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

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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 $ln\ \gamma^0_{B\ in\ solid\ Si} = (16317 \pm 282)(\frac{1}{T}) - (7.06 \pm 0.18)$.


## 1. Introduction

Among various semiconductor materials for manufacturing solar cells, silicon accounts for around 90% 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/cm$^3$), 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.

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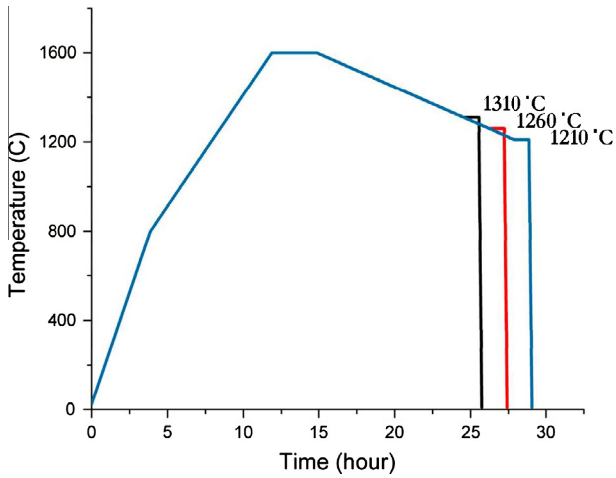


**Fig. 1.** Temperature history of the samples for different quenching temperatures.

### 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 Fig. 1. Samples were quenched from 1483 K, 1533 K, and 1583 K 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, Eqs. (1)–(3) can be obtained as follow:

$$\mu_{B(S) in\ solid\ Si} = \mu_{B(l) in\ Fe-Si\ melt} \tag{1}$$

$$RT \ln a_{B(S) in\ solid\ Si} = \Delta G_B^{0\ fusion} + RTa_{B(l) in\ Fe-Si\ melt} \tag{2}$$

$$\ln \gamma_{B(S) in\ solid\ Si} + \ln X_{B(S) in\ solid\ Si} = \frac{\Delta G_B^{0\ fusion}}{RT} + \ln \gamma_{B(l) in\ Fe-Si\ melt} + \ln X_{B(l) in\ Fe-Si\ melt} \tag{3}$$

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 Eq. (4).

$$\ln k_B = \ln \frac{X_{B\ in\ solid\ Si}}{X_{B\ in\ Fe-Si\ melt}} = \frac{\Delta G_B^{0\ fusion}}{RT} + \ln \frac{\gamma^0_{B\ in\ Fe-Si\ melt}}{\gamma^0_{B\ in\ solid\ Si}} - \varepsilon^B_{Fe\ in\ solid\ Si} X_{Fe\ in\ solid\ Si} - \varepsilon^B_{B\ in\ solid\ Si} X_{B\ in\ solid\ Si} \tag{4}$$

In the case of infinite dilution of boron, the self interaction coefficient of boron, $\varepsilon^B_{B\ in\ solid\ Si}$, can be neglected and Eq. (4) can be rewritten as:

$$\ln k_B^* = \frac{\Delta G_B^{0\ fusion}}{RT} + \ln \frac{\gamma^0_{B\ in\ Fe-Si\ melt}}{\gamma^0_{B\ in\ solid\ Si}} - \varepsilon^B_{Fe\ in\ solid\ Si} X^*_{Fe\ in\ solid\ Si} \tag{5}$$

where $k_B^*$ is the distribution coefficient of boron at infinite dilution and $X^*_{Fe\ in\ solid\ Si}$ 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 $5 \times 10^{-7}$ (1583KC) [23].

Combining Eqs. (4) and (5), Eq. (6) is obtained which was used for estimating $k_B^*$ and $\varepsilon^B_{B\ in\ solid\ Si}$.

$$\ln k_B^* - \varepsilon^B_{B\ in\ solid\ Si} X_{B\ in\ solid\ Si} = \ln k_B + \varepsilon^B_{Fe\ in\ solid\ Si} (X_{Fe\ in\ solid\ Si} - X^*_{Fe\ in\ solid\ Si}) \tag{6}$$

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 Eq. (6) can be calculated for each sample. Considering $X_{B\ in\ solid\ Si}$ 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 (Fig. 2).

Self interaction parameter of boron at different temperatures determined from the slope of the regression lines in Fig. 2 are as follow: −96 ± 12 (1583 K), −111 ± 28 (1533 K) and −159 ± 45 (1483 K). The variation of $\varepsilon^B_B$ in solid Si with temperature is depicted in Fig. 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 $\varepsilon^B_B$ 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

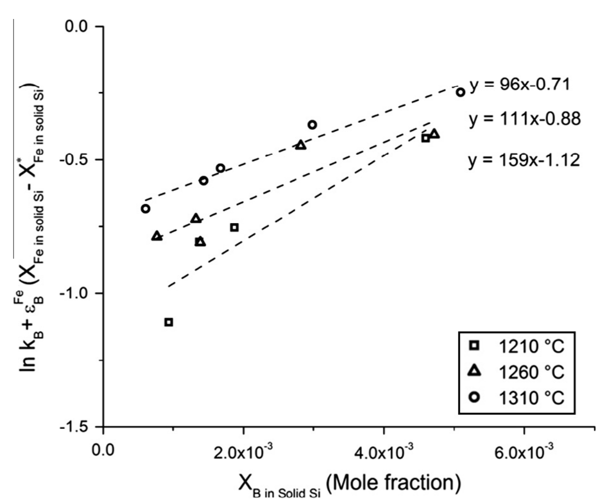


**Fig. 2.** Evaluation of self interaction parameter of boron and its distribution coefficient at infinite dilution.