Thermodynamics of Si and Ti in Solid Fe at 1 273 K

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Equilibrium experiments were carried out with solid Fe and liquid Ag to investigate the interactions between Si and Ti in solid Fe. The thermodynamic properties of Si in \(\gamma\)-Fe and \(\alpha\)-Fe phases were studied by determining the distribution equilibrium of Si in the Fe and the Ag phases. Using the activity coefficient and the self-interaction parameter of Si in solid Fe, the interaction parameter of Si and Ti in both the solid Fe phases—\(\gamma\)-Fe and \(\alpha\)-Fe—was determined as follows:

\[
\begin{align*}
\varepsilon^\gamma_{Si} &= 460 \pm 78 \text{ in } \gamma\text{-Fe}, \\
\varepsilon^\alpha_{Si} &= 350 \pm 7 \text{ in } \alpha\text{-Fe}
\end{align*}
\]

The analysis results for Si and Ti in the solid Fe phase showed reasonable agreement with previous research in \(\alpha\)-Fe region. Furthermore, the influence of the interaction between Si and Ti in the solid Fe phases on the formation of secondary inclusions such as Ti-based inclusions was discussed. It was concluded that, during solidification, the interactions among solutes such as Si and Ti should be properly considered because the formation of not only the secondary inclusions but also ferrites may depend on the thermodynamic properties of the solutes.

KEY WORDS: \(\gamma\)-Fe; \(\alpha\)-Fe; interaction parameter; silicon; titanium; secondary inclusions.

1. Introduction

Alloying elements such as aluminum, silicon, manganese, and titanium are widely used in high temperature metallurgical processes such as iron and steel making processes. When the concentration of molten iron is controlled using the alloying elements, non-metallic inclusions may be formed as by-products. It is well known that the inclusions greatly influence the quality of the final steel product. In addition, the type, amount, and structure of the inclusions depend on the type of alloying element used. Therefore, in order to gain better control on the quality of metallurgical products, a number of researchers have focused on understanding the thermodynamic properties of alloying elements in steel.

Many of these properties have been determined in liquid steel; however, the phenomena occurring during solidification, which greatly influence the quality of steel, are yet to be studied in detail. During hot rolling, the precipitation of secondary inclusions and the distribution of solutes between solid and liquid should be carefully traced and controlled. Otherwise, the final products may encounter unexpected defects. Therefore, it is critical to determine the thermodynamic properties of the solutes in solid steel during solidification. A better understanding of these properties will help in the development of better technologies to meet the growing demand for high quality products.

For instance, it has been reported that Si and Ti show an exceptionally large interaction in the distribution equilibrium between liquid Fe and Ag.\(^1\) Since both Si and Ti are frequently employed as oxidizing agents in iron and steel making processes, their repulsive interaction requires detailed attention. Similarly, the interaction between Si and Ti in solid Fe at relatively low temperature is also expected to have a considerable impact on the product quality. In particular, the thermodynamic properties of Ti in solid Fe are of importance in acicular ferrite formation and grain refinement, wherein Ti compounds such as TiO or TiN are employed.

As a matter of fact, the thermodynamic properties of elemental solutes of gaseous species, such as H\(_2\), N\(_2\), and O\(_2\), have been studied in a number of experimental works. However, there have been very few reports on the thermodynamics of not only Si or Ti but also other metallic elements which behave as a substitutional solute. Therefore, in the present study, the interaction between Si and Ti in solid Fe was experimentally investigated at 1 273 K using the distribution equilibrium between solid Fe and liquid Ag. Using the determined parameters, the behavior of Si and Ti during solidification was discussed.

2. Experimental

In order to investigate the thermodynamic behaviors of Si and Ti in solid Fe, the equilibrium between Fe\((s)\)–Ag\((l)\) was employed in this study. Details in the experimental principle are more or less similar to those of the previous research.\(^1\) When Si in solid iron and liquid silver phases is in equilibrium and solute contents in Ag phase are considerably low, Eq. (1) can be written from the chemical potential of Si in both phases.

\[
\ln X^\gamma_{Si \text{ in Fe}(s)} + \ln \gamma^\gamma_{Si \text{ in Fe}(s)} + \varepsilon^\gamma_{Si} X^\gamma_{Si \text{ in Fe}(s)} + \varepsilon^\gamma_{Ti} X^\gamma_{Ti \text{ in Fe}(s)} = \ln X^\gamma_{Si \text{ in Ag}(l)} + \ln \gamma^\gamma_{Si \text{ in Ag}(l)} \quad \cdots (1)
\]
Here, pure solid is chosen as the standard state of Si. And $\gamma^\alpha_{Si}$ and $\varepsilon^i_{ij}$ stand for the activity coefficient of Si in the infinite dilute solution and the 1st order interaction parameter between i and j, respectively. Rearrangement of Eq. (1) will lead to Eq. (2), by separating $X_{Ti}$ in Fe(s) and the experimentally determinable terms.

$$\ln X_{Si}^{Ag(l)} - \ln X_{Si}^{Fe(0)} = \varepsilon^Si_{Si}^{Ag(l)} X_{Si}^{Fe(0)}$$

$$= \varepsilon^Si_{Si}^{Ag(l)} X_{Si}^{Fe(0)} + \ln \gamma^Si_{Si}^{Ag(l)} - \ln \gamma^Si_{Si}^{Ag(l)} \quad \text{(2)}$$

By plotting the left side of Eq. (2) versus $X_{Ti}$ in Fe(0), the interaction parameter of Si and Ti in solid Fe can be obtained from the slope, because the activity coefficients of Si at infinite dilution in both phases are independent of the Ti content in solid Fe. Nonetheless, for the validity of this principle, it should be confirmed that the contents of Si and Ti in silver phase are sufficiently low to be the infinite dilute solution.

On the other hand, the correct value for the self-interaction parameter of Si in solid Fe at low temperatures is necessary to evaluate $\varepsilon^i_{ii}$. Since there have been few reports on the thermodynamic properties of (metallic) alloying elements in solid Fe, direct measurements may be required. In the system without Ti, the equilibrium of Si in solid Fe and liquid Ag phases can be expressed as Eq. (3), which is similar to Eq. (2).

$$\ln X_{Si}^{Ag(l)} - \ln X_{Si}^{Fe(0)} = \varepsilon^Si_{Si}^{Ag(l)} X_{Si}^{Fe(0)}$$

$$= \varepsilon^Si_{Si}^{Ag(l)} X_{Si}^{Fe(0)} + \ln \gamma^Si_{Si}^{Ag(l)} - \ln \gamma^Si_{Si}^{Ag(l)} \quad \text{(3)}$$

The self interaction parameter of Si in solid Fe could be evaluated with the analytical result of Si contents in both phases. The activity coefficient of Si at infinite dilution in the solid Fe phase also could be obtained simultaneously. As for the value in liquid Ag phase, used in the present study, the previous research by Sakao et al. was referred.

Sample preparation and experimental procedures were carried out as described below. Ag–Si(–Ti) alloy of various compositions was prepared by premelting silver (shot, 99.999%, Nilaco Corp.), silicon (piece of wafer, 99.9999%, Nilaco Corp.), and titanium (foil, 99.95%, Nilaco Corp.) in a porous alumina crucible at 1 273 K under deoxidized Ar atmosphere. The pre-melted alloy was cut and polished into small pieces (approx. 5 × 5 × 5 mm) for equilibrium experiment. On the other hand, an iron container to hold Ag alloy piece was manufactured with iron foil (0.05 mm thick) using a spot welder.

The iron container holding the Ag alloy piece was placed in a small alumina crucible and inserted into a quartz tube along with the Ti powder, which was used to absorb the entrapped oxygen. The interior of the quartz tube was flushed with deoxidized Ar flow for more than 1 h before being set in an electrical resistance furnace equipped with SiC heating elements. The temperature was kept at 1 273 ± 1 K with the aid of a Proportional-Integral-Differential controller. After the predetermined time for the preliminary experiments (18 h in most cases), the quartz tube was drawn out from the furnace and air-cooled under a flow of Ar. Further quenching seemed to be hardly necessary because the samples were usually solidified within approximately 2 s.

Since the physical separation of the iron and silver phase turned out to be very difficult, the sample after the equilibration was subjected to chemical separation to secure the amount of matrix needed for analysis. From a carefully ground sample, the iron phase was selectively dissolved into dilute hydrochloric acid (1:4). The weight change after the dissolution was taken as the amount of iron in the solution. The remaining silver phase was further polished in order to prevent emulsified iron phase from the analysis. The Si and Ti contents in the iron and silver phases were determined by ICP-MS (SPQ9000, Seiko Instrument Co., Japan). In the case where solid Si precipitated in the solidified Ag phase, the precipitates in the filter paper, which filtered the silver dissolved solution, were dissolved in 1M KOH aqueous solution for 24 h. The Si content in the alkali solution was also similarly determined by ICP-MS.

3. Results and Discussion

First of all, the diffusion distances of Si and Ti in solid Fe were estimated in order to determine the equilibrium time. Due to lack of reliable data on solute diffusion in $\gamma$-Fe at the temperature of our interest, parts of the reported data, such as the activation energy for the diffusion of Si and Ti in $\alpha$-Fe, have been referred to and are shown in Table 1. From the exponential relationship, it was found that approx. 3 h is needed for Si and Ti to diffuse 50 μm, which is the thickness of the iron foil. Although the solute diffusion is expected to be much slower in $\gamma$-Fe, 18 h was considered to be sufficient for the diffusion and the equilibrium of Si and Ti in solid Fe. Additionally, a number of preliminary experiments showed that the Si and Ti contents in the iron phase were nearly constant after more than 18 h of equilibration as shown Fig. 1. It was also verified that the contents of Si

|                | $D_0$ [$10^{-4}$ m$^2$/s] | $Q$ [10$^3$ J/mol] |
|----------------|--------------------------|---------------------|
| Si$^{11}$      | 0.735                    | 219.8               |
| Ti$^{48}$      | 68                       | 261.1               |

| Experimental time (hour) | Si | Ti |
|-------------------------|----|----|
| 0                       | 0  | 0  |
| 5                       | 0  | 0  |
| 10                      | 0  | 0  |
| 15                      | 0  | 0  |
| 20                      | 0  | 0  |
| 25                      | 0  | 0  |

Fig. 1. Contents of Si and Ti in solid Fe versus duration of experiment.
Silicon is known to be one of the alloying elements that has smaller free energy change for the dissolution of Si in γ-Fe can be qualitatively accepted. Similarly, a negative value for the self-interaction parameter of Si in γ-Fe may correspond to its instability in the γ-phase. On the other hand, the activity of Si should be constant through α- and γ-Fe coexisting region, which could be determined to be between 0.018 < X_{Si} < 0.084 at 1 273 K from the Fe–Si phase diagram shown Fig. 2(a). The values of the activity of Si at the boundaries of α/α + γ and α + γ/γ were estimated to be in the same order (2 ~ 4 × 10^{-4}) using the present values and the previous research, and therefore, the present values of the activity coefficient and the self-interaction parameter of Si in γ-Fe could be verified.

By obtaining the self-interaction parameter of Si in solid Fe, the interaction parameter of Si and Ti in solid Fe could be determined in a similar manner. The equilibrium contents of Si and Ti in both the solid Fe and Ag phases were analyzed after the equilibrium experiments with Fe(s)/Ag-Si-Ti(l). As shown Table 3, Si and Ti contents in Ag phase were found to low enough to support the assumption of the infinite dilution solution in Eq. (1). Especially, Ti content could not be properly determined under the detection limit of analysis in most cases. Equation (2) could be plotted

### Table 2. Analysis results of Si in Fe and Ag phases for determining $\alpha_{Si}^\alpha$.

| Sample | Si in Fe | Si in Ag | Si in Fe | Si in Ag | Left-hand Side of Eq. (3) |
|--------|---------|---------|---------|---------|--------------------------|
| AS15-4 | 0.814   | 6.46x10^{-3} | 1.61x10^{-2} | 2.48x10^{-4} | -4.170                   |
| AS16-4 | 0.466   | 4.64x10^{-3} | 9.22x10^{-3} | 1.78x10^{-4} | -3.946                   |
| AS17-1 | 0.244   | 2.79x10^{-3} | 4.84x10^{-3} | 1.07x10^{-4} | -3.812                   |
| AS17-1 | 0.244   | 2.85x10^{-3} | 4.84x10^{-3} | 1.10x10^{-4} | -3.789                   |
| AS17-2 | 0.611   | 5.18x10^{-3} | 1.21x10^{-2} | 1.99x10^{-4} | -4.105                   |
| AS18-1 | 0.195   | 2.28x10^{-3} | 3.88x10^{-3} | 8.75x10^{-5} | -3.792                   |
| AS19-1 | 2.524   | 8.45x10^{-3} | 4.90x10^{-2} | 3.25x10^{-4} | -5.016                   |
| AS19-1 | 2.524   | 1.02x10^{-2} | 4.90x10^{-2} | 3.92x10^{-4} | -4.827                   |
| AS19-2 | 1.558   | 3.75x10^{-3} | 3.05x10^{-2} | 1.44x10^{-4} | -5.536                   |
| AS19-4 | 0.624   | 5.03x10^{-3} | 1.23x10^{-2} | 1.93x10^{-4} | -4.156                   |

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against $X_{\text{Ti in Fe}}$ using the analytic results. In order to determine the slope of the regression line as the interaction parameter of Si and Ti, the intercept was fixed using the activity coefficient of Si in the infinite dilute solution. Since it has been found that the value of the activity coefficient of Si is different in $\gamma$-Fe and $\alpha$-Fe (hypothetical) as discussed earlier, the analytical result was also separately considered with respect to the Si and Ti contents in Fe. When the mole fraction of Si in the iron phase is considerably larger than 0.02 or the Ti content is of a similar order of magnitude as the solubility in $\gamma$-Fe ($X_{\text{Si}} = 0.0052$), the result have been tentatively regarded to be that in $\alpha$-Fe. From the slopes of Fig. 3, the interaction parameters between Si and Ti in $\alpha$- and $\gamma$-Fe iron at 1273 K could be estimated:

$$\varepsilon_{\text{Si Ti in Fe}} = 460 \pm 78 \text{ in } \gamma\text{-Fe}, \quad \varepsilon_{\text{Si Ti in Fe}} = 350 \pm 7 \text{ in } \alpha\text{-Fe}$$

Since it was difficult to distinguish between $\alpha$- and $\gamma$-Fe, the results that were not clearly distinguishable were discarded in order to avoid any uncertainty. Using the parameters determined in the present study, the change in the solubility of Si versus Ti content could be approximately evaluated as shown in Fig. 4. The Si solubility sharply decreases as Ti content increases and the present analysis results for $\alpha$- and $\gamma$-Fe are also represented as open and solid circles in Fig. 4. The choices of the solid iron phase according to Si and Ti contents are in fairly good agreement with the predicted solubility using the parameter presently determined.

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Table 3. Analysis results of Si and Ti in Fe and Ag phases for determining $\varepsilon_{\text{Si Ti}}$.

| Sample   | mass% | mole fraction | Left-hand | Side of Eq. (2) |
|----------|-------|---------------|-----------|-----------------|
|          | Si in Fe | Ti in Fe | Si in Ag | Si in Fe | Ti in Fe | Si in Ag |                      |
| AST01-4  | 0.259 | 6.93×10⁻³ | 9.87×10⁻³ | 1.55×10⁻⁴ | 8.43×10⁻⁵ | -3.551 |
| AST02-2  | 0.146 | 1.00×10⁻² | 1.80×10⁻³ | 1.17×10⁻⁴ | 6.93×10⁻⁵ | -3.629 |
| AST03-1  | 1.670 | 1.52×10⁻² | 4.29×10⁻³ | 1.75×10⁻⁴ | 1.65×10⁻⁴ | -5.898 |
| AST03-3  | 0.719 | 1.63×10⁻³ | 6.22×10⁻³ | 1.87×10⁻⁵ | 2.39×10⁻⁴ | -3.570 |
| AST04-3  | 0.386 | 4.57×10⁻² | 4.96×10⁻³ | 5.30×10⁻⁴ | 1.90×10⁻⁴ | -3.416 |
| AST04-4  | 0.295 | 3.14×10⁻² | 4.01×10⁻³ | 3.65×10⁻⁴ | 1.54×10⁻⁴ | -3.423 |
| AST06-3  | 0.371 | 7.88×10⁻² | 6.19×10⁻³ | 9.15×10⁻⁴ | 2.38×10⁻⁴ | -3.165 |
| AST07-1  | 0.651 | 8.96×10⁻² | 1.57×10⁻² | 1.04×10⁻⁴ | 6.03×10⁻⁵ | -5.602 |
| AST07-3  | 0.357 | 7.15×10⁻² | 5.11×10⁻³ | 8.30×10⁻⁴ | 1.96×10⁻⁴ | -3.327 |
| AST07-6  | 1.016 | 2.31×10⁻² | 2.11×10⁻³ | 2.00×10⁻² | 2.67×10⁻⁴ | 8.12×10⁻⁵ | -5.879 |

Fig. 3. Relationship between left-hand side of Eq. (2) and $X_{\text{Ti in Fe}}$ in (a) $\gamma$-Fe and (b) $\alpha$-Fe.

Fig. 4. Estimated solubility of Si and Ti in $\gamma$-Fe and analysis results of the present study.
sions such as TiO or TiN, which have been known to be favorable for the formation of acicular ferrite. The activity coefficient of Ti in solid Fe in the infinite dilute solution can be expressed as Eq. (4), where only the interactions with silicon as well as oxygen and nitrogen are taken into account.

\[
\ln C_i^0 = \sum C_i^0 \ln C_i^0 + \sum C_i^N \ln C_i^N + \sum C_i^S \ln C_i^S
\]  

(4)

As for the interaction parameters of oxygen and nitrogen on titanium, the values at high temperature or the extrapolated values were referred because of a lack of data at low temperature \( (e_{Ti}^O = -1.8, e_{Ti}^N = -19500/T + 8.3, e_{Ti}^S = 3.97) \) (present study). The contents of oxygen and nitrogen were assumed to be similar to those of Ti-killed steel, i.e., 0.005 (mass%) and 0.003 (mass%), respectively. A simple calculation showed that the activity coefficient of Ti in solid Fe drastically increased as Si content increases. Compared to the case where only oxygen and nitrogen interact with titanium, \( f_{Si}^0 \) in Fe(\( \gamma \)) seems to be approximately 10 and 100 times larger than the value when the mass% of Si is 0.25 and 0.5, respectively. When the formation energy of TiN(s) in molten iron\(^{7)\} \) is extrapolated to 1 273 K, the solubility product of TiN in solid Fe can be semi-quantitatively estimated as shown in Fig. 5. The figure well describes that the formation of TiN is greatly enhanced as Si content increases.

Moreover, the activity of Si significantly influences on the \( \delta/\gamma \) and \( \gamma/\alpha \) transformation temperatures and the formation of other secondary inclusions other than Ti-based inclusions, such as MnS.\(^{8)\} \) In order to control the formation of the secondary inclusions and ferrite, which are interrelated, during solidification, it is extremely essential to collect the proper data in solid Fe. The thermodynamics of Si and Ti in solid Fe, which is one of the most important information required for better process control, could be successfully presented.

4. Conclusion

The thermodynamic properties of Si and Ti in solid Fe were investigated using the distribution equilibrium of the solutes between solid Fe and liquid Ag. Firstly, the activity coefficient of the infinite dilute solution and the self-interaction parameter of Si in \( \gamma \)-Fe were evaluated as listed below, and compared to those in \( \alpha \)-Fe.

\[
\ln C_{Si}^{\gamma} = -7.72 \pm 0.05 \quad C_{Si}^{\alpha} = -36.3 \pm 5.0
\]

Based on the thermodynamic properties of Si in solid Fe, the interaction parameter between Si and Ti in both the solid Fe phases—\( \alpha \)-Fe and \( \gamma \)-Fe—was separately determined at 1 273 K, as listed below.

\[
C_{Si}^{\gamma} = 460 \pm 78 \quad C_{Si}^{\alpha} = 350 \pm 7
\]

The interaction between Si and Ti in solid Fe (\( \gamma \) and \( \alpha \)-Fe) is strongly positive, compared to those in liquid Fe at 1 873 K. Therefore, it is necessary to correctly consider the influence of the interaction between them on phenomena such as the formation of secondary inclusions.

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