Thermodynamics of Titanium, Nitrogen and TiN Formation in Liquid Iron

Thermodynamics of titanium, nitrogen and TiN formation in liquid iron was investigated using the metal–nitride–gas equilibration under different nitrogen partial pressures in the temperature range of 1873–1973 K. The nitrogen solubility in liquid iron increased with increasing titanium content. Pure solid TiN was formed at critical contents of titanium and nitrogen in liquid iron. The experimental results were thermodynamically analyzed using Wagner’s interaction parameter formalism to determine the first-order interaction parameter between titanium and nitrogen, the first-order self interaction parameter of titanium, and the equilibrium constant for the dissolution of pure solid TiN in liquid iron given as follows.

\[
\begin{align*}
e_N^T & = -8507/T + 4.18, \\
e_N^N & = -29110/T + 14.3 \\
e_T^T & = 0.048(1873–1973 K) \\
TiN(s) & = Ti + N \\
\log K_{TiN} & = 15780/T + 5.63
\end{align*}
\]

KEY WORDS: liquid iron; titanium; nitrogen; TiN; equilibrium constant; interaction parameters.

1. Introduction

Titanium is often added in liquid steels to improve mechanical properties of final products via the grain refinement during hot rolling and to improve corrosion resistance of stainless steels by stabilizing carbon and nitrogen. Titanium is a strong nitride-forming element in liquid steel, and the formation of TiN can provide both merits and demerits in steel processing. For instance, TiN precipitated during cooling or solidification of liquid steel can help the formation of equi-axed cast structure, while an excessive formation of TiN inclusions can cause a nozzle clogging during continuous casting and various defects in final products. It is therefore desirable to control the formation of TiN during liquid steel processing.

In order to predict under what condition TiN will form, it is essential to have accurate thermodynamic data of titanium and nitrogen in liquid steels as a function of temperature. In spite of such importance, there are still some uncertainties in the literature values including the recommended values of the Japan Society for the Promotion of Science (JSPS). Furthermore, the recommended values of JSPS for the equilibrium constant, \(K_{\text{TiN}}\) for the formation of TiN and the interaction parameter values of \(e_N^T\) and \(e_T^T\) in liquid iron were taken from different sources in which the data were determined by different experimental systems. This situation will cause significant errors in predicting the reaction equilibrium of TiN formation in Fe–Ti–N melt.

In the present study, thermodynamics of titanium, nitrogen and TiN formation in liquid iron was investigated using the metal–nitride–gas equilibration technique in the temperature range of 1873–1973 K. The sampling method utilizing a high frequency induction furnace was used to determine the equilibrium relations of titanium and nitrogen in iron melts containing up to 0.52 mass% Ti at different nitrogen partial pressures. The effect of titanium content on nitrogen solubility in liquid iron was measured. The solubility product of titanium and nitrogen in liquid iron saturated with pure solid TiN was also measured as a function of temperature. Using Wagner’s formalism, the interaction parameters of titanium and nitrogen and the equilibrium constant of TiN formation in liquid iron were determined.

The validity of thermodynamic parameters determined in the present study was examined together with previous investigations.

2. Experimental Procedures

Five hundred grams of high purity electrolytic iron (99.95 mass% purity, 200 mass ppm O, <5 mass ppm N, 18 mass ppm C, <10 mass ppm Si), contained in an \(\text{Al}_2\text{O}_3\) crucible (OD: 56 mm, ID: 50 mm, H: 96 mm) was melted in...
the temperature range of 1873–1973 K by a 15 kW/30 kHz high frequency induction furnace as shown in Fig. 1. The alumina crucible was placed in a graphite crucible and a porous alumina crucible as outer crucibles. The reaction chamber consisted of a 96 mm OD quartz tube open at both ends and was connected to a gas delivery system.

After melting the iron, the temperature of the melt was monitored by a Pt/Pt–13mass%Rh thermocouple sheathed with an 8 mm OD alumina tube immersed in the melt. Any possible influence of high frequency noise on the temperature reading was avoided by grounding the circuit of the thermocouple. Preliminary trials confirmed that no significant noise was detected. The temperature fluctuation of iron melt could be controlled within 2 K during experiment by the PID controller of the induction furnace. The temperature reading of the PID controller was calibrated by the sourcing DC voltage calibrator for the thermal EMF of R-type thermocouple.

After the temperature of iron melt was reached to a desired value, an Ar–10%H2 gas was blown onto the melt surface at a high flow rate of ~5 000 mL/min for 2 h to deoxidize the melt. The oxygen content in the iron melt after this procedure was in the range of 15–20 mass ppm. Then the gas was switched to a mixture of Ar–10%H2 and N2 gases (P_{N2} = 0.10, 0.11 and 0.2 atm). The flow rate of gas mixture was controlled by a mass flow controller in the range of 1 000 to 2 000 mL/min depending on nitrogen partial pressures in the gas.

Strong agitation of melt by an induction furnace resulted in a fast attainment of equilibrium nitrogen solubility in liquid iron within 1 h at a given nitrogen partial pressure. After confirming the saturation of nitrogen in liquid iron by sampling and in-situ analysis, pellets of sponge titanium (99.5 mass% purity) were dropped into liquid iron through an 18 mm ID quartz tube. After the predetermined equilibrium time of 1 h, a metal sample of about 10 g was sucked by a 4 mm ID quartz tube connected to a syringe (10 mL) and quenched rapidly in water within 2 s. Titanium addition and sampling were repeated until a stable TiN layer was formed on the surface of the iron melt.

The metal samples were carefully cut for the chemical analysis. Four specimen of each metal sample were prepared for the analysis of nitrogen and oxygen. The nitrogen and oxygen contents in the metal sample were measured by the inert gas fusion-infrared absorptiometry technique with an accuracy of ±1 mass ppm. For the analysis of titanium and silicon, the metal sample (0.2 g) was dissolved in 20 mL of HCl(1+1) in a glass beaker of 50 mL capacity heated in a water bath for 2 h. The leaching test of TiN powder (99% purity, <10 μm) in various acid solutions indicated that TiN was nearly insoluble in dilute HCl(1+1) solution heated in a water bath up to 6 h. In author’s previous studies,13) the detailed procedure for chemical analysis is available. After each experimental run, the Fe–Ti–N melt contained in an alumina crucible was quenched rapidly by
helium gas blowing onto the melt. The quenched metal sample was cross-sectioned and examined with an optical microscope for the presence of TiN inclusions. The center part of metal sample was virtually clean without any noticeable TiN inclusions. However, TiN inclusions of $\sim 20 \mu m$ in size were observed near the melt surface covered with a TiN layer by SEM-EDS analysis as shown in Fig. 2.

3. Results and Discussion

One of the main concerns in the measurement of equilibrium nitrogen solubility with titanium content by the sampling method was how to retain the dissolved titanium and nitrogen in metals during sampling. As shown in Table 1, a separate test was conducted at 1 973 K to see if any delay in quenching would result in a substantial error in determining soluble titanium and nitrogen contents by the secondary precipitation of TiN. The result showed that quenching the samples in water within 3 s did not invalidate the results.

The other experimental concern was the possibility of reduction reaction of quartz tube with titanium in the sample melt during immersion in the melt for sampling. Top and bottom parts of quenched metal samples were separately analyzed to check if there was any difference in titanium and silicon contents. As shown in Table 2, the silicon pickup in the top part was negligible. However, the bottom part of metal samples picked up significant amount of silicon and contained less titanium. This result may be attributed to the possibility that the lower part of quartz tube was heated enough to react with the sample melt while the upper part retained cool and sucked metal was rapidly cooled resulting in little reaction with quartz tube. On the other hand, nitrogen and oxygen contents in top and bottom parts of metal samples were nearly the same as shown in the table. Therefore, the top part of metal samples was used for the chemical analysis in the present study.

3.1. Effect of Titanium on Nitrogen Solubility

The experimental results of nitrogen solubility measurement with titanium additions in liquid iron under different nitrogen partial pressures are summarized in Table 3. Figure 3 shows the variation of equilibrium nitrogen solubility in Fe–Ti–N melt with titanium additions under different

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_N$ (atm)</th>
<th>w% Ti</th>
<th>w% Si</th>
<th>w% N</th>
<th>w% O</th>
<th>Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 973</td>
<td>0.2</td>
<td>0</td>
<td>0.0196</td>
<td>0.0000</td>
<td>0.0030</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.0195</td>
<td>0.0032</td>
<td>0.0015</td>
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<tr>
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<td>0.0024</td>
<td>0.0025</td>
<td>0.0020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0026</td>
<td>0.0000</td>
<td>0.0080</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. The experimental results of Ti and N equilibration in liquid iron.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_N$ (atm)</th>
<th>w% Ti</th>
<th>w% Si</th>
<th>w% N</th>
<th>w% O</th>
<th>Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 923</td>
<td>0.2</td>
<td>0</td>
<td>0.0156</td>
<td>0.0020</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.0159</td>
<td>0.0018</td>
<td>0.0014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0182</td>
<td>0.0018</td>
<td>0.0016</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.0026</td>
<td>0.0001</td>
<td>0.0018</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Variation of dissolved Ti and N in metal samples with delayed quenching.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$P_N$ (atm)</th>
<th>[%Ti]</th>
<th>[%Si]</th>
<th>[%N]</th>
<th>Delayed Time(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 973</td>
<td>0.11</td>
<td>0.299</td>
<td>0.0009</td>
<td>0.0155</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.299</td>
<td>0.0015</td>
<td>0.0153</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.271</td>
<td>0.0043</td>
<td>0.0136</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.212</td>
<td>0.0071</td>
<td>0.0151</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2. The contents of Ti, Si, N, and O in analyzed parts of extracted samples.
nitrogen partial pressures at 1,873, 1,923 and 1,973 K. As shown as open symbols in the figure, the nitrogen solubility increases linearly as the titanium content increases in liquid iron. When the titanium content exceeds a critical value, the nitrogen solubility sharply decreases as shown as solid symbols in the figure due to the formation of TiN in the melt.

The dissolution of nitrogen before the saturation of TiN in liquid iron alloys can be written as

$$\Delta G^\circ = 3598 + 23.89T \text{ J/mol} \quad (1)$$

where $K_1$ is the equilibrium constant for Reaction (1), $P_{N_2}$ is the nitrogen partial pressure and $f_N$ is the Henrian activity coefficient of nitrogen in 1 mass% standard state in liquid iron.

Using Wagner’s relation, the equilibrium constant $K_1$ can be rewritten as the following relation using the first order interaction parameters:

$$K_1 = \frac{f_N^{N_2} [\% N]}{P_{N_2}} \quad (2)$$

where $f_N^{N_2}$ is the equilibrium constant for Reaction (1), $P_{N_2}$ is the nitrogen partial pressure and $f_N$ is the Henrian activity coefficient of nitrogen in 1 mass% standard state in liquid iron.

Using Wagner’s relation, the equilibrium constant $K_1$ can be rewritten as the following relation using the first order interaction parameters:

$$\log K_1 = \log f_N^{N_2} + \log[\% N] - \frac{1}{2} \log P_{N_2} = e_N^{Ti} [\% Ti] + e_N^{N} [\% N] + \log[\% N] - \frac{1}{2} \log P_{N_2} \quad (3)$$

where $e_N^{Ti}$ and $e_N^{N}$ are the first-order interaction parameters of titanium and nitrogen on nitrogen, respectively, and the value of $e_N^{N}$ is known to be 0 in the temperature range of 1,873–1,973 K. As mentioned earlier, the silicon content in top parts of metal samples was very low, and aluminum and oxygen contents were lower than 20 and 30 mass ppm, respectively. Therefore, the effect of silicon, aluminum and oxygen on titanium and nitrogen was assumed to be negligible.

Therefore, the value of $e_N^{Ti}$ in Eq. (4) can be determined from the experimental results of nitrogen solubility in Fe–Ti melts as a function of titanium content before the saturation

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Fig. 3. Equilibrium relations between [\% Ti] and [\% N] in Fe–Ti–N melts at different $P_{N_2}$ pressures and temperatures.

Fig. 4. Relations between $\log f_N^{N_2}$ and [\% Ti] in Fe–Ti–N melt.
of TiN. Figure 4 shows the values of log $f^T_N$ plotted vs. titanium concentration by weight percent in liquid iron using the relation expressed by Eq. (4). At all temperatures, the data determined at different nitrogen partial pressures show excellent linear relationships. The first-order interaction parameter, $e^T_N$, can be determined by a linear regression analysis of data in Fig. 4 as $-0.36$, $-0.23$, and $-0.13$ at 1873, 1923, and 1973 K, respectively. The temperature dependence of $e^T_N$ values can be expressed as $-8.507/T+4.18$. Using Wagner’s reciprocal relationship, the value of $e^T_N$ can be expressed as $-29.110/T+14.3$.

Table 4 compares the $e^T_N$ values determined by previous workers. Evans and Pehlke used the Sieverts’ method to measure the effect of titanium on nitrogen solubility in liquid Fe–Ti alloys containing up to 0.32 mass% Ti as a function of nitrogen partial pressure. They determined the value of $e^T_N$ as $-0.53$ at 1873 K, and they reported the temperature dependence of $e^T_N$ value as $-6.200/T+2.7$ in the temperature range of 1873–2023 K. However, in the earlier work using the same method by Pehlke and Elliott, no satisfactory measurements could be obtained with Fe–Ti melts by the Sieverts’ method. They pointed out that the formation of a stable nitride in the Sieverts chamber would increase the apparent absorption of nitrogen.

Maekawa et al. used the sampling method utilizing a high frequency induction furnace to measure the nitrogen solubility in liquid Fe–Ti alloys at the atmospheric nitrogen pressure at 1973 K. They reported the value of $e^T_N$ as $-0.63$ from the nitrogen solubility data in liquid iron at titanium concentration range of 0.1–0.3 mass%. However, at their high nitrogen contents, the melts might have been saturated with TiN.

Morita and Kunisada did the similar experiment at reduced nitrogen partial pressures of 0.04–0.36 atm to measure the effect of titanium on nitrogen solubility and the solubility product for TiN formation in Fe–Ti–N melts. They determined the $e^T_N$ value as $-0.60$ at 1873 K from the nitrogen solubility data with titanium additions, and they reported the temperature dependence of $e^T_N$ value as $-5.700/T+2.45$ in the temperature range of 1873–1973 K.

Recently, Ishii and Fuwa also carried out the same experiment at reduced nitrogen partial pressures of 0.04–0.17 atm, and determined the $e^T_N$ value as $-7.240/T+3.0$ in the temperature range of 1853–1953 K. However, they pointed out that titanium was very reactive, and this could cause some errors in measuring the nitrogen solubility in Fe–Ti melts by the sampling method. Therefore, in the present study, separate tests were conducted to avoid errors in determining dissolved titanium and nitrogen in metals during sampling procedure as mentioned earlier. The validity of $e^T_N$ values determined by various authors will be discussed more in detail in the next section.

### 3.2. Thermodynamics of TiN Formation in Liquid Iron

The solubility product of titanium and nitrogen in liquid iron for TiN saturated condition was determined as shown as solid symbols in Fig. 3. Formation of pure TiN precipi-

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.36 (-8507/T+4.18)</td>
<td>0.048</td>
<td>-2.792 (-15780/T+5.63)</td>
<td>1873-1973</td>
<td>0.52%</td>
<td>Sampling (Fe-Ti-N)</td>
<td>Present Study</td>
</tr>
<tr>
<td>-0.53 (-6200/T+2.7)</td>
<td>0.058</td>
<td>-2.584 (-16413/T+6.19)</td>
<td>1973-2023</td>
<td>0.32%</td>
<td>Sieverts (Fe-Ti-N)</td>
<td>8</td>
</tr>
<tr>
<td>*-0.60 (-5700/T+2.45)</td>
<td>0.53(1873K)</td>
<td>*-2.760 (-19800/T+7.78)</td>
<td>1873-1973</td>
<td>0.5%</td>
<td>Sampling (Fe-Ti-N)</td>
<td>4</td>
</tr>
<tr>
<td>-0.63 (-7240/T+3.0)</td>
<td>0.29(1973K)</td>
<td></td>
<td>1973</td>
<td>0.3%</td>
<td>Sampling (Fe-Ti-N)</td>
<td>7</td>
</tr>
<tr>
<td>-0.90 (-7240/T+3.0)</td>
<td>0.26(1973K)</td>
<td></td>
<td>1853-1953</td>
<td>0.15%</td>
<td>Sampling (Fe-Ti-N)</td>
<td>9</td>
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<tr>
<td>0.048</td>
<td></td>
<td>1900</td>
<td></td>
<td>1%</td>
<td>Estimation from the data of Hadley et al. and Kelly et al. (Fe-Ti-D)</td>
<td>10</td>
</tr>
<tr>
<td>0.042</td>
<td></td>
<td>1873</td>
<td></td>
<td>12%</td>
<td>EMF (Fe-Ti-D)</td>
<td>11</td>
</tr>
<tr>
<td>*0.048</td>
<td></td>
<td>1873</td>
<td></td>
<td>8.8%</td>
<td>EMF (Fe-Ti-D)</td>
<td>5</td>
</tr>
<tr>
<td>0.023</td>
<td></td>
<td>1873</td>
<td></td>
<td>2.1%</td>
<td>Ag bath Iso-activity</td>
<td>12</td>
</tr>
</tbody>
</table>

*: Recommended values of JSPS
The reaction equilibrium for the dissolution of pure solid TiN in liquid iron can be written as

\[ \text{TiN} (s) = \text{Ti} + \text{N} \]  

\[ K_{\text{TiN}} = \frac{h_1 h_2}{a_{\text{TiN}}} = f_{\text{Ti}} f_{\text{N}} [\%\text{Ti}][\%\text{N}] \]  

where \( K_{\text{TiN}} \) is the equilibrium constant for Reaction (5) and, \( h_1 \) and \( h_2 \) are the Henrian activities of titanium and nitrogen relative to 1 mass\% standard state in liquid iron, and \( f_{\text{Ti}} \) and \( f_{\text{N}} \) are the activity coefficients of titanium and nitrogen, respectively. Under the present experimental condition, the activity of TiN is unity.

The equilibrium constant, \( K_{\text{TiN}} \), can be rewritten as the following relation using Wagner’s formalism \(^6\):

\[
\log K_{\text{TiN}} = \log f_{\text{Ti}} + \log f_{\text{N}} + \log [\%\text{TiN}] \\
= e^{(\%\text{Ti})} e^{(\%\text{N})} + e^{(\%\text{Ti})} e^{(\%\text{N})} + e^{(\%\text{Ti})} e^{(\%\text{N})} \\
+ \log [\%\text{Ti}] [\%\text{N}] 
\]  

(7)

where \( e_{\%\text{Ti}} \) is the first-order self interaction parameter of titanium in liquid iron, and the values of \( e_{\%\text{N}} \) and \( e_{\%\text{Ti}} \) were obtained in the preceding section.

In order to determine the values of \( \log K_{\text{TiN}} \) and \( e_{\%\text{Ti}} \), Eq. (7) can be rearranged as

\[
- e^{(\%\text{Ti})} e^{(\%\text{N})} - \log [\%\text{Ti}] - \log [\%\text{N}] \\
= e^{(\%\text{Ti})} - \log K_{\text{TiN}} 
\]  

(8)

Figure 5 shows plots for the relation of Eq. (8) using the solubility product data determined at a nitrogen partial pressure of 0.11 atm. It is apparent from the figure that the data points determined at different temperatures show excellent linear relationships. Therefore, the values of \( \log K_{\text{TiN}} \) and \( e_{\%\text{Ti}} \) can be simultaneously obtained from the relations shown in Fig. 5. The values of \( \log K_{\text{TiN}} \) obtained by extrapolating the lines are found to be -2.792, -2.577 and -2.365 at 1873, 1923 and 1973 K, respectively. The value of \( e_{\%\text{Ti}} \) can be obtained from the slope of lines as a constant value of 0.048 in the temperature range of 1873–1973 K.

The temperature dependence of \( \log K_{\text{TiN}} \) values is shown in Fig. 6, and it can be expressed as -15780/T + 5.63. The standard free energy of decomposition of TiN in liquid iron is then given by Eq. (9).

\[ \Delta G^\circ = 302200 - 107.8T \text{ J/mol} \]  

The \( \log K_{\text{TiN}} \) values determined by other workers are also shown in Fig. 6 and Table 4 for comparison. Evans et al. \(^3\) measured the solubility product of titanium and nitrogen for TiN formation in liquid Fe–Ti alloys by the Sieverts’ method in the temperature range of 1873–2023 K, by determining the break points in the Sieverts’ law lines of nitrogen solubility for the precipitation of TiN with increasing nitrogen partial pressure. They determined \( \log K_{\text{TiN}} \) values as -16.433/T + 6.19 from their experimental results of solubility product and interaction parameter values between titanium and nitrogen in liquid iron using the relation of Eq. (7). In their calculation, however, they used the \( e_{\%\text{Ti}} \) value of 0.045 converted from the \( e_{\%\text{Ti}} \) value of 9.0 at 1900 K reported by Chipman \(^0\) using the Lupis’ conversion relationship. \(^10\) Evans et al. could not determine the \( e_{\%\text{Ti}} \) value in liquid iron from their own data due to the lack of experimental accuracy in determining the solubility product of TiN using the Sieverts’ method. As pointed out by Pehlke et al., \(^16\) the Sieverts’ method could not give reliable solubility product data for iron melts containing titanium which forms a stable nitride.

Morita et al. \(^4\) measured the solubility product of TiN in liquid iron by the similar method as the present study. They determined the values of \( \log K_{\text{TiN}} \) and \( e_{\%\text{Ti}} \) simultaneously from the same relation of Eq. (8) using their solubility product data and interaction parameter values between titanium and nitrogen in liquid iron. As shown in Fig. 6 and Table 4, the \( \log K_{\text{TiN}} \) value of -2.760 at 1873 K reported by Morita et al. is nearly the same as the result of present study. However, the temperature dependency of \( \log K_{\text{TiN}} \) values differs significantly. In Morita et al.’s work, \(^5\) they measured the melt temperature indirectly by a thermocouple located at the bottom of crucible. In the present study, the melt temperature was directly measured by the immersion of an alumina sheathed thermocouple, and it was controlled within 2 K throughout the experiment by the PID controller of the induction furnace as described earlier. Morita et al. \(^4\) reported the \( e_{\%\text{Ti}} \) values in liquid iron as 0.53, 0.29 and 0.26 at 1873, 1923 and 1973 K, respectively. The \( e_{\%\text{Ti}} \) values in liquid iron determined by various authors are compared in Table 4. \(^4,5,10–12\) In spite of different experimental techniques, the values of \( e_{\%\text{Ti}} \) are quite well agreed in the
range of 0.042–0.048 at 1873 K except for the values obtained by Morita et al.\textsuperscript{4} and Yuanchang et al.\textsuperscript{6}) The recommended value for $e_{\text{Ti}}^{\text{II}}$ in JSPS (0.048 at 1873 K) was taken from the data of Janke et al.\textsuperscript{7} who studied the titanium deoxidation equilibrium in liquid iron by the EMF method. The $e_{\text{Ti}}^{\text{II}}$ value of 0.048 at 1873–1973 K determined in Fe–Ti–N system in the present study is well agreed with the values determined in Fe–Ti–O system.\textsuperscript{5,9,11)

In the present study, three important thermodynamic variables of log $K_{\text{TiN}}$, $e_{\text{N}}^{\text{II}}$ and $e_{\text{Ti}}^{\text{II}}$ were determined adequately in one consistent experimental method. Careful concerns on the sampling method, the selection of the position of sample for analysis and the temperature measurement method improved the accuracy in measuring the equilibrium solubility product for TiN formation in liquid iron.

Figure 7 compares the predictions of equilibrium solubility product of titanium and nitrogen for TiN formation in liquid iron in the temperature range of 1873–1973 K. The lines were calculated using Eq. (7) from log $K_{\text{TiN}}$ and interaction parameters determined by the present study and other workers\textsuperscript{4,8} including the recommended values of JSPS\textsuperscript{3} as shown in Table 4. The experimental data for the solubility product of TiN measured by Morita et al.\textsuperscript{4} Evans et al.\textsuperscript{4} and Ishii et al.\textsuperscript{5} are also shown in the figure. As discussed earlier, the solubility product data measured by the Sieverts’ method\textsuperscript{9} shows significantly higher values than the data measured by the sampling method. At 1873 K, the solubility product data measured by Morita et al.\textsuperscript{4} are in good agreement with the results of present study. However, at higher temperatures of 1923 and 1973 K, the solubility product data and predicted lines of Morita et al.\textsuperscript{4} are much higher than those determined in the present study. In Fig. 7, the solubility product data measured by Ishii et al.\textsuperscript{5} at 1903 and 1953 K are also shown. They are in excellent agreement with the solubility product lines at the same temperatures calculated using the thermodynamic data determined in the present study. The lines for the solubility product calculated from the recommended values of JSPS\textsuperscript{3} are not in agreement with any of those experimental data\textsuperscript{4,8,9}. As mentioned earlier, the recommended values of JSPS for the equilibrium constant, $K_{\text{TiN}}$ and the interaction parameters of $e_{\text{N}}^{\text{II}}$ and $e_{\text{Ti}}^{\text{II}}$ in liquid iron were taken from different investigations.\textsuperscript{4,5}

4. Conclusions

The metal–nitride–gas equilibration technique utilizing a high frequency induction furnace provided an accurate measurement of the equilibrium nitrogen solubility and the solubility product for TiN formation in Fe–Ti–N melts under different nitrogen partial pressures. The nitrogen solubility in liquid iron increased with increasing titanium content. The first-order interaction parameter between titanium and nitrogen was determined as follows in the temperature range of 1873–1973 K.

$$e_{\text{N}}^{\text{II}} = -8507/T + 4.18, \quad e_{\text{Ti}}^{\text{II}} = -29110/T + 14.3$$

Pure solid TiN was formed at critical titanium and nitrogen contents in liquid iron. Using Wagner’s interaction parameter formalism, the first-order self interaction parameter of titanium and the equilibrium constant for the dissolution of pure solid TiN in liquid iron were determined in the temperature range of 1873–1973 K.

$$e_{\text{Ti}}^{\text{II}} = 0.048 \quad (1873–1973 \text{ K})$$

$$\text{TiN (s)} = \text{Ti} + \text{N}$$

$$\log K_{\text{TiN}} = \text{14.3} - \frac{15780}{T} + 5.63$$

Acknowledgement

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