

Communication

Carbon Solubility in the CaO-SiO₂-3MgO-CaF₂ Slag System

JUN-YONG PARK, SUNG-MO JUNG,
and IL SOHN

The carbon solubility in the CaO-SiO₂-3MgO-CaF₂ slag system at 1773 K (1500 °C) was investigated under CO/Ar and CO/N₂ gases. Higher extended basicity [(CaO + MgO)/SiO₂] increased the carbon solubility in the slag as the activity of free oxygen ions ($a_{O^{2-}}$) promoted the reaction of the free carbide mechanism. Higher CaF₂ also resulted in higher carbon dissolution into the slag as fluorine ions interact with the bridged oxygen (O⁰) in the melt structure to increase the activity of the free oxygen ions in the melt. Structural information obtained from the Fourier transformed infra-red (FT-IR) and Raman revealed a depolymerization of the network structure as the simpler structural units of NBO/Si = 4 increased and the Si-O-Si bending vibrations decreased with higher basicity and CaF₂ content. This correlated well with higher free oxygen ions (O²⁻) in the slag system and subsequently higher carbon dissolution. A correlation of the theoretical optical basicity (Λ_{th}) with the logarithm of the carbon content in slag showed a relatively similar trend and an increase of carbon was observed with higher optical basicity.

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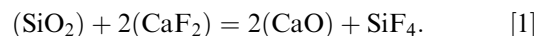
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The dominant carbon dissolution mechanisms in slags have been well-known to be the incorporated carbide or free carbide mechanisms depending on the composition and in particular the extended basicity (basic oxides/acidic oxides).^[1-6] And when sufficient nitrogen is present in some slag systems, cyanide (-CN) has also been known to form with the incorporated and free carbide to significantly increase the carbon and nitrogen content of the slag compared to nitrogen-free reacting systems, as verified by the present authors in the CaO-10SiO₂-Al₂O₃-CaF₂ slag system.^[1,4] The relative contents of slag constituents are provided in wt pct in the present paper.

In this study, the carbon solubility in the CaO-SiO₂-MgO-CaF₂ slag system has been investigated. The effect of the extended basicity [(CaO + MgO)/SiO₂] and CaF₂

content on the carbon solubility has been provided. In addition, the carbon solubility of the slag was correlated to the melt structure using Fourier transformed infra-red (FT-IR) and Raman spectroscopy of as-quenched slags from 1773 K (1500 °C).

Reagent grade chemicals (Junsei; Tokyo, Japan) of CaCO₃ (99.5 pct), SiO₂ (99.5 pct), MgO (98 pct), and CaF₂ (99 pct) were used. A total of 4 g was pre-melted in a Pt-10Rh crucible for 5 hours at 1773 K (1500 °C) with Ar gas flowing at 4.2 cm³/s. The post-experimental chemical compositions were analyzed using X-ray fluorescence spectroscopy (XRF; S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany), as provided in Table I. There are slight changes in the composition of the slags and the post-experimental compositions were used in subsequent results. In past work by Kor and Richardson,^[7] it was inferred that the CaF₂ and H₂O could react to form CaO and HF, which could affect not only the partial pressure of H₂O, but also the activity of O²⁻ in the slag as CaO is increased. Changes in the activity of O²⁻ can have a significant effect on the carbon solubility.^[4,6] However, in the present work, ultra high purity grade gases (99.9999 pct) were passed through columns of drierite and soda lime to remove impurities such as H₂O and CO₂ that may be present in the gases and there is likely negligible amount of moisture to react with the CaF₂ in the slag. Thus, the very slight change in the weighed and post-experimental chemical analysis of the slag, if any, is likely due to the formation of SiF₄ according to earlier work by Mitchell^[8] expressed in Eq. [1].



The CaF₂ and SiO₂ loss decreases with increasing CaO and seems to agree with the findings of Mitchell and Kumar *et al.*^[9] This change in the composition can increase the oxygen activity resulting in higher carbon solubility. However, as the CaF₂ content decreases, lower carbon solubility can occur^[4] and thus there could be a mutual competing effect of CaF₂ and CaO following volatilization through Reaction [1]. It should be noted that reference samples containing reagent grade chemicals of CaF₂ at concentrations of 3, 5, 8, 10, 12, and 15 wt pct was used to obtain a calibration curve for specifically CaF₂ since compositional changes in CaF₂ could occur in the CaO-SiO₂-CaF₂-3MgO system and accurate determination of the fluorine content is of importance. Furthermore, preliminary experiments showed the small changes in the composition for the present slag system occurred during the 5 hours pre-melting stages and compositional changes through volatilization was not significant during the 24 hours high temperature chemical equilibrium experiments. This compositional change during the pre-melting stages and the kinetics is a topic of further research. All results in the present study use the post-experimental chemical compositions and accounts for minute changes in the slag composition and its effect on the carbon solubility, if any.

Details of the experimental apparatus have been discussed elsewhere,^[4] but the slag sample was placed in a carbon crucible (OD: 1.5 cm, ID: 1.1 cm, H:

JUN-YONG PARK, Graduate Student, and IL SOHN, Associate Professor, are with Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea. Contact e-mail: ilsohn@yonsei.ac.kr SUNG-MO JUNG, Professor, is with the Graduate Institute of Ferrous Technology, POSTECH, San31, Hyoja-dong, Nam-gu, Pohang, Gyeongbuk 790-784, Korea.

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Table 1. Pre- and Post-experimental Composition Obtained from the XRF and the Carbon Content Analyzed Using the LECO C/S Analyzer

Sample No.	Pre-experimental (wt pct)				Post-experimental (wt pct)					Carbon (wt pct) STDEV	Extended Basicity (C + M)/S
	CaO	SiO ₂	CaF ₂	MgO	CaO	SiO ₂	CaF ₂	MgO	AVG		
CSFM1N	39	48	10	3	42	46	9	3	0.05871	0.0008	1.0
CSFM2N	44	44	10	3	46	42	9	3	0.0608	0.0028	1.2
CSFM3N	49	38	10	3	50	39	9	3	0.0626	0.0023	1.4
CSFM4N	49	49	0	3	51	46	0	3	0.0586	0.0022	1.2
CSFM5N	46	46	5	3	48	44	5	3	0.0620	0.0017	1.2
CSFM6N	41	41	15	3	43	39	14	3	0.0655	0.004	1.2

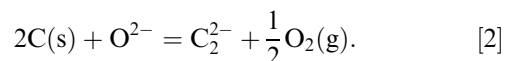
7.2 cm) within a Müllite reaction tube under a mixture of CO with Ar or N₂ gases (6:4) of 4.2 cm³/s. A MoSi₂ (Kanthal; Hallstahammar, Sweden) vertical resistance furnace was set at a target temperature of 1773 K (1500 °C). The oxygen partial pressure was maintained using the C/CO equilibrium reaction resulting in an oxygen partial pressure of approximately 10⁻¹⁶ atm, which is above the oxygen partial pressure for the decomposition of the Müllite reaction tube. Preliminary work with slags showed the equilibrium reaction time for the slag/carbon to be approximately more than 18 hours; thus, the equilibration time was taken to be 24 hours.^[4] The sample was removed from the hot zone of the furnace after the reaction was completed and quickly quenched with Ar gas. Carbon was measured by a CS-300 analyzer (LECO; St. Joseph, MI).

FT-IR (Spectrum-100; PerkinElmer, Waltham, MA) and Raman (PD-RSM300; Photon Design, Tokyo, Japan) spectroscopy on as-quenched slag samples were used to ascertain structural information of the slags. A sample of 2 mg was mixed with 200 mg of KBr, which was then pressed into 10 mm diameter and 1-mm-thick disk pellets for FT-IR analysis.^[10,11] The characteristic structural units of the silicate based slags verified with the FT-IR and Raman are typically concentrated within the wavenumber between 1400 and 400 cm⁻¹, where the various symmetric stretching and bending vibrations of the Si-O bonds constitute the greater part of the slag structure.

From the Raman spectroscopy (PD-RSM300; Photon Design; Tokyo, Japan), the obtained spectra can be deconvoluted and the area integrated to ascertain quantitative information on the amounts of the individual silicate structural units within the melt.

Figure 1 shows the carbon solubility in the CaO-SiO₂-3MgO-9CaF₂ slag at 1773 K (1500 °C) as a function of the extended basicity [(CaO + MgO)/SiO₂ ratio] under a CO and Ar or N₂ gas mixture. The carbon solubility in the slag seems to slightly increase with higher basicity under both atmospheric conditions. Although the amount of carbon is much less, this trend is similar to the results obtained from past work done by the authors in an alumina rich CaO-10SiO₂-Al₂O₃-10CaF₂ slag at 1773 K (1500 °C) shown by the open circles, which is expected for a (CaO + MgO)/SiO₂ above unity.^[4] If the free carbide ion dominates in the compositional range of the present study, the carbide ions increase with

increasing activity of free oxygen ions according to Reaction [2].



The carbon solubility in the CaO-10SiO₂-Al₂O₃-10CaF₂ slag system is also provided and shows comparable trends with the CaO/(SiO₂ + Al₂O₃) ratio. From the comparison of the absolute values of the aluminate-rich and silicate-rich slag systems, it can be inferred that the aluminate-rich slags are more effective in dissolving carbon. Furthermore, unlike the carbon solubility of the CaO-10SiO₂-Al₂O₃-10CaF₂ system, where significant cyanide (-CN) formed under a CO/N₂ atmosphere, the present CaO-SiO₂-3MgO-9CaF₂ system under identical conditions did not show dramatic differences in the carbon content with CO/Ar and CO/N₂ atmospheres. Only a slight increase in the carbon content was verified with the CO/N₂ combination and thus suggests only minimal formation of -CN compounds. The carbon content of the present study showed comparable results to Berryman and Sommerville.^[2] The increasing trend was similar to their results above a CaO/SiO₂ of 0.9, where the free carbide mechanism begins to dominate. In the present work, the oxygen partial pressure is less than 10⁻¹⁶ atm, where the carbide formation is dominant and the carbonate formation mechanism is not expected.^[12]

The effect of CaF₂ on the carbon solubility in the CaO-SiO₂-3MgO-CaF₂ slag at 1773 K (1500 °C) and fixed extended basicity of 1.2 is shown in Figure 2. Higher CaF₂ content seems to increase the carbon solubility of the slag in both CO/Ar and CO/N₂ atmospheres. CaF₂ has been known to be a network modifier, which can interact with the bridged oxygen (O⁰) in the silicate melts to release free oxygen ions (O²⁻). Thus with the addition of CaF₂, the activity of free oxygen ions would likely increase and similar to higher basicity push Reaction [1] forward to increase the carbon solubility in the slag. The carbon content in the melt at 1773 K (1500 °C) for CO/N₂ was found to be higher than the CO/Ar condition. This difference in the carbon content is to be the aforementioned additional formation of cyanide compounds within the slag as was observed by Park and Sohn.^[4]

The carbon solubility in the present slag system at 1773 K (1500 °C) was found to be directly affected by

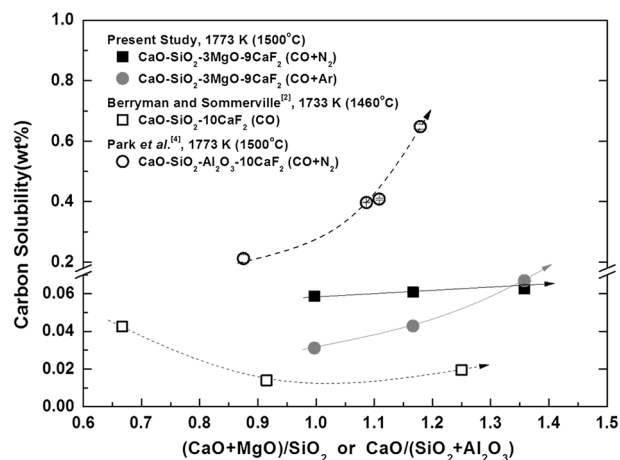


Fig. 1—Effect of the extended basicity $[(\text{CaO} + \text{MgO})/\text{SiO}_2]$ on the carbon solubility in the $\text{CaO-SiO}_2\text{-3MgO-9CaF}_2$ slag system at 1773 K (1500 °C).

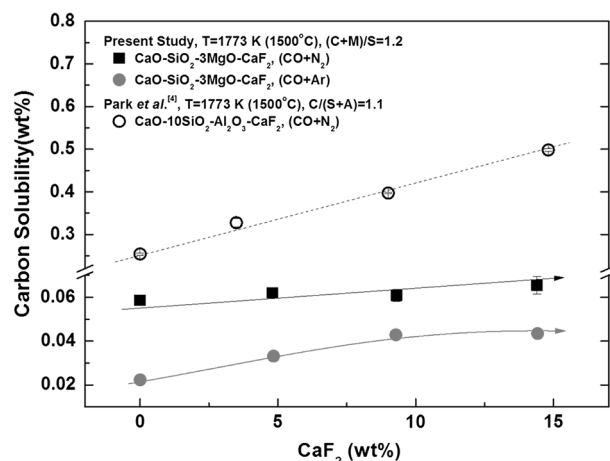
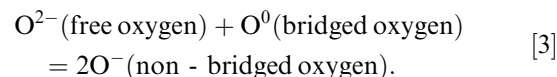


Fig. 2—Effect of CaF_2 content on the carbon solubility in the $\text{CaO-SiO}_2\text{-3MgO-CaF}_2$ slag system at fixed $(\text{CaO} + \text{MgO})/\text{SiO}_2$ of 1.2 and 1773 K (1500 °C).

the compositional variations of the extended basicity and CaF_2 additions. These modifications in the composition and carbon solubility can also be correlated to the slag structure. Using FT-IR and Raman spectroscopy of as-quenched slags from 1773 K (1500 °C), the changes in the basicity and CaF_2 can influence the various structural units that comprise the molten slag. Figure 3(a) describes the Si-O tetrahedral stretching vibrations as a function of the basicity in the $\text{CaO-SiO}_2\text{-3MgO-9CaF}_2$ slag system. The depth of the NBO/Si = 4 trough convoluted within the symmetric $[\text{SiO}_4]$ -tetrahedral stretching vibrations located approximately at 850 cm^{-1} generally increases with higher basicity and the right peak of the NBO/Si = 4 shifts toward lower wavenumber.^[13,14] NBO/Si is the number of non-bridged oxygen per tetrahedral cation and a higher value corresponds to a less complex and simple structural unit, which can be identified with depolymerization of the melt structure. As the peak shifts toward lower

wavenumbers, the center of gravity within the symmetric $[\text{SiO}_4]^{4-}$ -tetrahedral stretching bands moves toward lower wavenumbers. This suggests that the simple structural units of the NBO/Si = 4 are becoming more pronounced and a depolymerization of the slag is occurring with higher basicity, which is expected as the free oxygen ions provided at higher basicity can interact with the bridged oxygen to form non-bridged oxygens as anticipated by Reaction [3].^[15-17]



In addition, the Si-O-Si bending and its transmittance trough located near 700 cm^{-1} shifts toward lower wavenumbers and becomes less pronounced with higher basicity. Considering the Si-O-Si bending vibrations are characteristic of complex structural units, higher basicity seems to decrease the intensity of the Si-O-Si bending and suggest a depolymerization of the network to simpler structural units. Figure 3(b) shows the effect of CaF_2 on the slag structure. With higher CaF_2 content, the depth of the NBO/Si = 4 trough becomes deeper and more pronounced indicating a depolymerization to simpler structures corresponding to NBO/Si = 4. Thus, with higher basicity the slag structure becomes more depolymerized with the supply of excess free oxygen ions and subsequently increases the activity of free oxygen ions to increase the carbon solubility by pushing Reaction [1] forward. The Si-O-Si bending also becomes less pronounced further supporting the depolymerization of the structure and subsequent affinity for the free carbide mechanism to be dominant as the bridged oxygen ions decrease.

A more quantitative analysis can be performed using Raman spectroscopy of the as-quenched slags. Table II provides the fraction of structural units obtained from the integration of the deconvoluted Raman spectra comprising the slag as a function of basicity. It was apparent that the fraction of structural units including NBO/Si = 1 and NBO/Si = 3 decreased, while the NBO/Si = 2 and NBO/Si = 4 increased with higher basicity. This illustrates the network modification of the slag structure with higher basicity as the complex structures of NBO/Si = 1 become depolymerized and increase the fraction of less complex NBO/Si = 2 and NBO/Si = 4 structural units within the melt. This corresponds well with the results of the FT-IR and the carbon solubility plots with higher basicity.

Similar to the FT-IR, Figure 4 shows the depolymerization of the structure with higher CaF_2 content in the slag. As expected, higher CaF_2 sequentially decreases the complex structural units of NBO/Si = 1 and NBO/Si = 3, while the less complex structural units of NBO/Si = 2 and NBO/Si = 4 increase. From the FT-IR and Raman results, the complex silicate structural units decrease with higher basicity and CaF_2 content subsequently lowering the available bridged oxygen ions and increasing the free oxygen ion activity to facilitate the dominance of the free carbide mechanism and increase the carbon dissolution into the melt.

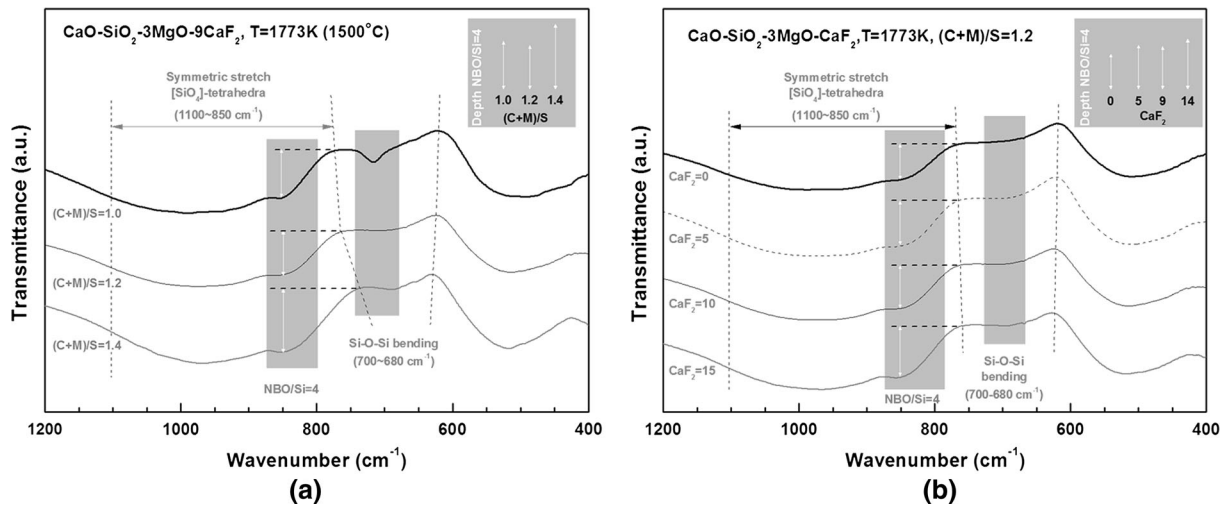


Fig. 3—FT-IR spectra of as-quenched slags from 1773 K (1500 °C) as a function of (a) extended basicity at fixed CaF_2 of 9 wt pct and (b) CaF_2 content at fixed extended basicity of 1.2.

Table II. Fraction of Structural Units in the $\text{CaO-SiO}_2\text{-3MgO-9CaF}_2$ Slag Estimated from the Integration of the Deconvoluted Raman Spectra of As-quenched Slags from 1773 K (1500 °C) as a Function of Extended Basicity [(wt pct $\text{CaO} + \text{wt pct MgO})/(\text{wt pct SiO}_2)]$ at Fixed CaF_2 of 9 wt pct

Extended Basicity [($\text{CaO} + \text{MgO}$)/ SiO_2]	Fraction of Structural Units	
	NBO/Si = 1 + 3	NBO/Si = 2 + 4
1.0	0.60	0.40
1.2	0.48	0.52
1.4	0.36	0.64

The compositional variations in the present study include changes in both the apparent basicity defined as the mass ratio of CaO/SiO_2 and CaF_2 . To comprehend both effects into a single variable, the theoretical optical basicity first proposed by Duffy and Ingram^[16] has been used in Figure 5. The details of the theoretical optical basicity (Λ_{th}) have been described in detail elsewhere, but the calculation can be obtained from Eq. [4].^[18]

$$\Lambda_{\text{th}} = \frac{\sum_{i=1}^j x_i \times n_i \times \Lambda_i}{\sum_{i=1}^j x_i \times n_i}, \quad [4]$$

where the theoretical optical basicity of the compound is calculated from the addition of each individual pure component i optical basicity (Λ_i) of a j component comprised system. In the $\text{CaO-SiO}_2\text{-3MgO-CaF}_2$ system considered in the present study, there are four components and the theoretical optical basicity of the pure constituents CaO , SiO_2 , MgO , and CaF_2 estimated from the average electron density according to Nakamura *et al.*^[18] was 1.00, 0.47, 0.92, and 0.67, respectively. x_i is the mole fraction of component i and n_i is the number of anions with respect to unit cation in the compound. Figure 5 shows a relatively similar trend of the logarithm of carbon content as a function

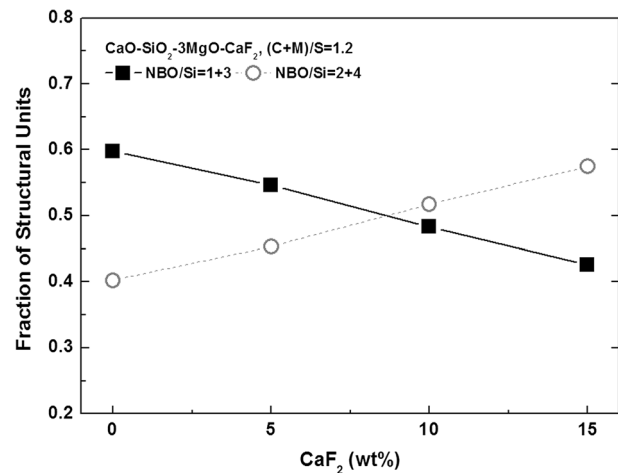


Fig. 4—Fraction of structural units in the $\text{CaO-SiO}_2\text{-3MgO-9CaF}_2$ slag estimated from the integration of the deconvoluted Raman spectra of as-quenched slags from 1773 K (1500 °C) as a function of CaF_2 content at fixed extended basicity of 1.2.

of the theoretical optical basicity, which correlates well with the depolymerization of the melt structure and subsequent increase in the carbon content with both increasing CaO/SiO_2 and CaF_2 content in the slag. The overall trend in carbon with optical basicity seems to agree well with work done by others.^[19,20]

The effect of the extended basicity and CaF_2 on the carbon solubility in the $\text{CaO-SiO}_2\text{-3MgO-CaF}_2$ slag system at 1773 K (1500 °C) was investigated under CO/Ar and CO/N_2 . In the present study, the carbon solubility increased with increasing activity of free oxygen ions or increasing basicity. The carbon seems to dissolve as a carbide ion. Higher CaF_2 also resulted in higher carbon dissolution into the slag as the network modifying fluorine ions interacts with the bridged oxygen in the melt structure to increase the activity of

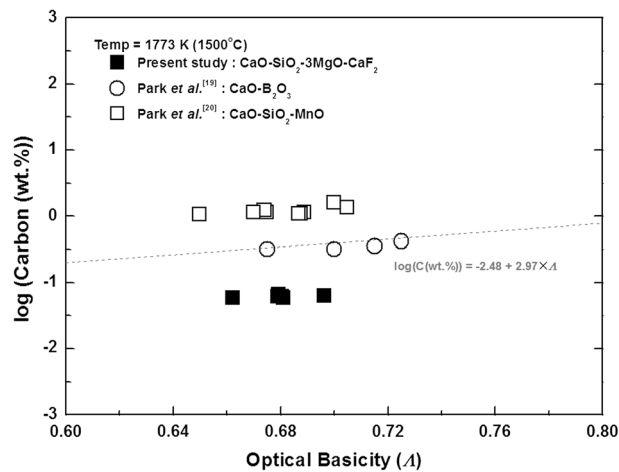


Fig. 5—Logarithm of the carbon content in the in the CaO-SiO₂-3MgO-CaF₂ slag system at 1773 K (1500 °C) as a function of the theoretical optical basicity (A).

the free oxygen ions in the melt subsequently driving the forward reaction of the free carbide mechanism. Slightly higher carbon content was observed for the CO/N₂ atmosphere compared to CO/Ar, which may be the formation of the cyanide compounds within the melt. Structural information obtained from the FT-IR and Raman revealed a depolymerization of the network structure as the simpler structural units of NBO/Si = 4 increased with higher basicity and CaF₂ content. The Si-O-Si bending vibration also decreased with higher basicity and CaF₂ to support the depolymerization of the melt and decreasing the bridged oxygen ions and increasing the activity of free oxygen ions to facilitate the free carbide mechanism. A correlation of the theoretical optical basicity with the logarithm of the carbon content in slag showed a similar trend and an increase of carbon was observed with higher optical basicity.

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