Formation of Titanium Carbonitride from Hot Metal

Yun Li, Yongquan Li1) and Richard J. Fruehan

Center for Iron and Steelmaking Research, Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213 USA. 1) Technical Center, Baosteel Co. Ltd., Guoyuan, Baoshan, Shanghai 201900, China.

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1. Introduction

Ironmakers need to prolong the campaign of the blast furnace (BF) while maintaining high productivity, in order to lower the unit capital cost. Premature hearth failure is the main factor limiting blast furnace campaign life. In addition to the proper lining designing, it is crucial to minimize the hearth wall erosion. It was well known that the so-called “titanium bear,”1) which is a precipitate of carbide, nitride and carbonitride of titanium, may form in the BF hearth area if TiO2 presents in the feed. In order to measure the activity coefficient of titanium, the solubility of titanium in carbon-saturated iron was measured and found to be 1.3, 1.0, and 0.3 mass% at temperatures of 1798, 1772, and 1670 K, respectively. The activity coefficient of titanium in carbon-saturated iron is expressed as log fT = −5.41 + 6890/T. Based on the results the conditions for Ti(C,N) formation and the amount of TiO2 addition to a blast furnace were calculated. At 1773 K and 1.0 atm of nitrogen, the minimum titanium in hot metal to form Ti(C,N) was determined to be 0.2 mass%. Under typical blast furnace operation conditions, a titanium load of 3.6–5.2 kg TiO2/THM is required. It was conclude that in situ observation using confocal scanning laser microscope provided us a unique and reliable technique to study thermodynamic of some molten metal systems.

KEY WORDS: blast furnace; titanium carbonitride; hot metal; solubility.

2. Experimental

In situ observation of the formation of the TiC and Ti(C,N) crystals from hot metal was the main experimental method used in this study. A confocal scanning laser microscope (CSLM) equipped with an infrared image furnace was used in the experiments. Detailed description of CSLM are given elsewhere.10,11) 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 loaded to the ring-like platinum sample holder in the CSLM system. The thermocouple used to control the in-
frared furnace, and the temperature from which is recorded, is welded on the platinum sample holder. The temperature difference between the thermocouple and the sample was carefully calibrated using ultra-high purity iron, Fe–Csat, and copper.

The carbon-saturated iron samples were prepared by melting high purity iron chips in an ultra-high purity graphite crucible in argon. In a typical experiment, about 1.3 g of carbon saturated iron together with appropriate amount of Fe–4.0mass%Ti master alloy was put in a 10-mm i.d. alumina crucible and loaded to the infrared image furnace. It was heated to a predetermined temperature, at which no precipitation was expected, under an ultra-high purity argon (99.999 vol% Ar) 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 ultra-high purity nitrogen (99.999 vol% N2) soon after the predetermined temperature was reached. The melt was kept at that temperature for 30 min 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.

To study the characteristics of Ti(C,N) formation under a large temperature gradient, which can exist in blast furnace hearth where local erosion occurred, ‘long crucible’ experiments were carried out. A long (16.5 cm) and thin (0.6 cm) alumina crucible, with a graphite block attached at both ends, were put in a horizontal tube furnace to create a temperature difference from 1 773 K at the hot end to 1 499 K at the cold end in the hot metal. The Fe–Csat–Ti sample was initially heated to 1 773 K in a homogenous temperature zone under argon. After the temperature was stabilized, nitrogen was introduced. The sample was kept there for 30 min before it was pushed to the predetermined temperature gradient zone for additional 30 min. The quenched sample was sectioned and examined using SEM.

3. Results

3.1. Precipitation of Ti(C,N) from Fe–Csat–Ti–N

Precipitation was observed at the surface of the liquid metal during cooling. Figure 1 shows a confocal laser image of the crystals observed on a Fe–0.37mass%Ti–C melt at 1 773 K. In that particular experiment the precipitation started soon after the introduction of nitrogen. The crystals have a rather regular shape of a square or a rectangle. A secondary electron image and EDX element mapping images of the crystal on the surface of a quenched sample are shown in Fig. 2. It appears that the crystals are titanium nitride. In the crystal, the titanium and nitrogen contents are high whereas carbon content is much lower than that in the background iron. The activity of TiC in a Fe–Csat–0.37mass%Ti melt at 1 773 K is about 0.28 based on the data of Sumito et al.12) and Morizane et al.6) In the ideal solid solution of TiC(N) with $\alpha_{\text{TiC}}=0.28$, the carbon content should be 5.5 mass% which is higher than the carbon content in the metal. However, the EDX mapping showed much lower carbon content in the crystal than that in the metal. Therefore, the crystals are likely to be primari-
the metal movement. The crystals with smooth surfaces did not stick together even if they touched. Figure 4 shows the SEM image of the crystals and the EDX element mapings. The results indicate 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 CKα, NKα, and L peaks of Ti. Unlike the crystals shown in Fig. 2, the carbon content in these crystals appear to be higher than that in the metal. This indicates that Ti(C,N) rather than TiN was formed, presumably due to the lower activity of TiN (less than one) in this case.

The precipitation temperature was determined as the temperature at which the first Ti(C,N) crystals was observed during cooling. 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 5.0 min after each drop. Gradually finer steps were used when the temperature approached the precipitation temperature determined previously. This was done in order to ‘pin point’ the precipitation temperature. The results are listed in Table 1. 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 hard to dissolve; or more precisely, the rate of dissolution is 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.

3.2. Precipitation of Ti(C,N) from Fe–C sat–Ti–N under Large Temperature Gradient

Results in Table 1 indicated that the precipitation temperature of Ti(C,N) decreases with titanium concentration in hot metal. In other words for hot metal with a given titanium concentration, Ti(C,N) will form at low temperature zone. This could be the mechanism of the formation of Ti(C,N) rich ‘bear’ in the blast furnace hearth: when local erosion occurs, the temperature decreases and Ti(C,N) forms until the temperature recovers to a level above the Ti(C,N) precipitation temperature. To demonstrate this process, experiments with large temperature gradient were carried out. Figure 5 shows the SEM images near the crucible wall in sections at different temperatures. Most of crystals are accumulated in the cold end of the long crucible. With the temperature increase, the number and the size of the Ti(C,N) crystals decrease. Only a few small crystals were found at the hot end. This is in good agreement with the results from the precipitation temperature measurement on the cofocal scanning laser microscope.

4. Discussion

4.1. Minimum Titanium Content in Fe–C sat–Ti Required to form Ti(C,N)

As discussed recently by Bergsma and Fruehan, titani-
um carbonitride may form in Fe–C sat melt if both Ti and N exist, and when
\[ K_{TiC}a_{Ti} + K_{TiN}P_{N2}^{1/2}a_{Ti} = 1.0 \] ........................(1)

The minimum titanium concentration to form titanium carbonitride in carbon-saturated iron was deduced as
\[ [Ti, \text{mass}\%] = \frac{1}{(K_{TiC} + K_{TiN}P_{N2}^{1/2})f_{Ti}} \] ........................(2)

where \( K_{TiC} \) and \( K_{TiN} \) are the equilibrium constants of the reactions (3) and (4), respectively.

\[ 1/2 N_{2}(g) + [Ti](1 \text{mass}\%) = TiN(S) \] ..............(4)

As reviewed recently by Jonsson, the available thermodynamic data for the Fe–Ti–N system agrees fairly well with each other. Morita and Kunisada’s data for the standard free-energy change for reaction (4) was recommended and given by
\[ \Delta G_{\text{f}}^\circ = -360 200 + 165.06T \text{ (J/mol)} \] ........................(5)

However, the available thermodynamic data for the Fe–C 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, 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.
\[ \Delta G_{\text{f}}^\circ = -153 700 + 57.53T \text{ (J/mol)} \] ........................(6)

For the prediction of the minimum titanium concentration required to form Ti(C,N) in Fe–C sat–Ti–N melts using Eq. (2), values of \( K_{TiC} \) and \( K_{TiN} \) can be calculated from the free energies given by Eqs. (5) and (6). The remaining information required is the activity coefficient of titanium, \( f_{Ti} \), relative to 1 mass% titanium in the liquid melts. Considering the fact that the solubility of nitrogen in this system is below 0.01 mass%, the effect of nitrogen on the activity coefficient of titanium is negligible based on the interaction coefficient data given by Morita and Kunisada. Therefore, the activity coefficient of titanium in Fe–C sat–Ti–N melts can be taken as the same value as in the Fe–C 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 sat–Ti melts. The solubility of titanium in carbon saturated iron was studied by Sumito et al. and recently by Morizane et al. From Morizane’s result, the activity coefficient of Ti at 1 773 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
\[ \log f_{Ti} = -\frac{1 269}{T} - 0.96 \] ........................(7)

The minimum titanium concentration required to form Ti(C,N) in Fe–C sat–Ti–N melts, predicted using Eq. (2) with values of \( K_{TiC} \), \( K_{TiN} \), and \( f_{Ti} \) calculated using Eqs. (6), (5) and (7), respectively, are shown in Fig. 6 as the solid line. The experimental data are also shown in the same figure. It was found that the experimental results differ significantly from the prediction. The activity coefficient of titanium was recently re-evaluated by Li and Fruehan. The new value of \( f_{Ti} \) in Fe–C sat–Ti system is given by
\[ \log f_{Ti} = \frac{6 890(\pm 50)}{T} - 5.41(\pm 0.01) \] ........................(8)

At 1 773 K the activity coefficient of Ti is 0.03, slightly higher than 0.023 obtained by Morizane et al., but the temperature dependence differs considerably with that obtained by Sumito et al. Using Eqs. (6), (5), and (8) for the calcu-
lution of $K_{\text{Ti:C}}$, $K_{\text{Ti:N}}$, and $f_{\text{Ti}}$, respectively, the minimum Ti concentration was re-calculated using Eq. (2). The result is presented in Fig. 6 as a broken line. From Fig. 6 it can be seen that the re-calculated values are closer to the experimental results than previous prediction in the temperature range relevant to the blast furnace operation.

Delve et al.\textsuperscript{16} measured the solubility of titanium in carbon-saturated iron under 1.0 atm of nitrogen. Their results showed a lower titanium solubility. In their analysis only the acid-soluble portion of titanium was considered. However, part of titanium originally in solution in the liquid iron would inevitably be transformed into Ti(C,N) during solidification. Therefore, their data is likely lower than the actual titanium solubility.

4.2. Use Titanium-Bearing Feed in the Blast Furnace to Protect the Hearth

As discussed previously,\textsuperscript{9} it is necessary to control the amount of titanium-bearing ore added to the blast furnace to effectively protect the hearth refractories while maintain a smooth operation. The calculations by Bergsma and Fruehan\textsuperscript{9} were basically repeated using the new thermodynamic data. Based on the new value for $f_{\text{Ti}}$, and taking a typical blast furnace operation condition being a hot metal temperature of 1 773 K and $P_{\text{N}_2}$ of 2.3 atm, the minimum titanium concentration to form Ti(C,N) is about 0.18 mass%.

The required titania concentration in the slag is 1.8 to 2.6 mass% taking [mass%Ti]/(mass%TiO\textsubscript{2}) ratio being between 0.07 and 0.1. For a typical slag volume of 200 kg/tHM, the corresponding titanium load of 0.18 mass% titania in the slag is 3.6 to 5.2 kgTiO\textsubscript{2}/tHM. Chao et al.\textsuperscript{21} reported that the TiO\textsubscript{2} intake for the ‘preventive approach’ is generally 3–5 kgTiO\textsubscript{2}/tHM unless a ‘remedial approach’, with a much higher TiO\textsubscript{2} load but short in duration, is required when excessive erosion is detected. It appears that the prediction based on the results from the present study agrees fairly well with that used in blast furnace operation. Figure 7 shows the predicted, based on the experimental data from the present study, minimum titanium load in blast furnace required for the formation of Ti(C,N) in the hearth. Results from previous study\textsuperscript{9} indicated that titanium distribution between hot metal and blast furnace slag has the following relationship with silicon distribution.

$$\frac{[\text{Ti}]}{(\text{TiO}_2)} = 5.2 \frac{[\text{Si}]}{(\text{SiO}_2)} - 0.006 \hspace{1cm} (9)$$

Typical blast furnace slag contains about 35 mass% of SiO\textsubscript{2}. The ratio [Ti]/(TiO\textsubscript{2}) in Fig. 7 can therefore be translate to silicon content in hot metal, a more practical number for blast furnace operators. The minimum titanium load required to form Ti(C,N) is plotted as an function of [Si] mass% and temperature of the hot metal in Fig. 8.

It should be noted that above estimation is based on the bulk condition in the blast furnace. In fact the formation of Ti(C,N) in the bulk liquid iron would be detrimental since it would increase the viscosity of the hot metal, and when float up and absorbed in the slag, increase the viscosity of the slag. A perfect scenario is the titanium in the hot metal is slightly lower than that is required to form Ti(C,N) at the bulk hot metal temperature. When local erosion occurs, the local temperature will drop and Ti(C,N) will form prefer-
able at that location until enough ‘titanium bear’ is formed and the temperature recovers to the level above the Ti(C,N) precipitation temperature.

5. Summary and Conclusions

(1) A confocal scanning laser microscope with an infrared image furnace was successfully used for in situ observation of TiC and Ti(C,N) precipitation from Fe–C sat–Ti melt. The new experimental technique has the advantage over the traditional equilibrium technique by eliminating the uncertainties associated with sample quenching.

(2) The solubility of titanium in carbon-saturated iron without the presence of nitrogen is 1.3, 1.0, and 0.3 mass% at temperature of 1 798, 1 772, and 1 670 K, respectively.

(3) The minimum titanium in carbon-saturated iron required to form Ti(C,N) was determined at $P_{N_2} = 1.0$ atm in the temperature range of 1 645 to 1 785 K.

(4) Under typical blast furnace operation conditions, a titanium load of 3.6–5.2 kgTiO$_2$/tHM is required to effectively protect the hearth by forming Ti(C,N) rich accretion.

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REFERENCES