Carbon distribution behavior between molten iron and $CaO-Al_2O_3-FeO-SiO_2-MgO$ slag at 1873 K

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ABSTRACT

The carbon solubility of the CaO-Al_2O_3-FeO-SiO_2-MgO slag, the main system formed in the Ruhrstahl-Heraeus (RH) vacuum degasser, was measured at 1873 K to understand the effect of slag compositions on the carbon contamination in the ultra-low carbon (ULC) steels. The stable form of carbon was demonstrated to be carbonate by plotting the log [(wt%C)/a_C] ratio against the log p(O_2) which ranged $-11 < \log p(O_2,\text{atm}) < -9$. The carbon solubility of the CaO-Al_2O_3-FeO-SiO_2-MgO slag can be estimated using thermodynamic model. The distribution ratio of carbon increased with increasing concentration of FeO due to the FeO reduction reaction and increased basicity of slag. The carbonate capacity of the CaO-Al_2O_3-FeO-SiO_2-MgO slag can be expressed as a linear function of the activity of lime and the optical basicity.

INTRODUCTION

Ultra-low carbon (ULC) steel sheets are widely used in the automotive industry due to its superior performance such as superior ductility or formability. There have been many improvements in the decarburization reaction in Ruhrstahl-Heraeus (RH) process for the production of ULC steel. However, after decarburization stage, carbon contamination has frequently occurred due to changes in the slag composition during the deoxidation stage. Therefore, understanding the solubility of carbon in RH-type molten slag is highly important.

Many researchers investigated the carbide solubility in various slag systems using graphite crucibles. Schwerdtfeger and Schubert (1977) reported the solubility of carbon in the CaO-Al_2O_3 slag following gas-slag equilibration. The carbide (C_2^{2-}) solubility increased with increasing basicity (i.e., CaO/Al_2O_3 ratio) of the slag. Park and his coworkers (Park and Min, 1999; Park and Min, 2004; Park, Park and Lee, 2010) reported that carbide solubility in the CaO-Al_2O_3-CaF_2, CaO-B_2O_3, and CaO-SiO_2-MnO systems also increased with increasing content of CaO.

Kuwata and Suito (1996) reported the carbon solubility in molten slag using slag-metal equilibrium with CaO or Al_2O_3 crucible. The carbide ion was found to exist as a (C^{2-}) single anion in the slag as shown in Eq. [1]. Consistent with other studies, the carbon solubility increased with increasing basicity.

$$C(s) + (O^{2-}) = (C^{2-}) + 1/2\, O_2(g) \qquad [1]$$

Many researchers have demonstrated that carbonate solubility increased with increasing basicity, following reaction in gas-slag experiments in various systems (Ikeda and Maeda, 1989; Rachev, Tsukihashi and Sano, 1991; Simeonov, Fukita and Maeda, 1992).

$$CO_2(g) + (O^{2-}) = (CO_3^{2-}) \qquad [2]$$

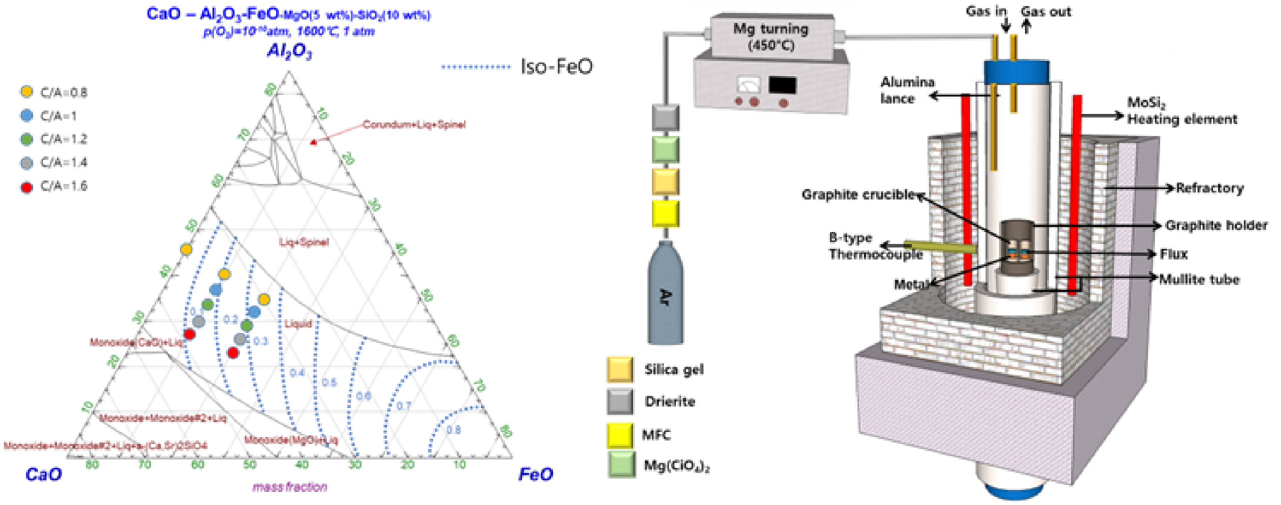
Ikeda and Maeda (1989) showed that carbonate solubility increased with increasing contents of basic oxides such as CaO in the CaO-CaF_2-$CaCl_2$ and CaO-CaF_2-SiO_2 systems. Additionally, Simeonov, Fukita and Maeda (1992) found that if CaO is replaced by Li_2O, the carbonate capacity is decreased due to the apparent basicity of CaO being higher than Li_2O. Rachev, Tsukihashi and Sano (1991) showed that carbonate capacity also increased with increasing contents of BaO. Moreover, the carbonate capacity increased with increasing optical basicity.

No published experimental data was found on the carbon solubility of FeO-containing slags. For this reason, the distribution ratio of carbon between FeO-containing slag and molten iron was measured at 1873 K in MgO crucible.

EXPERIMENTAL PROCEDURE

Carbon-saturated iron was prepared to ensure a uniform carbon concentration in the metal. The carbon-saturated iron was made by heating electrolytic iron in a carbon crucible using a high frequency induction furnace and stirring at 1723 K for one hour under an Ar (99.999%) atmosphere. The carbon concentration of the carbon-saturated iron was confirmed to be 5.3 wt% using a combustion analyser. The slags were prepared using reagent grade Al_2O_3, FeO, SiO_2, MgO and CaO calcined from $CaCO_3$ at 1273 K. The equilibration experiments with 7g slag, 4.95g electrolytic iron and 0.05g C-saturated iron were performed in MgO crucibles. The equilibration time was 24 hr under purified Ar atmosphere at 1873 K. After equilibration, the samples were quenched by Ar flushing and water.

A Super-Kanthal electric resistance furnace, shown in FIG 1, was used for the equilibration of the $CaO-Al_2O_3-FeO-SiO_2-MgO$ slag with molten iron at 1873 K under an Ar (99.999%) atmosphere. The temperature was controlled within ±2 K using a B-type thermocouple.



(a) (b)

FIG 1 – (a) Experimental slag compositions, (b) schematic diagram of the experimental apparatus.

After the equilibration, the carbon concentrations of the slag and metal samples were determined by using the combustion analyser (CS 800, ELTRA) and each component in the slags were determined by using an ICP-AES (ACROS II, Spectro). The N/O combustion analyser (ONH-p, ELTRA Co.) was used to determine oxygen content in metal samples.

RESULTS AND DISCUSSION

Kuwata and Suito (1996) reported that carbon dissolves as carbide ion following Eqs. [3] to [5], and dissolves as carbonate ion following Eqs. [6] to [8] when $\log(wt\%C)\ /a_C$ is plotted against $\log p_{O_2}$. If the carbon dissolves as carbide ion, the slope is -1/2 from Eq. [5], and dissolves as carbonate with the slope of unity from Eq. [8].

$$[\mathrm{C}] + (O^{2-}) = (C^{2-}) + 1/2O_2(g) \qquad [3]$$

$$K_{[3]} = (a_{C^{2-}} \cdot p_{O_2}^{1/2})/(a_C \cdot a_{O^{2-}}) \qquad [4]$$

$$\log(wt\%C)/a_C = -(1/2)\log p_{O_2} + \log\,(K \cdot a_{O^{2-}}/f_{C^{2-}}) \qquad [5]$$

$$[\mathrm{C}] + (O^{2-}) + O_2(g) = (CO_3^{2-}) \qquad [6]$$

$$K_{[6]} = a_{CO_3^{2-}}/(a_C \cdot a_{O^{2-}} \cdot p_{O_2}) \qquad [7]$$

$$\log(wt\%C)/a_C = \log p_{O_2} + \log\,[(M_C/M_{CO_3})\,K \cdot a_{O^{2-}}/f_{CO_3^{2-}} \qquad [8]$$

To investigate the general form of carbon in the slags, FIG 2 shows both the $\log(wt\%C)\ /a_C$ plotted against the oxygen partial pressure calculated with the Fe-FeO equilibrium reaction and carbon solubility calculated with Pelton-Eriksson-Serrano model (i.e., capacity model) (Pelton, Eriksson and Serrano, 1993). The activity of carbons was calculated from Wagner formalism using the first-order interaction parameters, which are listed in Table 1 (Hino and Ito, 2010). The slope of the linearly fitted line was about 0.8, which was close to the slope of unity expected from Eq. [8]. Therefore, the carbon in the RH-type molten slag can be defined as carbonate ion in the present study.

TABLE 1 – Interaction Parameters used in the Present Study.

e_i^j	j = C	O
i = C	0.14	-0.34
O	-0.45	-0.17

Jung (2006) calculated the carbide and carbonate capacities in the CaO-Al_2O_3 binary slag system using the capacity model and found that the calculated results were well matched with the experimental data. In the present study, the carbonate capacities calculated with the capacity model were also in good agreement with the measured data as shown in FIG 2

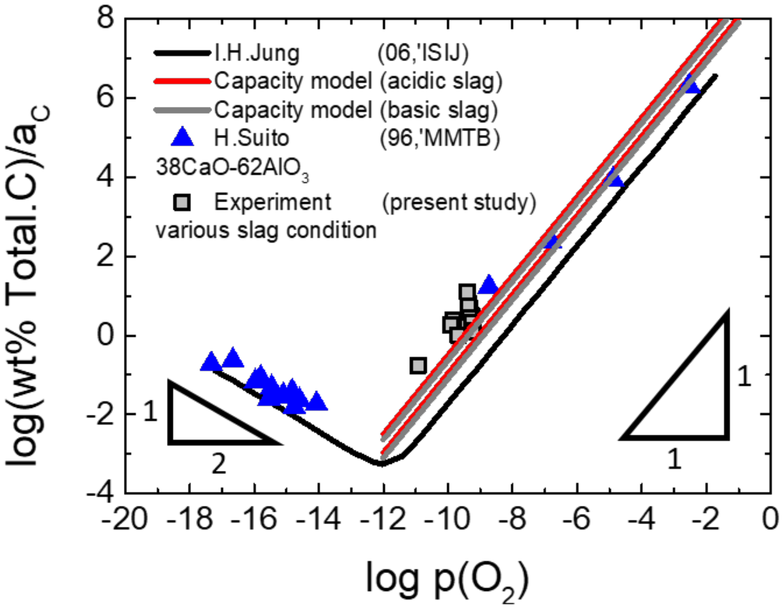


FIG 2 – Experimental and calculated results of carbon solubility plotted against oxygen partial pressure in logarithmic form for the FeO-containing slags.

The carbonate dissolution reaction can be defined as given in Eq. [2], and thus carbonate capacity is given below. (Ikeda and Maeda, 1989; Rachev, Tsukihashi and Sano, 1991; Simeonov, Fukita and Maeda, 1992).

$$C_{CO_3^{2-}} = K \cdot a_{O^{2-}}/f_{CO_3^{2-}} = (wt\%\ CO_3)/p_{CO_2} = (M_{CO_3}/M_C) \cdot [(wt\%C)/p_{CO_2}] \qquad [9]$$

$$\mathrm{Log}C_{CO_3^{2-}} = log a_{O^{2-}} - log f_{CO_3^{2-}} + constant \qquad [10]$$

Because the activity of free oxygen cannot be directly measured due to thermodynamic constraints, the activity of basic oxide such as CaO can be used as an indirect basicity index. FIG 3 represents the relationship between the carbonate capacity and the activity of CaO. The activity of CaO was calculated using FactSage^{TM}(ver 8.2.). A good linear correlation between them on a logarithmic scale can be found with the slope of 0.85. Although there are some experimental scatters, the slope of the fitted line is relatively close to the theoretical value of unity even though there are some scatters.

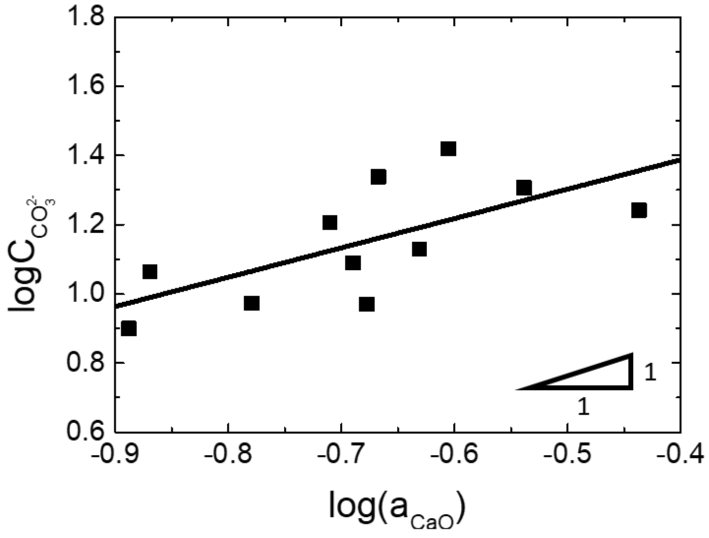


FIG 3 – Dependence of the carbonate capacity on the activity of CaO in molten slag.

CONCLUSIONS

Carbon solubility in the CaO-Al_2O_3-FeO-SiO_2-MgO slag was measured at 1873 K at oxygen partial pressure between $-11 \leq \log p_{O_2} \leq -9$ to determine the dissolution mechanism of carbon in the FeO-bearing slags by using the slag-metal equilibration reaction. The carbon solubility was plotted in terms of $\log\,(wt\%C)/a_C$ against $\log p_{O_2}$ to determine the stable form of carbon in the slag. Carbon was found to be dissolved as CO_3^{2-} and the carbonate capacity $C_{CO_3^{2-}}$ increased with increasing activity of CaO which can be the basicity index. Also, the calculated results using a capacity model were well matched with the experimental data.

REFERENCES

Ikeda, T., Maeda, M. 1989. Solubility of Carbon Dioxide in CaO-$CaCl_2$-CaF_2 Molten Fluxes, *Tetsu-to-Hagané*, 75(5): 742-749.

Jung, I.H. 2006. Thermodynamic modeling of gas solubility in molten slags (I)—carbon and nitrogen, *ISIJ International*, 46(11), 1577-1586.

Kuwata, M., Suito, H. 1996. Solubility of carbon in CaO-Al_2O_3 melts, *Metallurgical and Materials Transactions B*, 27(1), 57-64.

Park, J.H., Min, D.J. 1999. Solubility of carbon in CaO-B_2O_3 and BaO-B_2O_3 slags, *Metallurgical and Materials Transactions B*, 30(6), 1045-1052.

Park, J.H., Min, D.J. 2004. Carbide Capacity of CaO-SiO_2-CaF_2(-Na_2O) Slags at 1773 K, *ISIJ International*, 44(2), 223-228.

Park, J.H., Park, G.H., Lee, Y.E. 2010. Carbide capacity of CaO–SiO_2–MnO slag for the production of manganese alloys. *ISIJ International*, 50(8), 1078-1083.

Hino, M., Ito, K. 2010. *Thermodynamic for steelmaking,* pp 76-89 (Tohoku University Press: Sendai).

Pelton, A.D., Eriksson, G. Romero-Serrano, A. 1993. Calculation of sulfide capacities of multicomponent slags, *Metallurgical Transactions B*, 24(5), 817-825

Rachev, I.P., Tsukihashi, F. Sano, N.F. 1991. The thermodynamic behavior of sulfur in BaO-BaF_2 slags, *Metallurgical Transactions B*, 22(3), 333-338.

Schwerdtfeger, K., Schubert, H.G. 1977. Solubility of nitrogen and carbon in CaO-Al_2O_3 melts in the presence of graphite. *Metallurgical Transactions B*, 8(3), 535-540.

Simeonov, S., Fukita, K. Madea, M. 1992. Influence of Li_2O on the carbonate capacity of CaO-CaF_2-Al_2O_3 Melts, *Metallurgical Transactions B*, 23(2), 183-187.