1. Introduction

Recently, TWinning Induced Plasticity (TWIP) steel has received much attention for the automotive applications because of their excellent combination of strength and ductility.1,2) TWIP steel shows the special features by the addition of various alloying elements such as Mn (15–20 mass%), Al (1–3 mass%), Si (~0.3 mass%) and C (0.4–0.6 mass%).3,4) However, such high Mn and Al concentration in steel will significantly change the physicochemical conditions of non-metallic inclusion formation during steelmaking and casting processes compared to the conventional Al-killed steels containing ~1% Mn and 0.03–0.05% Al. In particular, the addition of a large amount of Mn significantly increases the N solubility in liquid iron and decreases the solidification temperature.

5) Also, a strong nitride forming element Al can form a large amount of AlN inclusions in liquid steel. AlN is considered as a detrimental phase for the hot ductility of steels.6)

In order to control the formation of AlN inclusions based on the supersaturation of N and Al in liquid alloy steels, it is necessary to have an accurate thermodynamic information for the critical solubility limit of N and AlN in such steel grades during cooling and solidification. There have been many studies on the N solubility and AlN formation in liquid iron alloys. However, most of the available data have been measured at the limited ranges of alloying concentration and temperature. In the authors’ recent studies,5,7,8) it was found that the second-order effect of alloying elements on N in liquid iron was necessary for the accurate prediction of the N solubility in high alloy steels. Also, the second-order cross-product effect on N in liquid iron significantly affected the accuracy of both N solubility and AlN solubility product in multi-component alloy systems. For example, the experimental results of the N solubility and the AlN solubility product in Fe–Al–C melt cannot be reproduced without considering the simultaneous effect of C and Al on N in liquid iron as shown in Fig. 1.8)

Therefore, in the present study, the nitrogen solubility in Fe–Mn and Fe–Si binary melts was measured at 1 773–1 873 K over the wide concentration range in order to precisely determine the first- and second-order effect of
Mn and Si on N in liquid iron. The simultaneous effect of two different alloying elements on N in liquid iron was also determined by measuring the N solubility in Fe–Mn–Si, Fe–Al–Si, Fe–Mn–C and Fe–Si–C ternary melts. The interactions among N and alloying elements were thermodynamically analyzed in terms of the interaction parameters using the Wagner’s formalism.9) The validity of the interaction parameters determined in the present study was checked by measuring the N solubility and AlN solubility product for a typical TWIP steel composition melt of Fe-25% Mn-0.3% Si-0.6% C-Al at 1 723–1 873 K.

2. Experimental

The gas-liquid metal and gas-liquid metal-nitride equilibrium experiments were carried out to determine the N solubility and AlN solubility product in liquid iron alloys, respectively. Detailed descriptions of the experimental apparatus and procedure are available in the authors’ recent studies.5,8)

Five hundred grams of high purity electrolytic iron charged in an Al2O3 crucible (outer diameter (OD): 56 mm, inner diameter (ID): 50 mm, height (H): 96 mm) was melted using a 15 kW/30 kHz high-frequency induction furnace. After melting the iron, the melt temperature was directly measured by a Pt/Pt-13 mass% Rh thermocouple sheathed with an alumina tube immersed in the melt, and the Ar-10% H2 gas was blown onto the melt surface at a high flow rate of ~2 L/min to deoxidize the melt. After 2 hours of gas blowing, the oxygen content in the melt decreased to a value less than 20 mass ppm, and then the gas was switched to a mixture of N2 and Ar-10% H2 gases to keep the aimed nitrogen partial pressures. The flow rate of the gas mixture was 1 L/min.

In order to determine the effect of Mn and Si on N in liquid iron, pellets of high purity Mn (99.999% purity) or Si (99.999% purity) were added to liquid iron through an 18 mm OD quartz tube after confirming the equilibrium nitrogen solubility in liquid iron under various nitrogen partial pressures. After each addition, a new nitrogen solubility equilibrium was attained within 1 hour. This was confirmed by the sampling and in-situ analysis of nitrogen at 15 min intervals. Si and Mn additions were repeated up to 54.34 mass% and 12.53 mass%, respectively.

The simultaneous effects of two different alloying elements on N in liquid iron were determined by measuring the nitrogen solubility in Fe–Mn–Si, Fe–Al–Si, Fe–Mn–C, and Fe–Si–C melts in the temperature range from 1 773 to 1 873 K. After the first alloying element was added for a desired composition in the melt under a specified nitrogen partial pressure, the second alloying element was added and repeated. It was also confirmed that the new nitrogen solubility equilibrium was attained within 1 hour for the ternary liquid iron alloys.

As a verification experiment, the N solubility and AlN solubility product in a multi-component high Mn steel melt were measured as a function of temperature. After the equilibrium N solubility was attained for a Fe-25% Mn-0.3% Si-0.6% C melt at 1 773 K under a nitrogen partial pressure of 0.14 atm, Al was added repeatedly up to 1.38 mass% while the melt temperature was increased to 1 823 and 1 873 K. After new nitrogen solubility equilibrium was attained at 1 873 K, the melt temperature was then lowered to 1 823, 1 773 and 1 723 K successively and held for 1 hour at each temperature prior to metal sampling. The metal samples were analyzed for nitrogen and aluminum contents as well as the secondary AlN inclusions precipitated during cooling of the melt.

Metal samples were extracted by a 4 mm ID quartz tube, quenched rapidly in ice water and carefully cut for the chemical analysis. Nitrogen content in the metal sample was analyzed by the nitrogen/oxygen analyzer (LECO TC-600 apparatus, St. Joseph, MI), and carbon content was analyzed by the carbon/sulfur analyzer (CS-800, Eltra, Neuss, Germany). For the analysis of manganese, silicon and aluminum, the metal sample (0.2 g) was dissolved in 20 mL of HCl (1+1 solution) in a glass beaker of 50 mL capacity heated in a water bath for 2 hours. After dissolving the sample, the solution was transferred to the measuring flask (1 000 mL) with filtration, and analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO ARCOS apparatus, Kleve, Germany). For analyzing silicon in high Si containing metal samples, the gravimetric method9) was also used.

The AlN inclusions formed in the melt during the verification experiment were analyzed by the potentiostatic electrolytic extraction method. 0.5 g of the metal sample was dissolved in the 10% acetyl-acetone (AA) solution under a total electric charge of 300 mA for 8 hours. 10% AA solution was prepared by dissolving 2.5 g of tetra-methylammonium in 25 mL of acetic acid, and the 225 mL of methanol was added in a glass beaker with a capacity of 300 mL. The inclusions were collected by the suction filtration using a membrane filter with an open pore size of 0.1 μm. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS, Hitachi, S4800) was used to analyze the inclusion morphology and composition.

3. Results and Discussion

3.1. N Solubility in Liquid Iron Alloys

The dissolution of nitrogen in liquid iron alloys can be written as

\[
\frac{1}{2} N_2(g) = N \quad \text{..........................} (1)
\]

\[
\Delta G_N^\circ = 3.598 + 23.89T \text{ J/mol}^{11)}
\]

\[
K_N = \frac{f_N^{[\% \text{N}]} \quad \text{..................}}{P_{N_2}^{1/2}} = f_N K_N^\circ
\]

where \(K_N\) is the equilibrium constant for Reaction (1) and, \([\% \text{N}]\) is the equilibrium nitrogen content in mass%, \(f_N\) is the Henrian activity coefficient of nitrogen for which the reference state is the infinitely dilute solution, i.e., \(f_N=1\) when \([\% \text{N}] \rightarrow 0\). \(P_{N_2}\) is the nitrogen partial pressure in atm over the melt surface, \(K_N\) is the apparent equilibrium constant.

Using Wagner’s formalism,9) the activity coefficient of nitrogen, \(f_N\) in Fe–Mn–Al–Si–C can be expressed as the following relation using the interaction parameters:
log$_{N}$ = log$_{K_N}$ - log($\% N$) + $\frac{1}{2}$ log$_{p_{N}}$

= $\sum_{i=Mn,Al,Si,C} e_{i} [\% i] + \sum_{i=Mn,Al,Si,C} r^{ij}_{i} [\% i][\% j]$ ...... (3)

+ $\sum_{i=Mn,Al,Si,C} r^{ij}_{i} [\% i][\% j]$

where $e_{i}$ and $r^{ij}_{i}$, respectively, are the first- and second-order interaction parameters of elements on nitrogen in liquid iron. $r^{ij}_{i}$ is the second-order cross-product parameter on nitrogen in liquid iron which indicates the simultaneous effect of two different alloying elements ($i$ and $j$) on the activity coefficient of nitrogen in liquid iron. The self-interaction parameter of N in liquid iron, $e_{i}^{N}$ and $r^{N}_{i}$ are known to be zero. In the present study, a mixture of N$_2$ and Ar-10% H$_2$ gases was used to keep the aimed nitrogen partial pressures and low oxygen level in the melt. The oxygen content was determined as less than 20 mass ppm under this condition and the hydrogen content was calculated to be 2.5–7.5 mass ppm depending on nitrogen partial pressures using the recommended data in JSPS. Therefore, the effect of oxygen and hydrogen on nitrogen solubility can be assumed to be negligible.

In the authors’ recent studies, the $e_{i}^{N}$ values ($i = Al, C, Mn and Si$) have been determined together with the $r^{ij}_{i}$ values ($i = Al and C$). In Fe–Al–N system, AlN would form at a relatively low Al concentration as shown in Fig. 1, and the nitrogen solubility in Fe–Al melts could be described using only $e_{i}^{N}$ value ($r^{N}_{i} = 0$) before the formation of AlN. In Fe–C–N system, the first- and second-order interaction parameters of C on N in liquid iron was required to reproduce the N solubility at high C concentration region. In Fe–Mn–N and Fe–Si–N systems, it was not clear about the second-order effect of Mn and Si on N solubility at high concentration region. Moreover, the cross-product effect of those alloying elements on N solubility in multi-component systems has been studied much. Therefore, in the present study, the first- and second-order effects, $e_{i}^{N}$ and $r^{N}_{i}$, and the second-order cross-product effects, $r^{ij}_{i}$, were determined by measuring the N solubility in the binary (Fe–Mn and Fe–Si) and ternary (Fe–Mn–Si, Fe–Mn–C, Fe–Al–Si and Fe–Si–C) iron alloy melts over the wide concentration range and temperature.

### 3.1.1. N Solubility in Binary Fe–Mn Melts

The N solubility in liquid iron containing manganese up to 54.34 mass% was measured under the reduced nitrogen partial pressures in the temperature range of 1 773–1 873 K. The experimental results are summarized in Table 1. The experimental results are plotted as the $K_N (=[N]/p_{N}^{0})$ against Mn concentration in Fig. 2 together with previous data determined in the similar temperature range.

The present experimental results agree well with the previous data over the wide range of Mn content up to 25 mass%, and the N solubility increases more significantly with Mn content at high concentration in Fe–Mn melt.

One of the experimental concerns in dealing with liquid iron containing high manganese content is its manganese vapor pressure. Therefore, the nitrogen partial pressure over the melt surface was corrected by the following equation:

$p_{N} = (1 - p_{Mn}) \left( \frac{Q_{N}}{Q_{N_{H_{2}}} + Q_{N}} \right)$ ......... (4)

where $p_{Mn}$ is the equilibrium manganese vapor pressure of the melt in atm, and $Q_{N_{H_{2}}}$ and $Q_{N}$ are the flow rates of Ar-10% H$_2$ and N$_2$ gases in L/min, respectively. The value of $p_{Mn}$ was calculated from the following equation:

$$p_{N} = (1 - p_{Mn}) \left( \frac{Q_{N}}{Q_{N_{H_{2}}} + Q_{N}} \right)$$
where $a_{Mn}$ is the manganese activity referred to pure liquid manganese in liquid Fe–Mn alloys. The activity data for Fe–Mn binary alloy may be found in the compilation of Hultgren et al.\textsuperscript{20} and the term $p_{Mn^0}$ is the vapor pressure of pure manganese.\textsuperscript{21}

**Figure 2.** Variation of $K_N$ values with Mn content in liquid iron.

\[
p_{Mn^0} = a_{Mn} \cdot p_{Mn^0} \quad \text{..................................... (5)}
\]

$K_N = a_{N_{Mn}} = a_{N} \cdot a_{Mn}$. \textsuperscript{7,9}

**Figure 3.** Relation of $\log N_{Mn}^{f}$ vs [% Mn] in liquid iron.

$30$ mass% at various nitrogen pressures from $0.06$ to $1$ atm in a vacuum induction furnace in the temperature range from $1 786$ to $1 873$ K. They reported the second-order $e_{N_{Mn}}$ value of $-0.000045$ in combination with the first-order $e_{N_{Mn}}$ value of $-0.02$ determined by Ishii et al.\textsuperscript{18} Senk et al. took this lowest $e_{N_{Mn}}$ value among those values in Table 2 for the best agreement of their nitrogen solubility. However, their data at low and high nitrogen partial pressures showed big scatters. This may be attributed to the effect of manganese vapor pressure at reduced nitrogen partial pressures in their experiment.

Therefore, from a regression analysis of the data determined in the present study taking the first-order $e_{N_{Mn}}$ value of $-0.023$ determined in the authors’ recent study at $1 773–1 873$ K,\textsuperscript{5,19} the second-order $e_{N_{Mn}}$ parameters were determined as $0.000059 \pm 0.000003$, $0.00007 \pm 0.000005$ and $0.000081 \pm 0.000008$ at $1 773$, $1 823$ and $1 873$ K, respectively. The temperature dependency of $e_{N_{Mn}}$ value can then be determined as $-0.763/T + 0.000489$. The calculated relations of the $K_N = [\% N]/p_{Mn^0}$ and $\log N_{Mn}^{f}$ vs. Mn content in Fe–Mn–N melts using the interaction parameters

$\text{Fig. 2.}$ Variation of $K_N$ values with Mn content in liquid iron.

$\text{Fig. 3.}$ Relation of $\log N_{Mn}^{f}$ vs [% Mn] in liquid iron.
determined in the present study and other values reported by Paek et al.5 and Senk et al.5 are compared in Figs. 2 and 3. The present results show an excellent correlation with all data determined over the wide range of Mn content at different temperatures.

### Table 2. Interaction parameters of Mn on N in liquid iron.

<table>
<thead>
<tr>
<th>$\epsilon^\text{Mn}$ (1 873 K)</th>
<th>$\eta^\text{Mn}$ (1 873 K)</th>
<th>Temp. Range (K)</th>
<th>[% Mn] Range</th>
<th>$p_\text{N}_2$ (atm)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.023</td>
<td>-0.763/T + 0.000489</td>
<td>1 773–1 873</td>
<td>&lt;54.4</td>
<td>0.1,0.2</td>
<td>Sampling</td>
<td>Present study</td>
</tr>
<tr>
<td>-0.020</td>
<td>-0.000045</td>
<td>1 773–1 873</td>
<td>&lt;30</td>
<td>0.06–1</td>
<td>Sampling</td>
<td>(15)</td>
</tr>
<tr>
<td>-0.023</td>
<td>-</td>
<td>1 823–1 873</td>
<td>&lt;22</td>
<td>0.1–0.8</td>
<td>Sampling</td>
<td>(5)</td>
</tr>
<tr>
<td>-0.020</td>
<td>-</td>
<td>1 873</td>
<td>&lt;6</td>
<td>1</td>
<td>Sieverts</td>
<td>(11)</td>
</tr>
<tr>
<td>-0.02045</td>
<td>-</td>
<td>1 823–1 973</td>
<td>&lt;4</td>
<td>1</td>
<td>Sieverts</td>
<td>(17)</td>
</tr>
<tr>
<td>-0.0245</td>
<td>-</td>
<td>1 873</td>
<td>&lt;6</td>
<td>1</td>
<td>Sampling</td>
<td>(16)</td>
</tr>
<tr>
<td>-0.020</td>
<td>-</td>
<td>1 813–1 953</td>
<td>&lt;9</td>
<td>1</td>
<td>Sampling</td>
<td>(18)</td>
</tr>
<tr>
<td>-0.596/T + 0.011 (−0.0209)</td>
<td>-</td>
<td>1 823–1 923</td>
<td>&lt;25</td>
<td>1</td>
<td>Sampling</td>
<td>(19)</td>
</tr>
</tbody>
</table>

Figure 4 shows the variation of $K'_N$ values with Si content in liquid iron.

3.1.2. N Solubility in Binary Fe–Si Melts

The N solubility in liquid iron containing silicon up to 12.53 mass% was measured under the reduced nitrogen partial pressures at 1 823 and 1 873 K. The experimental results are summarized in Table 1. Figure 4 shows the variation of $K'_N$ values with Si content in liquid iron at 1 823 and 1 873 K together with previous data.11,17,18,22,23 Among those data, the present N solubility data agreed well with the data determined by Pehlke and Elliott11 over the wide range of Si concentration at 1 873 K.

Figure 5 shows the $\log_{10}^S N$ values vs. [% Si] calculated using Eq. (3) from the present experimental results and the previous data of N solubility in Fe–Si melts at 1 823 and 1 873 K. The $\log_{10}^S N$ values increase almost linearly up to about 4 mass% Si in the melt showing that the relation can be well described by using the first-order $e_{SN}$ value only. However, it cannot be applied to the higher Si range as shown by the dotted line using only the first-order interaction parameter values determined by Pehlke and Elliott.11 Table 3 shows the first-order interaction parameter values of $e_{SN}$ for Fe–Si–N melt reported by several groups. In Pehlke and Elliott’s work, they measured the nitrogen solubility in Fe–Si melt containing Si up to about 10 mass% using the Sieverts method, but they determined only the first-order $e_S$ value from their experimental data up to 5 mass% Si. They neglected the second-order effect at higher Si content.11
Therefore, from a regression analysis of the data determined in the present study taking the first-order $e_N^0$ value of 0.047 determined by Pehlke and Elliott, the second-order $r_N^j$ parameters were determined as 0.0013±0.00014 at 1 823 and 1 873 K. No temperature dependence of these values was observed in the temperature range from 1 823 to 1 873 K. The calculated relations of the $K_N$ and $\log f_N^{Si}$ vs. Si content in Fe–Si–N melts using the interaction parameters determined in the present study and other values reported by Pehlke and Elliott and Schenck are compared in Figs. 4 and 5. The present results show an excellent correlation with all data determined over the wide range of Si content at different temperatures.

### Table 3. Interaction parameters of Si on N in Liquid Iron.

<table>
<thead>
<tr>
<th>$e_N^0$ (1 873 K)</th>
<th>$r_N^j$ (1 873 K)</th>
<th>Temp. Range (K)</th>
<th>[% Si] Range</th>
<th>$p_{N2}$ (atm)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.047</td>
<td>0.0013</td>
<td>1 823–1 873</td>
<td>&lt;12.53</td>
<td>0.3–1 Sampling</td>
<td>Present study</td>
<td></td>
</tr>
<tr>
<td>0.047</td>
<td>–</td>
<td>1 879</td>
<td>&lt;5</td>
<td>1</td>
<td>Sieverts (11)</td>
<td></td>
</tr>
<tr>
<td>0.047</td>
<td>–</td>
<td>1 823–1 873</td>
<td>&lt;4</td>
<td>1</td>
<td>Sampling (17)</td>
<td></td>
</tr>
<tr>
<td>0.060</td>
<td>–</td>
<td>1 853–1 953</td>
<td>&lt;3</td>
<td>1</td>
<td>Sampling (18)</td>
<td></td>
</tr>
<tr>
<td>0.0673</td>
<td>–</td>
<td>1 823–1 923</td>
<td>&lt;2</td>
<td>1</td>
<td>Sampling (23)</td>
<td></td>
</tr>
<tr>
<td>0.065</td>
<td>–</td>
<td>1 873</td>
<td>&lt;5</td>
<td>0.13–1 Sampling</td>
<td>(22)</td>
<td></td>
</tr>
</tbody>
</table>

3.1.3. N Solubility in Ternary Fe–Mn–Si, Fe–Al–Si, Fe–Mn–C and Fe–Si–C Melts

In order to determine the simultaneous effect of two different alloying elements on the N solubility in liquid iron, the N solubility was measured in ternary Fe–Mn–Si, Fe–Al–Si, Fe–Mn–C and Fe–Si–C melts under various nitrogen partial pressures at 1 773–1 873 K. The experimental results are summarized in Table 4.

Using the relation shown in Eq. (3), the second-order cross-product parameters on nitrogen in liquid iron, $r_N^j$ can be determined from the experimental results of ternary alloy melts by plotting the relation of $\log f_N^{Si}[\% i] – r_N^j [\% i]^j$ vs. $[\% i][\% j]$ as shown in Fig. 6. All data points show the excellent linear relationships and the $r_N^j$ values can be determined from the slopes of the data. Therefore, the values of $r_{Mn, Si}$, $r_{Al, Si}$, $r_{Mn, C}$, and $r_{Si, C}$ were determined as 0±0.00001, 0±0.0005, 0.0019±0.0002 and 0.0013±0.0005, respectively, by the regression analysis. The temperature dependence of the parameters could be neglected in the temperature range from 1 773 to 1 873 K.

Figure 7 summarizes the $r_N^j$ values for various ternary liquid iron alloys determined in the present study as well as the authors’ recent studies. It is worth to note that the cross-product effects of pair alloying elements on nitrogen are strong in the alloys containing carbon due to its strong interaction on nitrogen and alloying elements in liquid iron.

Table 5 summarizes the interaction parameters determined in the present study as well as in the author’s recent studies. Therefore, the nitrogen solubility in multi-component Fe–Mn–Si–C–Al alloy melts of various compositions can be calculated by the following relation obtained from Eq. (3):

### Table 4. N solubility in Fe–Mn–Si, Fe–Al–Si, Fe–C–Si and Fe–Mn–C melts.

<table>
<thead>
<tr>
<th>System</th>
<th>Temp. (K)</th>
<th>$p_{N2}$ (atm)</th>
<th>[% Mn]</th>
<th>[% Al]</th>
<th>[% Si]</th>
<th>[% C]</th>
<th>[% N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Mn–Si–N</td>
<td>1 773 0.9</td>
<td>19.85</td>
<td>1.26</td>
<td>0.0999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Al–Si–N</td>
<td>1 873 0.3</td>
<td>8.40</td>
<td>0.34</td>
<td>0.0361</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Mn–C–N</td>
<td>1 873 0.3</td>
<td>26.30</td>
<td>0.63</td>
<td>0.1340</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Si–C–N</td>
<td>1 773 0.75</td>
<td>10.00</td>
<td>1.00</td>
<td>0.0321</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Si–C–Al</td>
<td>1 873 0.4</td>
<td>13.4</td>
<td>1.57</td>
<td>0.0158</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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In order to check the validity of interaction parameters determined in the present study, a verification experiment was carried out by measuring the N solubility in Fe-25% Mn-0.3% Si-0.6% C-Al melt which is a typical TWIP steel composition. After the equilibrium N content was attained in Fe-25% Mn-0.3% Si-0.6% C melt under a nitrogen partial pressure of 0.14 atm at 1773 K, Al was added repeatedly while the melt temperature was increased from 1773 K to 1823 and 1873 K. After each Al addition and temperature increase, new nitrogen solubility equilibrium was attained within 1 hour. The experimental results are summarized in Table 6.

Figure 8 compares the experimental results of N solubility with predicted values in the melt as a function of Al content at different temperatures. The predicted N solubility using the second-order cross-product parameters, $r_{ij}^N$, are in excellent agreement with the experimental data as shown as solid symbols in the figure. The N solubility predicted without considering $r_{ij}^N$ values was much higher than the measured values. This result emphasizes the necessity of the second-order cross-product parameters in predicting the nitrogen solubility in the multi-component liquid alloy system.

### 3.2. AlN Formation in Fe–Mn–Si–Al–C Melts

The reaction equilibrium for the dissolution of pure solid AlN in liquid iron can be written as:

$$
\Delta G_{\text{AlN}} = 303.500 - 134.6T \text{ J/mol}^{14}
$$

$$
K_{\text{AlN}} = \frac{h_{\text{Al}} h_{\text{N}}}{\alpha_{\text{Al}} f_{\text{N}}} \left[ \% \text{ Al} \right] \left[ \% \text{ N} \right]
$$

where $K_{\text{AlN}}$ is the equilibrium constant for Reaction (7) and, $h_{\text{Al}}$ and $h_{\text{N}}$ are the Henrian activities of aluminum and nitrogen relative to the 1 mass% standard state in liquid iron, and $f_{\text{Al}}$ and $f_{\text{N}}$ are the activity coefficients of aluminum and nitrogen, respectively. The activity of AlN is unity under the
Table 5. Interaction parameter of alloying elements in liquid iron used in the present study.

<table>
<thead>
<tr>
<th>System</th>
<th>Interaction parameter</th>
<th>Value (at 1873 K)</th>
<th>Temp. (K) [% i] range</th>
<th>$P_{N_2}$ (atm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Mn–N</td>
<td>$e_{Mn}^N$</td>
<td>−0.023</td>
<td>1 773–1 873 [% Mn] &lt; 54.4</td>
<td>0.1–0.3</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>$r_{Mn}^N$</td>
<td>−0.763/T + 0.0000489 (0.000081)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Si–N</td>
<td>$e_{Si}^N$</td>
<td>0.047</td>
<td>1 823–1 923 [% Si] &lt; 12.53</td>
<td>0.3–1</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>$r_{Si}^N$</td>
<td>0.0013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Al–N</td>
<td>$e_{Al}^N$</td>
<td>0.017</td>
<td>1 823–1 973 [% Al] &lt; 2.5</td>
<td></td>
<td>(14)</td>
</tr>
<tr>
<td></td>
<td>$r_{Al}^N$</td>
<td>0</td>
<td>1 823–1 973 0.8 [% Al] &lt; 4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–C–N</td>
<td>$e_{C}^N$</td>
<td>0.08</td>
<td>1 773–1 873</td>
<td>0.3, 0.8</td>
<td>(7)</td>
</tr>
<tr>
<td></td>
<td>$r_{C}^N$</td>
<td>0.014</td>
<td></td>
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</tr>
<tr>
<td>Fe–Mn–C–N</td>
<td>$r_{Mn,C}^N$</td>
<td>0.0019</td>
<td>1 773–1 873 [% Mn] &lt; 27.25, [% C] &lt; 1.01</td>
<td>0.3, 0.9</td>
<td>Present study</td>
</tr>
<tr>
<td>Fe–Si–C–N</td>
<td>$r_{Si,C}^N$</td>
<td>0.013</td>
<td>1 773–1 873 [% C] &lt; 2.62, [% Si] &lt; 1.36</td>
<td>0.4, 0.75</td>
<td>Present study</td>
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<tr>
<td>Fe–Mn–Si–N</td>
<td>$r_{Mn,Si}^N$</td>
<td>0</td>
<td>1 773–1 873 [% Mn] &lt; 24.63, [% Si] &lt; 1.3</td>
<td>0.3, 0.9</td>
<td>Present study</td>
</tr>
<tr>
<td>Fe–Al–Si–N</td>
<td>$e_{Al}^{Si}$</td>
<td>0.037</td>
<td>1 823–1 923 [% Al] &lt; 1.2, [% Si] &lt; 1.82</td>
<td>0.1, 0.3</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>$r_{Al}^{Si}$</td>
<td>0</td>
<td>1 823–1 923 [% Al] &lt; 1.68, [% Si] &lt; 1.5</td>
<td>0.3, 1</td>
<td>Present study</td>
</tr>
<tr>
<td>Fe–Mn–Al–N</td>
<td>$r_{Mn,Al}^N$</td>
<td>0</td>
<td>1 823–1 873 [% Mn] &lt; 20.3, [% Al] &lt; 0.38</td>
<td>0.1–0.8</td>
<td>(5)</td>
</tr>
<tr>
<td>Fe–Al–C–N</td>
<td>$r_{Al,C}^N$</td>
<td>0.038</td>
<td>1 773–1 873 [% Al] &lt; 0.91, [% C] &lt; 2.03</td>
<td>0.19–0.8</td>
<td>(8)</td>
</tr>
<tr>
<td></td>
<td>$e_{Al}^C$</td>
<td>0.03</td>
<td>1 773–1 873 [% Al] &lt; 2.45, [% C] &lt; 3.9</td>
<td>0.19–0.8</td>
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<tr>
<td></td>
<td>$r_{Al}^C$</td>
<td>0</td>
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Table 6. $N$ solubility and AlN solubility product in Fe-25% Mn-0.3% Si-0.6% C-Al melts.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1 773</td>
<td>26.04</td>
<td>0.34</td>
<td>0.61</td>
<td>0</td>
<td>0.0473</td>
<td>0.0473</td>
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<tr>
<td></td>
<td>26.02</td>
<td>0.34</td>
<td>0.60</td>
<td>0.24</td>
<td>0.0456</td>
<td>0.0464</td>
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<tr>
<td></td>
<td>26.07</td>
<td>0.33</td>
<td>0.60</td>
<td>0.55</td>
<td>0.0461</td>
<td>0.0453</td>
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</tr>
<tr>
<td>1 823</td>
<td>25.70</td>
<td>0.34</td>
<td>0.61</td>
<td>0.54</td>
<td>0.0428</td>
<td>0.0439</td>
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<tr>
<td></td>
<td>25.13</td>
<td>0.34</td>
<td>0.60</td>
<td>0.83</td>
<td>0.0403</td>
<td>0.0419</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.01</td>
<td>0.33</td>
<td>0.60</td>
<td>1.12</td>
<td>0.0397</td>
<td>0.0397</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.87</td>
<td>0.33</td>
<td>0.61</td>
<td>1.38</td>
<td>0.0380</td>
<td>0.0389</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24.41</td>
<td>0.33</td>
<td>0.60</td>
<td>1.35</td>
<td>0.0327</td>
<td>0.0325 AlN</td>
<td></td>
</tr>
<tr>
<td>1 773</td>
<td>23.86</td>
<td>0.32</td>
<td>0.58</td>
<td>1.30</td>
<td>0.0196</td>
<td>0.0197 AlN</td>
<td></td>
</tr>
<tr>
<td>1 723</td>
<td>23.46</td>
<td>0.34</td>
<td>0.59</td>
<td>1.24</td>
<td>0.0117</td>
<td>0.0114 AlN</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. Correlation between calculated and measured $N$ solubility in Fe-25%Mn-0.3%Si-0.6%C-Al-N melt.
present experimental condition, the equilibrium constant, $K_{\text{AlN}}$ can be expressed as the following relation using the interaction parameters:

$$
\log K_{\text{AlN}} = \frac{-15850}{T} + 7.03
$$

where $e_i$, $r_i$, and $r_{ij}^s$ are the first- and second-order interaction parameters of elements on N and Al, respectively, and $r_{ij}^{ss}$ is the second-order cross-product interaction parameter on N in liquid Fe–Mn–Si–C–Al–N alloy.

The values of $e_i$, $r_i$, and $r_{ij}^s$ in liquid Fe–Mn–Si–C–Al–N alloy were determined in the preceding section from the nitrogen solubility data in the present study and the author’s recent studies. The values of $e_i$, and $r_i$ have been also determined from the AlN solubility data in liquid Fe–Mn–Si–C–Al–N alloy melt as functions of melt composition and temperature. For an example, an AlN solubility diagram for a commercial TWIP steel composition of Fe-25% Mn-0.3% Si-0.6% C-Al-N can be constructed at different temperatures from 1873 to 1723 K as shown as solid lines in Fig. 9. The dotted lines were calculated without considering the cross-product effect of alloying elements on nitrogen, $r_{ij}^{ss}$ in the melt. In order to check the validity of the contour lines shown in Fig. 9, a verification experiment was carried out by measuring the AlN solubility product in the same melt as a function of melt temperature. After the equilibrium N content of 0.038 mass% was attained in Fe-25% Mn-0.3% Si-0.6% C-Al-N melt under a nitrogen partial pressure of 0.14 atm at 1873 K (point A) which was well below the AlN solubility product line, the melt temperature was lowered to 1823, 1773 and 1723 K successively and held for 1 hour at each temperature prior to metal sampling. The metal samples were analyzed for nitrogen and aluminum contents as well as the secondary AlN inclusions precipitated during cooling of the melt.

The variation of nitrogen and aluminum contents with melt temperature change are summarized in Table 6. They changed from the point A to B, C and D in Fig. 9 as the melt temperature decreased from 1873 to 1823, 1773 and 1723 K, respectively. The experimental results showed an excellent agreement with predicted critical Al and N contents for the AlN inclusion formation at each temperature. The predicted lines calculated without considering the cross-product effect of alloying elements on nitrogen showed higher values compared to the experimental data. The metal samples were analyzed for the inclusions by the potentiostatic electrolytic extraction method and the SEM-EDS analysis. There was no AlN inclusions observed in the sample A at 1873 K. Figure 10 shows the SEM images of AlN inclusions in the metal sample B at 1823 K. The inclusions extracted by the potentiostatic electrolytic extraction
method were identified as the AlN inclusions of 1–10 μm size by the SEM-EDS analysis.

4. Conclusions

The interaction parameters of alloying element on nitrogen in liquid iron have been determined from the nitrogen solubility in liquid Fe–Mn, Fe–Si, Fe–Mn–Si, Fe–Mn–C, Fe–Al–Si, Fe–Si–C and Fe–Mn–Si–C–Al melts over a wide range of composition and temperature. By taking into account the interaction parameters determined in the present study, the interaction parameters of silicon on aluminum was newly determined. These parameters could be used to accurately predict the nitrogen solubility and the AlN solubility product in multi-component Fe–Mn–Si–C–Al system. The main finding of this study can be summarized as follows:

(1) The first and second-order interaction parameters of manganese and silicon on nitrogen in liquid Fe–Mn–N and Fe–Si–N melts over a wide range of melt composition can be expressed as:

\[
e_{N}^{\text{Mn}} = -0.023, r_{N}^{\text{Mn}} = \frac{-1.164}{T} + 0.000703 \quad (\text{Mn} \leq 54.34\%, \, 1773 \sim 1873 \, \text{K})
\]

\[
e_{N}^{\text{Si}} = 0.047, r_{N}^{\text{Si}} = 0.0013 \quad (\text{Si} \leq 12.53\%, \, 1823 \sim 1873 \, \text{K})
\]

(2) The effects of cross-products on nitrogen in liquid Fe–Mn–Si–N, Fe–Al–Si–N, Fe–Mn–C–N and Fe–Si–C–N melts can be expressed as:

\[
r_{N}^{\text{Mn, Si}} = 0 \quad (\text{Mn} \leq 26.43\%, \, \text{Si} = 0.33 \sim 1.3\%, \, 1773 \sim 1873 \, \text{K})
\]

\[
r_{N}^{\text{Al, Si}} = 0 \quad (\text{Al} \leq 1.12\%, \, \text{Si} = 0.93 \sim 1.82\%, \, 1823 \sim 1873 \, \text{K})
\]

\[
r_{N}^{\text{Mn, C}} = 0.0019 \quad (\text{Mn} \leq 27.23\%, \, \text{C} \leq 1.01\%, \, 1773 \sim 1873 \, \text{K})
\]

\[
r_{N}^{\text{Si, C}} = 0.013 \quad (\text{Si} \leq 1.36\%, \, \text{C} \leq 2.62\%, \, 1773 \sim 1873 \, \text{K})
\]

(3) The first- and second-order interaction parameters of silicon on aluminum in liquid Fe–Si–Al–N melts were determined as:

\[
e_{\text{Al}}^{\text{Si}} = 0.037, r_{\text{Al}}^{\text{Si}} = 0 \quad (\text{Al} = 0.83 \sim 1.68\%, \, \text{Si} \leq 2\%, \, 1823 \sim 1873 \, \text{K})
\]

Acknowledgment

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project No.: 11-C22-1D).

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