Carbon Dissolution Behaviors in MO(M=Ca, Ba)–B₂O₃ Slags

Sung-Hwan KIM, Yung-Jun KIM,1) Jung-Ho PARK1) and Chang Hee RHEE2)

Formerly Graduate Student, Department of the Materials Science and Engineering, Pohang University of Science and Technology, Pohang, now at KyoungNam Metal Co. Ltd in Changwon, Korea.
1) Graduate student, Department of the Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Korea. 2) Department of the Materials Science and Engineering, Pohang University of Science and Technology, Pohang, Korea.

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Carbon is known to dissolve into slag as carbide ion (C₂⁻) under a low oxygen partial pressure. In order to clarify these mechanisms of carbon dissolution, carbon solubility was measured both in acidic and basic slags under various oxygen partial pressures and temperatures. In basic slags, carbon solubility in MO(M=Ca, Ba)–B₂O₃ slags decreased with increasing the oxygen partial pressure and increased with increasing basicity confirming the carbide ion formation mechanism. But in acidic slags, carbon solubility in MO(M=Ca, Ba)–B₂O₃ slags decreased with increasing basicity and oxygen partial pressure. In order to explain these phenomena, the probable mechanism was discussed and suggested on the basis of experimental results. The model of nitrogen dissolution into slag was compared to that of carbon dissolution to find similar effects of basicity on the dissolution behaviors.

KEY WORDS: carbide; carbon dissolution; basicity; oxygen partial pressure; mechanism; acidic; basic.

1. Introduction

The solubility of carbon in various slag systems has been studied by many researchers1–8) and several reaction mechanisms of carbon in liquid slag were proposed.

Schwerdtfeger et al.1) measured carbon and nitrogen solubility in CaO–Al₂O₃ melts at 1873 K, and proposed that carbon would dissolve either as a cyanide (CN⁻) ion or carbide (C₂⁻) ion. On the other hand, Suito et al.6) explained carbon dissolution behavior in CaO–Al₂O₃ liquid slag by introducing carbide/carbonate (CO₃²⁻) ion formation mechanism.

Song7) measured carbon dissolution in CaO–Al₂O₃ and CaO–SiO₂ liquid slag at 1873 K. As shown in Fig. 1, with increasing oxygen partial pressure, carbon content in liquid slag decreased at low oxygen partial pressure, while it increased at relatively high oxygen partial pressure.

To explain this, carbide/carbonate ion mechanism was used, the intercept of two different behaviors was found at \( P_{O_2} = 10^{-10} \) atm.

In this study, the carbon dissolution in MO(M=Ca, Ba)–B₂O₃ slags with wide range of basicity was measured to clarify the mechanisms of carbon dissolution into slag system by changing the composition of the basic oxides, oxygen partial pressures, and temperature. Based on the experimental results, reaction mechanisms in basic and acidic slag were proposed and compared to other studies.

2. Experimental

A schematic diagram of experimental apparatus is shown in Fig. 2. The experiments were carried out by equilibrating the slags contained in a graphite crucible (ID 16 mm, OD 20 mm, Height 50 mm) under CO–Ar gas mixture.

Temperature was controlled within ±3 K. Master slags were prepared by melting a mixture of reagent grade CaO (calcined 5 hr at 1473 K for removing the remaining CaCO₃), BaO, and B₂O₃ in a graphite crucible under Ar atmosphere for 2–3 hr. The crucible with 7 g of mixed slags was put into the hot zone of a furnace and maintained 18 hr. The time for equilibration was preliminary determined.

After equilibration, the samples were quenched by Ar gas, and crushed for chemical analysis. CaO in the slags...
was analyzed by permanganate titration, BaO by gravimetric method, and carbon by LECO thermal analyzer.

3. Results and Discussion

3.1. Effects of Basicity on Carbon Dissolution

Carbon dissolution behaviors with basicity change in CaO–B₂O₃ and BaO–B₂O₃ slags are shown in Fig. 3. Experiments were carried out by the composition change of the basic oxide (CaO, BaO) and the activities of basic oxide used in this graph were estimated by using the Min’s data. In this study, the activity of basic oxide was used as a scale of basicity.

In both systems, carbon dissolution decreased with increasing basicity, and showed a minimum, then increased with basicity. For the purpose of explanation, the region in which carbon dissolution decreased with basicity would be called as acidic region and the region in which carbon dissolution increased with basicity would be called as basic region in this paper from here.

To compare the results more clearly, the concept of carbide capacity was introduced.

The definition of carbide capacity is shown in Eq. (1). As it can be seen in Eq. (1), the carbide capacity depends on the basicity (a_{O^2-}) and the oxygen partial pressure at fixed temperature.

\[ C_e = \left( \text{wt}\% C \right)^{2m} \cdot \frac{a_{O^2-}^{m}}{a_{C}^{n}} = K \cdot \frac{a_{O^2-}^{m}}{f_{C^{n+}}} \]  

Where \( K \) is the equilibrium constant, \( f_{C^{n+}} \) is an activity coefficient of a carbide ion and \( a_{O^2-} \) is an activity of a free oxygen ion.

The results of carbide capacity are plotted with the results of other studies in Fig. 4. While other studies show a linear relationship between carbide capacity and \( X_{\text{CaO}} \), increasing carbide capacity with \( X_{\text{CaO}} \) showed different behavior between basic and acidic region in this study, indicating the possibility of different carbon dissolution mechanisms in each region.

3.2. Effects of Oxygen Partial Pressure on Carbon Dissolution in the Basic Region

To clarify the effects of oxygen partial pressure on carbon dissolution in basic slags, the oxygen partial pressure was varied from 10⁻¹⁶ atm to 10⁻¹⁰ atm using C/CO equilibrium (2C+O₂=2CO) in each case with slags saturated...
by basic oxide. The results are shown in Figs. 5(a) and 5(b). Both diagrams show that the carbon content in slag decreased with increasing oxygen partial pressure; having the slope of −0.42 in CaO–B2O3 and −0.5 in BaO–B2O3 slags, respectively.

Considering the effects of both basicity and oxygen potential, following mechanism may explain carbon dissolution behavior in the basic region.

\[
2(C)+2(O^{2-})=2(C_{2}^{2-})+\frac{1}{2}(O_{2}) \quad \text{............(2)}
\]

If the carbon dissolution into slags follows Eq. (2), theoretically, the effects of oxygen partial pressure should be −1/2 and the effects of basicity are unity. The effects of oxygen potential in this study (−0.42 for CaO–B2O3 system and −0.5 for BaO–B2O3 system) agree well with the theoretical value, while the effects of basicity is much lower than the theoretical value (0.46 for CaO–B2O3 system and 0.39 for BaO–B2O3 system).

The same tendency was found in previous study. Song measured carbon solubility change with basicity using CaO–SiO2 and CaO–Al2O3 system at 1873 K and reported that the effects of basicity on carbon dissolution in CaO–SiO2 system is smaller than in CaO–Al2O3 system. Song suggested that the change of the activity coefficient of CaC2 influence the results. In order to check the validity of this assumption, the thermodynamic calculations below were conducted, and the calculated values of activity coefficient of carbide in basic region (log aMO > −3) were plotted in Fig. 6(b) including previous data by Song.

In the CaO–B2O3 system, CaC2 would be formed as a reaction product according to following reaction:

\[
3(C)+(CaO)=\frac{(CaC_{2})}{2}+\{CO\} \quad \text{..........(3)}
\]

\[
\Delta G^{\circ}=469686-220667T \text{(J/mol)} \quad \text{..........(3)}
\]

From the equilibrium constant of above reaction and the change of free energy, the activity coefficient of CaC2 is calculated as follows,

\[
K=\frac{a_{CaC_{2}} \cdot P_{CO}}{a_{C} \cdot a_{CaO}} \quad \text{..........(4)}
\]

\[
\log \gamma_{CaC_{2}}=-\frac{24561}{T}+7.06+\log a_{CaO}+3 \log a_{C} \quad \text{..........(5)}
\]

Similarly, the activity coefficient of BaC2 in BaO–B2O3 system can be calculated as follows:
As shown in Fig. 6(b), $\gamma_{\text{CaC}_2}$ and $\gamma_{\text{BaC}_2}$ increased with basicity. It is noticed that the change of the activity coefficient of BaC$_2$ with basicity is larger than that of CaC$_2$.

According to the Eqs. (5) and (9), the increase of activity coefficient with basicity would reduce the effect of basicity on carbon dissolution, and the more change of activity coefficient would mean that more discrepancy from the theoretical value. From the fact that BaO–B$_2$O$_3$ system has larger slope in Fig. 6(b), more discrepancy from theoretical value in BaO–B$_2$O$_3$ than in CaO–B$_2$O$_3$ system can be explained.

Based on the results in this study and the thermodynamic calculations above, the formation of carbide ion would be feasible by Eq. (2).

3.3. Effects of Oxygen Partial Pressure on Carbon Dissolution in Acidic Region

The experiments were carried under various oxygen partial pressure with 40wt%CaO–B$_2$O$_3$ at 1773 K, 30wt% BaO–B$_2$O$_3$ at 1698 K, respectively. The results were shown in Fig. 7. The effects of oxygen partial pressure on carbon dissolution were similar in both basic and acidic region, but the effects of basicity in acidic slags were different from the results in basic slag. Compared to the value of 0.46 in CaO–B$_2$O$_3$ and 0.39 in BaO–B$_2$O$_3$ in basic slag, the effects of basicity in acidic slags had negative value, which is −0.75 in CaO–B$_2$O$_3$ and −0.24 in BaO–B$_2$O$_3$ (Fig. 3).

To explain the carbon dissolution behavior in wide range of basicity, carbon is assumed to dissolve into liquid slag not only as a single ion (C$_2$$^\text{2-}$) but also as a replaced component in polymerized ion network, similar to nitrogen ion dissolution mechanism, as shown in Fig. 8.

![Fig. 7. Carbon contents at various oxygen partial pressure in acidic region. (a) CaO–B$_2$O$_3$ (b) BaO–B$_2$O$_3$](image)

![Fig. 8. Schematic representation of nitride capacity as a function of basicity.](image)
Case 2. When nitrogen is combined to network partly

\[
\frac{1}{2} \{N_2\} + 2(O^\text{-}) = (N^\text{0}) + \frac{1}{2} \{O_2\} + \frac{3}{4} \{O_2\} \quad \text{........(13)}
\]

When free ion model is used, oxygen ions in the liquid slag are assumed to be free ions. In the highly basic region, this assumption can be applied pretty well, so free ion model becomes dominant model to describe the nitrogen dissolution behavior.

On the other hand, network model is applied with the assumption that nitrogen substitute oxygen ions in the network. This model can be applied acidic region where acidic oxide makes network in the liquid slag.

If carbon dissolution behavior follows the carbide ion formation in Eq. (2), there is a similarity to free ion model of nitrogen in basic region. Assuming that network model of nitrogen can also be applied to carbon dissolution behavior in acidic region, the reaction mechanisms may be formulated as follows:

When carbon is combined to network completely

\[
(C) + 3(O^\text{-}) = (C^\text{0}) + (O^\text{2-}) + \{O_2\} \quad \text{........(14)}
\]

When carbon is combined to network partly

\[
(C) + 3(O^\text{-}) = (C^\text{0}) + (O^\text{2-}) + \{O_2\} \quad \text{........(15)}
\]

In the CaO–B₂O₃ system, dependence on \( p_{O_2} \) is -0.5 and dependence on basicity is -0.75 respectively. These are almost the average of the values derived from above two reaction mechanisms.

On the other hand, dependence on oxygen potential is -0.35 and dependence on basicity is -0.24 in the BaO–B₂O₃ system. It cannot be explained quite well with the reaction mechanism proposed here and other studies, but it shows the possibility that carbon dissolution in the BaO–B₂O₃ system in acidic region is not determined by sole reaction mechanism but the combination of several reaction mechanisms. It can be also thought that the carbide can be made in acidic region with complex ion and the basicity dependence can become less negative.

It can be said here that the carbon dissolution behavior in acidic region of BaO–B₂O₃ and CaO–B₂O₃ cannot be explained clearly by just one reaction mechanism but more than two reaction mechanisms coexisted. The amount of contribution cannot be shown quantitatively here, but still this study shows the possibility of coexistence of more than two reaction mechanisms in acidic region. The study about the structure of binary slag system will help the verification of this possibility and the understanding of carbon dissolution mechanisms in slag.

3.4. Effects of Temperature on Carbon Dissolution

In order to check the effects of temperature, carbon dissolution behavior was studied in slag systems (52.5 wt%CaO–B₂O₃, 75wt%BaO–B₂O₃ and 30wt%CaO–B₂O₃, 35wt%BaO–B₂O₃). In the basic region, which is shown in Fig. 9, slopes are -0.48 in the CaO–B₂O₃ and -0.47 in the BaO–B₂O₃ system. Using the Van’t Hoff equation, Eq. (16), the enthalpy change of carbon dissolution into slags in basic region can be calculated. The results are 89.79 kJ/mol in the BaO–B₂O₃ and 91.71 kJ/mol in the CaO–B₂O₃ systems respectively. In Fig. 10, the slope of CaO–B₂O₃ system is -0.47, and that of the BaO–B₂O₃ system is -0.43, which can be related to the enthalpy change of carbon dissolution in acidic region, the values are 89.79 kJ/mol in the CaO–B₂O₃ and 82.14 kJ/mol in the BaO–B₂O₃ system respectively.

\[
\Delta H^\circ = -R \frac{d \ln K}{d(1/T)} = -R \frac{d \ln X_C}{d(1/T)} \quad \text{........(16)}
\]

These results show that the carbon dissolution into the CaO–B₂O₃ and the BaO–B₂O₃ systems is an endothermic reaction and the values are almost same in each (basic and acidic) region.

Because the activities are not exactly same in the selected compositions in both slags, the enthalpy change could include the effect of activity change, too. Although the enthalpy values obtained here do not show sole effect of temperature change on carbon dissolution, it can be used to compare with the value of other systems and the stability of ion or ion complex in each slag system can be compared using these data.
4. Summary

(i) Carbon solubility in the CaO–B₂O₃ and the BaO–B₂O₃ slags decreased with increasing basicity in acidic region while it increased with basicity change in the basic region. Carbon solubility increased with decreasing oxygen partial pressure in both regions.

(ii) Based upon the results, the carbon dissolution behavior in the CaO–B₂O₃ and the BaO–B₂O₃ systems can be explained by following reaction mechanisms.

(1) Carbide ion formation reaction is dominant in the basic region

\[ 2(C) + (O^-) = (C_2)^2^- + \frac{1}{2} \{O_2\} \]

(2) Following two reactions can be proposed to explain carbon dissolution in the acidic region.

- When carbon is combined to network completely

\[ (C) + (O^-) = (C^0) + \frac{1}{2} \{O_2\} + \frac{1}{4} \{O_2\} \]

- When carbon is combined to network partly

\[ (C) + 3(O^-) = (C^-) + (O^2^-) + \{O_2\} \]

(iii) In basic region, activity coefficient of reaction product (carbide ion) increased with the increase of basicity. This is one of the reason the basicity dependence of the basic slag system is below the theoretical value 1, which is proposed by carbide ion formation mechanism.

(iv) The carbon dissolution behavior in slag system has different mechanisms with the change of basicity. Only one reaction mechanism cannot explain the behavior especially in acidic region.

(v) Carbon dissolution increased at higher temperature. The enthalpy change of carbon dissolution is calculated with Van’t Hoff equation. The results are 89.79 kJ/mol in BaO–B₂O₃ and 91.71 kJ/mol in CaO–B₂O₃ in basic region, and 82.14 kJ/mol in BaO–B₂O₃ system and 89.79 kcal/mol in CaO–B₂O₃ in the acidic region.

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