

Solubility of Carbon in CaO-B₂O₃ and BaO-B₂O₃ Slags

JOO HYUN PARK and DONG JOON MIN

The solubility of carbon in molten CaO-B₂O₃ and BaO-B₂O₃ slags at high temperatures was measured to understand the dissolution mechanism of carbon into the slags. The B₂O₃-bearing slags, which have a wide range of liquids, at the temperature of interest have been applied to investigate the effect of basicity on the solubility of carbon from the saturation of acidic or basic components. The solubility of carbon, as a function of the composition of slags, shows a minimum value, and it is suggested that carbon dissolves by different mechanisms in the acidic and basic slags, respectively. From the infrared spectra measurements, the wave number indicating the B-C bond was found to be about 1150 cm⁻¹ in the acidic region of slags; hence, the incorporation of carbon into the borate network was confirmed qualitatively. The carbide capacity was compared to the nitride capacity, showing that the dissolutions of carbon and nitrogen into the slags are similar.

I. 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 under the condition of an ultralow level has been required. Therefore, the possibility of control of carbon content in molten steel was suggested, and the solubility of carbon in the molten slags has been investigated by many other researchers.^[2-13]

In previous works, the solubility of carbon was strongly dependent on oxygen partial pressure^[8,10-12] and basicity ($a_{O^{2-}}$) of slags.^[6-13] 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,^[2,9] 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 cases of nitrogen^[10,14-17] and silver^[18,19,20] dissolution in molten slags, two types of dissolution mechanisms, with variation in the basicity of slags, have been reported.

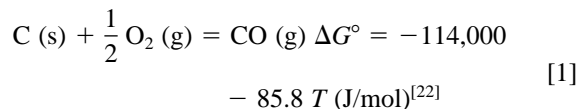
In the present study, the solubility of carbon in the B₂O₃-bearing slags, which had been known to have a wide range of liquids, was measured to understand the reaction mechanism of carbon dissolution into the slags.^[21] In addition, the carbide capacity was suggested and compared to the nitride capacity.

II. EXPERIMENTAL

A superkanthal electric furnace was used for equilibration of molten slag and gas phase. 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, B₂O₃,

and CaO calcined from CaCO₃. The schematic diagram of the experimental apparatus is shown in Figure 1.

The slag samples of 10 g were held in graphite crucibles under CO atmosphere for controlling oxygen partial pressure by C/CO equilibrium, as shown in Eq. [1].



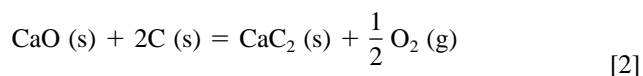
For measuring the effect of oxygen partial pressure on the solubility of carbon, a mixture of CO and Ar was supplied by using MFC (Matheson, model 8284 (Montgomeryville, PA)). The impurities of CO and Ar were removed by passing through CaSO₄, Na₂O · CaO, silica gel, and, especially, Mg turnings at 753 K for Ar.

The time for equilibration was predetermined to be 18 hours, as shown in Figure 2. 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*

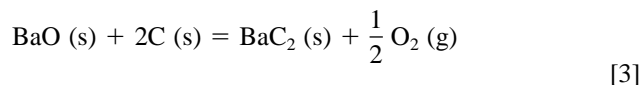
*LECO is a trademark of LECO Corporation, St. Joseph, MI.

(CS-300) analyzer. The uncertainty of the measured data could be estimated to be about ± 3.25 pct. Therefore, it could be concluded that the experimental data in the present work is reproducible.

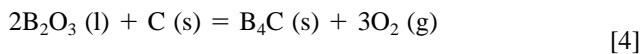
The possibility of carbide formation could be evaluated using thermodynamic data available in the literature for the following reactions:^[22,23,24]



$$\Delta G^\circ = 568,000 - 144 T \text{ (J/mol)}$$



$$\Delta G^\circ = 442,000 - 99.5 T \text{ (J/mol)}$$



$$\Delta G^\circ = 2,420,000 - 414 T \text{ (J/mol)}$$

The evaluated values of the activity of the carbides for the present experimental conditions, in each case, are less than

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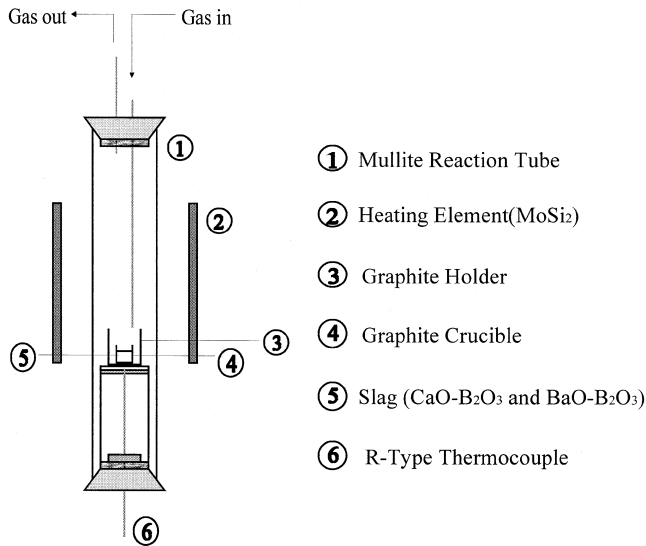


Fig. 1—Schematic diagram of the experimental apparatus.

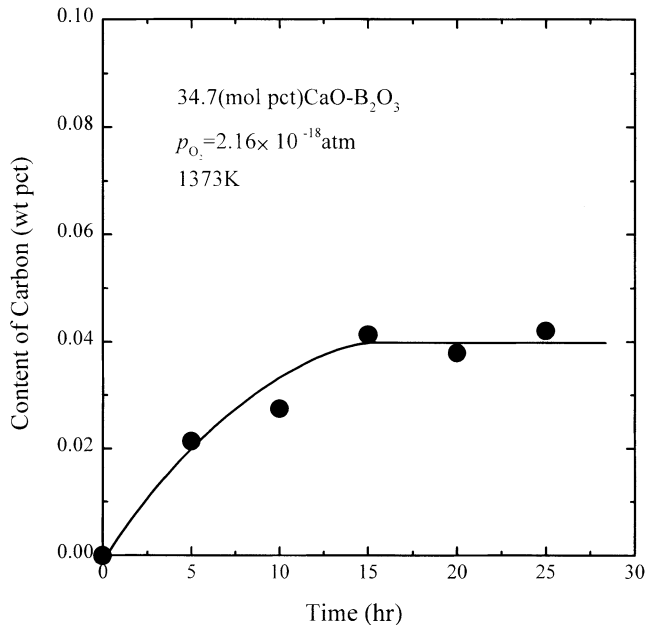


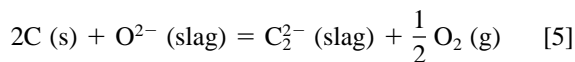
Fig. 2—Changes of carbon content in the 34.7 mol pct CaO-B₂O₃ system with equilibration time at 1373 K under CO atmosphere.

0.05. Therefore, the discussion in the present study will be limited to the dissolved carbides in molten slags.

III. RESULTS AND DISCUSSION

A. Dependence of Carbon Solubility on Oxygen Partial Pressure in CaO_{satd}-B₂O₃

Carbon has been known to dissolve into the basic slags by the following reaction:^[10,13]



$$K_{[5]} = \frac{a_{C_2^{2-}} \cdot p_{O_2}^{1/2}}{a_C^2 \cdot a_{O^{2-}}} \quad [6]$$

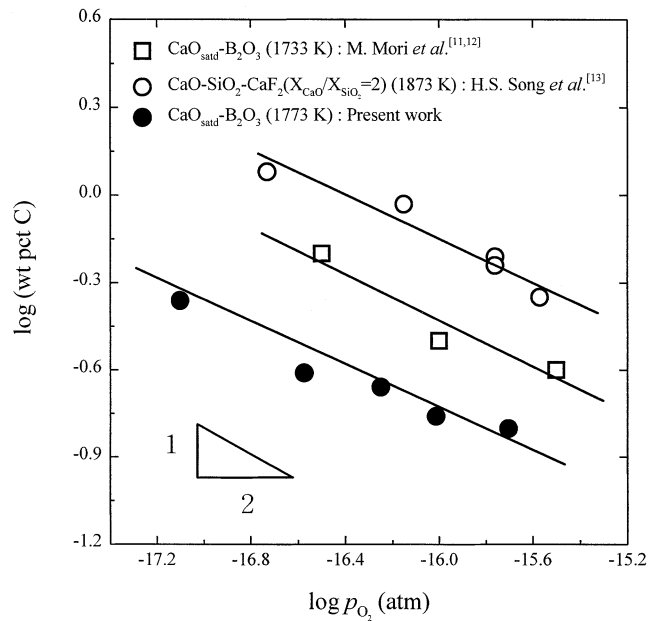


Fig. 3—Dependence of carbon solubility on oxygen partial pressure in the CaO_{satd}-B₂O₃ and CaO-SiO₂-CaF₂ slags.

where $K_{[5]}$, a_i , and p_{O_2} are the equilibrium constant of Eq. [5], 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:

$$\log(\text{wt pct } C_2^{2-}) = -\frac{1}{2} \log p_{O_2} + \log a_{O^{2-}} - \log f_{C_2^{2-}} + \log K_{[5]} \quad [7]$$

where $f_{C_2^{2-}}$ is the activity coefficient of C_2^{2-} ion.

From Eq. [7], the solubility of carbon is expected to have a linear relationship with the oxygen partial pressure in logarithmic form, and the slope of the line will be $-1/2$, under conditions of a fixed composition and temperature. The solubility of carbon in the CaO_{satd}-B₂O₃ system at 1773 K is shown as a function of oxygen partial pressure, with the results of previous studies, in Figure 3. The slope of the line is -0.368 , which is slightly lower than the expected value of -0.5 . However, because the slope is similar to the values measured in previous studies, *i.e.*, from -0.40 to -0.36 ,^[11,12,13] it can be suggested that Eq. [5] is available in the basic slags.

B. Dependence of Carbon Solubility on Slag Composition

Solubility of carbon in the CaO-B₂O₃ slag at 1773 K and in the BaO-B₂O₃ slag at 1698 K, under $p_{CO} = 1$ atm, is shown in Figure 4, with the results of previous studies.^[2,3,7,10,13] The solubility of carbon in the B₂O₃-bearing slags decreases by increasing the content of basic oxides and shows a minimum solubility, followed by an increase with increasing contents of basic oxides. It is noticed that the solubility of carbon shows a minimum value in the B₂O₃-bearing slags. Therefore, it was suggested that there would be a possibility for

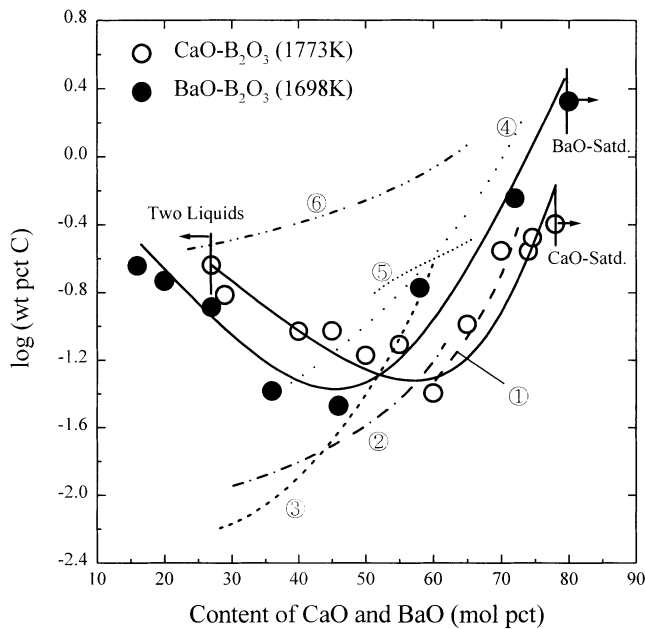


Fig. 4—Solubility of carbon in various slags as a function of the content of CaO and BaO in the molar basis (① CaO-Al₂O₃ (1883 K) by Swisher,^[2] ② CaO-SiO₂ (1873 K) by Song,^[10,13] ③ CaO-Al₂O₃-CaF₂ (1873 K) by Song,^[10] ④ CaO-SiO₂-Al₂O₃ (1873 K) by Ponomarenko and Kozlov,^[3] ⑤ BaO-MnO (1573 K) by Watanabe *et al.*,^[7] and ⑥ CaO-SiO₂-CaF₂ (1873 K) by Song^[10]).

the dissolution of carbon by another mechanism on the left-hand side of the minimum point, *i.e.*, in the acidic region. If Eq. [5] is valid over the entire composition range, $f_{C_2^{2-}}$ must increase much faster than $a_{O^{2-}}$ with increasing contents of basic oxides, which seems unlikely.^[14,15]

In the CaO-B₂O₃ slag, the minimum solubility of carbon was observed at about 60 pct of CaO in molar basis. It was also observed at about 45 mol pct of BaO in the BaO-B₂O₃ slag. Comparing the solubility of carbon at the composition of CaO and BaO saturation in both slags, the latter is about 5 times larger than the former, indicating that BaO is more basic than CaO.

The dissolution mechanism of carbon into the slags can be examined more quantitatively by considering the relationship between the solubility of carbon and the activity of basic oxides.

C. Relationship between Carbon Solubility and the Activity of Basic Oxides

In Eq. [7], the solubility of carbon was expected to have a linear relationship with the basicity ($a_{O^{2-}}$) in logarithmic form; the slope of the line would be unity, under conditions of a fixed temperature and oxygen partial pressure, assuming that the activity coefficient of carbide ion would not be affected by the slag composition. The solubility of carbon is shown as a function of the activity of basic oxides in Figure 5. The activities of CaO and BaO in B₂O₃-bearing slags are available in the literature.^[15,25]

In the basic region of the CaO-B₂O₃ slag, a good linearity is not shown. The slope of the line is 0.583, which is smaller than the expected value of unity. The reason for the discrepancy from the theoretical expectation is that the structure

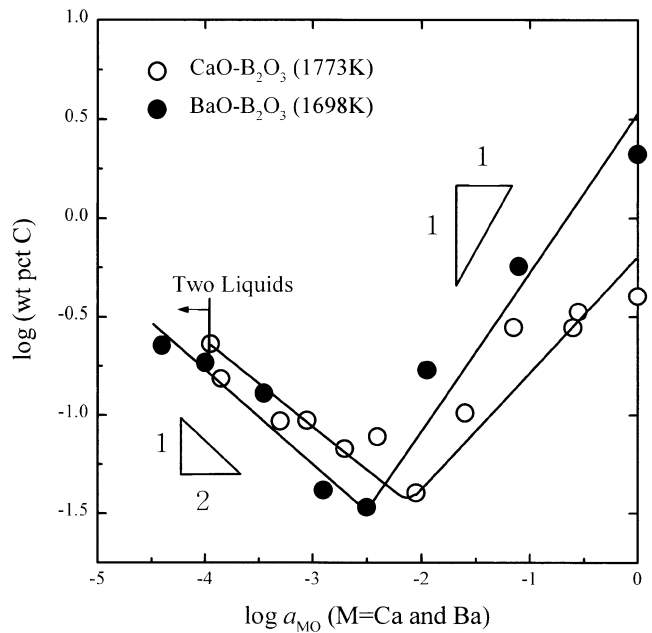


Fig. 5—Relationship between the solubility of carbon and the activity of basic oxides in the CaO-B₂O₃ and BaO-B₂O₃ slags.

of molten slags affects the basicity,^[18] or that the activity coefficient of carbide ion would be varied with slag composition. However, in the BaO-B₂O₃ slag, the solubility of carbon and the activity of BaO in logarithmic scale have a linear relationship in the basic region with a slope of 0.804. Therefore, it was suggested that dissolution of carbon into the basic region would occur by Eq. [5].

In addition, the solubility of carbon in the BaO-B₂O₃ system was about 4 times higher than that of the CaO-B₂O₃ system, on average, in the basic region. In the previous work by the present authors, BaO showed more basic characteristics than CaO, about 5 times in the basic region of slags from the measurement of the silver solubility as a new measure of basicity.^[19,20] Therefore, the difference of the solubility of carbon, in the basic region for both slags, would imply the difference of the relative basicity of CaO and BaO.

However, in the acidic region of slags, it was difficult to explain the reaction mechanism of carbon dissolution based on Eq. [5]. Therefore, it was expected that there would be another reaction for carbon dissolution into the acidic slags. The solubility of carbon in the acidic region decreases with the increasing activity of basic oxides, which corresponds to the basicity of slags. The slopes of the lines for the CaO-B₂O₃ and the BaO-B₂O₃ systems are negative values of -0.411 and -0.474, respectively. Therefore, the basicity term, O²⁻, should be placed on the right-hand side in the dissolution reaction, with a stoichiometric coefficient of 1/2.

In addition, the solubility of carbon in the BaO-B₂O₃ system was about 29 pct lower than that of the CaO-B₂O₃ system, on average, in the acidic region. In the previous work by the present authors, BaO showed more basic characteristics than CaO, about 33 pct in the acidic region of slags using the solubility of silver as a new measure of basicity.^[19,20] Therefore, the difference of the solubility of

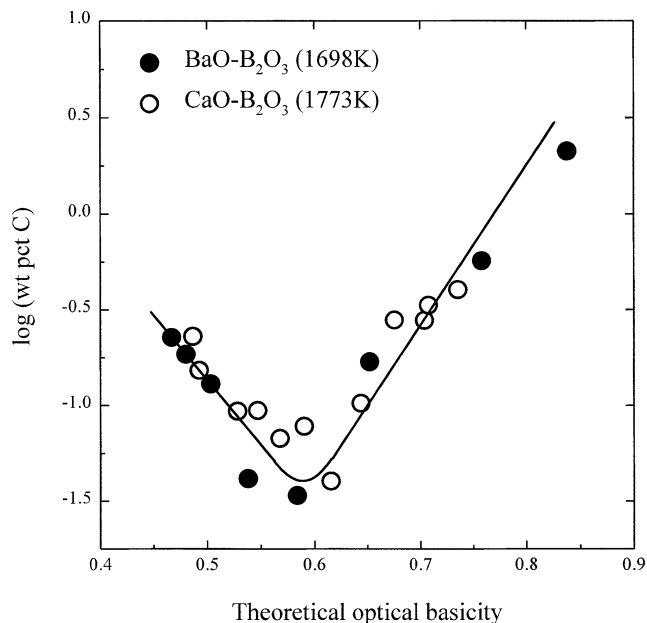


Fig. 6—Relationship between carbide capacity and theoretical optical basicity in the CaO-B₂O₃ and BaO-B₂O₃ slags.

carbon in the acidic region for both slags would imply the difference of the relative basicity of CaO and BaO.

The dissolution mechanism of carbon into the slags can also be discussed by introducing the theoretical optical basicity as an indirect measure of basicity.

D. Relationship between Carbon Solubility and Theoretical Optical Basicity

The optical basicity would be defined from a shift of the $^1S_0 \rightarrow ^3P_1$ transition of ions having a $d^{10} s^2$ configuration as Tl^+ , Pb^{2+} , and Bi^{3+} , in the ultraviolet region by the orbital expansion effect.^[26,27,28] CaO was chosen as a standard matrix for the probe ions. The basicity of a slag is simply given by

$$\Lambda = \Lambda_1 X_1 + \Lambda_2 X_2 + \dots \quad [8]$$

where $\Lambda_i (=1/\gamma_i)$, γ_i being the basicity-moderating parameter) is the optical basicity of pure oxide i , and $X_i (=z_i \cdot r_i / 2)$, z_i and r_i being the oxidation number of cations and the ratio of the cations with respect to the total number of oxides, respectively) is the equivalent fraction of oxide i . Although the Λ_i is measured by the spectroscopic method, there seems to be a correlation to the Pauling electronegativity (χ_i) of the involved metal ions by Eq. [9].

$$\gamma_i = 1.36(\chi_i - 0.26) \quad [9]$$

In Figure 6, $\log(\text{wt pct C})$ is plotted as a function of the optical basicity calculated by Eqs. [8] and [9]. Each of the slags has a good linear relationship, on either side of the minimum point, at about 0.6 of Λ , and different mechanisms of carbon dissolution can be found, as shown in Figures 4 and 5.

It is also necessary to confirm the dependence of the solubility of carbon on oxygen partial pressure, at a fixed

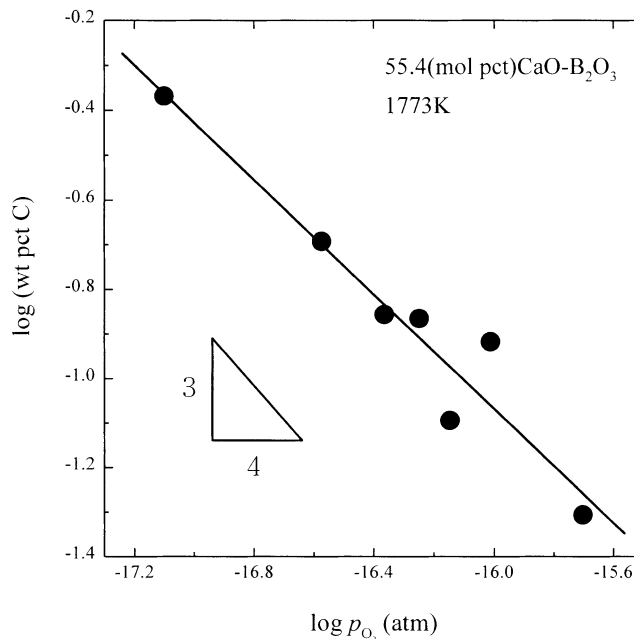


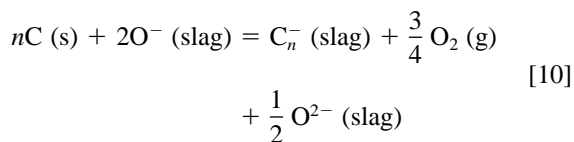
Fig. 7—Dependence of the solubility of carbon on oxygen partial pressure in the 55.4 mol pct CaO-B₂O₃ system at 1773 K.

temperature and composition, to determine the dissolution mechanism of carbon in the acidic region of slags.

E. Dependence of Carbon Solubility on Oxygen Potential in 55.4 (Mol Pct) CaO-B₂O₃

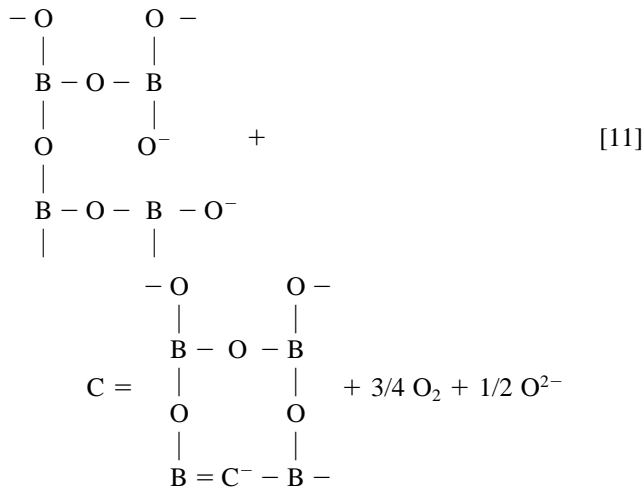
Dependence of the solubility of carbon on oxygen partial pressure was measured in the 55.4 (mol pct) CaO-B₂O₃ system as a relatively acidic slag, at the same temperature, 1773 K. In Figure 7, the solubility of carbon linearly decreases with increasing oxygen partial pressure with a slope of -0.641 . Therefore, the dependence of the solubility of carbon on oxygen partial pressure in the acidic region would be larger than that in the highly basic region of slags.

As in the case of nitrogen,^[10,14-17] Eq. [10] could be proposed to explain the experimental results in Figures 5 and 6, by introducing the nonbridging oxygen ion

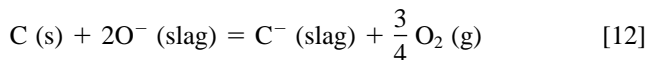


That is, the carbide ion incorporated in the network would be considered, instead of the free carbide ion existing, in the basic slags, as in Eq. [5].

Considering the composition of $\text{MO} \cdot 2\text{B}_2\text{O}_3$ ($M = \text{Ca}$ and Ba), for example, which was known as an acidic composition by the results of Figure 4, the structure of molten slags could be represented by the ' $\text{B}_4\text{O}_7^{2-}$ ' diborate as a main polymeric group.^[29] Therefore, Eq. [10] could be expressed by Eq. [11], based on the fact that B_2O_3 would be a network former in these slags:



From Eq. [11], it was suggested that the 'B-O-B' bonds would be replaced by the 'B = C⁻ - B' bonds by introducing a carbon atom into the borate network. Therefore, if the value of *n* in Eq. [10] is assumed to be unity, the dissolution reaction of carbon into the acidic slags can be generalized as the following reaction:



$$K_{[12]} = \frac{a_{\text{C}^-} \cdot p_{\text{O}_2}^{3/4} \cdot a_{\text{O}^{2-}}^{1/2}}{a_{\text{C}} \cdot a_{\text{O}^-}^2}$$

The carbide ion dissolved following Eq. [5], in the basic slags, may be referred to as "free carbide" and that following Eq. [12], in the acidic slags, as "incorporated carbide."

The incorporation of carbide into the borate network was confirmed by the FT-IR measurements, as in the case of nitrogen, where the Si-N bond was found in the silicate melts.^[14,15,30,31]

F. Infrared Spectra Measurements

The infrared (IR) transmittance of the slag samples was measured by using Fourier transform infrared (FT-IR) spectrometry. The IR transmittance of the CaO-B₂O₃ slags is shown as a function of wave numbers in different compositions for comparison (Figure 8). The results are in general agreement with those of the literature.^[32,33] That is, the main peak for the B-O stretching vibration is shifted to higher wave numbers with increasing B₂O₃ content in slags. In addition, the peaks indicating the simple anionic group are shown by increasing the content of CaO, which modifies the borate structure.

The IR region indicating the B-C bond is shown in the literature to be about 1255 to 1145 cm⁻¹.^[33] In the present measurements, those wave numbers were found to be 1153, 1151, and 1155 cm⁻¹, in the composition of 40.1, 50.4, and 60.3 (mol pct) CaO, respectively, *i.e.*, in the acidic region. Therefore, it was suggested that carbon would dissolve into the acidic slags as an incorporated carbide, as mentioned in Eq. [11]. On the other hand, the peak indicating the B-C bond is not found in 74.3 (mol pct) CaO-B₂O₃ and CaO_{satd}-B₂O₃ systems, *i.e.*, in the basic slags. Therefore, it was

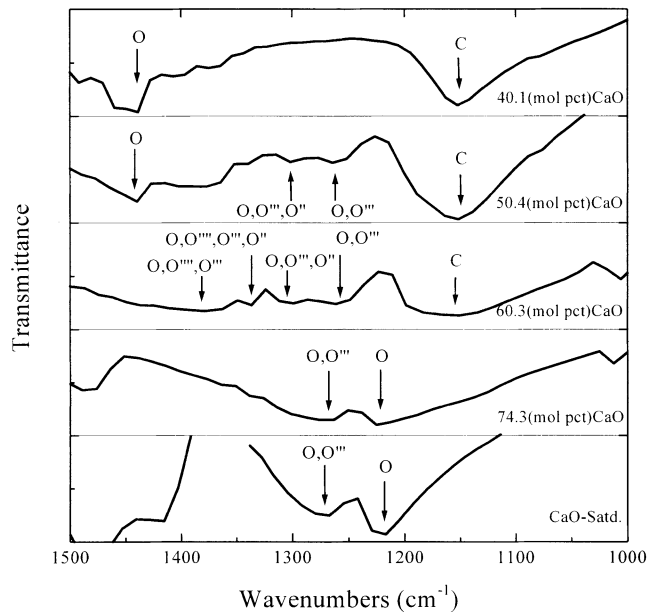


Fig. 8—IR transmittance of the CaO-B₂O₃ slags as a function of wave numbers in different compositions (O: B-O bond, O^{''}: B₄O₇²⁻, O^{'''}: BO₃⁻, O^{''''}: BO₂⁻, and C: B-C bond).

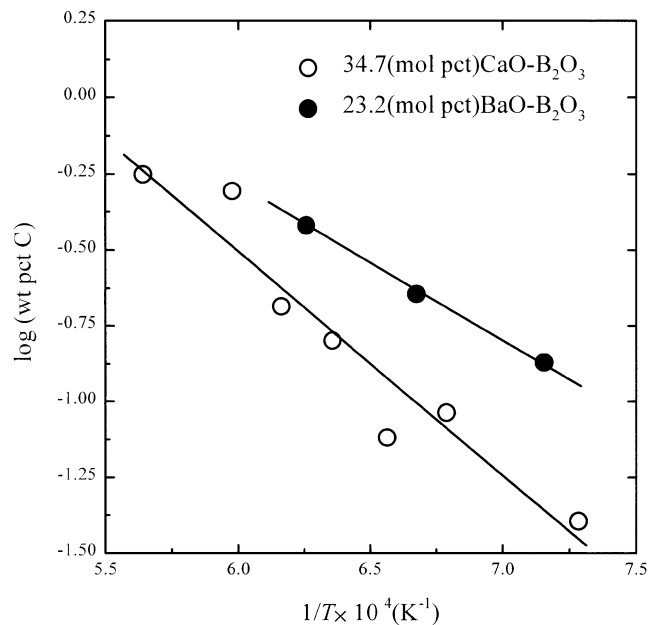


Fig. 9—Dependence of the solubility of carbon on temperature in the acidic region for the CaO-B₂O₃ and BaO-B₂O₃ slags.

suggested that carbon would dissolve as a free carbide in the basic region. 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 states of carbon in slags.

G. Dependence of Carbon Solubility on Temperature

Dependence of the solubility of carbon on temperature in the 34.7 (mol pct) CaO-B₂O₃ and 23.2 (mol pct) BaO-B₂O₃ systems is shown in Figure 9. The compositions of both

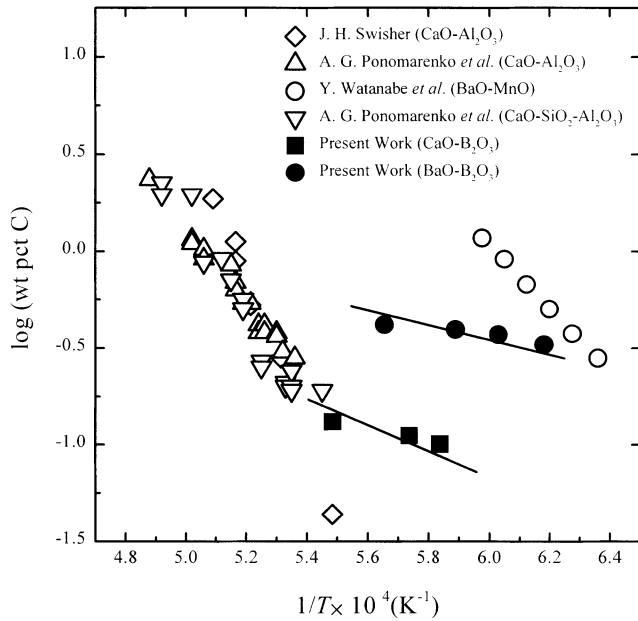


Fig. 10—Dependence of the solubility of carbon on temperature in the basic region for the CaO-B₂O₃, BaO-B₂O₃, and various slags.

slags were chosen for the same activity of basic oxides in the molten slags, *i.e.*, $a_{\text{CaO}} = a_{\text{BaO}} = 2.41 \times 10^{-4}$, to examine the unique effect of temperature on the solubility of carbon. The solubility of carbon in both slags increases with increasing temperature. The enthalpy changes for dissolution of carbon into the acidic slags can be calculated from the slope of the lines by the Gibbs–Helmholtz equation.^[34] The enthalpy changes for each slag are 144 and 95.7 kJ/mol, respectively, indicating that the dissolution is an endothermic reaction. From this result, it can be proved qualitatively that Eq. [12] is a possible reaction in the acidic region of slags.

The effect of temperature on the solubility of carbon in the basic region is shown in Figure 10, with the results of previous works for comparison. The slag compositions were 72.1 (mol pct) CaO-B₂O₃ and 73.4 (mol pct) BaO-B₂O₃ for the same activity of basic oxides, *i.e.*, $a_{\text{CaO}} = a_{\text{BaO}} = 0.121$. The solubility of carbon in both slags increases with increasing temperature. The enthalpy changes for each slag can be estimated to be 59.4 and 36.4 kJ/mol, respectively, indicating that the dissolution into the highly basic slags is an endothermic reaction. The enthalpy changes of the B₂O₃-bearing slags are less than those of aluminate and aluminosilicate melts. This may result from the difference of the effect of temperature on $f_{\text{C}_2^-}$ for each slag system.

H. Relationship between Carbide Capacity and Nitride Capacity

Free and incorporated carbide capacities can be defined by the following equations from Eqs. [6] and [11], respectively:

$$C_{\text{C}_2^-} = \frac{K_{[5]} \cdot a_{\text{O}^{2-}}}{f_{\text{C}_2^-}} = (\text{wt pct C}_2^-) \cdot p_{\text{O}_2}^{1/2} \quad [14]$$

$$C_{\text{C}^-} = \frac{K_{[12]} \cdot a_{\text{O}^{2-}}}{f_{\text{C}^-} \cdot a_{\text{O}^{2-}}^{1/2}} = (\text{wt pct C}^-) \cdot p_{\text{O}_2}^{3/4} \quad [15]$$

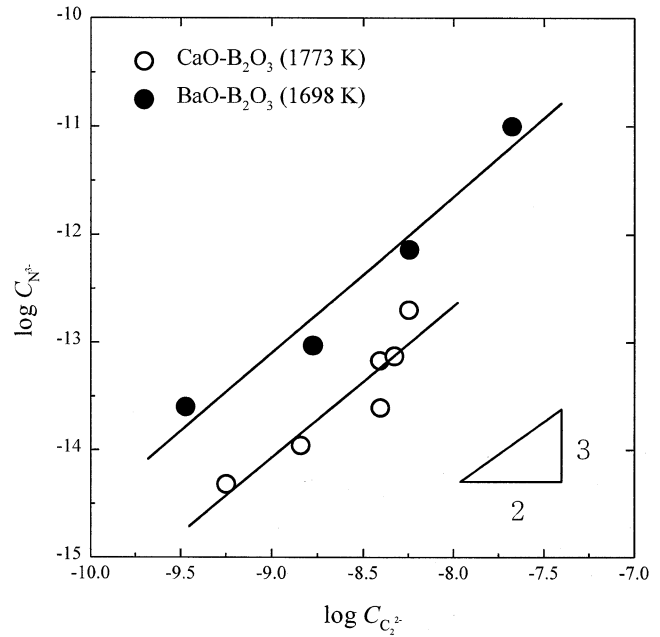
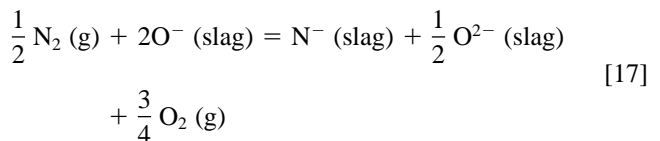
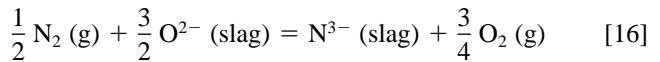


Fig. 11—Relationship between free nitride and carbide capacities in the basic region for the CaO-B₂O₃ and BaO-B₂O₃ slags.

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

The dissolution of nitrogen into the basic and acidic slags is suggested by Eqs. [16] and [17], respectively.^[10,14–17]



The nitride capacities in each case are defined as follows:

$$C_{\text{N}^{3-}} = \frac{(\text{wt pct N}^{3-}) \cdot p_{\text{O}_2}^{3/4}}{p_{\text{N}_2}^{1/2}} = \frac{K_{[16]} \cdot a_{\text{O}^{2-}}^{3/2}}{f_{\text{N}^{3-}}} \quad [18]$$

$$C_{\text{N}^-} = \frac{(\text{wt pct N}^-) \cdot p_{\text{O}_2}^{3/4}}{p_{\text{N}_2}^{1/2}} = \frac{K_{[17]} \cdot a_{\text{O}^{2-}}}{a_{\text{O}^{2-}}^{1/2} \cdot f_{\text{N}^-}} \quad [19]$$

Eliminating the $a_{\text{O}^{2-}}$ term from Eqs. [14] and [18] and [15] and [19], the relationship between the carbide capacity and the nitride capacity in the basic and acidic regions is derived, respectively, as follows:

$$\log C_{\text{N}^{3-}} = \frac{3}{2} \log C_{\text{C}_2^-} + \log \frac{f_{\text{C}_2^-}^{3/2}}{f_{\text{N}^{3-}}} + \log \frac{K_{[16]}}{K_{[5]}^{3/2}} \quad [20]$$

$$\log C_{\text{N}^-} = \log C_{\text{C}^-} + \log \frac{f_{\text{C}^-}}{f_{\text{N}^-}} + \log \frac{K_{[17]}}{K_{[12]}} \quad [21]$$

Thus, nitride capacity may be expected to have a linear relationship with carbide capacity in the logarithmic scale if the other terms are constant, and the theoretical slope will be 3/2 and 1, respectively. In Figure 11, $\log C_{\text{N}^{3-}}$ from the

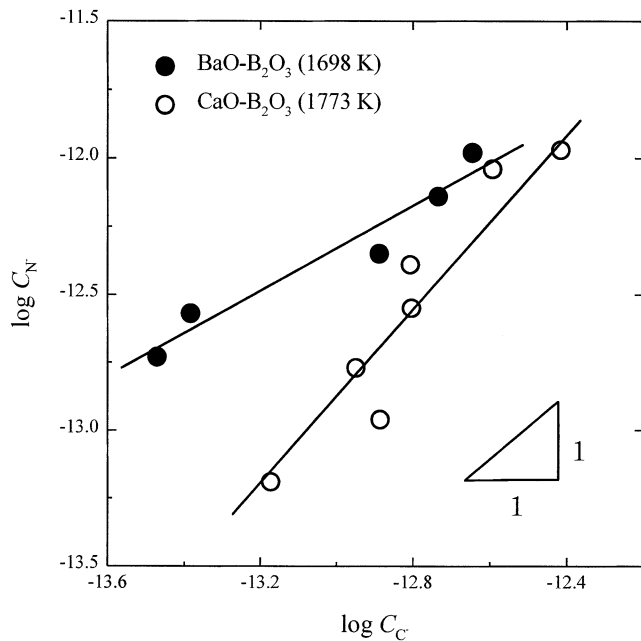


Fig. 12—Relationship between incorporated nitride and carbide capacities in the acidic region for the CaO-B₂O₃ and BaO-B₂O₃ slags.

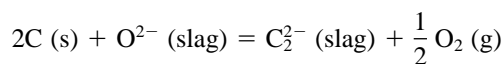
literature is plotted as a function of $\log C_{C^{2-}}$ in the basic region for the CaO-B₂O₃ and the BaO-B₂O₃ slags.^[15] The slope of the former is 1.72 and that for the latter is 1.59, which are relatively close to the expected value of 3/2. Therefore, the $f_{C^{2-}}^{3/2}/f_{N^{3-}}$ ratio in Eq. [20] may be nearly constant in the basic region of each slag system.

Figure 12 shows the relationship between $\log C_{N^-}$ and $\log C_{C^-}$ in the acidic region. The slope of the CaO-B₂O₃ system is 1.43, slightly higher than the expected value of unity, and that of the BaO-B₂O₃ system is 0.696, which is lower than the expected value. From these differences, it could be suggested that f_{C^-} would be larger than f_{N^-} in the CaO-B₂O₃ system, and *vice versa* in the BaO-B₂O₃ system, in Eq. [21]. As seen in Figures 11 and 12, the dissolution of carbon and nitrogen into the slags shows similar behavior in each slag.

IV. CONCLUSIONS

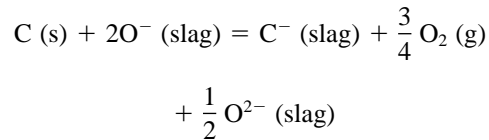
The solubility of carbon in molten CaO-B₂O₃ and BaO-B₂O₃ slags was measured at 1773 and 1698 K, respectively, to understand the dissolution mechanism of carbon into the slags. The results of this study can be summarized as follows.

1. The solubility of carbon as a function of the composition of slags shows a minimum value, which is observed at about 60 mol pct CaO in the CaO-B₂O₃ slag and at about 45 mol pct BaO in the BaO-B₂O₃ slag.
2. The dissolution of carbon into the basic region of slags is confirmed by the following reaction:



3. The dissolution mechanism of carbon into the acidic region of slags can be suggested by the following reaction

from the effect of basicity and oxygen partial pressure on the solubility of carbon:



4. The wave numbers obtained from the infrared spectra measurements indicate that the B-C bond is about 1150 cm⁻¹ in the acidic region of the CaO-B₂O₃ slag; hence the incorporation of carbon into the borate network is confirmed qualitatively.
5. The dissolution of carbon and nitrogen into the slags shows a similar behavior in B₂O₃-bearing slags based on the relationship between carbide capacity and nitride capacity.

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REFERENCES

1. Z. Morita and T. Emi: *An Introduction to Iron and Steel Processing*, Kawasaki Steel 21st Century Foundation, Tokyo, 1997.
2. J.H. Swisher: *Trans. TMS-AIME*, 1968, vol. 242, pp. 2033-37.
3. A.G. Ponomarenko and Y.E. Kozlov: *Russ. Metall.*, 1974, No. 5, pp. 61-66.
4. K. Schwerdtfeger and H.G. Schubert: *Metall. Trans. B*, 1977, vol. 8B, pp. 535-40.
5. K. Schwerdtfeger and H.G. Schubert: *Metall. Trans. B*, 1977, vol. 8B, pp. 689-91.
6. R.A. Berryman and I.D. Sommerville: *Metall. Trans. B*, 1992, vol. 23B, pp. 223-27.
7. Y. Watanabe, K. Kitamura, I.P. Rachev, F. Tsukihashi, and N. Sano: *Metall. Trans. B*, 1993, vol. 24B, pp. 339-47.
8. M. Kuwata and H. Suito: *Metall. Mater. Trans. B*, 1996, vol. 27B, pp. 57-64.
9. K.R. Lee and H. Suito: *Steel Res.*, 1996, vol. 67, pp. 87-92.
10. H.S. Song: Ph.D. Thesis, Pohang University, Pohang, Korea, 1996.
11. M. Mori, K. Morita, and N. Sano: *Metall. Mater. Trans. B*, 1997, vol. 28B, pp. 1257-59.
12. M. Mori, K. Morita, and N. Sano: *CAMP-ISIJ*, 1997, vol. 10, p. 211.
13. H.S. Song, D.S. Kim, C.H. Rhee, and D.J. Min: *J. Kor. Inst. Met. Mater.*, 1998, vol. 36, pp. 448-53.
14. K. Ito and R.J. Fruehan: *Metall. Trans. B*, 1988, vol. 19B, pp. 419-25.
15. D.J. Min and R.J. Fruehan: *Metall. Trans. B*, 1990, vol. 21B, pp. 1025-32.
16. H.S. Song, P.C.H. Rhee, and D.J. Min: *Steel Res.*, 1996, vol. 67, pp. 221-26.
17. H.S. Song, D.S. Kim, D.J. Min, and P.C.H. Rhee: *Proc. 5th. Int. Conf. Molten Slags, Fluxes, and Salts '97*, Sydney, Jan. 5-8, 1997, ISS, Warrendale, PA, pp. 583-87.
18. J.H. Park and D.J. Min: *J. Kor. Inst. Met. Mater.*, 1999, vol. 37, pp. 346-52.
19. J.H. Park and D.J. Min: *Metall. Mater. Trans. B*, 1999, vol. 30B, pp. 000-00.
20. J.H. Park and D.J. Min: *Mater. Trans. JIM*, to be published.
21. M. Kowalski, P.J. Spencer, and D. Neuschutz: *Slag Atlas*, 2nd. ed., Verlag Stahleisen GmbH, Dusseldorf, 1995, pp. 49-50.
22. E.T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, NY, 1980, pp. 1-24.
23. T. Wakasugi and N. Sano: *Metall. Trans. B*, 1989, vol. 20B, pp. 431-33.
24. H. Ono, A. Kobayashi, F. Tsukihashi, and N. Sano: *Metall. Trans. B*, 1992, vol. 23B, pp. 313-16.
25. F.D. Richardson: *Physical Chemistry of Melts in Metallurgy*, Academic Press, London, 1974, vol. 1, pp. 132-40.

26. J.A. Duffy and M.D. Ingram: *Phys. Chem. Glasses*, 1975, vol. 16, pp. 119-23.
27. J.A. Duffy and M.D. Ingram: *J. Inorg. Nucl. Chem.*, 1975, vol. 37, pp. 1203-06.
28. J.A. Duffy, M.D. Ingram, and I.D. Sommerville: *J. Chem. Soc. Faraday Trans. I*, 1978, vol. 74, pp. 1410-19.
29. F. Muller and S. Demirok: *Glastech. Ber.*, 1989, vol. 62, pp. 142-49.
30. H.O. Mulfinger: *J. Am. Ceram. Soc.*, 1966, vol. 49, pp. 462-67.
31. Y. Iguchi, S. Kashio, T. Goto, Y. Nishina, and T. Fuwa: *Can. Metall. Q.*, 1981, vol. 20, pp. 51-56.
32. E. Martinez and N. Sano: *Metall. Trans. B*, 1990, vol. 21B, pp. 97-104.
33. G. Socrates: *Infrared Characteristic Group Frequencies*, 2nd. ed., John Wiley & Sons, Chichester, 1994, pp. 195-243.
34. D.R. Gaskell: *Introduction to Metallurgical Thermodynamics*, 2nd. ed., McGraw-Hill, New York, NY, 1981, pp. 109-10.