simple for calculation (the calculated value of γ_{SL} depends on two parameters, i.e. temperature and percentage composition of Cu atom). It can be treated as the foundation of application for the γ_{SL} calculation of liquid–solid interfacial free energy in other immiscible systems.

Keywords: Immiscible; Liquid–Solid Interface Free Energy; Multiple Equilibrium; Pb–Cu System; Warren Theory.

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1 Introduction

The liquid–solid interfacial free energy is the uniquely measurable quantity that acquires the balance characteristics of metal series liquid–solid interface [1], and it plays a vital role in the studies on nucleation, crystal growth, wetting, sintering and thermal cracking, etc. In addition, the bonding strength between matrix and reinforced substance in composite materials and the density of sintered alloy powder in powder metallurgical materials are all closely related with the appropriate liquid–solid interfacial free energy [2]. Eustathopoulos [3] reviewed the early years works from all kinds of experiments to modeling and calculations about interfacial free energy and provided general references. Ten years before, Kaptay [4] built a set of new general algorithm that can apply to most of the metallic systems.

Experimental methods for conventional studies on liquid–solid interfacial free energy comprise MPE (multiphase equilibrium method) [5], SD (sessile drop method) [6], PD (pendant drop method) [7], RD (rising drop method) [8], TG (temperature gradient method) [9], etc. However, due to the complexity of experimental technology and operation conditions, the most majority of studies on free energy in immiscible system are restricted.

In this case, a theoretical modeling method came into being. Miedema and Broeder et al. were among those who conducted early researches in this field [10]. As indicated in their studies, the liquid–solid interface of any metallic bonding can be calculated through the adoption of a simple method, and its interface can be divided into two parts, i.e. physical item and chemical item. Among them, the physical item depends on the latent heat of fusion from the solid surface atomic layer while the entropy of interfacial atomic layer can be applied to characterize the disorder of surface atomic layer in the liquid fraction, whereas the chemical item can be determined by the energy obtained from the alloying reaction through the contact of different metal atom.

Subsequently, at the end of last century, Prof. Warren [11] from Chalmers University in Godesberg, Sweden, improved on the theories of previous scientists and applied the γ_{SL} calculation of liquid–solid interfacial free energy into the binary system and quasi-binary system between metal and metal, as well as metal and compound, to the extent that certain gas–solid interface energy γ_{SV} can be satisfied.

In his theory, due to the complex interference factors of chemical action item between the common binary system, the approximate theoretical calculation was still not simple.

In this article, based on the research outcomes of previous scientists, the author has derived the method for the calculation of solid–liquid interface energy of immiscible metal system [12, 13], a hot issue in current studies. Its biggest advantage lies in the fact that only the interaction

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potential of item on structural in binary system needs to be considered. As a result, the complex interferences of chemical action items in common system are avoided, and the calculation process is simplified, at the same time, it can get a good agreement between calculated value and experimental value. Pb–Cu immiscible system [14–17], the currently focus of study, is taken as an example, so as to carry out the thermodynamic formula derivation of liquid–solid interfacial energy, establish the model for calculating the immiscible liquid–solid interfacial energy and compare the calculated value and the experimental value.

2 Method Details

According to Warren's solid–liquid interface theory, as shown in Figure 1, Pb–Cu interface layer can be considered as the diatomic layer, respectively, mixed with rare alien atoms. Hypothetically, the area surrounded by α and β is composed of Pb and Cu atoms and lies in a state of liquid mixing. For Cu single atom layer on the upper and lower sides of β plane, it is feasible to omit Pb due to only few Pb atoms can dissolved in Cu atom layer and change the composition. β_{upper} is in the liquid phase, whereas β_{lower} is in the solid phase. For α interface, Pb atoms on both sides are in the liquid phase, with the same composition and structure.

According to Warren theory, the overall interface free energy γ_{SL} can be represented as

$$\gamma_{\text{SL}} = \gamma_{\text{Pb}} + \gamma_{\text{Pb–Cu}} + \gamma_{\text{Cu}} \tag{1}$$

wherein, γ_{Pb} represents the interfacial energy of α_{upper} and α_{lower} liquid phase Pb, $\gamma_{\text{Pb–Cu}}$ represents the interfacial energy of Pb and Cu atom in the nonequilibrium mixed state. γ_{Cu} represents the interfacial energy generated between β_{upper} and β_{lower} atom layer due to the structural difference in solid-phase Cu.

According to Warren's assumption, the uniformity of structure and composition of Pb atoms in β_{upper} and β_{lower} can be approximately considered as $\gamma_{\text{Pb}} = 0$. Therefore, the formula for interfacial energy in Pb–Cu immiscible liquid–solid system can be

$$\gamma_{\text{SL}} = \gamma_{\text{Pb–Cu}} + \gamma_{\text{Cu}} \tag{2}$$

Hypothetically, when the balance state is reached, the atomic percentage of Cu in liquid phase is x_1, whereas x_2 in solid phase, x_3 in α_{lower} and β_{upper} liquid phase diatomic layer. As Pb–Cu binary system belongs to the immiscible system, it is thus feasible to make the approximation as below:

$$x_1 \approx 0;$$
$$x_2 \approx 1;$$

and then, the mixing free energy of Pb which has an equilibrium atomic percentage of x_3, $\Delta G = 0$, therefore:

$$\gamma_{(\text{Pb–Cu})L} = (\Delta G_1 - \Delta G_2)n/N = \Delta G_1 n/N \tag{3}$$

wherein, N stands for the Avogadro constant, n for number of atoms per unit area in diatomic layer (/m²), ΔG_1 for the liquid-phase free energy of Cu with its atomic percentage content as x_3 (J/m²), $\Delta G_2 = \Delta G = 0$. According to the studies of Jackson [18], partial free energy of Pb–Cu homogeneous liquid phase can be divided into two components, i.e. (1) free energy required in the transition from solid-state Cu to liquid state; (2) uniform free energy of mixing between liquid-state Pb and liquid-state Cu. At this time, the liquid-state Cu belongs to nonequilibrium phase under the temperature in discussion. Thus, with regard to Pb–Cu composition-free energy curve, following Kaufmann and Bernstein [19]. We can obtain total free energy of Pb–Cu in liquid:

$$\Delta G_L = \Delta G_3 x_3 + RT[x_3 \ln x_3 + (1-x_3)\ln(1-x_3)] + Cx_3(1-x_3) \tag{4}$$

wherein, ΔG_3 stands for the free energy of liquid-state pure Cu (J/m²), The x_3 is the content of Cu in liquid phase, R for gas constant, and C for undetermined coefficient, and T is the temperature (K).

As shown in Figure 1, there are extremely few contents of Cu atom in β_{upper} and β_{lower} liquid surface, it is thus feasible to simplify γ_{Cu} as the demanding for interfacial free energy between pure Pb solid phase and fused mass of itself. In this regard, the approximate calculation formula can be depended.

$$\gamma_{\text{Cu}} = kT_{\text{mCu}}/V_{\text{Cu}}^{2/3} \tag{5}$$

wherein, T_{mCu} stands for the melt point of Cu, V_{Cu} stands for the molar volume of Cu, k stands for the experiment constant. According to the pure metal measurement of γ_{SL} [14], the evaluation ranges between 5×10^{-4} and 8×10^{-4} and the medium value of 6.5×10^{-4} is often taken in calculations. Meanwhile, the unit for T_{mCu} and γ_{Cu} can be K and J/m².

To derivate x on both sides of formula (4), and let it equal to 0, then we can obtain the minimum value point on the curve of the composition vs free energy of liquid state, where the:

$$\frac{\mathrm{d}\Delta G_L}{\mathrm{d}x} = \Delta G_3 + RT[\ln x - \ln(1-x)] + C(1-2x)$$

And when $\mathrm{d}G_L/\mathrm{d}x = 0$, the $x = x_1$, x_1 is the saturated content of the Cu atomic percentage in the Pb liquid in the interface area; so from (7), we can get the expression of constant C as follow:

$$C^* = -[\Delta G_3 + RT(\ln x_1 - \ln(1-x_1))]/(1-2x_1) \tag{6}$$

For immiscible system, x_1 is often quite little, and when it approach 0, the $RT\ln(1-x_1)$ and $2x_1$ approach 0 either, then we can even get a simplified equation of C and have still a good approximation of C in the mean time as

$$C \approx -\Delta G_3 - RT\ln x_1 \tag{7}$$

For the solution within C (J/m²) characterized interface layer, due to the degree of deviation from the solution in ideal state,

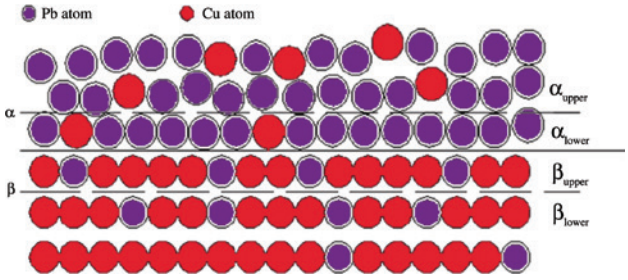

Figure 1: Model for Pb/Cu liquid–solid interface.

the solubility of Pb is nearly zero in Cu. Thus, formula (6) can be deemed as (7).

Hypothetically, the atoms within the interface layer belong to simple queuing, and if we define n as the atoms number per unit interface area, it is equal to the sum of the liquid and solid interface atom number per unit area. So n (atoms number/m^2) within the unit area of biatom interface layer can be

$$n = 2/[(V_{Cu}/N)^{2/3}x_3 + (V_{Pb}/N)^{2/3}(1-x_3)] \tag{8}$$

wherein, V_{Pb} and V_{Cu} (m^3/mol), respectively, stand for the molar volume of Pb and Cu, N stands for the Avogadro constant, and x_3 is the Cu atomic percentage content in atomic interface bilayer.

As the liquid–solid interface layer of Pb–Cu immiscible system is very thin, which bring great difficulty to the actual measurement of x_3. However, the basic calculation formula can be met.

$$x_3 = (n_L x_1 + n_S x_2)/(n_L + n_S)$$

wherein, n_S and n_L, respectively, stand for the atoms number of the unit area of solid-side atomic layer and liquid-side atomic layer within the interface bilayer (/m^2).

Due to,

$$n_L = (N/V_L)^{2/3} = (N/V_{Pb})^{2/3}$$
$$n_S = (N/V_S)^{2/3} = (N/V_{Cu})^{2/3}$$

We can obtain:

$$x_3 = (V_{Cu}^{-2/3}x_2 + V_{Pb}^{-2/3}x_1)/(V_{Cu}^{-2/3} + V_{Pb}^{-2/3}) \tag{9}$$

ΔG_3 can be approximately represented as the melted free energy of pure Pb.

$$\Delta G_3 = \Delta H_{Cu}(1 - T/T_{mCu}) \tag{10}$$

wherein T_{mCu} and ΔH_{Cu}, respectively, stand for the melting point of pure Cu and the latent heat of fusion.

By substituting formula (7) to (10) into formula (3)

$$\gamma_{Pb-Cu} = 2N^{-1/3}[V_{Cu}^{2/3}x_3 + V_{Pb}^{2/3}(1-x_3)]^{-1}\{\Delta H_{Cu}(1 - T/T_{mCu})$$
$$x_3^2 + RT[x_3\ln x_3 + (1-x_3)\ln(1-x_3) - x_3(1-x_3)\ln x_1]\} \tag{11}$$

By substituting formula (11) into formula (1), we can obtain

$$\gamma_{SL} = kT_{mCu}/V_{Cu}^{2/3} + 2N^{-1/3}[V_{Pb}^{2/3}x_3 + V_{Cu}^{2/3}(1-x_3)]^{-1}\{\Delta H_{Cu}$$
$$(1 - T/T_{mCu})x_3^2 + RT[x_3\ln x_3 + (1-x_3)\ln(1-x_3) - x_3(1-x_3)\ln x_1]\} \tag{12}$$

In immiscible system, x_2 approach 0, if we have x_1, then x_3 can derive by formula (10), and formula (12) just has two parameters unknown: T and x_1. If we have the values of T and x_1, the interfacial energy of immiscible metal system can be calculated easily.

For estimate the error induced by the approximation of C, we can give (11*) and (12*) which use C^* as final contrast equations, like the same procession derived above we can get

$$\gamma_{Pb-Cu} = 2N^{-1/3}[V_{Cu}^{2/3}x_3 + V_{Pb}^{2/3}(1-x_3)]^{-1}\{\Delta H_{Cu}(1 - T/T_{mCu})$$
$$x_3 + RT[x_3\ln x_3 + (1-x_3)\ln(1-x_3)] - x_3(1-x_3)C^*]\}$$

if we substituted (6) into this equation, we get (11*):

$$\gamma_{Pb-Cu} = 2N^{-1/3}[V_{Cu}^{2/3}x_3 + V_{Pb}^{2/3}(1-x_3)]^{-1}\{\Delta H_{Cu}(1 - T/T_{mCu})x_3$$
$$+RT[x_3\ln x_3 + (1-x_3)\ln(1-x_3)] - x_3(1-x_3)$$
$$[\Delta H_{Cu}(1 - T/T_{mCu}) + RT\ln x_1 - RT\ln(1-x_1)]/(1-2x_1)\} \tag{11*}$$

the we get (12*):

$$\gamma_{SL} = kT_{mCu}/V_{Cu}^{2/3} + 2N^{-1/3}[V_{Pb}^{2/3}x_3 + V_{Cu}^{2/3}(1-x_3)]^{-1}$$
$$\{\Delta H_{Cu}(1 - T/T_{mCu})x_3 + RT[x_3\ln x_3 + (1-x_3)\ln(1-x_3)]$$
$$-x_3(1-x_3)[\Delta H_{Cu}(1 - T/T_{mCu}) + RT\ln x_1 - RT\ln(1-x_1)]/(1-2x_1)\} \tag{12*}$$

3 Experimental and Calculation Values

In order to verify the rationality of established calculation model, we have made comparisons between calculation results and measuring results. By using MPE [5], we have obtained the overall interfacial free energy in Pb–Cu immiscible system at certain temperatures. MPE is applicable in the determination of liquid–solid interfacial free energy in simple binary system, and its requirements for the system to be measured shall comprise the possession of the simple eutectic or monotectic phase diagram. The solubility of liquid phase A in the solid phase B is small enough to be ignored. Its main principle is to obtain γ_{SL} by utilizing the equilibrium relationship of various tensions within liquid–solid and gas–solid interface under the thermal equilibrium condition and by measuring the dihedral angle of α and φ within liquid–solid and liquid–gas interface, as well as the three-phase contact angle among solid, liquid, and gas (as shown in Fig. 2).

The equilibrium equation is listed as below:

$$\gamma_{SS} = 2\gamma_{SV}\cos\frac{\alpha}{2} \tag{13}$$

$$\gamma_{SS} = 2\gamma_{SL}\cos\frac{\varphi}{2} \tag{14}$$

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\cos\theta \tag{15}$$

wherein γ_{SS} = solid–solid interfacial energy, it can be inferred from the above three formulas:

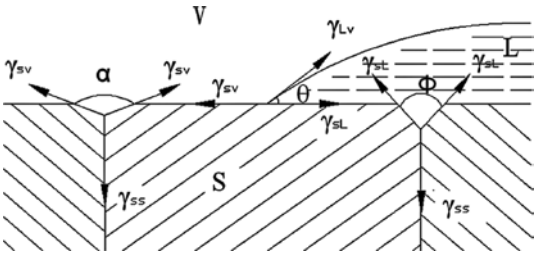

Figure 2: Tension equalization diagram of solid–liquid–gas-phase interface.

Table 1: Comparisons between the experimental values and calculation values of overall interfacial free energy in Pb–Cu immiscible system.

T(K)	ΔH_{Cu} (J/mol) [20]	V_{Pb} (10^{-6} m^3/mol) [21]	V_{Cu} (10^{-6} m^3/mol) [21]	x_1	x_3	γ_1 (mJ/m^2) (MPE Experiment)	γ_D (J/m^2) (DA methods Experiment)	γ_2 (J/m^2) (Theory)
1173	13263.28	20.843	7.4975	0.030	0.6742	0.402	0.357	0.350
1123	13263.28	20.718	7.4713	0.030	0.6738	0.411	0.368 [22]	0.357
1073	13363.28	20.594	7.4457	0.031	0.6738	0.419//0.380 ± 0.065 [5]	0.380 [22]	0.361
1023	13263.28	20.470	7.4204	0.031	0.6734	0.451	0.390	0.368
1093	13263.28	20.664	7.4558	0.115 [3]	0.7022	0.390 ± 0.065 [3]	0.375 ± 0.065 [22]	0.348//0.282
1193	13263.28	20.892	7.5089	0.235 [3]	0.7431	0.348 ± 0.065 [3]		0.361//0.278
1000	13263.28	20.413	7.4089	0.06 [11]	0.6849	0.410 [23]		0.328//0.339 [11]

$$\gamma_{SL} = \frac{\gamma_{LV} \cdot \cos\frac{\varphi}{2} \cdot \cos\theta}{\cos\frac{\alpha}{2} - \cos\frac{\varphi}{2}} \tag{16}$$

In the formula (16), γ_{LV} can be determined independently, and γ_{SL} can be determined after the measurement of θ, φ, and α.

During the specific experimental measurements, θ can be obtained by directly absorbing the droplet and the outline image of matrix, whereas φ and α can be measured by means of optical interference. The advantage of this method is that the principle is simple and there is no need for very demanding conditions of experimental equipment. Furthermore, γ_{SS} and γ_{SV} can be determined at the same time. However, the main demerits lie in the facts that the restrictions for the chemical composition of binary system are relatively high and the experimental error is relatively high.

The correlation table for test results and the calculation values obtained through the application of this theoretical model is listed as Table 1.

From Table 1, the calculated value of free energies has errors not more than 10 %, and the result is between the MPE methods and DA (dihedral angle) methods results, and has the similar tendency with the experimental values. It has an acceptable error and can satisfy the need of deal with the interfacial energy of Pb–Cu like immiscible metallic systems.

Compare with the MPE methods experimental results of [3], the Pb–Cu system, solid–liquid interfacial energy is 390 ± 65 mJ/m^2 in 1093 K, $x_1 = 0.115$; and 348 ± 55 mJ/m^2 in 1193 K, $x_1 = 0.235$, our model's result is not contradictory to it. As to the results of model of [4], the Pb–Cu system's solid–liquid interfacial energies are about between 350 and 370 mJ/m^2, and it has a ± 20 % of uncertainty. So, maybe the simplified model is considerable accepted in situation of convenient use.

Other reference data also listed in Table 1 to give a contrast. γ_1 and γ_2 represent experimental and calculated values of the liquid–solid interfacial free energy, respectively. x_1 is the molar fraction of Cu in liquid phase. γ_1 and x_1 are obtained by MPE, γ_D ref [22]; $x_2 \approx 1$; x_3 calculated from formula (10).

$\Delta H_{Cu} = 13263.28$ J/mol from [20]. (13050 J/mol from [24], 13042 J/mol from [25], cause the [20]).

V_{Pb} and V_{Cu} are computed from the formula of [21], respectively. Reference [21] provided a formula of molar volumes of pure solid fcc metals and their liquid, according to the temperature and the melting point of Cu and Pb, we adopted $V_{Pb} = 17.92 + 2.483 \times 10^{-3} \times T$ (10^{-6} m^3/mol) for the Pb-liquid $T > 600.6$ K; and adopted $V_{Cu} = 7.042 + 3.159 \times 10^{-5} \times T^{1.355}$ (10^{-6} m^3/mol) for Cu-fcc $T < 1358$ K. (And [25] give 18.170×10^{-6} m^3/mol for V_{Pb} and 7.1920×10^{-6} m^3/mol for V_{Cu}, not T-dependent.)

Table 2 is the error estimate induced by C or C^* when $x_1 = 0.03$ or less than 0.06 ($x = 0.06$ for 1000 K).

$\gamma_{2\_}C$ is the results calculated from C ((7) and (12)), and $\gamma_{2\_}C^*$ is the results calculated from C^*((6) and (12*)), in different temperature and x_1, respectively, Error_in $= (C - C^*)/C^*$, and Error_out $= (\gamma_{2\_}C - \gamma_{2\_}C^*)/\gamma_{2\_}C^*$.

From Table 2, we can see that when we use C as the estimate of C^* and x_1 is less than 0.06, the final solid–liquid interface energies have a result error not big than 8 %, and the experimental result errors are

Table 2: The input error and output error of different C.

T(K)	$\gamma_{2\_}C$	$\gamma_{2\_}C^*$	Error_out	Error_in
1173	0.3256	0.3505	− 0.0701	− 0.0685
1123	0.3337	0.3569	− 0.0651	− 0.0687
1073	0.3387	0.3612	− 0.0621	− 0.0712
1023	0.3469	0.3680	0.0572	− 0.0715
1093	0.3224	0.3475	0.0722	− 0.0685
1193	0.3385	0.3609	0.0621	− 0.0688
1000	0.3535	0.3734	0.0532	− 0.0692

not less than 16 %. And we can see that when $x_1 = 0.115$ and $x_1 = 0.235$ ($T = 1093$ K and 1193 K, respectively) in Table 1, the error induced by C and C^* can reach (0.282–0.348)/0.348 = 18.9 % and (0.278–0.361)/0.361 = 22.9 %, respectively, at the mean time, as the x_1 increased, the result error increased either.

4 Conclusions

(a) According to the theory of Warren solid–liquid interface, the author has proposed a thermodynamic calculation method that aims to calculate the interfacial free energy in immiscible system, established a kind of relatively simple physical model and proved that the said model possesses better fitness with the experimental value and within the permissible error range, through comparisons between theoretical calculations and experimental test values and by taking Pb–Cu binary system as an example.
(b) The changes in the interfacial free energy of immiscible system within the same research system is mainly in direct proportion to the changes in the temperature adopted in experiment and the atomic fraction of actually measured solid-phase atom in liquid phase. Consequently, the complex of chemical item disturbance in classical theory can be averted.

As indicated in the above-mentioned calculation results and measuring results, the computational model established in this article is rational, and its calculation results are trustworthy. Through the adoption of this model, it is possible to provide accurate calculation data for the liquid–solid interfacial free energy in binary immiscible system. Before the formation of a very mature theoretical system, it can provide new theoretical support. It is believed that there is bound to have greater breakthroughs in the researches of interfacial energy in immiscible system and the preparation of new materials, along with the progress of current computational materials science.

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