Thermodynamics of boron distribution in solvent refining of silicon using ferrosilicon alloys

Leili Tafaghodi Khajavi, Kazuki Morita, Takeshi Yoshikawa and Mansoor Barati

Version Post-print/Accepted Manuscript


Copyright/License This work is licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/4.0/.

How to cite TSpace items

Always cite the published version, so the author(s) will receive recognition through services that track citation counts, e.g. Scopus. If you need to cite the page number of the author manuscript from TSpace because you cannot access the published version, then cite the TSpace version in addition to the published version using the permanent URI (handle) found on the record page.

This article was made openly accessible by U of T Faculty. Please tell us how this access benefits you. Your story matters.
Thermodynamics of Boron Distribution in Solvent Refining of Silicon using Ferrosilicon Alloys

Leili Tafaghodi Khajavi¹, Kazuki Morita², Takeshi Yoshikawa², Mansoor Barati¹

¹Department of Materials Science and Engineering, University of Toronto, 184 College Street, Suite 140; Toronto, Ontario M5S 3E4, Canada
²Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan
E-mail: leili.tafaghodikhajavi@utoronto.ca

ABSTRACT

Distribution coefficient of boron between purified solid silicon and iron-silicon melt at infinite dilution of boron was evaluated to investigate the effectiveness of boron removal from silicon by solvent refining using iron. The estimated values for distribution coefficient of boron at infinite dilution are: 0.49±0.01 (1583 K), 0.41±0.03 (1533 K) and 0.33±0.04 (1483 K). The distribution coefficient increases with temperature showing less boron removal at higher temperatures. The estimated values for self interaction parameter of boron are as follow: -96±12 (1583 K), -111±28 (1533 K) and -159±45 (1483 K). Activity coefficient of boron in solid silicon was obtained and related to temperature as $lny_B^{0\text{ in solid Si}} = (16317 \pm 282) \left(\frac{1}{T}\right) - (7.06 \pm 0.18)$.

Keywords: Silicon, thermodynamics, solvent refining, impurity, boron
1. Introduction

Among various semiconductor materials for manufacturing solar cells, silicon accounts for around 90 percent of PV materials [1, 2]. The concentration of impurity elements significantly influences the semiconductor properties of silicon; consequently the impurity content must be precisely controlled.

Solvent refining is one of the alternative approaches that has been considered as a cost efficient and energy efficient purification steps for producing solar grade silicon. This study employs solvent refining as a purification process in which high purity silicon dendrites are precipitated from an alloy of Si with an element, known as getter, by controlled cooling and solidification. The purification that takes place during crystal growth is mainly due to the impurity rejection by the solidification front.

Various metallic elements including Al [3-12], Cu [13-15], Ni [16], Sb [17] and Sn [18] have been used as the getter. A detailed comparison between the effectiveness of these elements has been presented elsewhere [19]. Al is the alloying element that has been studied the most among other candidates. An advantage of employing Al in solvent refining of Si is that they have a single eutectic phase diagram without intermetallic compounds. Morita and his colleagues [3-8, 12] investigated the effectiveness of Al as the getter by studying the thermodynamics of the impurity elements in Al-Si system. As the densities of silicon and aluminum are very close (2.33 vs. 2.70 g/cm³), it is challenging to separate them by gravity separation techniques. Although removing aluminum with acid leaching is a promising technique, it consumes large amounts of acid and also results in major losses of Al. In response to this issue, a new method has been developed on the basis of induction stirring to agglomerate solidified silicon crystals during the solidification of Si-Al alloy [6, 8]. Cu has the advantage of lower solid solubility in silicon compared to Al, Sn, and Sb. However, from economic point of view Cu is less favorable than Al. Furthermore it is not effective in removing phosphorus and boron [19].
In the current study, iron was employed as the alloying element. Iron was a preferred getter [20] because of its lower cost, good affinity for B, high density to facilitate the separation of the alloy from Si crystals, and the possibility of using the by-product alloy as ferrosilicon addition in steelmaking. Also, it has a solid solubility in silicon significantly lower than both Cu and Al. This will result in less residual iron in the purified silicon [19]. Amongst various impurities in solar silicon, removal of boron has proven to be most difficult as it is not responsive to directional solidification (due to large segregation coefficient) or vacuum treatment due to its low vapor pressure. Of particular interest in solvent refining of silicon is enhancing boron removal by alloying Si with a proper getter that lowers the segregation coefficient effectively. Thus it is critical to evaluate the thermodynamic properties of boron in solid silicon and in iron-silicon melt in order to understand B behavior in Fe-Si and possibly optimize the removal conditions.

2. Materials and Methods

The experimental work involved melting and controlled solidification of an iron-silicon-boron alloy (80 wt% Si- 20 wt% Fe), followed by separation of the precipitated silicon and analysis of both the silicon phase and the total sample. The temperature profile of the samples quenched at different temperatures is depicted in Figure 1. Samples were quenched from 1483K, 1533K, and 1583K in order to investigate the effect of temperature on boron distribution and thermodynamic properties of boron. The quenching temperature being above the eutectic temperature of iron and silicon system (1400 K) [21] results in formation of solid silicon and a iron-silicon alloy with composition corresponding to the liquidus line of the binary phase diagram. After quenching, the samples were crushed and leached to separate the alloy from refined silicon phase. The alloy dissolves during leaching and the silicon particles remain as solid residue. The next step includes digestion of silicon samples followed by ICP-OES analysis to obtain the concentration of boron. The concentration of iron in the purified silicon phase was measured using EPMA. Further details on separation, digestion, and analysis of the phases are provided in an earlier article[22].
3. Results and Discussion

3.1. Self Interaction Parameter of Boron and Distribution Coefficient at Infinite Dilution

Distribution coefficient of boron at different concentrations and temperatures along with the interaction parameter of iron on boron has been investigated in the authors’ previous paper [22]. In order to study the distribution of impurities in solvent refining of silicon for solar applications where the concentration of impurities would be in the order of few or sub ppm, the distribution coefficient at infinite dilution of boron should be evaluated.

Assuming equilibrium conditions and pure solid and liquid boron as standard states for boron in solid silicon and iron-silicon melt respectively, Equations 1-3 can be obtained as follow:

\[ \mu_B(\text{in solid Si}) = \mu_B(\text{in Fe-Si melt}) \]  \hspace{1cm} (1)
\[
RT \ln a_{B(\text{in solid Si})} = \Delta G^0_{B \text{ fusion}} + RT a_{B(\text{in Fe-Si melt})} \quad (2)
\]

\[
\ln y_{B(\text{in solid Si})} + \ln x_{B(\text{in solid Si})} = \frac{\Delta G^0_{B \text{ fusion}}}{RT} + \ln y_{B(\text{in Fe-Si melt})} + \ln x_{B(\text{in Fe-Si melt})} \quad (3)
\]

The variation in the molar ratio of iron to silicon is negligible because of the small content of boron in the alloy melt. Consequently the activity coefficient of boron in iron-silicon melt is considered to be constant and the distribution coefficient of boron can be expressed as Equation 4.

\[
\ln k_B = \ln \frac{x_{B \text{ in solid Si}}}{x_{B \text{ in Fe-Si melt}}} = \frac{\Delta G^0_{B \text{ fusion}}}{RT} + \ln \frac{y_{B \text{ in Fe-Si melt}}}{y_{B \text{ in solid Si}}} - \varepsilon_{Fe \text{ in solid Si}}^B x_{Fe \text{ in solid Si}} - \varepsilon_{B \text{ in solid Si}}^B x_{B \text{ in solid Si}} \quad (4)
\]

In the case of infinite dilution of boron, the self interaction coefficient of boron, \(\varepsilon_{B \text{ in solid Si}}^B\), can be neglected and Equation (4) can be rewritten as:

\[
\ln k_B^* = \frac{\Delta G^0_{B \text{ fusion}}}{RT} + \ln \frac{y_{B \text{ in Fe-Si melt}}}{y_{B \text{ in solid Si}}} - \varepsilon_{Fe \text{ in solid Si}}^B x_{Fe \text{ in solid Si}} \quad (5)
\]

where \(k_B^*\) is the distribution coefficient of boron at infinite dilution and \(x_{Fe \text{ in solid Si}}^*\) is the solid solubility of iron in silicon which is equal to \(3 \times 10^{-7}\) \((1483\) K\), \(4 \times 10^{-7}\) \((1533\) K\), and \(5 \times 10^{-7}\) \((1583\) K\) [23].

Combining Equations (4) and (5), Equation (6) is obtained which was used for estimating \(k_B^*\) and \(\varepsilon_{B \text{ in solid Si}}^B\).

\[
\ln k_B^* - \varepsilon_{B \text{ in solid Si}}^B x_{B \text{ in solid Si}} = \ln k_B + \varepsilon_{Fe \text{ in solid Si}}^B (x_{Fe \text{ in solid Si}} - x_{Fe \text{ in solid Si}}^*) \quad (6)
\]

Distribution coefficient of boron, interaction coefficient of boron on iron and the concentration of iron in silicon are known, consequently the right-hand side of Equation (6) can be calculated for each sample. Considering \(x_{B \text{ in solid Si}}^*\) as "X" and the right-hand side of the mentioned equation as "Y", linear regression using least square method,
yields the natural logarithm of the distribution coefficient at infinite dilution as the intercept of the line (Figure 2).

![Graph showing ln(kb) vs. X_B in solid Si](image)

**Figure 2.** Evaluation of self interaction parameter of boron and its distribution coefficient at infinite dilution.

Self interaction parameter of boron at different temperatures determined from the slope of the regression lines in Figure 2 are as follow: -96±12 (1583 K), -111±28 (1533 K) and -159±45 (1483 K). The variation of $\varepsilon_B^p$ in solid Si with temperature is depicted in Figure 3. The negative values indicate the attraction between boron atoms and their tendency for clustering in Si, which has been observed in other studies involving B behavior in Si [24-31]. The absolute value of $\varepsilon_B^p$ in solid Si decreases with increasing temperature implying the smaller attractive force between boron atoms at higher temperatures.
The calculated values for distribution coefficient at infinite dilution are: 0.49±0.01 (1583 K), 0.41±0.03 (1533 K) and 0.33±0.04 (1483 K). The distribution coefficient at infinite dilution decreases with decreasing temperature which is advantageous towards solvent refining. In other words according to the results, higher boron removal can be achieved at lower temperatures.

This trend can be explained by the relative stability of iron and silicon borides. The standard Gibbs energies for formation of borides were estimated using the available thermodynamic data [32, 33]. As it can be seen in Figure 4, the standard Gibbs energies for formation of silicon and iron borides increase with temperature, which indicates a decrease in the affinity of iron and silicon for boron, similar trend can be found for aluminum.
The relative stability of borides can be determined from the position of each line in the above figure. Basically, it appears that borides of both Al and Fe are more stable than that of Si.

The absolute value of the difference between the standard Gibbs free energies of iron borides and silicon boride decreases with temperature, showing that as the temperature increases, the iron-boron compounds become more unstable than those of silicon-boron, thus less affinity between iron and boron compared to silicon and boron. The bigger the difference, the less the affinity of iron for boron compared to silicon. It should be emphasized that by increasing temperature, the affinity of both iron and silicon for boron decreases, but the iron affinity for boron decreases more than that of silicon. It is worth mentioning that according to the results obtained by Yoshikawa and Morita [4], the distribution coefficient of boron between silicon and aluminum also increases with temperature. As it can be seen in Figure 4, similar to the case of iron and silicon, the absolute value of the difference between the standard Gibbs free energies of aluminum borides and silicon boride decreases with temperature which is consistent with the
increase of boron distribution coefficient between silicon and aluminum as temperature increases.

3.2. Activity Coefficient of Boron in Solid Silicon

Rearranging Equation (5), activity coefficient of boron in solid silicon can be written as:

\[
RT\ln \gamma_{B}^{0}_{\text{in solid Si}} = RT\Delta G_{B}^{0}_{\text{fusion}} + RT\ln \gamma_{B}^{0}_{\text{in Fe-Si melt}} - RT\ln k_{B}^{*} - RT\epsilon_{Fe}^{B} \frac{X_{Fe}^{*}}{X_{Si}^{*}}
\]

(7)

Interaction coefficient of boron on iron [22] and the distribution coefficient of boron at infinite dilution have been calculated based on the experimental result. Thus the activity coefficient of boron in solid silicon can be estimated if the activity coefficient in the alloy melt is known.

The Gibbs-Duhem integration method developed by Toop [34] was employed to estimate the activity coefficient of boron in the alloy melt. Knowing the chemical composition of a ternary system, the activity coefficient of element 2 in the 1-2-3 ternary system can be evaluated based on the activity coefficient of element 2 in 1-2 and 2-3 binary systems, and the excess Gibbs energy for 1-3 binary system at the given concentration ratio (Equation 8).

\[
RT\ln \gamma_{2}^{0}_{1-2-3} = [\frac{x_{1}}{1-x_{2}}RT\ln \gamma_{2}^{0}_{1-2} + \frac{x_{3}}{1-x_{2}}RT\ln \gamma_{2}^{0}_{2-3}]x_{2} - (1-x_{2})^{2}G_{1-3}^{\text{excess}}\frac{x_{1}}{x_{3}}
\]

(8)

Taking 1 for silicon, 2 for boron and 3 for iron, Equation (8) can be rewritten as follows:

\[
RT\ln \gamma_{B}^{0}_{\text{in Si-Fe melt}} = [X_{Si}RT\ln \gamma_{B}^{0}_{\text{Si melt}} + X_{Fe}RT\ln \gamma_{B}^{0}_{\text{Fe melt}}] - G_{\text{Si-Fe melt}}^{\text{excess}}
\]

(9)

It is clear that the activity coefficient of boron in Si-Fe melt can be evaluated using the activity coefficient of boron in molten silicon [35] and that in molten iron [36]. It should be noted that the above activity coefficients of boron in silicon and iron are estimated by extrapolating from activity coefficient values at higher temperatures, i.e. 1693-1923K in silicon and 1723-1823K in iron.
The excess Gibbs energy of mixing for silicon-iron melt was obtained from Miettinen’s work [37] knowing the mole fraction of iron and silicon in the alloy melt at each temperature, i.e. silicon mole fraction equals 0.75 (1483 K), 0.79(1533 K), 0.82(1583 K). Similar to the case of the activity coefficients, the temperature range for $G_{Si-Fe \text{ melt}}^{\text{excess}}$ in Miettinen’s experiments (1573-1823 K) is higher than what is employed in this study.

$$G_{Si-Fe \text{ melt}}^{\text{excess}} = X_{Fe} \cdot X_{Si} \cdot [-164435 + 41.99T - 21.523T(X_{Fe} - X_{Si}) + (52220 + 5.726T)(X_{Fe} - X_{Si})^2 + (-28955 + 26.275T)(X_{Fe} - X_{Si})^3]$$ \hspace{1cm} (10)

The activity coefficient of boron in the alloy melt was obtained by substituting the activity coefficient of boron in silicon and in iron as well as the excess Gibbs free energy values in Equation 9.

The interaction parameter between iron and boron at three different temperatures was estimated in authors’ previous work [22]. The distribution coefficient of boron at infinite dilution was presented in Section 3.1. Substituting the values for interaction parameter and distribution coefficient along with the boron activity coefficient in the alloy and the standard Gibbs free energy of fusion into Equation (9), activity coefficient of boron in solid silicon can be evaluated through least square regression as:

$$\ln \gamma_{B \text{ in solid } Si}^{0} = (16317 \pm 282) \left( \frac{1}{T} \right) - (7.06 \pm 0.18)$$ \hspace{1cm} (11)
The $\gamma_B^{0} \text{ in solid Si}$ obtained based on the experimental results of this study (1483-1583 K) and the one based on the extrapolation from Yoshikawa’s result at 1273-1473K [4] are presented in Figure 5. It can be seen that there’s a very good agreement between the values obtained in the two studies. It should be emphasized that the equation suggested by Yoshikawa et al. was obtained for a different temperature range compared to the ones that were examined in this study and it can be the reason for the minor difference between the values estimated for activity coefficient. It should also be noted that due to extrapolation from higher to lower temperatures, there might be some inaccuracy involved in evaluating the activity coefficient of boron in the silicon-iron system. This can be considered as another source for the difference between the obtained values in the two studies.
Figure 5: Comparison between the activity coefficients of boron in solid silicon obtained in this study and the one by Yoshikawa et al.

4. Conclusions

The values obtained for distribution coefficient at infinite dilution are: 0.49±0.01 (1583 K), 0.41±0.03 (1533 K) and 0.33±0.04 (1483 K). All the above values are smaller than the distribution coefficient of boron in conventional directional solidification which makes solvent refining more effective for boron removal compared with directional solidification. Distribution coefficient of boron at infinite dilution increases with temperature which shows better boron removal at lower temperatures. The relative stability of iron and silicon borides is in line with the variation of distribution coefficient with temperature. Self interaction parameter of boron are as follow: -96±12 (1583 K), -111±28 (1533 K) and -159±45 (1483 K). The values obtained for self interaction parameter of boron in silicon were negative indicating an attraction between boron atoms in silicon. The absolute value of self interaction parameter of boron decreases with increasing temperature, implying the smaller attraction between boron atoms at higher temperatures.
Activity coefficient of boron in Si-Fe alloy was estimated and used to evaluate the activity coefficient of boron in solid silicon as: 

\[ \ln \gamma_{B}^{0}_{\text{in solid Si}} = (16317 \pm 282) \left( \frac{1}{T} \right) - (7.06 \pm 0.18) \]

**Acknowledgement**

Financial support for this research work from NSERC is greatly appreciated.
References


