Thermodynamic Interaction between Chromium and Titanium in Liquid Fe–Cr Alloys Containing 30 mass% Cr

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Thermodynamic interaction of chromium on titanium in liquid Fe–Cr alloys was studied by measuring the effect of chromium on the solubility product of TiN in liquid Fe–Cr–Ti–N alloys by the metal–nitride–gas equilibration technique in the temperature range from 1 873 to 1 973 K. Titanium nitride formed in the melt was identified as a pure solid stoichiometric TiN. As the chromium content increases in the melt saturated with TiN, the critical nitrogen solubility increases significantly, while the titanium solubility decreases. Using Wagner’s formalism, the present results were thermodynamically analyzed to determine the first- and the second-order interaction parameters between chromium and titanium given as follows.

\[ e^{\theta}_{TiCr} = 406.7/T - 0.193 \]  \[ r^{\theta}_{TiCr} = -20.6/T - 0.011 \]  (0<mass% Cr<30)

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

1. Introduction

Recently, ferritic stainless steels containing chromium up to 30 mass% with ultra-low carbon and nitrogen contents have been developed for a good corrosion resistance and a high formability to replace austenitic stainless steels. Titanium is often added in these steel grades to improve the corrosion resistance by stabilizing carbon and nitrogen and the mechanical properties via the grain refinement. Recently, TiN or titanium oxides, TiO\(_x\) precipitated as secondary inclusions in liquid steel during cooling or solidification are known to help the formation of equi-axed cast structure.\(^1\)\(^-\)\(^3\) On the other hand, an excessive formation of those inclusions can cause a nozzle clogging problem during continuous casting and various defects in final products.\(^4\)\(^-\)\(^6\)

In order to control those inclusions during steel processing, it is essential to have accurate thermodynamic information of titanium in liquid stainless steels containing high chromium. In spite of its importance, the thermodynamic relation between chromium and titanium in liquid Fe–Cr–Ti alloys is not consistent in the literature,\(^7\)\(^-\)\(^11\) and little information is available at temperatures other than 1 873 K.

In the present study, the thermodynamic interaction between chromium and titanium in liquid iron was determined by measuring the effect of chromium on the solubility product of TiN in Fe–Cr–Ti–N melts containing a wide range of chromium up to 30 mass% in the temperature range from 1 873 to 1 973 K.

2. Experimental Procedures

The metal–nitride–gas equilibration technique utilizing a 15 kW/30 kHz high frequency induction furnace was employed to measure the critical solubility product of Ti and N in liquid Fe–Cr–Ti–N alloys to form TiN under various nitrogen partial pressures. The experimental system is shown in Fig. 1. Detailed descriptions of experimental apparatus and procedure are available in author’s recent studies on Fe–Ti–N, Fe–Ti–Al–N and Fe–Cr–N systems.\(^12\)\(^-\)\(^14\)

Five hundred grams of high purity electrolytic iron contained in an Al\(_2\)O\(_3\) crucible (OD: 56 mm, ID: 50 mm, H: 96

Fig. 1. A schematic diagram of experimental system.
mm) was melted in the temperature range from 1 873 to 1 973 K. The melt temperature was monitored by a Pt/Pt–13 mass% 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. Previous studies 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% H\textsubscript{2} gas was blown onto the melt surface at a high flow rate of \(\sim 5\,000\text{ mL/min} \) 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% H\textsubscript{2} and N\textsubscript{2} gases to have nitrogen partial pressures from 0.01 to 0.1 atm. The flow rate of each gas was controlled by a mass flow controller at a total flow rate in the range from 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 analysis, pellets of sponge titanium (99.5 mass% purity) were dropped into liquid iron through an 18 mm ID quartz tube. After each titanium addition, some amount of solid reaction product, presumably TiN, was dissolved in the melt again and completely disappeared after this procedure was in the range of 15–20 mass ppm. For the analysis of chromium and titanium, 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. Chromium and titanium dissolved in the sample solution was then analyzed by the ICP-AES using the appropriate standard solutions containing the similar amount of Fe as in the sample solutions. The analytical limit for chromium and titanium in metal sample was 5±1 mass ppm.

After each experiment, the melt remained in an Al\textsubscript{2}O\textsubscript{3} crucible was quenched by blowing helium gas onto the melt surface. In order to check the presence of inclusions including TiN in the quenched melt, about 10 g of metal sampled near the upper surface of the melt was dissolved in dilute HCl (1+1) solution heated in a water bath for 72 h. After the complete dissolution of metallic portion, the residue was filtrated and analyzed by the X-ray diffraction analysis (XRD, High power X-ray diffractometer System, Rigaku D/MAX-2500/PC).

3. Result and Discussion

3.1. Inclusion Identification

As shown in Fig. 2(a), the inclusions formed in the melt were identified as TiN, TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} phases. The result was also compared with the XRD pattern of the stoichiometric TiN powder (99% purity, <10 \(\mu\text{m}\), Aldrich Chemical Co.) shown in Fig. 2(b). By comparing 2 values of the diffraction peaks, the titanium nitride formed in Fe–Cr–Ti–N melt in the present study can be considered as a pure solid stoichiometric TiN.

3.2. Effect of Chromium on Solubility Product of TiN in Liquid Iron

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

\[\text{TiN} (s) = \text{Ti} + \text{N}_{2} \]  

with

\[\Delta G_{f}^{\circ} = 302 200 – 107.87 \text{ J/mol} \]  

where

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

where \(K_{\text{TiN}}\) is the equilibrium constant for Reaction (1), \(h_{\text{Ti}}\) and \(h_{\text{N}}\) are the Henry’s 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. The activity of TiN in Eq. (3) is unity in the present study.

Figure 3 shows the variations of equilibrium nitrogen solubility in Fe–Ti–N melt with titanium additions under the nitrogen partial pressures from 0.01 to 0.1 atm at different temperatures. Reduced nitrogen pressures were used to keep nitrogen content low in the melt and hence to avoid an excessive formation of TiN on titanium additions. The nitrogen solubility increases linearly as the titanium content increases in liquid iron when the melt is not saturated with TiN as shown as open symbols in the figure. However, when the titanium content exceeds a critical value, the nitrogen solubility decreases with titanium additions due to a stable formation of TiN as shown as solid symbols in the figure.

The solid lines in Fig. 3 are the equilibrium solubility products of titanium and nitrogen for TiN formation, calcu-
lated using the thermodynamic data determined in author’s previous study on Fe–Ti–N melt.\textsuperscript{12)} The predicted lines for the solubility product of TiN at different temperatures are in excellent agreement with experimental data in the present study.

Figure 4 shows the effect of chromium additions on the solubility of titanium and nitrogen for TiN saturation under a nitrogen partial pressure of 0.01 atm at 1 873 K. As the chromium content increases, the nitrogen solubility increases significantly while the titanium content decreases. Figure 5 shows the effect of chromium additions on the solubility product of TiN, log$[\%\text{Ti}]$/$[\%\text{N}]$ at different temperatures. TiN solubility product increases with chromium additions, and it reaches a maximum value at chromium content of 20 mass%.

In order to determine the thermodynamic relation between chromium and titanium from the TiN solubility data in Fe–Cr–Ti–N melts, the equilibrium constant, $K_{\text{TiN}}$ can be rewritten as the following relation using Wagner’s formalism.\textsuperscript{16)}

\[
\log K_{\text{TiN}} = \log f_{\text{Ti}} + \log f_{\text{N}} + \log[\%\text{Ti}]/[\%\text{N}]
\]

\[
= e_{\text{Ti}}^{\text{T}}[\%\text{Ti}] + r_{\text{Ti}}^{\text{T}}[\%\text{T}]^2 + e_{\text{Cr}}^{\text{T}}[\%\text{Cr}] + r_{\text{Cr}}^{\text{T}}[\%\text{Cr}]^2
\]

\[
+ e_{\text{N}}^{\text{N}}[\%\text{N}] + r_{\text{N}}^{\text{N}}[\%\text{N}]^2 + e_{\text{N}}^{\text{T}}[\%\text{N}] + r_{\text{N}}^{\text{T}}[\%\text{T}]^2
\]

\[
+ e_{\text{Cr}}^{\text{N}}[\%\text{Cr}] + r_{\text{Cr}}^{\text{N}}[\%\text{Cr}]^2 + e_{\text{Cr}}^{\text{N}}[\%\text{N}] + r_{\text{Cr}}^{\text{N}}[\%\text{N}]^2
\]

\[
+ \log[\%\text{Ti}]/[\%\text{N}]
\]

\[
\cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS
where $e^{Ti}_N$, $e^{N}_N$, $r^{Ti}_N$ and $r^{N}_N$ are the first- and second-order interaction parameters of elements on titanium and nitrogen in liquid Fe–Cr–Ti–N alloy, respectively. In author’s recent work, thermodynamics of Fe–Ti–N and Fe–Cr–N melts were studied as a function of temperature. The values of $\log K_{TiN}$ and the interaction parameters used in Eq. (4) are summarized in Table 1. The value of $r^{Ti}_Ti$ was assumed to be zero in the present study.

Then, Eq. (4) can be rewritten as

$$\log f^{Cr}_Ti = e^{Cr}_Ti[\%Cr] + r^{Cr}_Ti[\%Cr]^2$$

$$= \log K_{TiN} - e^{Ti}_Ti[\%Ti] - e^{N}_N[\%N] - e^{Cr}_Ti[\%Ti]$$

$$- e^{Cr}_Ti[\%Cr] - r^{Cr}_Ti[\%Cr]^2 - \log[\%Ti][\%N]$$

where $f^{Cr}_Ti$ is the interaction coefficient of chromium on titanium and is a measure of the effect of a specific concentration of chromium on the behavior of titanium in liquid iron. As mentioned earlier, the oxygen content in the melt was very low, and aluminum and silicon contents were lower than 20 and 30 mass ppm, respectively. Therefore, the effect of oxygen, aluminum and silicon on titanium and nitrogen was assumed to be negligible.

Therefore, the values of $e^{Cr}_Ti$ and $r^{Cr}_Ti$ in Eq. (5) can be determined from the TiN solubility data in Fe–Cr–Ti–N melts. Figure 6 shows the values of $\log f^{Cr}_Ti$ plotted vs. percent chromium in Fe–Cr–Ti melt using the relation expressed by Eq. (5) in the temperature range from 1 873 to 1 973 K. The $\log f^{Cr}_Ti$ value increases linearly with chromium content in the melt at 1 873 K. Therefore, the values of $e^{Cr}_Ti$ and $r^{Cr}_Ti$ can be determined as 0.024 and 0, respectively, at 1 873 K by a linear regression analysis of data. At higher temperatures of 1 923 and 1 973 K, the second-order effect of chromium on titanium is appreciable. Therefore, the values of $e^{Cr}_Ti$ and $r^{Cr}_Ti$ at 1 923 and 1 973 K can be determined as

<table>
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<tbody>
<tr>
<td>Fe-Cr-N</td>
<td>$e^{Cr}_N$</td>
<td>-0.06</td>
<td>-147.8/T+0.019</td>
<td></td>
</tr>
<tr>
<td>(Cr&lt;30mass%)</td>
<td>$r^{Cr}_N$</td>
<td>0.0006</td>
<td>-2.58/T+0.0021</td>
<td>14</td>
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<tr>
<td>Fe-Ti-N</td>
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<td>-8507/T+4.18</td>
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<tr>
<td></td>
<td>$r^{Ti}_N$</td>
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<tr>
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<td>$e^{N}_N$</td>
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<td>$e^{Cr}_Ti$</td>
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<tr>
<td></td>
<td>$r^{Cr}_Ti$</td>
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</tbody>
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\[
\log K_{TiN} = -2.792 - 15780/T+5.63
\]

**Table 1.** Thermodynamic parameters used in the present study.

**Fig. 6.** Relation between $\log f^{Cr}_Ti$ vs. [\%Cr] in Fe–Cr–Ti melts.
0.018 and 0.00021, and 0.013 and 0.00056, respectively, by a regression analysis of data in Fig. 6. The temperature dependency of $e_{TiCr}^C$ and $r_{TiCr}^C$ values can then be determined as $406.7/T - 0.1933$ and $-20.6/ T + 0.011$, respectively, from the results shown in Figs. 7 and 8.

The interaction parameters determined in the present study are compared with previous results7–11) in Table 2. Wada and Pehlke7) measured the effect of chromium on TiN precipitation in their nitrogen adsorption experiments in Fe–Cr–Ti melt using the Sieverts’ method in the temperature range from 1 823 to 2 073 K. They reported the values of $e_{TiCr}^C$ and $r_{TiCr}^C$ as 0.022 and $-0.0001$, respectively, at 1 873 K from their limited experimental data (10 and 20 mass% Cr). They could not determine the temperature dependency of interaction parameter values due to the scattering of experimental data at other temperatures.

Ozturk et al.8) measured the TiN solubility in Fe–Cr melts in the presence of pure solid TiN pellets under 1 atm nitrogen pressure. They determined the value of $e_{TiCr}^C$ as 0.024 at 1 873 K from a plot of log$f_{Ti}$ vs. chromium content up to 18 mass% in Fe–Cr–Ti–N melt using the relation expressed by Eq. (7).

In their calculation, however, the strong interaction between titanium and nitrogen was not considered at high nitrogen content under 1 atm nitrogen pressure. In order to obtain the true value of $e_{TiCr}^C$ in Fe–Cr–Ti–N melt, the interaction coefficient of chromium on titanium, $f_{TiCr}^C$ should be determined as defined in Eq. (5).

Recently, Choi et al.9) reported the value of $e_{TiCr}^C$ as 0.032 at 1 873 K by measuring the activity of titanium in Fe–Cr–Ti–O melts containing chromium up to 31 mass% using a galvanic cell technique. They measured the oxygen activity in the melts using an oxygen sensor as functions of titanium and chromium contents. They assumed a pure solid Ti$_3$O$_5$ as the equilibrium oxide phase in Fe–Cr–Ti–O melts containing titanium less than 0.25 mass% according to other worker’s results for Fe–Ti–O melts.17–20) However, as pointed out in their study, it was not certain to form a pure solid Ti$_3$O$_5$ phase free from other oxides of Fe and Cr. The identification of equilibrium titanium oxide phases and their

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**Table 2.** Interaction parameters between Cr and Ti in Fe–Cr–Ti alloy melt at 1 873 K.

<table>
<thead>
<tr>
<th>$e_{TiCr}^C$</th>
<th>$r_{TiCr}^C$</th>
<th>Temp. Range(K)</th>
<th>[%Cr] Range</th>
<th>$P_N$(atm)</th>
<th>Method</th>
<th>Ref.</th>
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<td>0.024</td>
<td>0</td>
<td>1873–1973</td>
<td>0 – 30</td>
<td>0.01 – 0.05</td>
<td>Sampling</td>
<td>Present Study</td>
</tr>
<tr>
<td>0.022</td>
<td>-0.0001</td>
<td>1873</td>
<td>10, 20, 30</td>
<td>1</td>
<td>Sieverts</td>
<td>7</td>
</tr>
<tr>
<td>0.024</td>
<td>0</td>
<td>1873</td>
<td>0 – 18</td>
<td>1</td>
<td>Sampling</td>
<td>8</td>
</tr>
<tr>
<td>0.032</td>
<td>0</td>
<td>1873</td>
<td>0 – 31</td>
<td>-</td>
<td>EMF</td>
<td>9</td>
</tr>
<tr>
<td>0.016</td>
<td>0.0005</td>
<td>1873</td>
<td>0 – 4.3</td>
<td>-</td>
<td>Iso–activity</td>
<td>10</td>
</tr>
<tr>
<td>0.028</td>
<td>0</td>
<td>1843–1923</td>
<td>0 – 16.2</td>
<td>0.1 – 1</td>
<td>Sampling</td>
<td>11</td>
</tr>
</tbody>
</table>

---

$\text{TiN(s)} = \text{Ti} + \frac{1}{2} \text{N}_2(g)$ .......................... (6)

$K_e = \frac{f_{Ti}[\%Ti]P_{N}^{1/2}}{a_{Ti}}$ .......................... (7)
purity or activity information are very important for the accurate thermodynamic analysis of Ti deoxidation equilibrium in liquid iron.\textsuperscript{13,21,22)}

As also shown in Fig. 6, the present authors previously measured the effect of chromium on the activity coefficient of titanium by determining the TiN solubility in Fe–Cr melts under various nitrogen partial pressures.\textsuperscript{11)} However, the time required for the metal–nitride–gas equilibration using a resistance furnace was too long when the equilibrium was approached from high and low titanium contents with respect to the equilibrium values. As a result, the correlation of \( \log f_{Ti}^{\text{TiN}} \) vs. chromium content in our previous work was not satisfactory enough as shown in the figure.

In the present study, strong agitation of the melt by inductive stirring resulted in a fast attainment of equilibrium nitrogen and titanium solubility for the TiN saturation under various nitrogen partial pressures. Moreover, the melt temperature control technique used in the present study allowed us to determine the temperature dependency of thermodynamic parameters more accurately. As a result, the correlations of \( \log f_{Ti}^{\text{TiN}} \) vs. chromium content are excellent over a wide range of chromium content at all temperatures as shown in Fig. 6.

### 3.3. TiN Solubility in Fe–Cr Alloy Melt

Rearranging Eq. (5), the following relation can be obtained to construct the TiN solubility diagram for Fe–Cr–Ti–N melts as functions of melt composition and temperature.

\[
\log[\%\text{Ti}] = \frac{e_{N}^Ti}{K_{Ti}} + (e_{Ti}^N + e_{N}^Ti) \cdot [\%\text{N}] + (e_{Cr}^Ti + e_{Ti}^N) \cdot [\%\text{Cr}]
\]

\[
\times e_{Cr}^Ti \cdot [\%\text{Cr}]^{2}
\]

Therefore, using the values of \( e_{Cr}^Ti \) and \( e_{Ti}^N \) determined in the present study and other parameter values given in Table 1, one can calculate the contour lines of critical nitrogen and titanium contents for the onset of TiN inclusion formation in ferritic stainless melts at a typical tundish temperature of 1 823 K as shown in Fig. 9. As the chromium content increases in liquid stainless steel, the critical nitrogen content to form TiN inclusions increases at a specific titanium content. Figure 10 shows the effect of melt temperature on the TiN solubility for a liquid Fe–20mass%Cr–Ti–N alloy. As the temperature decreases from a typical ladle treatment temperature of 1 923 K to a mold temperature of 1 793 K, the critical nitrogen and titanium contents decrease significantly.

A separate experiment was carried out to check the validity of TiN solubility contours shown in Fig. 10. A Fe–20%Cr alloy melt was equilibrated with an Ar–10%H\textsubscript{2}–1%N\textsubscript{2} gas (\( p_{N_2} = 0.01 \text{ atm} \)) at 1 923 K using a high frequency induction furnace as described earlier in experimental procedures. After confirming the saturation of nitrogen at 0.036 mass% in alloy melt (symbol [1]) at 1 923 K, the titanium content was increased to 0.15 mass% in the melt by the addition of sponge titanium pellets. After the predetermined equilibration time of 1 h, a metal sample was taken and water quenched. The nitrogen and titanium contents in the metal sample are shown as symbol [2] in Fig. 10. No TiN was formed under this condition as predicted by the contour line calculated at 1 923 K.

Then the melt temperature was decreased slowly by adjusting the PID controller of the induction furnace. During cooling process, the melt was inductively stirred to attain the new equilibrium quickly with respect to the melt temperature. Solid TiN precipitate started to form on the melt surface as the melt temperature decreased below 1 873 K. After an equilibration time of 1 h at 1 823 and 1 793 K, metal samples were taken and water quenched. The nitrogen and titanium contents in metal samples taken at 1 823 and 1 793 K are shown as symbols [3] and [4] in Fig. 10, respectively. They are in excellent agreement with the predicted values.

### 4. Conclusions

The metal–nitride–gas equilibration utilizing a high frequency induction furnace and a precise temperature control technique provided an accurate measurement of the equilibrium solubility of TiN in liquid Fe–Cr alloys in the temperature range from 1 873 to 1 973 K. The main findings of this study can be summarized as follows.

(1) As the chromium content increases in Fe–Cr–Ti–N melt saturated with TiN, the critical nitrogen solubility increases significantly, while the titanium solubility decreases.

(2) The experimental results were thermodynamically analyzed using Wagner’s interaction parameter formalism to determine the first- and the second-order interaction parameters between chromium and titanium in liquid
Fe–Cr–Ti containing up to 30 mass% Cr as follows.

e_{\text{Ti}}^{\text{Cr}} = 406.7/T − 0.1933 \quad r_{\text{Ti}}^{\text{Cr}} = −20.6/T − 0.011

3) Thermodynamic calculations to predict the TiN inclusion formation in a Fe–Cr–Ti–N alloy with melt temperature changes are in excellent agreement with the experimental results.

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