Experimental determination of activity interaction coefficients of components in Si-B-Fe and Si-B-Al ternary systems at 1723 K

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Abstract:

The interactions among impurity components in Si-based solution are the important thermodynamic parameters for the purification of silicon materials. A "same concentration" method was used to determine the activity interaction coefficients of Fe to B and Al to B in the silicon solution. Fe and Al were respectively dissolved into the binary Si-B solution at 1723 K with the holding time of 5 h, 7 h, 9 h and 11 h. The equilibrium concentrations of Fe, B in the Si-B-Fe system and Al, B in the Si-B-Al system were determined. The interaction coefficients of Fe to B and Al to B were obtained by fitting the solubility data of B, Fe and Al. The solubility relationships between B and [%Fe] and between B and [%Al] were obtained, respectively. It is found by the SEM and EPMA pictures of samples that the third component Fe or Al

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added to the binary Si-B solution have been fully alloyed, which verifies the accuracy of the experimental determination results. The significance of the activity interaction coefficient of B on boron removal from industrial silicon was analyzed.

Keywords: Si-based solution; ternary system; activity interaction coefficient; saturation solubility; physical characterization

1. Introduction

Solar grade silicon (SoG-Si) is a key material for solar photovoltaic conversion. A metallurgical route for producing SoG-Si that employs relatively inexpensive metallurgical grade silicon (MG-Si, ~99%) as the raw material is believed to be a promising approach for fabricating solar cells [1-3]. However, various impurities in silicon such as iron, aluminum, boron, etc. have a great negative impact on the photoelectric conversion performance of solar grade silicon [4]. In the process of metallurgical production of industrial silicon, boron is mainly removed by refining outside the furnace [5]. The temperature of silicon refining is around 1723 K. So the thermodynamic parameters $\varepsilon^{Fe}_B$ and $\varepsilon^{Al}_B$ about the phase equilibria and the liquid phase are necessary, since the boron removal from silicon by refining is relevant to the thermodynamic parameters such as solubility and activity in silicon [6-8]. Currently, there are no details on the thermodynamic parameters about boron removal from silicon under high temperature conditions.

Therefore, the research on the thermodynamic properties of metallurgical grade silicon has always been a research hotspot in the silicon industry [9]. Liu [10] et al. used the MIVM model to investigate the thermodynamic behavior of Al and Fe in Si
solution under the vacuum environment, and calculated the activity interaction coefficients between Fe and Al. Tao [11-13] used the MIVM model to calculate the interaction coefficient of each component in the Si-Fe-Al system, and obtained the activity interaction coefficient of Fe to Fe, Fe to Al and Al to Al in the silicon solution at 1687 K. The iso-activity curves of components Fe and Al in liquid Si-Al-Fe ternary system at 1823 K are drawn. Cui et al. [14] conducted the thermodynamic optimization of the binary Ca-Fe and the ternary Ca-Fe-Si systems based on the critical evaluation of all phase diagrams and thermodynamic properties data available in the literature, and predicted several pseudo-binary sections and isopleths in the ternary Ca-Fe-Si system. Iwata et al. [15] predicted the activity coefficients and the interaction coefficients of Ti, Fe, Al and Pb elements in infinite dilute Si solutions by the use of first-principles calculations based on density functional theory. They compared the theoretical calculations with the reported experimental results and found that considering the excess entropy would reduce the difference between theoretical and experimental measurements. Yang et al. [16] used the atom and molecule co-existence theory to calculate the thermodynamic properties of Si-Fe-Ca system, and obtained the activity interaction coefficient of Ca to Fe ($\varepsilon_{Fe}^{Ca}$) in Si solution at 1723-1873 K. Noguchi et al [17] determined the activity coefficient of B and the activity interaction coefficient of B and N in Si by equilibrating solid BN and liquid Si in a nitrogen atmosphere from 1723 to 1923 K, and obtained the favorable conditions for removing boron in Si liquid. Applying the atom and molecule co-existence theory model to the Si-Fe binary system, Yang et al. [18] studied the
infinite dilute activity coefficient and the self-interaction coefficient of Fe at the
temperature range of 1693-1993 K. Zhou et al. [19] used the “same activity” method
to determine the activity interaction coefficient of Al to Fe in Si solution at 1663-1723
K. Miki et al. [20-22] used the chemical equilibration method and the Knudsen
effusion method to determine the thermodynamic properties of elements such as Al,
Ca, Mg, Ti and Fe in Si, and obtained the relationship between the infinite activity
coefficients of Al, Ca and Mg in Si liquid and temperature. In addition, they also
obtained the relationship between the activity interaction coefficient and the
temperature of each element in Si alloys.

We determined the interaction coefficients $\varepsilon_{B}^{Fe}$ in the Si-B-Fe and $\varepsilon_{B}^{Al}$ in the
Si-B-Al systems using the “same concentration” method at 1723 K. In order to make
sure the dissolution balance of components B, Fe and Al at 1723 K, the alloying
samples were kept the temperature for the 5 h, 7 h, 9 h and 11 h respectively in the
process of experimental. The relationship between the saturated solubility of B and
[%Fe] or [%Al] were obtained. At the same time, the microstructures of the Si-B-Fe
and Si-B-Al alloying samples was physically characterized to verify the accuracy of
the experimental results.

2. Experimental

The Fe (>99.97%), Al (>99.95%), Si (>99.99%) and B (>99.9%) powders were
used as the raw materials in the experiments. As shown in the Si-B binary phase
diagram (Fig. 1) [23], the boron concentration on the liquidus at 1723 K is about 5.5%
mass ratio. Therefore, the raw materials were matched according the liquidus at 1723
K and the raw material composition used to prepare the experimental alloys is shown in Table 1. An excess of B in Si-B-Fe and Si-B-Al systems were ensured.

![Si-B binary phase diagram](image)

Fig. 1 Si-B binary phase diagram

The high-purity Si, B, Fe or Al were weighed and mixed uniformly and then placed in a corundum crucible of φ20-mm*33-mm, which were encased a graphite crucible of φ63-mm*90-mm. Since the content of Fe and Al added in the experiment is high, the influence of Al in corundum crucible on the experiment can be neglected. The crucibles were then placed in a vacuum tubular resistance furnace as shown in Fig. 2. In order to ensure that the materials were not oxidized, the furnace tube was first evacuated, and then a high purity argon gas (99.99%) was continuously supplied during the experiment. The temperature was raised to 1723 K and kept for 5, 7, 9, and 11 hours, respectively. After the full dissolution of B and Fe or Al in silicon solution, the high-temperature graphite crucible is quickly extracted from the furnace tube by molybdenum wire, and the silicon solution is quenched.
Fig. 2 Vacuum/atmosphere tubular resistance furnace and its structure

The alloying sample was firstly sanded with sandpaper and then cleaned with alcohol. It is cut into two pieces by a diamond wire cutter. One piece is ground into a powder in an agate mortar (less than 200 mesh) and another is burnished. The contents of B, Fe or Al in the powder samples were measured by the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Optima 8000, Perkin Elmer Corporation). And the burnished samples are detected by the Scanning Electron Microscopy (SEM, XL30ESEM, Netherlands) and the Electron Probe Microanalysis (EPMA, JXA-8230, Japan Electronics Co., Ltd.). The experimental process is shown in Fig. 3.
3. Results and discussion

3.1 Interaction coefficients $\varepsilon_{B}^{Fe}$ and $\varepsilon_{B}^{Al}$

The activity interaction coefficient refers to the activity coefficient effect of the component $j$ on another component $i$ in Si-$i$-$j$ solution, which is embodied the correction of activity coefficient of the component $i$. In this study, the “same concentration” method was used for the experimental determination work. When the components $j$ and $k$ ... are added to the Si-$i$ binary system, the components in the system reach the concentration balance within a certain time, and the effect of the components $j$ and $k$ ... on the activity coefficient of component $i$ can be calculated [24].

In this study, Fe or Al is added to the Si-B binary system, and the effect of Fe or Al on the activity coefficient of B was obtained. The Wagner equations [25, 26] corresponding to the Si-B-Fe system and the Si-B-Al system are shown in the formulas (1) and (2), respectively.

$$\ln f_B = e_B^{B}[%B] + e_B^{Fe}[%Fe]$$  \hspace{1cm} (1)

$$\ln f_B = e_B^{B}[%B] + e_B^{Al}[%Al]$$  \hspace{1cm} (2)
The results of chemical composition analysis by ICP for the Si-B-Fe and Si-B-Al ternary alloy samples at 1723 K with different holding time are shown in Table 2.

Since the boron is at a saturated state, the activity of B in silicon solution is 1.

\[ x_B \gamma_B = 1 \]  \hspace{1cm} (3)

Given as

\[ \gamma_0^B = \gamma_B / f_B \]  \hspace{1cm} (4)

Therefore,

\[ f_B = 1 / x_B \gamma_0^B \]  \hspace{1cm} (5)

We know from the literature that \( \gamma_0^B \) is 0.24 [27], so the calculation results of Si-B-Fe and Si-B-Al ternary alloy systems by the formulas (3)-(5) and the data of Table 2 are obtained and shown in Table 3.

According to Table 2 and Table 3, the fitting results of [%Fe] to \( \lg f_B \) and [%Al] to \( \lg f_B \) at 1723 K with different holding time in the Si-B-Fe and Si-B-Al ternary alloy systems are shown in Fig. 4(a) and Fig. 4(b). Due to the slight fluctuations in the current and temperature fields of the experimental furnace, there are subtle differences between the samples, but the fitted straight lines of multiple samples can compensate for this difference. From the fitting results, it is found that the dissolution equilibrium is reached. The fitting result of holding time 5 h is almost consistent with that of holding time 7 h in the Si-B-Fe ternary alloy system, and the fitting result of holding time 7 h is almost consistent with that of 9 h in the Si-B-Al ternary alloy system. Therefore, the concentrations of B and Fe or Al are in a dynamic equilibrium state with the holding time of 5 h and 7 h in Si-B-Fe ternary alloy system and the holding
time 7 h and 9 h in the Si-B-Al ternary alloy system.

Fig. 4 (a) Fitting results between [%Fe] and $\lg f_B$ at 1723 K; (b) Fitting results between [%Al] and $\lg f_B$ at 1723 K

Due to some uncontrollable factors and changes in the Fe and Al contents during the experiment, the saturation solubility of B in the Si solution also changed. However, it can be seen that the content of B is very low relative to the content of Fe and Al, and the solubility change of B is not very significant. Then, this study ignores the effect of B’s own solubility change on the experiment. According to the equations (1) and (2), it is seen that the slope of the fitted straight line is the activity interaction coefficient $\varepsilon_B^{Fe}$ or $\varepsilon_B^{Al}$, which is converted to $\varepsilon_B^{Fe}$ or $\varepsilon_B^{Al}$ by the formulas (6) and (7).

$$\varepsilon_B^{Fe} = 230 \frac{M_{Fe}}{M_{Si}} e_B^{Fe} + \frac{M_{Si}-M_{Fe}}{M_{Si}}$$

(6)
\[ \varepsilon_{B}^{Al} = 230 \frac{M_{Al}}{M_{Si}} \varepsilon_{B}^{Al} + \frac{M_{Si}-M_{Al}}{M_{Si}} \] (7)

The results of \( \varepsilon_{B}^{Fe} \) and \( \varepsilon_{B}^{Al} \) are shown in Table 4.

### 3.2 Physical characterization techniques

The SEM microstructures of Si-B-Fe and Si-B-Al ternary alloy samples by experiments at 1723 K are shown in Fig. 5. As can be seen, the phases are evenly distributed and there are some black areas in each of the figures. Fig. 6 is the EPMA analysis of each ternary alloy sample. It is found that the black region is the solid solution phase of Si and B, and the white regions in Fig. 6 (b) and (d) are the solid solution phase of Si and Fe. There are Al phase in Fig. 6 (f) and (h). In the alloy samples, the solid solution phases of Fe and B are not been found, and almost no solid solution phases of Al and B are found. As can be seen from the Fig. 6 (b) and (d) that B is enriched around the addition Fe, which reduces the B content in the silicon solution. As can be seen from the red circle part of Fig. 6 (f) and (h), most of the aluminum exists alone, and a small amount of aluminum diffuses into the Si-B phase that the Si-B-Al phase is formed.

![Fig. 5 SEM microstructures of Si-B-Fe and Si-B-Al ternary alloy samples](image-url)
Fig. 6 EPMA analysis of Si-B-Fe and Si-B-Al ternary alloy samples: (a) Si-B-Fe sample 1 for 5 h; (b) Si-B-Fe sample 3 for 5 h; (c) Si-B-Fe sample 1 for 7 h; (d) Si-B-Fe sample 3 for 7 h; (e) Si-B-Al sample 1 for 7 h; (f) Si-B-Al sample 3 for 7 h; (g) Si-B-Al sample 1 for 9 h; (h) Si-B-Al sample 3 for 9 h

From the above analysis, it can be concluded that the affinity between Si, Fe, Al and B in the Si solution at 1723 K has the relationship of Si-Fe>Si-B-Al-B>Fe-B. Wu et al. [28] used molecular dynamics to simulate the covalent interaction between Si, B, Al and Fe. That is, in a high temperature solution, Si is more likely to bind to Fe, and B is less inclined to bond with Fe. They concluded that the covalent interaction strength of Si-Fe is greater than that of Si-B, which is consistent with the experimental results of this study.
3.3 Features of $\varepsilon_{\text{Fe}}$ and $\varepsilon_{\text{Al}}$ on Si purification

The Si-B-Fe and Si-B-Al alloy solutions at 1723 K are in dynamic equilibrium states with holding time 5 h, 7 h and 7 h, 9 h, respectively. As shown in Fig. 7(a) and Fig. 7(b), the saturation solubility of boron in silicon solution decreases with the increase of Fe and Al contents.
Fig. 7 (a) Change of saturated solubility of B in silicon solution with the content of Fe; (b) Change of saturated solubility of B in silicon solution with the content of Al

Since the affinity of Fe to Si is greater than the affinity of Si and B, Si atoms are more likely to combine with Fe to form a compound, so that the compound formed by Si and B is reduced, resulting in a decrease in the saturation solubility of B. Its atomic behavior diagram is shown in Fig. 8(a). The addition of Al changes the original Si-B phase to the Si-B-Al phase, and Al extrudes a portion of the B atom, reducing the saturation solubility of B in Si. A schematic diagram of its atomic and molecular behavior is shown in Fig. 8(b).

Fig. 8 (a) Schematic diagram of substitution of Fe atom for B atom; (b) Schematic
diagram of Al atom replacing B atom

Presently, slag treatment is the most popular method for boron removal from silicon. However, the boron removal is disturbed by other impurity components in silicon. The experimental results show that the values of $\varepsilon_{B}^{Fe}$ and $\varepsilon_{B}^{Al}$ are positive and there exists the relationship of $\varepsilon_{B}^{Al} > \varepsilon_{B}^{Fe} > 0$. The third component Fe or Al will both increase the activity coefficient and decrease the saturation solubility of boron in silicon solution. It is also more beneficial to remove boron from silicon by combining with the slag agent due to the reduction of solubility and the increase of activity coefficient of boron. Therefore, the existence of a small amount of Fe or Al will have a positive effect on boron removal by slag treatment, and the effect of Al is more obvious.

Many researchers have previously studied the activity interaction coefficients of other components to B in Si [26, 29, 30]. The activity interaction coefficients of some elements to B in Si solution at 1723 K are shown in Fig. 9. The interaction coefficients of N, Mg and Ni to B are positive, and their existence can reduce the content of B in Si. The interaction coefficients of Ca, Ti, and Mn to B are negative, and their existence has an adsorption effect on B. Therefore, it is advantageous for boron removal from industrial silicon for the existence of Fe, Al, N, Mg, and Ni in the Si liquid and unfavorable for the existence of Ca, Ti, and Mn.
Fig. 9 Activity interaction coefficient of each component to B in Si solution at 1723K [26, 29, 30]

4. Conclusions

Using the “same concentration” method, the activity interaction coefficients of Fe to B and Al to B in Si-B-Fe and Si-B-Al ternary systems and other conclusions were determined by solubility equilibrium experiments at 1723 K.

(1) The interaction coefficients $\varepsilon_B^{Fe}$ and $\varepsilon_B^{Al}$ at 1723 K respectively are 2.7076 and 9.8287. Saturated solubility of B in Si-B-Fe and Si-B-Al ternary alloy systems at 1723 K decreases gradually with the increase of [%Fe] and [%Al].

(2) The microstructures of Si-B-Fe and Si-B-Al ternary alloy samples were characterized using SEM and EPMA techniques to testify the uniformity of alloy samples dissolved at 1723 K. Affinity relationship between Si, Fe, Al, and B was found: Si-Fe > Si-B > Al-B > Fe-B, which verifies the accuracy of the experimental results.
(3) The significance of $\varepsilon_F^{Fe}$ and $\varepsilon_F^{Al}$ is analyzed from the industrial point of view. The existence of a small amount of Fe and Al is benefit for Si slag refining removes B.

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Figure captions

Fig. 1 Si-B binary phase diagram

Fig. 2 Vacuum/atmosphere tubular resistance furnace and its structu; 1-Barometer; 2-Corundum furnace tube; 3-Silicon molybdenum rod; 4-Melt; 5-Control panel; 6-Argon; 7-Graphite crucible; 8-Corundum crucible; 9-Vacuum pump; 10-Refractory brick

Fig. 3 Experimental flow chart

Fig. 4 (a) Fitting results between [%Fe] and $\lg f_B$ at 1723 K; (b) Fitting results between [%Al] and $\lg f_B$ at 1723 K

Fig. 5 SEM microstructures of Si-B-Fe and Si-B-Al ternary alloy samples

Fig. 6 EPMA analysis of Si-B-Fe and Si-B-Al ternary alloy samples: (a) Si-B-Fe sample 1 for 5 h; (b) Si-B-Fe sample 3 for 5 h; (c) Si-B-Fe sample 1 for 7 h; (d) Si-B-Fe sample 3 for 7 h; (e) Si-B-Al sample 1 for 7 h; (f) Si-B-Al sample 3 for 7 h; (g) Si-B-Al sample 1 for 9 h; (h) Si-B-Al sample 3 for 9 h

Fig. 7 (a) Change of saturated solubility of B in silicon solution with the content of Fe; (b) Change of saturated solubility of B in silicon solution with the content of Al

Fig. 8 (a) Schematic diagram of substitution of Fe atom for B atom; (b) Schematic diagram of Al atom replacing B atom

Fig. 9 Activity interaction coefficient of each component to B in Si solution at 1723K [26, 29, 30]
Table captions

Table 1 Batching schemes of dissolution equilibrium experiments for Si-B-Fe and Si-B-Al systems at 1723 K

Table 2 Chemical compositions of components in Si-B-Fe and Si-B-Al systems at 1723 K with different holding time

Table 3 Fitting data of Si-B-Fe and Si-B-Al system at 1723 K

Table 4 Experimental results of activity interaction coefficients at 1723 K
Table 1 Batching schemes of dissolution equilibrium experiments for Si-B-Fe and Si-B-Al systems at 1723 K

| Exp. | Al/Fe (g) | B (g) | Si (g) |
|------|-----------|-------|--------|
| 1    | 0         | 0.57  | 9.43   |
| 2    | 1         | 0.6   | 9.43   |
| 3    | 2         | 0.7   | 9.43   |
| 4    | 4         | 0.8   | 9.43   |
Table 2 Chemical compositions of components in Si-B-Fe and Si-B-Al systems at 1723 K with different holding time

| Holding time (h) | Si-B-Fe System | Si-B-Al System |
|-----------------|----------------|----------------|
|                 | Sample | 1 | 2 | 3 | 4 | Sample | 1 | 2 | 3 | 4 |
| 5               | [%B]   | 4.44 | 2.98 | 2.67 | 2.26 | [%B]   | 2.80 | 2.62 | 2.08 | 1.30 |
|                 | [%Fe]  | 0.00 | 6.73 | 15.86 | 32.89 | [%Al]  | 0.00 | 1.28 | 6.95 | 13.19 |
| 7               | [%B]   | 3.86 | 2.76 | 2.61 | 2.29 | [%B]   | 4.81 | 3.11 | 1.69 | 1.11 |
|                 | [%Fe]  | 0.00 | 8.79 | 16.24 | 26.43 | [%Al]  | 0.00 | 2.52 | 8.77 | 14.29 |
| 9               | [%B]   | 1.95 | 3.46 | 3.26 | 1.16 | [%B]   | 4.79 | 3.08 | 1.60 | 1.05 |
|                 | [%Fe]  | 0.00 | 9.46 | 21.74 | 33.91 | [%Al]  | 0.00 | 2.58 | 8.92 | 14.33 |
| 11              | [%B]   | 2.06 | 2.48 | 3.84 | 1.15 | [%B]   | 4.71 | 3.21 | 2.51 | 1.65 |
|                 | [%Fe]  | 0.00 | 9.41 | 21.49 | 34.18 | [%Al]  | 0.00 | 6.96 | 13.10 | 17.65 |
Table 3 Fitting data of Si-B-Fe and Si-B-Al system at 1723 K

| Holding time (h) | Sample | Si-B-Fe system | Si-B-Al system |
|------------------|--------|----------------|----------------|
|                  |        | x_B            | lgf_B          |
|                  |        | 1   | 2   | 3   | 4   | 1   | 2   | 3   | 4   |
| 5                | x_B    | 0.350 | 0.239 | 0.211 | 0.177 | 0.318 | 0.298 | 0.236 | 0.148 |
|                  | lgf_B  | 11.90 | 17.43 | 19.75 | 23.54 | 13.10 | 13.98 | 17.66 | 28.15 |
| 7                | x_B    | 0.335 | 0.240 | 0.226 | 0.199 | 0.449 | 0.290 | 0.158 | 0.103 |
|                  | lgf_B  | 12.44 | 17.36 | 18.44 | 20.94 | 9.28  | 14.37 | 26.37 | 40.45 |
| 9                | x_B    | 0.200 | 0.351 | 0.332 | 0.117 | 0.455 | 0.293 | 0.152 | 0.100 |
|                  | lgf_B  | 20.83 | 11.87 | 12.55 | 35.61 | 9.16  | 14.22 | 27.41 | 41.67 |
| 11               | x_B    | 0.217 | 0.260 | 0.402 | 0.120 | 0.391 | 0.266 | 0.208 | 0.136 |
|                  | lgf_B  | 19.20 | 16.03 | 10.36 | 34.72 | 10.66 | 15.66 | 20.03 | 30.64 |
Table 4 Experimental results of activity interaction coefficients at 1723 K

| Parameters | Si-B-Fe system | Si-B-Al system |
|------------|----------------|----------------|
|            | 5 h            | 7 h            | 7 h            | 9 h            |
| $e^\text{Fe}_B$ | 0.3243         | 0.3060         |                |                |
| $e^\text{Al}_B$ |                | 2.1549         | 2.2541         |                |
| $\varepsilon^\text{Fe}_B$ | 147.31         | 139.94         |                |                |
| $\varepsilon^\text{Al}_B$ |                | 476.04         | 497.96         |                |