Communications

Thermodynamics of TiCN and TiC in Fe-C<sub>sat</sub> Melts

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As discussed elsewhere<sup>[1–4]</sup> in order to prolong the refractory life in a blast furnace, titanium ore is added with the objective of forming titanium carbonitride (TiCN) on the refractory for protection. In a recent article, Bergsma and Fruehan<sup>[2]</sup> discussed the thermodynamics of TiCN for blast furnace conditions. The current work was undertaken to confirm the fundamental thermodynamics of TiCN formation by observing the formation of TiCN in a confocal scanning laser microscope. As will be discussed, there was a significant difference between the observations and the predicted conditions required for Ti(C,N) formation using available thermodynamic data. The largest uncertainty in the calculation is in the value of the activity coefficient of Ti in Fe-C<sub>sat</sub> melts. Therefore, the activity coefficient was measured by using the solubility of TiC using the confocal scanning laser microscope.

Experimental: In-situ observation of the formation of the TiC and Ti(C,N) crystals from hot metal was used in this study. A confocal scanning laser microscope (CSLM) equipped with an infrared image furnace was used in the experiments. Detailed descriptions of CSLM are given elsewhere.<sup>[5,6]</sup> The unique design of the CSLM system made it possible to observe the details of the object’s surface at elevated temperatures.

The metal sample was held in an alumina crucible, which is supported by a ringlike platinum sample holder in the CSLM system. The thermocouple used to control the infrared furnace, and to measure temperature, is welded onto the platinum sample holder. The temperature difference between the thermocouple and the sample was carefully calibrated against the melting point of ultrahigh purity iron, carbon-saturated iron, and copper.

The carbon-saturated iron samples were prepared by melting high-purity iron chips in an ultrahigh purity graphite crucible in argon. In a typical experiment, about 1.3 g of carbon-saturated iron together with the appropriate amount of Fe-4.0 wt pct Ti master alloy was put in a 10-mm-i.d. alumina crucible and loaded into the infrared image furnace. It was heated to a predetermined temperature, at which no precipitation was expected, under an ultrahigh purity argon atmosphere. Immediately after melting, a heating rate of 30 K/s was used to avoid the formation of TiC during heating. The gas was switched to ultrahigh purity nitrogen soon after the predetermined temperature was reached. The melt was kept at that temperature for 30 minutes for the iron to be saturated with nitrogen. It was then cooled slowly at a rate of 0.1 K/s. In the experiments, for TiC formation observation, argon was used during the entire experiment. The images of the metal surface were displayed on a monitor and recorded on videotape. In this technique, we observed the formation of TiC and Ti(C,N) on the surface. However, the activities of components on the surface are the same as the bulk, and therefore, for the present purpose observing the surface is meaningful.

Precipitation of Ti(C,N) from Fe-C<sub>sat</sub>-TiN: Precipitation was observed at the surface of the liquid metal during cooling. Figure 1 shows a typical confocal laser image of the precipitates observed during cooling. Two types of crystals were observed: one with rough surfaces and another with smooth surfaces. The crystals with rough surfaces tend to agglomerate, but the bond is rather weak and can be broken by the metal movement. The crystals with smooth surfaces did not stick together even if they touched. Energy-dispersive X-ray element mapping of the quenched sample confirmed that the crystals are titanium carbonitride. The compositions of the crystals with rough and smooth surfaces appear to be identical. However, the exact compositions of the crystals cannot be analyzed using EDX because of the overlapping of the peaks among C<sub>Ka</sub>, N<sub>Ka</sub>, and L peaks of Ti.

The precipitation temperature was determined as the temperature at which the first Ti(C,N) crystal was observed during cooling. It should be pointed out that the crystal at precipitation temperature is very small and difficult to reprint due to limited image resolution. Larger and clearer images of the crystals were obtained at lower temperatures, as shown in Figure 1. Once the precipitation temperature was determined for a particular titanium concentration, several experiments were carried out with the same metal composition. In those repeat experiments, the temperature was dropped step by step and kept for 5 minutes after each drop. Gradually, finer steps were used when the temperature approached the precipitation temperature determined previously. This was done in order to “pinpoint” the precipitation temperature. The results are listed in Table I. The different precipitation temperatures for the same sample demonstrate the reproducibility. Determination of the precipitation temperature through the reverse direction, i.e., by observing the dissolving of the crystals, was attempted. The crystals were found to be hard to dissolve; or, more precisely, the rate of dissolution was extremely slow. Because of the gradual smearing of the optical window in the image furnace by iron vapor, the CSLM is not suitable for observing a process taking place over many hours or days.

Precipitation of TiC from Fe-C<sub>sat</sub>-Ti: As discussed later, there appears to be some uncertainty in the activity coefficient of Ti in Fe-C<sub>sat</sub> melts. Therefore, the precipitation temperature of TiC from Fe-C<sub>sat</sub>-Ti was determined in a similar way. In these experiments, ultrahigh purity argon was used during the entire experiment. The results are listed in Table II.

Discussion: As discussed recently by Bergsma and Fruehan,<sup>[2]</sup> titanium carbonitride may form in a Fe-C<sub>sat</sub> melt if both Ti and N exist, and when

\[ \frac{K_{TiC} h_{Ti} + K_{TiN} (P_{N2})^{1/2} h_{Ti}}{K_{TiC} + K_{TiN} P_{N2}^{1/2}} = 1 \]  

The minimum titanium concentration to form titanium carbonitride in carbon-saturated iron was deduced as

\[ \frac{[Ti, wt\,pct]}{[Ti, wt\,pct]} = \frac{1}{(K_{TiC} + K_{TiN} P_{N2}^{1/2})} \]
Table I. Precipitation Temperature of Ti(C,N) in Fe-C$_{\text{sat}}$-Ti under 1.0 Atm $N_2$

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ti, Mass Pct</th>
<th>Precipitation Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>1773, 1788, 1785</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>1773, 1770, 1775</td>
</tr>
<tr>
<td>3</td>
<td>0.18</td>
<td>1767, 1764</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>1762, 1758</td>
</tr>
<tr>
<td>5</td>
<td>0.12</td>
<td>1747, 1738, 1740</td>
</tr>
<tr>
<td>6</td>
<td>0.11</td>
<td>1694, 1696</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>1645, 1648</td>
</tr>
</tbody>
</table>

Table II. Precipitation Temperature of TiC in Fe-C$_{\text{sat}}$-Ti under Ar

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ti, Mass Pct</th>
<th>Precipitation Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.30</td>
<td>1797, 1800</td>
</tr>
<tr>
<td>9</td>
<td>1.00</td>
<td>1773, 1769</td>
</tr>
<tr>
<td>10</td>
<td>0.30</td>
<td>1667, 1672</td>
</tr>
</tbody>
</table>

where $K_{\text{TiC}}$ and $K_{\text{TiN}}$ are the equilibrium constants of Reactions [3] and [4], respectively:

\[
\text{[Ti]} \ (1 \text{ wt pct}) + \text{C} \ (s) = \text{TiC} \ (s) \quad [3]
\]

\[
\frac{1}{2}\text{N}_2 \ (g) + \text{[Ti]} \ (1 \text{ wt pct}) = \text{TiN} \ (s) \quad [4]
\]

As reviewed recently by Jonsson,$^7$ the available thermodynamic data for the Fe-Ti-N system agrees fairly well. Morita and Kunisada’s$^8$ data for the standard free-energy change for Reaction [4] was recommended$^7$ and given by

\[
\Delta G_{\text{TiN}}^0 = -360,200 + 165.06T \ (J/mol) \quad [5]
\]

However, the available thermodynamic data for the Fe-C$_{\text{sat}}$-Ti system varies significantly. Since it is beyond the scope of the present work to discuss the difference of free energies, the following expression, as used in the previous work,$^9$ was chosen as the standard free-energy change for Reaction [3] and the following discussion on the activity coefficient of titanium is based on this expression.

\[
\Delta G_{\text{Ti}}^0 = -153,700 + 57.53T \ (J/mol) \quad [6]
\]

For the prediction of the minimum titanium concentration required to form Ti(C,N) in Fe-C$_{\text{sat}}$-Ti-N melts using Eq. [2], values of $K_{\text{TiC}}$ and $K_{\text{TiN}}$ can be calculated from the free energies given by Eqs. [5] and [6]. The remaining information required is the activity coefficient of titanium, $f_{\text{Ti}}$, relative to 1 wt pct titanium in the liquid melts. Considering the fact that the solubility of nitrogen in this system is below 0.01 pct, the effect of nitrogen on the activity coefficient of titanium is negligible based on the interaction coefficient data given by Morita and Kunisada.$^8$ Therefore, the activity coefficient of titanium in Fe-C$_{\text{sat}}$-Ti-N melts can be taken as the same value as in the Fe-C$_{\text{sat}}$-Ti melts. Since the activities of carbon and titanium carbide in Reaction [3] are unity, the activity coefficient of titanium can be determined by measuring the solubility of titanium in the Fe-C$_{\text{sat}}$-Ti melts. The solubility of titanium in carbon-saturated iron was studied by Sumito et al.$^{10}$ and recently by Morizane et al.$^9$ From Morizane’s result, the activity coefficient of Ti at 1773 K was calculated to be 0.023 taking the free energy of Reaction [3] as Eq. [6] being in good agreement with Sumito’s results given by

\[
\log f_{\text{Ti}} = -1269 \cdot \frac{1}{T} - 0.96 \quad [7]
\]

The minimum titanium concentrations required to form Ti(C,N) in Fe-C$_{\text{sat}}$-Ti-N melts, predicted using Eq. [2], with values of $K_{\text{TiC}}$, $K_{\text{TiN}}$, and $f_{\text{Ti}}$, calculated using Eqs. [6], [5], and [7], respectively, are shown in Figure 2 as the solid line. The experimental data are also shown in the same figure. It was found that the experimental results differ from the prediction.

Close examination of the available data on the solubility of titanium in the Fe-C$_{\text{sat}}$-Ti melts found significant differences among previous studies, as shown in Figure 3. This suggests that a re-examination of the solubility of titanium is necessary. Samples containing 1.3, 1, and 0.3 wt pct Ti were used and the results are presented in Figure 3. The solubility of Ti from the present study is lower than Sumito’s and Morizane’s but higher than the others. It should be mentioned that in all previous studies the solubility of titanium was determined by chemical analysis of Ti in quenched