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Thermodynamic investigation of persistent complexes in Si–P melts

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Abstract : The Si–P alloy forms compounds SiP, Si_2P and SiP_2 in its solid phase. A statistical mechanical theory based on complex formation has been used to predict the possible compounds that could persist from the solid to the liquid state of Si–P melt at about 1750 K. The results show that Si_2P will exist in the liquid phase at lower concentrations of phosphorus. It also predicts the presence of Si_3P_2 which is strong and probably exists throughout the whole concentration range.

Keywords : Liquid alloys, concentration fluctuation, chemical complex.

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1. Introduction

The study of the thermodynamic properties of melts have engaged the attention of many authors in recent times. In this regard, a great deal of work has been done in understanding the thermodynamic properties of metal-metal melts and metal-non-metal melts. These studies also include the understanding of their energertics and size effects or what they called entropic and enthalpic contributions to the free energy of mixing [1].

Another class of melts include elements in the non-metal category or refer to them as the non-metal-non-metal melts. This class of melts has been investigated albeit with a lesser degree of interest both from the experimental and theoretical researchers. The Si–P melt belongs to this category. Few authors [2–6] have made both measurements and calculations on the thermodynamic properties of Si–P melts. The knowledge of the thermodynamic properties of Si–P melts is of research interest in that it provides a fundamental scientific basis for developing technologies of cleaning silicon of phosphorus, doping semiconductor and refining steel and alloy [2]. In addition liquid Si–P are characterized

by considerable negative deviations of the activity from Raoults law [2]. This is an indication to the existence of strong interactions in the melt. Ugai Ya et al [7] has pointed out that for Si–P alloy, a series of stable compounds such as Si_2P, SiP and SiP_2 are formed in the solid state. The persistent existence of these compounds into the liquid phase or formation of new ones in the liquid state has thermodynamic implications and require further investigation.

In this paper therefore, we attempt to investigate the applicability of the quasi chemical model on the non-metal-non-metal melts, specifically the Si–P melt. Hence using this model, we seek to determine the possible complexes which can persist from the solid into the liquid phase and perhaps new complexes which may be formed in the liquid phase. This study of the nature and strength of complexes existing in an alloy melt is gaining increasing importance. This importance results from the fact that chemical complexes have been associated with the formation of glassy materials in binary alloys [8]. For instance, it has been suggested that formation of chemical complexes in Fe–B

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liquid alloy is a factor that enhanced glass formation in the system [9], whereas in Ba–Mg [8], glass formation was mentioned to be hindered by the formation of chemical complexes in the liquid state of the alloy. We note here that the quasi-chemical model [10] was formulated and applied to the thermodynamic properties of liquid binary metallic alloys. We therefore attempt to extend its applicability to non-metals since it has been used successfully for metal-non-metal melts [11].

The fundamental idea about the quasi-chemical model is that the thermodynamic properties of a compound forming A–B alloy can be explained by treating the alloy as a pseudo ternary mixture of A atom, B atom and A_pB_q complexes. Details of the formulation are given in Ref. [5].

The excess free energy of mixing G_m^{es} of a liquid binary alloy is related to its free energy G_m by the expression,

$$G_m^{es} = G_m - RT[x\ln x + (1-x)\ln(1-x)]. \qquad (1)$$

Here, x is the concentration of atom A and R is the universal gas constant. The quasi-chemical expression for the excess free energy of mixing G_m^{es} is given as :

$$\frac{G_m^{es}}{RT} = z\int_0^x \left[\ln\sigma + (2kT)^{-1}\left(P_{aa}\Delta\varepsilon_{aa} - P_{bb}\Delta\varepsilon_{bb}\right)\right]$$
$$\times dx + \psi, \qquad (2)$$

where z is the coordination number, k, the Boltzman constant and

$$\ln\sigma = \frac{1}{2}\ln\frac{(1-x)(\beta+2x-1)}{x(\beta-2x+1)} \qquad (3)$$

with $\beta = [1 + 4x(1-x)(\eta^2 - 1)]^{\frac{1}{2}} \qquad (4)$

and $\eta = \exp\left(\dfrac{2\omega}{zkT}\right)$

$$\times \exp\left(\frac{2P_{ab}\Delta\varepsilon_{ab} - P_{aa}\Delta\varepsilon_{aa} - P_{bb}\Delta\varepsilon_{bb}}{kT}\right). \qquad (5)$$

ω, $\Delta\varepsilon_{ab}$, $\Delta\varepsilon_{aa}$, $\Delta\varepsilon_{bb}$ are the interaction parameters with ω denoting the interchange energy and $\Delta\varepsilon_{ij}$ being the change in the energy if ij bond is in the complex A_pB_q. P_{ij} denotes the probability that the bond is part of the complex and the expressions are given as follows :

$$P_{ab} = x^{p-1}(1-x)^{q-1}\left[2 - x^{p-1}(1-x)^{q-1}\right], \qquad (6)$$

$$P_{aa} = x^{p-2}(1-x)^q\left[2 - x^{p-2}(1-x)^q\right], \quad p \geq 2; \qquad (7)$$

$$P_{bb} = x^p(1-x)^{q-2}\left[2 - x^p(1-x)^{q-2}\right], \quad p \geq 2. \qquad (8)$$

The constant ψ is determined from the requirement that $G_m = 0$ at $x = 1$.

The activities of the metals are obtained by

$$a_m = x\gamma_m, \qquad (9)$$

where x is the concentration of the species and γ_m is its activity coefficient given by

$$\gamma_m = \left\{\frac{\beta - 1 + 2x}{x(1+\beta)}\right\}^{\frac{1}{2}z}, \qquad (10)$$

where β is as defined in eq. (4).

The concentration-concentration fluctuations in the long wavelength limit $S_{cc}(0)$ has been shown to be given by

$$S_{cc}(0) = x(1-x)\left\{1 + \frac{1}{2}z\left(\frac{1}{\beta} - 1\right) + \Omega\right\}^{-1} \qquad (11)$$

where Ω is the expression given below :

$$\Omega = \frac{zx(1-x)}{2\beta kT}\Theta \qquad (12)$$

and $\Theta = \left[2(1-2x)P'_{ab}\Delta\varepsilon_{ab} + (\beta - 1 + 2x)P'_{aa}\Delta\varepsilon_{aa}\right.$
$$\left. - (\beta + 1 - 2x)P'_{bb}\Delta\varepsilon_{bb}\right], \qquad (13)$$

where the prime on P denotes the first derivative with respect to x. The Warren-Cowley short range order parameter α_1 for the first nearest neighbours is expressed as

$$\alpha_1 = \frac{\beta - 1}{\beta + 1}. \qquad (14)$$

2. Results and discussion

The work of Zaitsev *et al* [3] provided the experimetal data for our investigations. The use of quasi-chemical model requires the subtle choice of parameters p and q which determine the stoichiometry of the complex A_pB_q formed in the liquid state. Usually, p and q may be taken from phase diagrams or conjectures. In the phase diagram of Si–P [12], no compounds were suggested for the liquid phase. However, in the solid phase SiP and the metastable Si$_2$P were suggested. In addition to these mentioned compounds, Ugai Ya *et al* [7] suggested the existence of the SiP$_2$ in the solid phase.

To acertain the applicability of the quasi-chemical model to the non-metal melt (Si–P) and to determine which of the compounds aforementioned persistently exist as a complex in the liquid phase, we pick the values of p and q for each compound taking P as the A atom and Si as the B atom and proceed to simultaneously determine the activity values a_P and a_{Si} and the free energy of mixing G_m/RT for the alloys. This is achieved using eq. (2) and eq. (9) by finding the interaction parameters ω, $\Delta\varepsilon_{ab}$, $\Delta\varepsilon_{aa}$ and $\Delta\varepsilon_{bb}$ which reproduce simultaneously and to a reasonable extent the

measured values of activity and free energy of mixing. This particular interaction parameters will be used in calculating the concentration-concentration fluctuation at long wavelength limit ($S_{cc}(0)$).

The choice of parameters $p = 1$ and $q = 1$ giving the complex SiP and the choice of $p = 2$ and $q = 1$ giving the complex SiP_2 could not reproduce simultaneously the measured thermodynamic data of activity and free energy of mixing with all possible variation of the interaction parameters by the authors. This rules out the possible existence of such complexes in the liquid phase. However, two sets of choices of p and q representing Si_2P and Si_3P_2 reproduced simultaneously and to a reasonable extent the measured activity and free energy of mixing. The interaction parameters used for the different choices of p and q are given in Table 1.

Table 1. Interaction parameters for the complexes in Si–P melts.

Complex	p	q	$\dfrac{\omega}{kT}$	$\dfrac{\Delta\varepsilon_{ab}}{kT}$	$\dfrac{\Delta\varepsilon_a}{kT}$	$\dfrac{\Delta\varepsilon_{bb}}{kT}$
Si_2P	1	2	–4.90	0.17	0.00	–0.59
Si_3P_2	2	3	–2.83	–0.07	–0.36	–1.50

The measured activities of phosphorus ($a(P)$) and silicon ($a(Si)$) and the corresponding calculated activities assuming the complexes Si_2P and Si_3P_2 are given in Figure 1. The calculated activities using these complexes appear close in their values except at low concentration of phosphorus for $a(P)$ and low concentration of silicon for $a(Si)$ where discrepancies are prominent. The calculated activity of
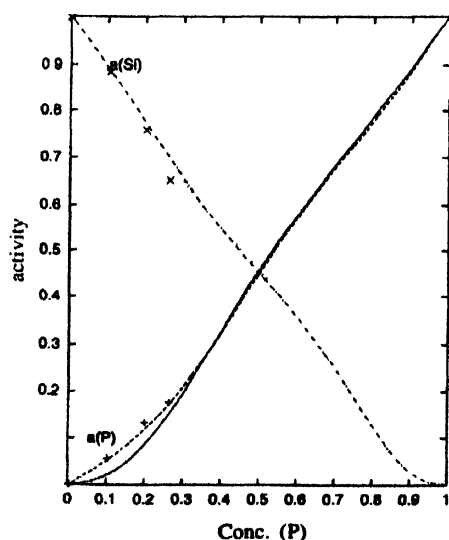
Figure 1. Activity of phosphorus $a(P)$ and activity of silicon $a(Si)$ vs concentration of phosphorus for the Si–P melt. Solid line — $a(P)$ for Si_2P complex, (- - -) — $a(P)$ for Si_3P_2 complex. (— · —) — $a(Si)$ for Si_3P_2 complex, dots — $a(Si)$ for Si_2P complex. (xxx) are the respective measured values of activity from Ref. [3].

phosphorus for the complex Si_3P_2 fits the measured values closely, hence suggesting the strong influence of this complex in the thermodynamic properties of the Si–P melt. At higher concentrations of phosphorus, the calculated activity due to the two complexes appear to agree.

The calculated free energy of mixing for the complexes are compared with measured values in Figure 2. The values for the complex Si_3P_2 predicted a lower minimum for the G_m/RT while the values for the complex Si_2P appear to agree more with the measured data. In all, the two sets of calculated values have good agreement with the measured values. With the above results, it will be good to note that apart from successfully describing the thermodynamic properties of Si–P melts, the model predicts the presence of Si_2P in the liquid phase. This is consistent with the suggestions of [4–6]. In addition, it suggests that a complex Si_3P_2 hitherto not mentioned may also exist in the liquid phase.
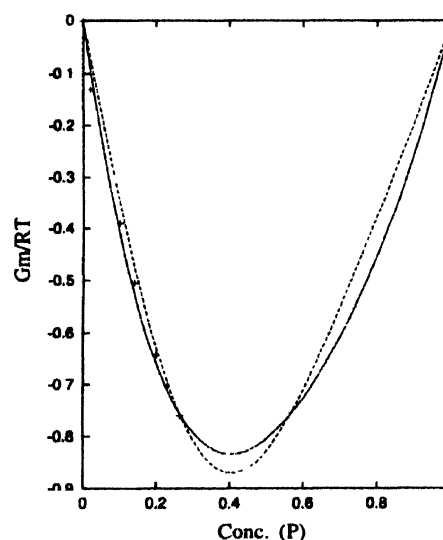
Figure 2. G/RT vs atomic fraction of P for Si–P melt. Solid lines — calculated values for Si_2P complex, dashes — calculated values for Si_3P_2 complex. (xxx) — experimental values deduced from Ref. [3].

To understand the nature and strength of the interactions producing these complexes persisting from the solid into the liquid state of Si–P alloy, it is of interest to calculate the concentration-concentration fluctuation at the long wavelength limit $S_{cc}(0)$ using the interaction parameters for each persisting complex as indicated in Table 1. Essentially, $S_{cc}(0)$ is defined in such a way that with x, being the concentration of A atoms in an A–B liquid alloy, the ideal values of $S_{cc}(0)$ is $x(1 - x)$. A liquid alloy is said to be compound forming in a concentration range for which its $S_{cc}(0) < x(1 - x)$. The liquid alloy is phase seperating when the $S_{cc}(0) > x(1 - x)$. In addition the knowledge of $S_{cc}(0)$

can successfully be used to assess the strength of the chemical complexes (A_pB_q) if it exists in the alloy [5]. The $S_{cc}(0)$ can be expressed in terms of activity as

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_m}{\partial x^2}\right)_{T,P,N}^{-1} = \frac{(1-x)a_A}{(\partial a_A/\partial x)_{T,P,N}}$$

$$= \frac{xa_B}{(\partial a_B/\partial(1-x))_{T,P,N}} \quad (15)$$

where A and B represent the A and B components of the melt. The experimental values of $S_{cc}(0)$ are obtained from measured activity data. Here, the values of the activity of phosphorus was fitted to a polynomial and $S_{cc}(0)$ was determined after the necessary differentiation.

Figure 3 shows the calculated $S_{cc}(0)$ for the Si_2P and Si_3P_2 complexes. It can be observed that the $S_{cc}(0)$ for the Si_2P complex has a qualitative trend of the experimental
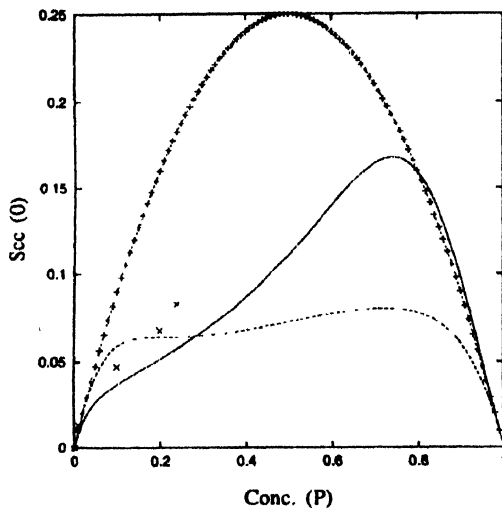
Figure 3. $S_{cc}(0)$ vs atomic fraction of P for Si–P melt. Solid lines — calculated values for Si₂P complex, dashes — calculated values for Si₃P₂ complex, (+—+) — ideal values, (xxx) — experimental values deduced from Ref. [3].

values. This further comfirms the presence of this complex in the melt. The shape of the curve of $S_{cc}(0)$ for the complex Si_2P and the values of the Warren Cowley short range order parameter α_1 (Figure 4) suggests that the existence of this complex will be predominant in the lower concentrations of phosphorus. However, for the complex Si_3P_2, the $S_{cc}(0)$ shows that this complex is strong and can exist throught the whole concentration range. The calculated Warren Cowley short range order parameter for the nearest neighbour shell α_1 given in Figure 4 indicates ordering with $\alpha_1^{min} \approx -0.044$ for Si_2P complex at about 0.24 atomic fraction of phosphorus and $\alpha_1^{min} \approx -0.025$ for Si_3P_2 at about 0.32 atomic fraction of phosphorus.
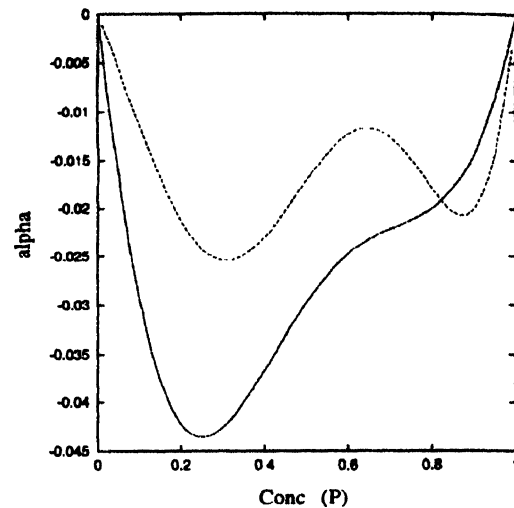
Figure 4. Warren Cowley short range order parameter α_1 vs atomic fraction of P for Si–P melt. Solid line — calculated values for Si₂P complex while dashes — calculated values for Si₃P₂ complex.

3. Conclusion

The quasi-chemical model has successfully described the thermodynamic properties of Si–P melt. The study indicated the presence of two complexes Si_2P and Si_3P_2 in the Si–P melts. We conclude that Si_2P compound persists into the liquid phase of the Si–P melt and is more prominent at concentrations lower than the equiatomic concentration of phosphorus. Although there is the presence of a new complex Si_3P_2 not indicated in the solid phase, we suggest that its existence is strong and pronounced throughout the whole concentration range.

Acknowledgments

References

[1]   O Akinlade, R N Singh and F Sommer *J. Alloys Compd.* **267** 195 (1998)

[2]   T Miki, K Morita and N Sano *Metall. Mater. Trans.* B27 917 (1997)

[3]   A I Zaitsev, A D Litvina and N E Shelkova *High Temp.* 39 2 (2001)

[4]   A I Zaitsev, A D Litvina, N E Shelkova and B N Mogutnov *Thermochim. Acta* **314** 307 (1998)

[5]   A I Zaitsev, A D Litvina and N E Shelkova Z. *Metallkd* 88 79 (1997)

[6]   A I Zaitsev and B M Mogutnov *High Temp. Mater. Sci.* 34 155 (1995)

[7]   A Ugai Ya, S I Miroshaichenko, E P Domasheoskaya and M A Vasil'evskaya *Neorg. Mater.* 9 7 (1973)

[8] P Ramachandra Rao, R N Singh and S Lele *J. Non Cryst. Solids* 64 387 (1984)

[9] L I Aptekar in C Hargitai, I Bakonyi, T Kemeny (eds.) *Proceedings of the Conference on Metallic Glasses : Science and Tech.*, Vol. 1 (Central Research Institute for Physics, Budapest) p 253 (1981)

[10] R N Singh *Can. J. Phys.* 65 309 (1987)

[11] B C Anusionwu and G A Adebayo *J. Alloys Compd.* 329 162 (2001)

[12] W G Moffatt *The Handbook of Binary Phase Diagrams* (General Electric Company, Schenectady, NY) (1980)