Thermodynamic Behavior of Carbon in Molten Slags

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The solubility of carbon in the MO-B₂O₃ (MO = CaO, BaO, and Na₂O) and CaO-RO (RO = SiO₂ and Al₂O₃) slags at high temperatures was measured to understand the thermodynamic behavior of carbon in molten slags. The solubility of carbon as a function of the composition of slags shows a minimum value, indicating that carbon dissolves by different mechanisms in the acidic and basic slags, respectively. The infrared spectra measurements indicate that the B-C bond is about 1150 and 1140 cm⁻¹ in the acidic region of the CaO-B₂O₃ and Na₂O-B₂O₃ slags; hence, the incorporation of carbon into the borate network is confirmed qualitatively. The dissolution of carbon and nitrogen into the slags shows a similar behavior in the B₂O₃-bearing slags, while the different behavior is shown in the CaO-SiO₂ and CaO-Al₂O₃ slags, based on the relationship between carbide capacity and nitride capacity.

KEY WORDS: carbon solubility; dissolution mechanism; infrared spectra measurement; B-C bond; carbon incorporation; borate network; nitrogen solubility; carbide capacity; nitride capacity

1. Introduction

A new breakthrough in steel materials has been achieved for various applications. For example, super fine and high strength steels have been developed for improving both strength and ductility.¹⁾ For these purposes, the severe control of impurities such as C and N under condition of an ultra low level has been required. Hence, the solubility of carbon in molten slags has been investigated by many other researchers.²⁻¹²⁾

In previous works, the solubility of carbon was strongly dependent on oxygen partial pressure and basicity ($a_{O^{2-}}$) of slags. The dependence of carbon solubility on oxygen partial pressure has been known explicitly, while the effect of basicity on carbon dissolution has not been cleared. For example, the solubility of carbon increased by the increase of SiO₂ content in the CaO-SiO₂-Al₂O₃ slag,^{2, 7)} while the solubility increased with increasing content of basic oxides in other basic slags. Therefore, it was not clear whether carbon dissolution would be enhanced by the basic or acidic components. In the case of nitrogen^{8, 12-14)} and silver¹⁵⁻¹⁷⁾ dissolution in molten slags, two types of dissolution mechanisms with the basicity of slags have been reported.

In the present study, the solubility of carbon in the B₂O₃-bearing slags, which had been known to have a wide range of liquids,¹⁸⁾ and in the CaO-SiO₂ and CaO-Al₂O₃ slags was measured to understand the reaction mechanism of carbon dissolution into the slags. In addition, the carbide capacity was suggested and compared to the nitride capacity.

2. Experimental Procedure

A super kanthal electric furnace was used for equilibration of molten slag and gas phases. The temperature was controlled within ± 2 K using an R-type (Pt-13Rh/Pt) thermocouple and a proportional-integral-differential (PID) controller. The slag samples were prepared using reagent-grade BaO, Na₂O, B₂O₃, SiO₂, Al₂O₃, and CaO calcined from CaCO₃. The schematic

diagram of the experimental apparatus is shown in previous articles.^{11, 16)}

The slag samples of 10g were held in graphite crucibles under CO atmosphere for equilibration. For the effect of oxygen partial pressure on the solubility of carbon, a mixture of CO and Ar was supplied by using mass flow controller (Matheson, Model 8284). The impurities of CO and Ar were removed by passing through CaSO₄, Na₂O • CaO, silica gel, and, especially, Mg turnings at 753 K for Ar.

The equilibration time was predetermined to be 18 hours. After equilibrating, the samples were quenched by Ar gas and crushed for chemical analysis. The content of carbon in slags was determined by a LECO (CS-300) analyzer. The uncertainty of the measured data could be estimated to be about ± 3.25 %.

The possibility of carbide formation could be evaluated using thermodynamic data available in the literature.^{19, 20)} Because the evaluated activities of the carbides for the present experimental conditions are less than 0.05, the discussion in the present study will be limited to the dissolved carbides in molten slags.

3. Results and Discussion

3.1. Dissolution Mechanism of Carbon in Basic Slags

Carbon has been known to dissolve into the basic slags by the following reaction:^{8, 10-12)}

$$K_{(1)} = \frac{a_{C_2^{2-}} \cdot p_{O_2}^{1/2}}{a_C^2 \cdot a_{O^{2-}}} \quad \dots (2)$$

where $K_{(1)}$, a_i , and p_{O_2} are the equilibrium constant of Eq. (1), the activity of i , and the oxygen partial pressure, respectively. Because graphite crucibles were used to fix the activity of carbon as unity, the following relation could be deduced:

Fig. 1. Dependence of carbon solubility on oxygen partial pressure in various slags (*: mass%).

$$\log(\text{mass}\%C_2^{2-}) = -1/2 \log p_{O_2} + \log a_{O^{2-}} - \log f_{C_2^{2-}} + \log K_{(1)} \quad \dots\dots\dots (3)$$

where $f_{C_2^{2-}}$ is the activity coefficient of C_2^{2-} ion. From Eq. (3), $\log(\text{mass}\%C_2^{2-})$ and $\log p_{O_2}$ are expected to have a linear relationship with a slope of $-1/2$, under conditions of a fixed composition and temperature. The solubility of carbon in the $\text{CaO}_{\text{satd}}\text{-B}_2\text{O}_3$ system (78.0 mol% CaO) at 1773 K is shown as a function of $\log p_{O_2}$, with the results of previous studies, in Fig. 1. Although the slope of the line, -0.37 is slightly lower than the expected value of -0.50 , it is close to the previous results.⁸⁻¹⁰⁾

The solubility of carbon in the $\text{MO-B}_2\text{O}_3$ slags ($\text{MO} = \text{CaO}, \text{BaO}, \text{and } \text{Na}_2\text{O}$) under $p_{\text{CO}} = 1 \text{ atm}$ shows a minimum value (Fig. 2). The presence of the minimum solubility indicates that there would be a possibility for the dissolution of carbon by two types of mechanisms on either side of the minimum point. Hereafter, the slag composition will be divided into the acidic and the basic regions, based on carbon solubility. If Eq. (1) is valid over the entire composition range, $f_{C_2^{2-}}$ must increase much faster than $a_{O^{2-}}$ with increasing content of basic oxides, which seems unlikely.^{13, 14)}

The dissolution mechanism of carbon can be examined more quantitatively by considering the relationship between the solubility of carbon and the activity of basic oxides. In Eq. (3), $\log(\text{mass}\%C_2^{2-})$ and $\log a_{O^{2-}}$ are expected to have a linear relationship with a slope of unity at a fixed temperature and oxygen partial pressure, assuming that $f_{C_2^{2-}}$ would not be affected by the slag composition. The solubility of carbon is shown as a function of the activity of basic oxides in Fig. 3, assuming that $a_{O^{2-}}$ is directly proportional to a_{MO} . The activity of CaO ,^{14, 21)} BaO ,^{14, 22)} and Na_2O ²³⁾ in the B_2O_3 -bearing slags are available in the literature.

In the basic region of the $\text{BaO-B}_2\text{O}_3$ and $\text{Na}_2\text{O-B}_2\text{O}_3$ slags, $\log(\text{mass}\%C)$ and $\log a_{\text{MO}}$ have a linear relation with the slope close to unity, although that in the $\text{CaO-B}_2\text{O}_3$ slag is slightly lower than the expected value of unity. Based on these results, it is confirmed that the dissolution of

Fig. 2. Solubility of carbon in the B_2O_3 -bearing slags as a function of the content of basic oxides in the molar basis.

Fig. 3. Relationship between carbon solubility and the activity of basic oxides in the B_2O_3 -bearing slags.

carbon into the basic slags can be described by Eq. (1).

However, in the acidic region of slags, it was difficult to explain the dissolution mechanism of carbon by Eq. (1). Hence, it was expected that there would be another reaction for carbon dissolution into the acidic slags.

3.2. Dissolution Mechanism of Carbon in Acidic Slags

The dependence of carbon solubility on oxygen partial pressure was measured at 1773 K in the 55.4 (mol%) $\text{CaO-B}_2\text{O}_3$ system. In Fig. 4, $\log(\text{mass}\%C)$ linearly decreases with increasing $\log p_{O_2}$ with a slope close to $-3/4$, which is higher than $-1/2$. Therefore, the dependence carbon solubility on oxygen partial pressure in the acidic region would be larger than that in the basic slags.

As shown in Fig. 3, the solubility of carbon in the acidic B_2O_3 -bearing slags decreases by increasing the activity of basic oxides. The slopes of the lines for the CaO- , BaO- , and the $\text{Na}_2\text{O-B}_2\text{O}_3$ slags are -0.41 , -0.47 , and -0.52 , respectively, which are close to -0.5 . Consequently, the basicity term, O^{2-} should be placed on the right-hand side

Fig. 4. Dependence of carbon solubility on oxygen partial pressure in the CaO-B₂O₃ slags at 1773 K.

in the dissolution reaction.

It has been known that there are three kinds of oxygen ions such as free (O^{2-}), non-bridging (O^-), and bridging oxygen ion (O^0) in molten slags. Generally, O^{2-} and O^- ions would participate in the reaction more dominantly rather than O^0 from the viewpoint of activation energy.¹³⁾ Therefore, carbon dissolution into the slags may be described by Eq. (4) based on the experimental results and the interactions between oxygen ions and carbon.

$$K_{(4)} = \frac{a_{C^-} \cdot p_{O_2}^{3/4} \cdot a_{O^{2-}}^{1/2}}{a_{C^-} \cdot a_{O^-}^2} \quad (5)$$

$$\log(\text{mass}\% C^-) = -3/4 \log p_{O_2} - 1/2 \log a_{O^{2-}} - \log f_{C^-} + \log K_{(4)} + 2 \log a_{O^-} \quad (6)$$

The carbide ion dissolved following Eq. (1), in the basic slags, may be referred to as “free carbide” and that following Eq. (4), in the acidic slags, as “incorporated carbide.” From Eq. (6), $\log(\text{mass}\% C^-)$ and $\log a_{O^{2-}}$ are expected to have a linear relationship with a slope of -1/2 at a fixed oxygen partial pressure and temperature. In Fig. 3, the slopes of the lines in the acidic B₂O₃-bearing slags are close to -1/2; thus f_{C^-} in Eq. (6) would be constant with the acidic slag composition. This is qualitatively confirmed from the estimated results that the activity coefficient of BC_{0.25} is independent of composition in each slag system, assuming that BC_{0.25} is the reference state of incorporated carbide. However, because the relationship between a_{O^-} and slag composition is not manifested, a more detailed investigation is required.

Considering the composition of MO • 2B₂O₃ (MO = CaO, BaO, and Na₂O), for example, exhibits the incorporation of carbon, the structure of molten slags could be represented by the ‘B₄O₇²⁻’ diborate as a typical polymeric group, although so many polymeric groups would exist in the melt.^{15, 21, 24)} Hence, the reaction for the incorporation of carbon can be expressed by Eq. (7), based on the fact that

Fig. 5. IR transmittance of the CaO-B₂O₃ and 20.6 (mol%) Na₂O-B₂O₃ slags as a function of wave numbers (*: mol%).

B₂O₃ is a network former in these slags:

From Eq. (7), it is suggested that the ‘B–O–B’ bonds would be replaced by the ‘B=C⁻–B’ bonds by introducing a carbon into the borate network. However, Eq. (7) is not an overall reaction for carbon incorporation, because the slag melt could be constituted by many other polymeric groups.

The incorporation of carbide into the borate network could be confirmed qualitatively by the Fourier transform infrared (FT-IR) measurements, as in the case of nitrogen, where the Si–N bond was found in the silicate melts.^{13, 14, 25)} In Fig. 5, the IR transmittance of the CaO-B₂O₃ and Na₂O-B₂O₃ slags is shown as a function of wave numbers in different compositions for comparison. The main peak for the B–O stretching vibration (1470 to 1180 cm⁻¹) is shifted to higher wave numbers with increasing B₂O₃ content.²⁶⁾ Also, the peaks indicating the simple anionic group, such as B₄O₇²⁻ (1380 to 1330 cm⁻¹), BO₃³⁻ (1380 to 1260 cm⁻¹), and BO₂⁻ (1350 to 1300 cm⁻¹) are appeared by increasing the content of CaO, which modifies the borate structure.²⁶⁾ In addition, these anionic groups are appeared in the 20.6 (mol%) Na₂O-B₂O₃ system, while occur in the composition higher than 50.4 (mol%) CaO in the CaO-B₂O₃ slag.

The IR region indicating the B–C bond is known to be about 1255 to 1145 cm⁻¹ in the literature.²⁶⁾ In the acidic Na₂O-B₂O₃ system, the peak was found to be about 1140 cm⁻¹, close to the results of the CaO-B₂O₃ slags.¹¹⁾ Based on these experimental results, it is suggested that carbon would dissolve into the acidic slags as incorporated carbide, as mentioned in Eq. (4), while as free carbide in the basic slags.

Fig. 6. Comparison of the dependence of carbon solubility on slag composition in various slags.

However, this is not conclusive proof of the incorporation of carbon into the borate network and a more detailed investigation is required to determine the coordination state of carbon in slags.

Fig. 6 exhibits the solubility of carbon in various slags as a function of the content of basic oxides. The effect of the slag components on carbon solubility can be discussed as follows.

In the B_2O_3 -bearing slags, the minimum solubility of carbon is observed at about 60 (mol%) CaO, 45 (mol%) BaO, and 30 (mol%) Na_2O , respectively. As in the case of silver solubility in the B_2O_3 -bearing slags, the shifts of the composition for the minimum carbon solubility to the acidic one indicate that Na_2O is more basic than BaO, followed by CaO, qualitatively.¹⁵⁻¹⁷⁾

In the CaO-RO (RO = B_2O_3 , SiO_2 , and Al_2O_3) slags, the solubility of carbon decreases in the order of CaO- SiO_2 , CaO- Al_2O_3 , and the basic CaO- B_2O_3 slags at the same content of CaO. This mainly due to the higher stability of carbide ion in the CaO- SiO_2 slag than those in other slags.⁸⁾

In addition, fluoride has been known to affect the thermodynamic behaviors of carbon and nitrogen in molten slags.^{8, 10, 12)} In the CaO- SiO_2 - CaF_2 and CaO- Al_2O_3 - CaF_2 slags, the carbon solubility is higher than those in the CaO- SiO_2 and CaO- Al_2O_3 slags, respectively. This may result from the effect of F^- ion on the depolymerization reaction of slag structure instead of O^{2-} ion, in some proportion; hence the more O^{2-} ions could be reacted with carbon by Eq. (1). Also, effect of CaF_2 on carbon solubility is more significant in the silicate than that in the aluminate melt.

3.3. Relationship between Carbide Capacity and Nitride Capacity

The free and incorporated carbide capacities can be defined by the following equations from Eqs. (2) and (5), respectively:

$$C_{C_2^{2-}} = \frac{K_{(1)} \cdot a_{O^{2-}}}{f_{C_2^{2-}}} = (\text{mass}\% C_2^{2-}) \cdot p_{O_2}^{1/2} \quad \dots\dots (8)$$

Fig. 7. Relationship between nitride and free carbide capacities in the CaO- SiO_2 , CaO- Al_2O_3 , and the basic region of the B_2O_3 -bearing slags.

$$C_{C^-} = \frac{K_{(4)} \cdot a_{O^{2-}}^2}{f_{C^-} \cdot a_{O^{2-}}^{1/2}} = (\text{mass}\% C^-) \cdot p_{O_2}^{3/4} \quad \dots\dots\dots (9)$$

where p_i , $K_{(n)}$, a_i , and f_i are the partial pressure of i , the equilibrium constant of reaction (n), the activity, and the activity coefficient of i , respectively.

Combining these carbide capacities with the nitride capacities given in the literature,^{8, 12-14)} the relationship between them in the basic and acidic slags is derived, respectively, as follows:

$$\log C_{N^{3-}} = 3/2 \log C_{C_2^{2-}} + \log \frac{f_{C_2^{2-}}^{3/2}}{f_{N^{3-}}} + \log K' \quad \dots\dots (10)$$

$$\log C_{N^-} = \log C_{C^-} + \log \frac{f_{C^-}}{f_{N^-}} + \log K'' \quad \dots\dots\dots (11)$$

Thus, nitride and carbide capacities are expected to have a linear relationship with the slope of 3/2 and 1, respectively, if the other terms are constant. In Fig 7, $\log C_{N^{3-}}$ from the literature is plotted as a function of $\log C_{C_2^{2-}}$ in the basic CaO- B_2O_3 and BaO- B_2O_3 slags.¹⁴⁾ The slope of the former is 1.4 and that for the latter is 1.5, which are relatively close to the expected value of 3/2. Hence, the $f_{C_2^{2-}}^{3/2} / f_{N^{3-}}$ ratio in Eq. (10) may be nearly constant in the basic region of each slag system.

The slope of the lines is negative in the CaO- SiO_2 and CaO- Al_2O_3 slags. The solubility of nitrogen in these slags decreased with increasing CaO content,^{27, 28)} indicating that nitrogen would dissolve as incorporated nitride; thus in the CaO- SiO_2 and CaO- Al_2O_3 slags, the following equation is deduced.

$$\log C_{N^-} = -1/2 \log C_{C_2^{2-}} + \log \frac{1}{f_{N^-} \cdot f_{C_2^{2-}}^{1/2}} + \log K''' + 2 \log a_{O^{2-}} \quad \dots\dots\dots (12)$$

Thus, $\log C_{N^-}$ is expected to have a linear relationship with $\log C_{C_2^{2-}}$ if the other terms are constant, and the theoretical slope will be -1/2. The slope of the line in the CaO- SiO_2 slag is -0.58 and that for the CaO- Al_2O_3 slag is -0.66, which is relatively close to the expected value of -1/2.

Fig. 8. Relationship between incorporated nitride and carbide capacities in the acidic region of the B_2O_3 -bearing slags.

Hence, the terms of $f_{N^-} \cdot f_{C^{2-}}^{1/2}$ and a_{O^-} may be constant. Based on these results, the thermodynamic behaviors of nitrogen and carbon in the B_2O_3 -bearing slags are similar, while different behaviors are shown in the $CaO-SiO_2$ and $CaO-Al_2O_3$ slags.

Fig. 8 exhibits the relationship between $\log C_{N^-}$ and $\log C_{C^{2-}}$ in the acidic B_2O_3 -bearing slags.^{14, 29)} The slope of the $CaO-B_2O_3$ system is 1.4, slightly higher than the expected value of unity, and those of the $BaO-$ and $Na_2O-B_2O_3$ systems are 0.78 and 0.64, lower than the expected value. From these differences, it can be suggested that f_{C^-} would be larger than f_{N^-} in the $CaO-B_2O_3$ system, and vice versa in the $BaO-$ and $Na_2O-B_2O_3$ systems, in Eq. (11). As seen in Figs. 7 and 8, the dissolution of carbon and nitrogen into the B_2O_3 -bearing slags shows a similar behavior.

4. Conclusions

The solubility of carbon in the $MO-B_2O_3$ ($MO = CaO$, BaO , and Na_2O) and $CaO-RO$ ($RO = SiO_2$ and Al_2O_3) slags was measured at high temperatures to understand the thermodynamic behavior of carbon in molten slags. The results of this study can be summarized as follows:

(1) The dissolution of carbon into the basic region of the B_2O_3 -bearing slags and into the $CaO-RO$ slags is confirmed by the following reaction:

(2) The dissolution mechanism of carbon into the acidic region of the B_2O_3 -bearing slags can be suggested by the following reaction from the effect of basicity and oxygen partial pressure on the solubility of carbon:

(3) The infrared spectra measurements indicate that the B-C bond is about 1150 and 1140 cm^{-1} in the acidic $CaO-B_2O_3$ and $Na_2O-B_2O_3$ slags; hence, the incorporation of

carbon into the borate network is confirmed qualitatively.

(4) The dissolution of carbon and nitrogen into the slags shows a similar behavior in the B_2O_3 -bearing slags, while different behavior is shown in the $CaO-SiO_2$ and $CaO-Al_2O_3$ slags, based on the relationship between carbide capacity and nitride capacity.

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