Effect of Fe Addition on the Activity Coefficient of Si in Cu–Fe–Si Melt at 1 623 K

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The activity coefficient of Si in Cu–Si alloy and Cu–Si–Fe alloys was determined using three principles at 1 623 K. Cu–Si(–Fe) alloys at a low Si concentration were equilibrated with SiO₂ in a graphite crucible under a controlled CO partial pressure. Cu–Si(–Fe) alloys at a medium Si concentration were equilibrated with SiC in a graphite crucible. And finally, Cu–Si(–Fe) alloys at a high Si concentration were equilibrated in a Si₃N₄ crucible under a controlled partial pressure of N₂. The activity coefficients of the alloys were calculated based on the equilibrium Si concentration. The results show that the activity coefficient of Si in Cu–Si–Fe alloy decreases with an increase in the concentration of Fe. The results were evaluated in terms of the interaction parameters in molten Cu for Wagner's formalism, and the interaction coefficient in the concentrated solution.

The evaluated thermodynamic properties of Cu–Si–Fe alloy indicated that the addition of Fe to Cu–Si alloy is effective in decreasing the activity of Si in the alloy.

KEY WORDS: thermodynamics; activity coefficient; interaction parameter; Cu–Si alloy.

1. Introduction

Flaky graphite cast iron and forged carbon steel have been commonly used for brake discs in high-speed trains. They have certain advantages such as high-strength and high resistance to cracking. On the other hand, a significant problem, a heat-affected zone called a heat spot, typically appears when using iron-based materials repeatedly at high speed. Therefore, a higher heat-resistant material is required. In addition, to decrease energy consumption during transport, a lighter-weight brake disc is preferable. For these reasons, the fabrication of light-weight and high-heat-resistant brake disc materials is crucial.

Carbon fiber is known to be a light-weight, high-strength material, and is considered a promising matrix material for use in brake discs. When Cu–Si alloy is added to a carbon fiber matrix, the resulting composite is expected to be a high performance material for brake discs. This type of composite can be prepared through the infiltration of Cu–Si alloy into a carbon fiber matrix at temperatures higher than 1 700 K.

However, when the concentration of Cu in the alloy is extremely high, the alloy cannot penetrate into the matrix owing to the poor wettability of Cu to graphite.¹⁾ On the other hand, when the concentration of Si is high, Si in the infiltrated alloy reacts with carbon to form SiC. Formation of excess SiC results in an embrittlement of the composite.²⁾ Therefore, it is necessary to control the formation of SiC

during the fabrication process of high-performance brake discs. Because the formation of SiC depends on the activity of Si in the alloy, it is needed to find an optimal composition that demonstrates low Si activity, which in turn suppresses the SiC formation.

Since Fe has a strong affinity with Si in the liquid phase,³⁾ the addition of Fe to Cu–Si alloy is expected to decrease the Si activity. The thermodynamic property of Cu–Si–Fe alloy system has been investigated to elucidate the Cu solubility in solid iron with the aim to avoid the liquid Cu formation from steel during hot rolling⁴⁾ and to determine the miscibility gap between Cu-rich and Fe-rich liquids to control the phase separation during the Fe–Cu-enriched waste incineration process.⁵⁾ However, both reports mainly focused on the Fe–Cu rich side and investigation on Cu–Si rich side is inadequate. Furthermore, there are discrepancies in reported thermodynamic property of the liquid Cu–Si alloys as described by Miki *et al.*⁶⁾

In the present study, the activity coefficients in liquid Cu–Si and Cu–Si–Fe alloys were determined using a chemical equilibration method. The effect of Fe on the thermodynamic properties of Si in Cu–Si alloys was evaluated in terms of the interaction parameters in molten Cu for Wagner's formalism⁷⁾ and the interaction coefficient in the concentrated solution.

2. Experimental

The experimental apparatus, which consists of a vertical SiC resistance furnace equipped with a mullite reaction

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tube, is shown in Fig. 1. The temperature was maintained at 1 623 K with an accuracy of ± 1 K using a proportional integral differential (PID) controller and a Pt-6%Rh/Pt-30%Rh thermocouple. In this work, three kinds of reaction were employed to determine the activity of Si within a wide range of alloy compositions.

Experiment 1 –measurement of activity of Si at the low Si concentration in Cu–Si and Cu–Si–Fe alloys at a low Si concentration–

The activity of Si in Cu–Si–Fe alloy was controlled by equilibrating the alloy with both SiO_2 and graphite under a CO atmosphere. The equilibrium reaction is expressed as Eq. (1).

The Gibbs energy change, ΔG_1° , and the equilibrium constant, K_1 , for the reaction of Eq. (1) are expressed as Eqs. (2) and (3), respectively.

$$\Delta G_1^\circ = 712\,900 - 367.2T \text{ (J/mol)}^8 \quad (2)$$

$$K_1 = \frac{a_{\text{Si}(\text{l})} \cdot p_{\text{CO}}^2}{a_{\text{SiO}_2(\text{s})} \cdot a_{\text{C}(\text{s})}^2} = \frac{\gamma_{\text{Si}(\text{l})} \cdot X_{\text{Si}} \cdot p_{\text{CO}}^2}{a_{\text{SiO}_2(\text{s})} \cdot a_{\text{C}(\text{s})}^2} \quad (3)$$

Here, the activities of SiO_2 and carbon ($a_{\text{SiO}_2(\text{s})}$, $a_{\text{C}(\text{s})}$) are considered to be unity, and the CO partial pressure (p_{CO}) is kept constant. Therefore, the activity of Si ($a_{\text{Si}(\text{l})}$) at 1 623 K under a controlled CO partial pressure can be determined, and the activity coefficient of Si in the molten alloy is subsequently obtained by measuring the equilibrium silicon concentration of the alloy (X_{Si}).

0.3 g of Cu–Si–Fe alloy and a 1.0 g SiO_2 pellet were charged in a graphite crucible, which was placed in the hot zone of the furnace. The above sample was kept under a given CO partial pressure ($p_{\text{CO}}=0.3\text{--}1$ atm) for a period of 90 h. The sample was then withdrawn from the furnace and quenched by flushing it with Ar gas. The concentrations of Si and Fe in the alloy were determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Fig. 1. Schematic diagram of experimental apparatus. 1) silica gel, 2) $\text{Mg}(\text{ClO}_4)_2$, 3) soda lime, 4) silicone plug, 5) mullite reaction tube, 6) electric resistance furnace, 7) thermocouple, 8) porous alumina block.

Experiment 2 –measurement of activity coefficient of Si at a concentration of around 15 at% in Cu–Si–Fe alloys–

The activity of Si in Cu–Si–Fe alloy at the critical composition of SiC formation was controlled by equilibrating the alloy with both SiC and graphite under an Ar atmosphere. The equilibrium reaction is expressed as Eq. (4).

The Gibbs energy change, ΔG_4° , and the equilibrium constant, K_4 , for the reaction of Eq. (4) are expressed as Eqs. (5) and (6), respectively.

$$\Delta G_4^\circ = 122\,800 - 37.2T \text{ (J/mol)}^8 \quad (5)$$

$$K_4 = \frac{a_{\text{Si}(\text{l})} \cdot a_{\text{C}(\text{s})}}{a_{\text{SiC}(\text{s})}} = \frac{\gamma_{\text{Si}(\text{l})} \cdot X_{\text{Si}} \cdot a_{\text{C}(\text{s})}}{a_{\text{SiC}(\text{s})}} \quad (6)$$

Here, the activities of SiC and carbon are considered to be unity. Therefore, the activity of Si at 1 623 K can be determined, and subsequently the activity coefficient of Si in Cu–Si–Fe alloy is obtained.

0.3 g of Cu–Si–Fe alloy and a 0.5 g piece of SiC were kept in a graphite crucible, which was placed in the hot zone of the furnace. The above sample was kept under an Ar atmosphere at 1 623 K for a period of 48 h. The sample was then removed from the furnace and quenched by flushing it with Ar gas. The concentrations of Si and Fe in the alloy were determined through X-ray fluorescence (XRF) spectrometry.

Experiment 3 –measurement of activity of Si at a high Si concentration in Cu–Si–Fe alloys–

The activity of Si in Cu–Si–Fe alloy was controlled by equilibrating the alloy with Si_3N_4 under a controlled partial pressure of N_2 . The equilibrium reaction is expressed as Eq. (7).

The Gibbs energy change, ΔG_7° , and the equilibrium constant, K_7 , for the reaction of Eq. (7) are expressed as Eqs. (8) and (9), respectively.

$$\Delta G_7^\circ = -292\,570 + 135.5T \text{ (J/mol)}^9 \quad (8)$$

$$K_7 = \frac{a_{\text{Si}(\text{l})} \cdot p_{\text{N}_2(\text{g})}^{2/3}}{a_{\text{Si}_3\text{N}_4(\text{s})}^{1/3}} = \frac{\gamma_{\text{Si}(\text{l})} \cdot X_{\text{Si}} \cdot p_{\text{N}_2(\text{g})}^{2/3}}{a_{\text{Si}_3\text{N}_4(\text{s})}^{1/3}} \quad (9)$$

Here, the activity of Si_3N_4 is considered to be unity, and the partial pressure of N_2 is kept constant. Therefore, the activity of Si at 1 623 K under a controlled partial pressure can be determined, and subsequently the activity coefficient of Si in the molten alloy is obtained.

0.3 g of Cu–Si–Fe alloy was kept in a silicon nitride crucible, which was placed in the hot zone of the furnace. This sample was kept under a controlled partial pressure of N_2 (5.34×10^{-4} atm by Ar – 534 ppm N_2 gas) for a period of 70 h. It was then removed from the furnace and quenched by flushing it with Ar gas. The concentrations of Si and Fe in the alloy were determined through XRF spectrometry.

3. Results and Discussions

3.1. The Cu–Si Binary System

The measured activity coefficients of Si in the Cu–Si alloy with a variation in the Si activity are summarized in **Table 1**. **Figure 2** summarizes the results along with values reported by other researchers.^{6,10–13} Here, the data are discussed in terms of the interaction parameters. The activity coefficient of a small concentration of Si ($X_{\text{Si}} < 0.15$) in Cu–Si alloy can be expressed using the first-order interaction parameter for Wagner's formalism⁷) as follows:

$$\ln \gamma_{\text{Si}} = \ln \gamma_{\text{Si}}^{\circ} + \varepsilon_{\text{Si}}^{\text{Si}} \cdot X_{\text{Si}} \quad (10)$$

where $\gamma_{\text{Si}}^{\circ}$ denotes the activity coefficient of Si in molten Cu–Si alloy in an infinite dilution relative to pure liquid Si, and $\varepsilon_{\text{Si}}^{\text{Si}}$ denotes the first-order self-interaction parameter of Si.

In **Fig. 3**, the logarithm of the activity coefficient of Si is plotted against the concentration of Si. The intercept and slope of the line in **Fig. 3** correspond to $\gamma_{\text{Si}}^{\circ}$ and $\varepsilon_{\text{Si}}^{\text{Si}}$, respectively. The values for $\gamma_{\text{Si}}^{\circ}$ and $\varepsilon_{\text{Si}}^{\text{Si}}$ were determined using the least-square regression as follows:

$$\gamma_{\text{Si}}^{\circ} = 0.0071 \pm 0.0006 \quad (11)$$

$$\varepsilon_{\text{Si}}^{\text{Si}} = 17.6 \pm 0.5 \quad (12)$$

The first-order self-interaction parameter of Si as determined in this paper shows reasonable agreement with the results obtained by Miki *et al.*⁶) The value of $\gamma_{\text{Si}}^{\circ}$ obtained in this work is one-fourth the value reported by Miki *et al.*,

while the values for $\gamma_{\text{Si}}^{\circ}$ obtained both in this work and by Bowles *et al.*¹³) are in good agreement.

All obtained data for activity coefficient of Si in Cu–Si alloy was regressed with α -function. The relationship between $(1-X_{\text{Si}})^2$ and $RT \ln \gamma_{\text{Si}}$ is shown in **Fig. 4**, along with other reported values. Regression of the present data gives the following equation of α -function.

$$\alpha = \frac{RT \ln \gamma_{\text{Si}}}{(1-X_{\text{Si}})^2} = -68400 + 162000X_{\text{Si}} - 94300X_{\text{Si}}^2 \quad (13)$$

Unfortunately, the activity data of Cu in Cu–Si alloy, especially at its dilute composition in Cu–Si alloy are not available so that the estimation of the activity of Cu by Gibbs-Duhem integration was not performed. The activity curve of Si at 1623 K calculated from α -function obtained in this

Fig. 3. Activity coefficient of Si in the Cu–Si alloy in the range of small concentration of Si at 1623 K.

Fig. 4. Relationship between $RT \ln \gamma_{\text{Si}}$ in the Cu–Si alloy and $(1-X_{\text{Si}})^2$.

Fig. 2. Relationship between $\ln \gamma_{\text{Si}}$ and silicon concentration in the Cu–Si alloy at 1623 K.

Fig. 5. Activity curve of Si in Cu–Si alloy at 1623 K.

Table 2. Results of the equilibrium experiments of Cu–Si–Fe alloys. P_{CO} was controlled to 1 in Exp. 1.

Sample No.	X_{Si}	X_{Fe}	a_{Si}	γ_{Si}	Experimental method
CSF-01	2.03×10^{-2}	6.17×10^{-3}	1.72×10^{-4}	8.48×10^{-3}	Exp. 1
CSF-02	2.12×10^{-2}	1.13×10^{-2}	1.72×10^{-4}	8.13×10^{-3}	Exp. 1
CSF-03	2.19×10^{-2}	1.69×10^{-2}	1.72×10^{-4}	7.87×10^{-3}	Exp. 1
CSF-04	2.18×10^{-2}	2.24×10^{-2}	1.72×10^{-4}	7.89×10^{-3}	Exp. 1
CSF-05	2.37×10^{-2}	2.88×10^{-2}	1.72×10^{-4}	7.26×10^{-3}	Exp. 1
CSF-06	2.33×10^{-2}	4.47×10^{-2}	1.72×10^{-4}	7.39×10^{-3}	Exp. 1
CSF-07	2.66×10^{-2}	5.57×10^{-2}	1.72×10^{-4}	6.49×10^{-3}	Exp. 1
CSF-08	2.54×10^{-2}	5.89×10^{-2}	1.72×10^{-4}	6.78×10^{-3}	Exp. 1
CSF-09	1.50×10^{-1}	1.13×10^{-2}	9.80×10^{-3}	6.54×10^{-2}	Exp. 2
CSF-10	1.54×10^{-1}	2.24×10^{-2}	9.80×10^{-3}	6.38×10^{-2}	Exp. 2
CSF-11	1.55×10^{-1}	3.08×10^{-2}	9.80×10^{-3}	6.32×10^{-2}	Exp. 2
CSF-12	1.62×10^{-1}	4.07×10^{-2}	9.80×10^{-3}	6.05×10^{-2}	Exp. 2
CSF-13	1.66×10^{-1}	5.09×10^{-2}	9.80×10^{-3}	5.90×10^{-2}	Exp. 2
CSF-14	1.96×10^{-1}	7.60×10^{-2}	9.80×10^{-3}	4.99×10^{-2}	Exp. 2
CSF-15	2.05×10^{-1}	8.66×10^{-2}	9.80×10^{-3}	4.79×10^{-2}	Exp. 2
CSF-16	2.06×10^{-1}	9.82×10^{-2}	9.80×10^{-3}	4.77×10^{-2}	Exp. 2
CSF-17	2.07×10^{-1}	1.04×10^{-1}	9.80×10^{-3}	4.74×10^{-2}	Exp. 2
CSF-18	0.715	5.51×10^{-3}	0.697	0.974	Exp. 3
CSF-19	0.695	9.45×10^{-3}	0.697	1.00	Exp. 3
CSF-20	0.719	2.62×10^{-2}	0.697	0.968	Exp. 3
CSF-21	0.731	3.21×10^{-2}	0.697	0.952	Exp. 3

work is shown in Fig. 5, along with the experimental data and other reported values.^{6,10–14} The experimental data and activity curve of Si are in good agreement compared to the data reported by Miki *et al.*,⁶ and Yan *et al.*¹⁴

3.2. The Cu–Si–Fe Ternary System

The equilibrium compositions and measured activity coefficients of Si are summarized in Table 2. The equilibrium Si concentration increases with an increase in the concentration of Fe in the alloy at a constant Si activity. The change in the activity coefficient of Si in the Cu–Si–Fe alloy against the concentration of Fe is shown in Fig. 6. The activity coefficient of Si in Cu–Si–Fe alloy decreases with an increase in the Fe concentration, and a tendency is most significant within the low Si activity range.

The change in the activity coefficient of Si against Fe concentration in Fig. 6 is affected by not only interaction of Fe on Si but change in Si concentration. So, the data for small concentrations of Si (exp.1) are discussed in terms of the interaction parameters for the Wagner's formalism first. The activity coefficient of Si in Cu–Si–Fe alloy at small concentrations of Si and Fe can be expressed through the first and second-order interaction parameters as follows:

$$\ln \gamma_{Si(l)} = \ln \gamma_{Si(l)}^{\circ} + \varepsilon_{Si}^{Si} \cdot X_{Si} + \varepsilon_{Si}^{Fe} \cdot X_{Fe} + \rho_{Si}^{Fe} \cdot X_{Fe}^2 \quad (14)$$

where ε_{Si}^{Fe} and ρ_{Si}^{Fe} are the first and second-order interaction parameters of Fe on Si, and $\gamma_{Si(l)}^{\circ}$ and ε_{Si}^{Si} are used of the data determined above. Eq. (15) is obtained by rearranging Eq. (14).

Fig. 6. Relationship between $\ln \gamma_{Si}$ and Fe concentration in the Cu–Si–Fe alloy at 1623 K.

Fig. 7. Relationship between the left hand side of Eq. (15) and Si concentration.

$$\ln \gamma_{Si(l)} - \varepsilon_{Si}^{Si} \cdot X_{Si} = \ln \gamma_{Si(l)}^{\circ} + \varepsilon_{Si}^{Fe} \cdot X_{Fe} + \rho_{Si}^{Fe} \cdot X_{Fe}^2 \quad (15)$$

In Fig. 7, the left-hand side of Eq. (15) is plotted against the concentration of Fe. ε_{Si}^{Fe} and ρ_{Si}^{Fe} were determined using the least-square regression as follows:

$$\varepsilon_{Si}^{Fe} = -16 \pm 3 \quad (16)$$

$$\rho_{Si}^{Fe} = 150 \pm 47 \quad (17)$$

The negative value of ε_{Si}^{Fe} indicates that the addition of Fe to Cu–Si alloy is effective in decreasing the activity of Si.

To express the effect of Fe addition on the activity coefficient of Cu at higher Si composition (exp.2 and 3), the following equation proposed by Fuwa and Chipman¹⁵ is employed.

$$\left(\frac{\partial \ln \gamma_{Si(l)}}{\partial X_{Fe}} \right)_{X_{Si}} = - \left[1 + \left(\frac{\partial \ln \gamma_{Si(l)}}{\partial X_{Si}} \right)_{X_{Fe}=0} \right] \left(\frac{\partial \ln X_{Si}}{\partial X_{Fe}} \right)_{a_{Si}} \quad (18)$$

Equation (18) indicates the interaction coefficient of Fe on Si in Cu–Si alloy at a fixed Si concentration in the concentrated solution, of which formula was derived to express the interaction of alloying element on C in carbon-saturated iron.¹⁵

By inserting $(\partial \ln \gamma_{Si(l)} / \partial X_{Si})_{X_{Fe}=0}$ from Eq. (13) and the composition change, $(\partial \ln X_{Si} / \partial X_{Fe})_{a_{Si}}$ into Eq. (18), the interaction coefficient was determined to be -12.0 at $X_{Si} = 0.138$ and -1.18 at $X_{Si} = 0.702$. Including Eq. (16), the interaction

of Fe on Si in Cu–Si alloy was found to be attractive in the wide composition range, but becomes smaller by increasing Si concentration in the alloy.

4. Conclusions

In order to clarify the effect of Fe addition on the activity of Si in Cu–Si alloy, the equilibrated concentrations and activity coefficients of Si in Cu–Si–Fe alloy at 1 623 K were determined using chemical equilibration methods. The data were evaluated in terms of the interaction parameters in molten Cu for Wagner's formalism and the interaction coefficient in the concentrated solution, and the thermodynamic properties were obtained as follows:

$$\gamma_{\text{Si(l)}}^{\circ} = 0.0071 \pm 0.0006 \quad \varepsilon_{\text{Si}}^{\text{Si}} = 17.6 \pm 0.5 \quad \varepsilon_{\text{Si}}^{\text{Fe}} = -16 \pm 3$$

$$\rho_{\text{Si}}^{\text{Fe}} = 150 \pm 47$$

$$\left(\frac{\partial \ln \gamma_{\text{Si(l)}}}{\partial X_{\text{Fe}}} \right)_{X_{\text{Si}}} = -12.0 (X_{\text{Si}} = 0.138), \quad -1.18 (X_{\text{Si}} = 0.702)$$

It was found that the activity coefficient of Si decreases with an increase in the concentration of Fe in Cu–Si alloy.

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