THERMODYNAMICS OF TiO_X IN BLAST FURNACE SLAGS

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ABSTRACT

The activity of TiO_x (TiO_2 or $TiO_{1.5}$) is an important thermodynamic parameter for predicting the formation of titanium nitride, carbide and carbonitride in the blast furnace hearth. The formation of TiN, TiC and Ti(C,N) is desirable because it protects the hearth bricks against local erosion. However excessive amounts adversely effect the operations due to high viscosity. A gas-slag-metal equilibration technique is being used to determine the activity of TiO_x in blast furnace type slags at 1773 K. The titanium content of iron-carbon alloys that is in equilibrium with slags was determined. The activities of $TiO_{1.5}$ and TiO_2 were determined from the preliminary experimental results. The composition of Ti(C,N) that may form in the blast furnace hearth was calculated. The mole fractions of $TiO_{1.5}$ and TiO_2 in blast furnace slags were estimated for the formation of TiC and Ti(C,N) from the available data in the literature.

1. INTRODUCTION

Titanium enters the blast furnace as a titanium oxide compound associated with iron oxide or is deliberately added to the blast furnace burden. Titanium increases the viscosity of the slag and causes some operational problems such as slag thickening and accretions.(1-9) The slag thickening and accretions is due to the formation of titanium carbonitride, Ti(C,N) and/or TiC. However, the formation of some titanium carbide and carbonitride is desirable because it protects the hearth bricks against local erosion. If sufficient amounts of titanium oxide are added into the charge of the blast furnace it reacts with carbon and nitrogen in the system to form titanium carbonitride, Ti(C,N), that forms a protective layer against local erosion of the refractory brick in the blast furnace hearth. However, if too much Ti(C,N) forms, the slag viscosity becomes very high and it is very difficult to tap the slag.

The effect of titania on the slag properties and on the blast furnace operations have been the subject of many investigations. Ohno and Ross(5) investigated the smelting behavior of titaniferous iron ores in the blast furnace. The thickening rate increases by an increase in titania content and decreased by an increase in basicity. The optimum slag composition was determined from the viscosity investigation to be lime to silica ratio of 0.63 to 1.06 with 20 to 40 % titania. The thickening of the slags took place in the presence of solid carbon and is slightly promoted by the presence of nitrogen. This may be due to the formation of titanium carbonitride.

Handfield and Charette(10) studied the viscosity of high titania containing slags originating from industrial electric arc smelting furnaces. They found that regardless of their FeO content, industrial high titania containing slags are very fluid melts once completely molten and the viscosity of these molten slags remains fairly constant, even with further increase in temperature. They concluded that the main factor seriously affecting the fluidity of industrial high titania slags is presence of the solid particles in the melt.

Fine and Arac(11) investigated the effect of TiO_2 on the liquidus temperatures of blast furnace type slags. They found that at low oxygen potentials, increasing the TiO_2 content of the slag from 0.83% to 3.27% increases the liquidus temperature of blast furnace slags, while at high oxygen potential, TiO_2 decreases the liquidus temperature.

Datta et al.(9) studied the high temperature properties of blast furnace slags containing high alumina and manganese oxide. It was found that a titania content up to 2% fluidizes the slag and also lowers the liquidus temperature. The titanium bearing accretions of the blast furnaces was between 2.5 and 5.5% and titanium bearing compounds in the slag showed traces of TiC, TiN, Ti_2N, TiO, Ti_2O_3, Ti_3O_5, and Ti_5O_9.

Benesch et al.(12,13) measured the distribution of titanium between slag and metal saturated with carbon at temperatures of 1723, 1773 and 1823 K. They found that the reduction of TiO_2 from the slag reached equilibrium after 6 hours. They obtained less than 0.3% Ti in carbon saturated iron in equilibrium with a slag containing 15% TiO_2 at 1773 K. They also observed that TiC was formed in all metal samples equilibrated with the slags, even the ones containing 0.5% TiO_2 which was not expected thermodynamically at 1773 K. Chukukere and Ross(7) also studied the reduction behavior of TiO_2 in blast furnace type slags containing 10% FeO. They found that titania is reduced faster from basic slag than acid slags and the amount of titania reduced increased with the basicity (CaO/SiO_2).

Tanabe and Suito(14) investigated the thermodynamics of nitrogen in the CaO - TiO_2 - $TiO_{1.5}$ system using a gas - slag equilibration technique was used. The oxygen potential in the system was controlled by H_2 - H_2O equilibrium. They found that titanium in the slags exist in the forms of Ti^{3+} and Ti^{4+}. The Ti^{4+} content of the slag was obtained by analyzing the slags for Ti^{3+} and total titanium after the experiments. It was indicated that the ratio of Ti^{3+} to Ti^{4+} strongly depends on oxygen potential and slag composition. A linear relationship with slope of -1/4 was obtained from a plot of $\log(\%\ Ti^{3+}/Ti^{4+})$ versus $\log P_{O_2}$. Their results indicate that at low oxygen potentials titanium in the slag is predominantly in the form of Ti^{3+}. It was also found that the Ti^{3+}/Ti^{4+} ratio decreases with increasing the

CaO content of the slag at constant temperature and oxygen pressure.

Equilibrium between CaO - Al_2O_3 - TiO_x slags and liquid Fe - 20% Cr alloy was studied by Kishi, Inoue and Suito(15) at 1873 K in order to determine the thermodynamics of nitrogen and oxygen in the system. The Ti^{3+} and Ti^{4+} contents of the slags were determined after the experiments. The $X_{TiO_{1.5}}/X_{TiO_2}^{3/4}$ values increases with log[% Ti]. The ratio of Ti^{3+}/Ti^{4+} is strongly dependent on the oxygen partial pressure. The activity coefficients of γ_{TiO_2} *and* $\gamma_{TiO_{1.5}}$ were calculated from the experimental data. The activity coefficient of TiO_2 does not change with the titanium content of the metal.

Schreiber et al.(16) studied the redox equilibria of Ti^{3+} and Ti^{4+} in blast furnace type slags (51.6% SiO_2, 2.3 % Al_2O_3, 19.2% CaO and 26.9% MgO) as a function of melt temperature and oxygen pressure. The experiments were carried out at oxygen pressures (10^{-5} to 10^{-9} atm) higher than the ones exist near blast furnace heart.

In order to predict the formation of Ti(C,N), TiC or TiN in the blast furnace, it is necessary to have information on the thermodynamics of TiO_x in blast furnace type slags. The activity of TiO_X in blast furnace type slags is unknown. Therefore, it is purpose of this investigation to determine the activity and activity coefficient of TiO_x in blast furnace type slags.

The results that are presented in this manuscript are preliminary ones. Experiments are underway to determine the activities of TiO_2 and $TiO_{1.5}$ in blast furnace slags. The effect of basicity on activities will be determined. The results will be presented at the meeting.

2. EXPERIMENTAL PROCEDURE

A gas-slag-metal equilibration technique was used to study the thermodynamics of TiO_x in blast furnace type slags. The experiments were carried out in a 4.3 cm in diameter and 114 cm long recrystallized alumina reaction tube in a carbon resistor furnace. A 32.7 mm inside diameter, 36.0 mm outside diameter, 50.0 mm height MgO crucible was used to contain the slag and metal. The MgO crucible was kept in position by a Mo wire basket. A Pt-Pt/10% Rh (S type) thermocouple inside a protection tube was placed in the bottom part of the hot zone in order to measure and to control the temperature of the system.

Master alloys containing different amounts of carbon was prepared by melting electrolytic iron (99.99%) and pure carbon (99.999%) in a magnesia crucible under an argon atmosphere using the high frequency induction furnace. The melts were quenched and cut to desired sizes. Carbon saturated alloys are melted in a graphite crucible.

A master slag was prepared by mixing desired amounts of analytical grades of CaO,

SiO_2, MgO and Al_2O_3. The mixture was mechanically mixed and melted in a magnesia crucible in the high frequency induction furnace using a graphite susceptor. The master slag was crushed to the desired size. The master slag was then analyzed and the chemical composition of the master slag is given in Table 1. The desired amount of titanium dioxide were added to the crushed premelted slag.

Table 1: Chemical Composition of Master Slag.

% CaO	% Al_2O_3	% MgO	% SiO_2
39.97	7.25	10.62	42.16

For each experiment, 20 grams of metal and 25 grams of slag was placed in a MgO crucible that was suspended from a molybdenum rod. The crucible and its contents were slowly lowered into the hot zone of the furnace which was kept at 1773 K under a purified argon atmosphere. Then the argon was replaced by pure CO when the sample was in the hot zone. The total flow rate of CO was kept at around 300 cc/min. After the desired equilibration time the sample was taken out from the furnace and quenched. The slag and the metal phases were separated. The metal samples were analyzed for titanium by using spectrophotometer and checked by ICP (ionic conductive plasma analysis). The metal was also analyzed for carbon. The slag samples were analyzed by using AAS (atomic absorption spectrometer) to determine Ca, Mg, Ti, and Al . The slags were also analyzed for Ti^{3+}. About 0.5 grams of slag was dissolved under a CO_2 atmosphere using a hot solution containing 60 ml of HCl (1+1), 40 ml of HF (1+1), and 20 ml of ferric chloride standard solution (1 w/v-% Fe^{3+}). Then the solution was titrated with potassium dichromate. During titration Fe^{2+} ions produced by the exchange reaction: $Fe^{3+} + Ti^{3+} = Fe^{2+} + Ti^{4+}$. The Ti^{4+} content was determined by subtracting Ti^{3+} content from total Ti content.

A series of experiments is being carried out to determine the activity coefficient of titanium in Fe-C alloys. For those experiments 25 grams of Fe-C alloy and a 6 g cylindrical pellet of TiC was held in a magnesia crucible and equilibrated under a purified argon atmosphere. The TiC pellets were made by using an isostatic press and they were sintered at 1973K. After 24 hours of equilibration time, the sample was pulled out and quenched in water. The metal sample was cleaned and analyzed for Ti.

3. RESULTS AND DISCUSSION

Preliminary experiments were conducted with metal containing 1.91%C and the slag containing 10% TiO_2 as a function of time to determine the equilibration time. It was attempted to each equilibrium both from metal and slag side. Titanium content of the metal as a function of equilibration time is plotted in Figure 1.

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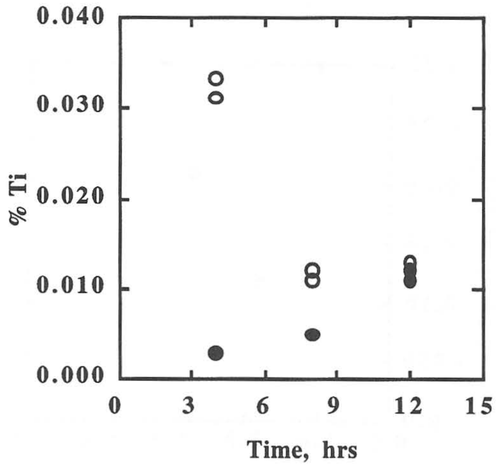

Figure 1: Titanium content of metal containing 1.91%C as a function of time at 1773 K.

The experimental results shown in Figure 1 indicate that the system has reached equilibrium and 12 hours of reaction time is sufficient to obtain equilibrium under present experimental conditions. Therefore, all of the subsequent experiments were conducted for 12 hours. In order to ensure equilibrium a small amount of titanium (0.015% Ti) was also added into the metal. The experimental results are plotted in Figure 1. The data shown in Figure 1 indicates that also the equilibrium titanium content of the metal is too low. Therefore, it was decided to increase the final titanium content of metal by increasing the activity of the carbon without precipitation of TiC.

In a series of experiments, metal saturated with carbon was used in order to have a higher equilibrium titanium level in the metal which can be analyzed more accurately. The preliminary results from the experiments with carbon saturated iron are summarized in Table 2. The data indicates that the Ti content of the metal increases with the Ti content of the slag. All the slag samples were analyzed for total titanium. The chemical analysis are under way to analyze the slag samples for Ti^{3+}. Only a few samples were analyzed for Ti^{3+} to date. The Ti^{4+} content of the samples was obtained from total Ti and Ti^{3+}.

Table 2. Titanium content of the carbon saturated metal at different Ti levels in slag.

% Ti in Slag	% Ti in Metal
1.82	0.37
2.71	0.73
4.14	0.84

Activity of $TiO_{1.5}$ and TiO_2

The titanium oxide, $TiO_{1.5}$, in a slag phase is reduced by carbon in metal according to the following overall reaction:

$$TiO_{1.5}(s) + 3/2C\ (s) = \underline{Ti}\ (1wt.\ \%) + 3/2CO(g) \qquad (1)$$

$$\Delta G^\circ = 550573 - 301.79T \text{ Joules}^{(17)} \qquad (2)$$

From equation (1), the following relation is obtained for the activity of $TiO_{1.5}$ using the equilibrium constant for reaction (1), K_1.

$$a_{TiO_{1.5}} = \frac{f_{Ti}\ [\%Ti]\ P_{CO}^{3/2}}{K_1\ a_C^{3/2}} \qquad (3)$$

Where a_i is the activity of i, P_{CO} is the pressure of carbon monoxide, f_{Ti} is the activity coefficient of titanium in 1 wt.% standard state and [% Ti] is the titanium content of the metal phase. Under the experimental conditions, the activity of carbon is unity and pressure of the CO is 1 atmosphere. The titanium content of the metal that is in equilibrium with the carbon saturated iron and TiC was measured by Sumito et al.(18) at different temperatures. From this data the activity coefficient of Ti, f_{Ti}, in carbon saturated iron is calculated to be 0.112 at 1773 K. Then the activity of $TiO_{1.5}$, with respect to pure solid, was calculated from equation (3) using experimental data presented in Table (2). The results are plotted in Figure (2). The data shown in Figure (2) indicates that the activity increases with the Ti content of the slag. It must be noted that these are just preliminary results. The activity coefficient of $TiO_{1.5}$ cannot be calculated at the present time because the mole fraction of $TiO_{1.5}$ in all the slag is unknown. The activity coefficients will be calculated once the slags are analyzed for Ti^{3+}. However the ratio of Ti^{3+}/Ti^{4+} ratios for different slags at different oxygen potentials were measured by Kishi et al.(15). Results indicate that the Ti^{3+}/Ti^{4+} ratio is strongly dependent on oxygen potential and slag composition. This data was not used to calculate the activity coefficient of $TiO_{1.5}$ since the slag compositions used by Kishi et al. are different than the ones used this in study.

Similarly, the activity of TiO_2 can be obtained from the following reaction.

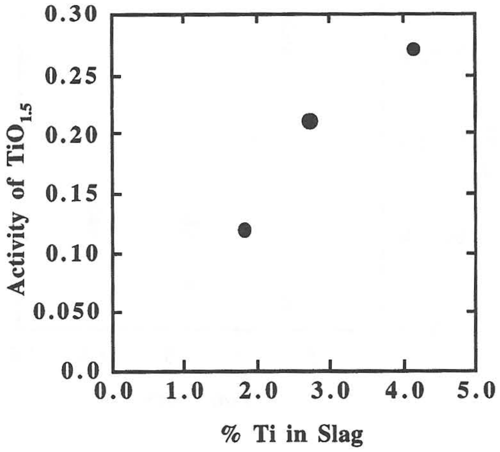

Figure 2. Activity of $TiO_{1.5}$ as a function of Ti in slag at 1173 K.

$$TiO_2(s) + 2C\,(s) = Ti\,(1\ wt.\%) + 2CO(g) \qquad (4)$$

$$\Delta G° = 681072 - 394.72T\ \text{Joules} \qquad (5)$$

The activity of TiO_2 with respect to pure solid TiO_2 was calculated from the data presented in Table (2) for the conditions used in the calculation of $TiO_{1.5}$. The calculated data is presented in Figure (3). Again the activity increases with the Ti content of the slag. The activity coefficients were not calculated due the reason indicated above. More detailed results will be presented at the symposium.

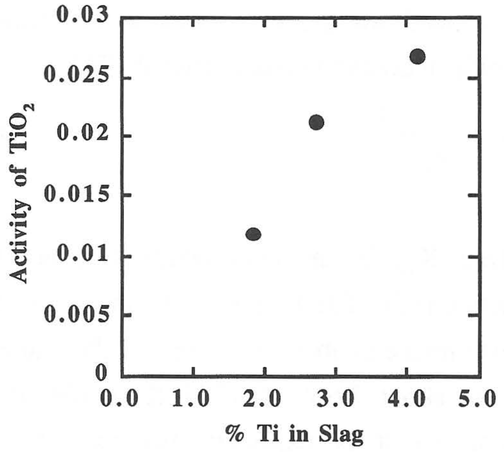

Figure 3. Activity of TiO_2 as a function of Ti in slag at 1173 K.

Calculation of Critical Slag Composition:

The precipitation of titanium carbide or carbonitride is desirable to the protection of hearth brick. Therefore it is important to estimate the amount of titania needed for the precipitation of titanium carbide, nitride or carbonitride. For example, the precipitation of titanium carbide from slag can be written as:

$$TiO_2\ (s) + 3C\ (s) = TiC\ (s) + 2CO\ (g) \quad (6)$$

$$\Delta G^\circ = 553460 - 338.44T \text{ Joules} \quad (7)$$

The following equation is obtained by using the equilibrium constant

$$X_{TiO_2} = \frac{P_{CO}^2}{\gamma_{TiO_2} K_6} \quad (8)$$

For the derivation of equation (8) it was assumed that activities of carbon and titanium carbide are unity in the blast furnace. The activity coefficient of TiO_2 in the blast furnace slag is not known. However, the activity coefficients of TiO_2 were determined by Kishi et al.(15) in the CaO - Al_2O_3 -TiO_x and BaO - Al_2O_3 - TiO_x systems at 1873 K. For a slag containing about 23.2% Ca, 29.5% Al, 2.9% Ti^{3+} and 3.7% Ti^{4+}, the value of γ_{TiO2} is 2.6. Activity coefficient of TiO_2 can be obtained at 1773 K assuming a regular solution model. The value of activity coefficient is 2.74 at 1773 K if the solution is regular. The blast furnace gas contains about 20 % CO in the combustion zone of the furnace and the total pressure is about 2 atm. The mole fraction of TiO_2 in equilibrium with pure solid C and TiC at P_{CO} of 0.4 atm is 0.0025. The mole fraction of TiO_2 must be greater than 0.0025 in order to form the TiC in the blast furnace hearth at 1773 K. However if P_{CO} is 0.80 atm the mole fraction of TiO_2 will be 0.011. Similar calculations also can be carried out for pure TiN.

Titanium carbide also forms from $TiO_{1.5}$. The precipitation reaction can be written as:

$$TiO_{1.5}\ (s) + 5/2C(s) = TiC(s) + 3/2\ CO(g) \quad (9)$$

$$\Delta G^\circ = 420701 - 246.14T \text{ Joules} \quad (10)$$

$$X_{TiO_{1.5}} = \frac{P_{CO}^{3/2}}{\gamma_{TiO_{1.5}} K_9} \quad (11)$$

The concentration of $TiO_{1.5}$ that is necessary to form TiC can also be obtained for the conditions used in the calculations for TiO_2 in a similar way. The activity of $TiO_{1.5}$ is 33 for a slag containing 23.2% Ca, 29.5% Al, 2.9% Ti^{3+} and 3.7% Ti^{4+} at 1873 K.(15) The activity coefficient of $TiO_{1.5}$ is 40.2 at 1773 K if one assumes a regular solution . The mole fraction of $TiO_{1.5}$ which is in equilibrium with pure solid C and TiC, and pressure of CO 0.8 atm at 1773 K obtained from equation (11) is 0.0061. The concentration of $TiO_{1.5}$ must be greater than 0.0061 in order to form TiC for the conditions used in the calculations. If P_{CO} is 0.4 atm the equilibrium mole fraction of $TiO_{1.5}$ will be 0.0022.

It must be noted that the calculated values are the best estimates based on the data available in the literature. The activity coefficients of TiO_2 and $TiO_{1.5}$ are strongly dependent on slag compositions and temperature. Therefore, the activity coefficients used for the calculations may be different from the ones for the blast furnace type slags. The activity coefficients of TiO_2 and $TiO_{1.5}$ are currently being measured. The above calculations will be made from the obtained data and will be present at the conference.

Titanium carbonitride may also precipitate in the blast furnace. The composition of titanium carbonitride that forms in the blast furnace can be estimated from the following reaction:

$$TiC(s) + 1/2N_2(g) = TiN(s) + C(s) \qquad (12)$$

$$\Delta G° = -177568 + 83.22T \text{ Joules} \qquad (13)$$

The activities of TiN and TiC in titanium carbonitride were measured by Ozturk and Fruehan.(19) The results indicate that the activities are equal to their respective mole fractions. The activity of carbon is unity in the blast furnace hearth. From the equilibrium constant of reaction (12) the following relation is obtained for the mole fraction of titanium carbide in titanium carbonitride at 1773 K.

$$X_{TiC} = \frac{1}{P_{N_2}^{1/2} K_{12} + 1} \qquad (14)$$

Where K_{12} is the equilibrium constant for reaction (12). The pressure of nitrogen in the blast furnace is about 1.2 atm and the value of K_{12} is about 7.665 at 1773 K. Under these conditions it is expected that the titanium carbonitride containing 10.6 mole % TiC and 89.4 mole % TiN forms. Similarly, the composition of titanium carbonitride can be estimated at different temperatures and nitrogen pressures. The mole fraction of TiC will be about 0.0934 if nitrogen pressure is 1.6 atm. One can also calculate the equilibrium concentrations of TiO_2 and $TiO_{1.5}$ which is in equilibrium with titanium carbonitride. The titanium content of the metal can be obtained from one of the following equilibrias since the composition of Ti(CN) is known:

$$Ti\ (1\ \text{wt.\%}) + C(s) = TiC(s) \qquad (15)$$

$$Ti\ (1\ \text{wt.\%}) + 1/2N_2(g) = TiN(s) \qquad (16)$$

The titanium content of the metal phase in equilibrium with titanium carbonitride containing 10.6 mole% TiC and 89.4 mole % TiN is about 0.015%. Then the activities of $TiO_{1.5}$ and TiO_2 can be calculated from reactions (1) or (4) since the equilibrium Ti content of the metal is known. The activities of TiO_2 and $TiO_{1.5}$ must be greater than 0.0026 and 0.0037 respectively in order to form the Ti(C,N). The concentrations of TiO_2 and $TiO_{1.5}$

cannot be calculated since activity coefficients in blast furnace slags are not known.

4. CONCLUSIONS

The activity of TiO_x is an important thermodynamic parameter for predicting the formation of TiC, TiN and Ti(C,N) in the blast furnace hearth. A gas-slag-metal equilibration technique is being used to determine the activity of TiO_x in blast furnace type slags at 1773 K. The titanium content of carbon saturated iron in equilibrium with slags containing titanium was determined. The activities of $TiO_{1.5}$ and TiO_2 were determined from the preliminary experimental results. The mole fractions of $TiO_{1.5}$ and TiO_2 in the blast furnace slag that is necessary to form TiC, TiN and Ti(C,N) were estimated from the available data in the literature. Calculations indicate that Ti(C,N) containing 10.6 mole % TiC and 89.6 mole % TiN may form in the blast furnace at 1773 K.

5. ACKNOWLEDGMENTS

The authors would like to thank the member companies of the Center for Iron and Steelmaking Research at Carnegie Mellon University, the Turkish Scientific and Research Council for providing financial support for A. Aydogdu and Nippon Steel Corporation for providing financial support to Y. Morizane.

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