Activities of SiO_2 in Some $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(-10\%\text{MgO})$ Melts with Low SiO_2 Contents at 1 873 K

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The activity of SiO_2 in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(-10\%\text{MgO})$ systems was measured at the region of $\%\text{SiO}_2 < 10\%$. The melts were equilibrated with a reference metal of Cu in a controlled oxygen partial pressure at 1 873 K. Iso- SiO_2 activity contours were drawn from the measured values. For the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system, the measurement result showed positive deviation from the previous data. It was also found that the SiO_2 activity decreased as CaO content increased. In the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2-10\%\text{MgO}$ system, the composition dependence of the SiO_2 activity seemed to be similar as the ternary system. On the other hand, the activity values were much lower than that of the ternary system. It could be attributed to the strong basic behaviour of MgO. Based on the result of the SiO_2 activity measurement, the equilibrium between the inclusions and liquid steel during ladle treatment was discussed.

KEY WORDS: activity of SiO_2 ; $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system; $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ system; deoxidation equilibrium; ladle process.

1. Introduction

Generally, non-metallic inclusions in steelmaking have detrimental influences on the final product. It has been a main issue for steelmakers to control the inclusions appropriately. Moreover, the increasing demand on the cleaner steel, such as tool steel, requires even more careful controls on the inclusions. In secondary refining of the tool steel, calcium aluminate liquid inclusions have been often observed. Most of the inclusions stay in the steel till the end of the processes. Since they are rather big in size ($\sim 10\ \mu\text{m}$), the calcium aluminate inclusions are very likely to degrade the quality of the final product.

Although a few experimental studies on the calcium aluminate inclusions in the ladle process have been carried out,^{1,2)} thermodynamic aspects have not been fully discussed yet due to the lack of thermodynamic data. Moreover, it has been found that 2 types of the liquid calcium aluminate inclusions coexist at the end of the ladle process.²⁾ Their distinctively different SiO_2 contents have suggested a careful consideration on the equilibrium during the ladle process. However, the activity data of the components of low SiO_2 melts are extremely insufficient.

Many researchers have tried to measure the activities in silicate melts.^{3–7)} Particularly, the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(-\text{MgO})$ system has been often studied because of its practical importance in the secondary refining as well as iron and steel-making. Kay and Tayler^{3,4)} reported the activities of SiO_2 in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(-\text{MgO})$ system at 1 823 K. They de-

rived the activities from the equilibrium partial pressure of CO in the reaction: $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$. Rein and Chipman⁵⁾ measured the activities of SiO_2 related to the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ system by an equilibrium technique. Slags and Fe-C-Si alloys were equilibrated in CO atmosphere at 1 873 K. The SiO_2 activities were obtained from the silicon distribution. Subsequently, the activities of other components were calculated using the Gibbs–Duhem integration method. However, there was difficulty in the determination of the Si distribution with low SiO_2 composition. In the works of Morita *et al.*,^{6,7)} the silicate slags and silicon alloys were equilibrated at 1 823 K and 1 873 K to determine the activity of SiO_2 by modified application of the Gibbs–Duhem equation. However, the integration methods might intrinsically bear significant error when SiO_2 content was too small.

This study aims at the determination of the SiO_2 activities in low SiO_2 region of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2(-\text{MgO})$ system using an equilibrium technique with copper as the reference metal. Based on the results of the measurement, the deoxidation equilibrium between the $\text{CaO-Al}_2\text{O}_3$ liquid inclusions and liquid steel in the secondary refining is discussed.

2. Experimental

In order to measure the activity of SiO_2 in the silicate melt, reference metal and synthetic oxide solution were equilibrated in a MoSi₂ resistance furnace, SS-1700-200,

NEMS. In **Fig. 1**, the experimental apparatus is shown. The temperature was controlled with a proportional integral differential (PID) controller equipped with Pt–6%Rh/Pt–30%Rh thermocouple. All experiments were carried out at 1873 K.

Copper, of which the activity coefficient of Si has been reported as 0.016 (infinite dilute solution)⁸⁾ was used as a reference metal. Reagent grade Al_2O_3 , SiO_2 , MgO and CaO , calcined from CaCO_3 were carefully mixed so as to obtain a certain composition. The mixture was premelted in a platinum crucible at 1923 K for 30 min. After quenching, the samples were crushed finely for sample preparation. The weighed-in compositions of the oxide melts are listed in **Table 1**.

In order to control the oxygen partial pressure, $\text{C(s)}/\text{CO(g)}$ equilibrium, which can be expressed as Eqs.

(1), (2) was used.

$$\log K_1 = \log \frac{p_{\text{CO}}}{a_{\text{C}} \cdot p_{\text{O}_2}^{1/2}} = \frac{6088}{T} + 4.33^{9)} \quad \text{.....(2)}$$

where a_{C} is the activity of carbon relative to pure solid, while p_{CO} and p_{O_2} are the partial pressure of CO(g) and $\text{O}_2(\text{g})$, respectively. The partial pressure of oxygen was evaluated to be 4.4×10^{-16} atm.

About 10 g of metallic copper rod ($\text{Cu} > 99.9\%$) and 10 g of the synthetic slag were filled in a graphite crucible, which was held in a larger graphite holder. The holder with the sample was inserted into the even temperature zone of the furnace. After holding at 1873 K for 18 h, which were confirmed to be enough to reach equilibrium by preliminary experiments, the sample was quenched. Thereafter, the metal and the slag were carefully separated for chemical analyses.

The content of Si in Cu was analyzed by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Seiko Instrument Co. The ICP-AES was also used for determination of the slag compositions. SiO_2 content in slag sample was analyzed by a gravimetry separately.

Fig. 1. Experimental apparatus.

Table 1. Charge compositions.

sample	charge compositions			
	CaO (mass%)	Al_2O_3 (mass%)	SiO_2 (mass%)	MgO (mass%)
ternary	301	49	40	11
	302	56	35	9
	303	48	43	9
	304	40	51	9
	305	47	47	6
	306	55	39	6
	307	40	54	6
	308	47	50	3
	309	40	57	3
	310	55	42	3
quaternary	401	41	40	9
	402	46	35	9
	403	37	44	9
	404	42	42	6
	405	46	38	6
	406	36	48	6
	407	41	46	3
	408	35	52	3
	409	45	42	3
	410	39	42	9
inclusions	411	47	35	11
	412	48	32	14

3. Results and Discussion

Using Eqs. (3)–(5), the activity of SiO_2 can be calculated by Si content in Cu and the oxygen partial pressure.

$$\log K_3 = \log \frac{a_{\text{Si}} \cdot p_{\text{O}_2}}{a_{\text{SiO}_2}} = - \frac{49799}{T} + 10.65^{10)} \quad \text{.....(4)}$$

$$a_{\text{Si}} = \gamma_{\text{Si}} \cdot X_{\text{Si}} \quad \text{.....(5)}$$

where a_{Si} is the activity of Si relative to pure liquid, while a_{SiO_2} is relative to pure solid.

3.1. Activity of SiO_2 in the CaO – Al_2O_3 – SiO_2 System

The results of the chemical analysis of the slag samples are presented in **Table 2**. A comparison of the results with the weighed-in compositions in Table 1 indicates that the slag compositions did not change significantly during the

Table 2. Analyzed compositions of the melts and SiO_2 activities in the CaO – Al_2O_3 – SiO_2 system.

sample	analyzed compositions			mass%Si in Cu	a_{SiO_2} ($\times 10^{-3}$)
	CaO (mass%)	Al_2O_3 (mass%)	SiO_2 (mass%)		
ternary system	301	49	40	0.38	1.02
	302	55	36	0.24	0.64
	303	47	44	0.34	0.91
	304	39	52	0.62	1.64
	305	48	46	0.27	0.72
	306	54	40	0.07	0.19
	307	40	54	0.37	0.99
	308	46	50	0.14	0.38
	309	40	56	0.18	0.47
	310	54	42	0.04	0.10

Fig. 2. Iso- a_{SiO_2} lines in the CaO- Al_2O_3 - SiO_2 system at 1873 K, Solid lines: Present work, dotted lines: Rein and Chipman.⁵⁾

Fig. 3. Dependence of a_{SiO_2} on mass%CaO/mass%SiO₂.

experiments. However, SiO_2 contents slightly increased in the low SiO_2 containing samples. Table 2 also presents the measured activities of SiO_2 in the CaO- Al_2O_3 - SiO_2 ternary system.

Based on the obtained values, iso- SiO_2 activity curves were constructed in the iso-thermal section of the CaO- Al_2O_3 - SiO_2 system at 1873 K. The contour lines are presented in Fig. 2. The iso-activity curves estimated by Rein and Chipman⁵⁾ are also reproduced in the figure for comparison. The present activity values of SiO_2 are higher than the suggestion by Rein and Chipman,⁵⁾ in spite of the similarity of the shape. Moreover, the SiO_2 activity obtained in the present study decreases more drastically with the increase of CaO content in comparison with the results by Rein and Chipman. Note also that significant decrease in the SiO_2 activity can be seen, as the composition approaches CaO-saturated line.

It should be mentioned that Rein and Chipman was not successful to determine the activity of SiO_2 at low SiO_2 region experimentally. Hence, a hypothetical point, at which CaO and $2\text{CaO} \cdot \text{SiO}_2$ are doubly saturated at 1873 K (marked as a solid circle in Fig. 2), was considered by these authors.⁵⁾ Using the Gibbs free energy change for the decomposition of the dicalcium silicate into CaO and SiO_2 , the activity of SiO_2 at the coexisting point of CaO and $2\text{CaO} \cdot \text{SiO}_2$ was estimated as 7.7×10^{-4} at 1873 K. By extrapolating from the measurement result at high SiO_2 content region through the hypothetical point, the authors derived the activity of SiO_2 in the rest of the low SiO_2 content region. However, the estimated value does not agree well

with the contours drawn by the same authors⁵⁾ as shown in Fig. 2.

According to the phase diagram of the CaO- Al_2O_3 - SiO_2 system,¹¹⁾ tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$ phase exists in equilibrium with liquid in CaO-rich side at 1873 K, instead of $2\text{CaO} \cdot \text{SiO}_2$. The result of the present study can be verified using the Gibbs energy of decomposition of the tricalcium silicate.

$$\log K_6 = -\frac{6211.2}{T} - 0.350^9) \dots\dots\dots (7)$$

The SiO_2 activity at the coexisting point of CaO and $3\text{CaO} \cdot \text{SiO}_2$ is evaluated to be 2.2×10^{-4} , which is in very good accordance with the measured value as presented in Fig. 2. This agreement would confirm the reliability of the present measurements.

In order to understand better the dependence of the SiO_2 activity on the CaO content, the SiO_2 activity coefficient is presented as a function of the ratio mass%CaO/mass% SiO_2 in Fig. 3. The activity coefficient of SiO_2 decreases evidently as the CaO content increases. It implies that CaO, which is a strong basic oxide, has an influence to decrease the activity coefficient of SiO_2 in the melt. Cations, Ca^{2+} in the melt are expected to break tetrahedral covalent bonds of SiO_2 resulting in lower SiO_2 activity.

3.2. Activity of SiO_2 in the CaO- Al_2O_3 - SiO_2 -MgO System

The measured values of the SiO_2 activities in the quaternary system along with the analyzed slag compositions are presented in Table 3. Most of the slag compositions were in the 10 mass% MgO section. Two additional slag compositions, which were relevant to the inclusions found in the ladle, were also studied. Similar as the ternary system, no significant change in the slag compositions was noticed after the experiments.

A comparison of Tables 2 and 3 shows that the SiO_2 activities in the quaternary system are generally lower than that in the ternary system, almost one order of magnitude. Since the content of MgO was only 10 mass%, the strong basic behavior of MgO to decrease the SiO_2 activity is very

Table 3. Analyzed compositions of the melts and SiO_2 activities in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{MgO}$ system.

sample	analyzed compositions				mass%Si in Cu	a_{SiO_2} ($\times 10^{-4}$)
	CaO (mass%)	Al_2O_3 (mass%)	SiO_2 (mass%)	MgO (mass%)		
quaternary system	401	42	41	8	9	0.17
	402	46	35	9	10	0.08
	403	38	46	8	8	0.13
	404	43	42	6	9	0.07
	405	46	38	6	10	0.05
	406	36	49	5	10	0.13
	407	41	46	3	10	0.05
	408	36	52	3	9	0.07
	409	45	42	4	9	0.03
	410	40	42	8	10	0.15
inclusions	411	47	36	11	6	0.13
	412	48	31	15	6	0.23

Fig. 4. Dependence of γ_{SiO_2} of the ternary and quaternary melts on $\text{mass}\% \text{CaO} / \text{mass}\% \text{Al}_2\text{O}_3$. **Fig. 6.** Microphotograph of a typical inclusion after vacuum degassing.²⁾ **Fig. 5.** Iso- a_{SiO_2} lines in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-10\% \text{MgO}$ system at 1873 K.

profound. To examine the effect of MgO on the activity of SiO_2 , the activity coefficients of SiO_2 is plotted against the ratio of $\text{mass}\% \text{CaO} / \text{mass}\% \text{Al}_2\text{O}_3$ at constant SiO_2 content for both of the ternary and quaternary systems in **Fig. 4**. Commonly in the 2 systems, the activity coefficient of SiO_2 decreases with the increase of the CaO content. It is also apparent that the activity coefficient of SiO_2 in the quaternary system with 10 $\text{mass}\% \text{MgO}$ is much lower than that of the ternary system. Only 10 $\text{mass}\% \text{MgO}$ would lower the activity coefficient of SiO_2 significantly by modifying SiO_2 network structure.

Iso-activity contours of SiO_2 in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-10\text{mass}\% \text{MgO}$ system at 1873 K were drawn in the iso-thermal section in **Fig. 5**. The figure shows again that the activity of SiO_2 decreases as CaO content increases and Al_2O_3 content decrease.

3.3. Liquid Oxide Inclusions at the End of Ladle Treatment

In previous studies,^{1,2,12)} it was found that a large number of liquid inclusions of calcium aluminate coexist with spinel inclusions before vacuum degassing. After vacuum degassing, most of the inclusions were calcium aluminate liquid inclusions.^{1,2,12)} An example of these inclusions is presented in **Fig. 6**. When dissolved Al level is low, 2 types of liquid calcium aluminate inclusions with considerably different SiO_2 contents were found to coexist even after vacuum degassing.²⁾ Since stirring is carried out during vacuum degassing for about half an hour, the inclusions have a good chance to reach or at least get close to the equilibrium with liquid steel. To understand the coexistence of the two types of liquid inclusions with different SiO_2 con-

Table 4. Composition ranges of the liquid inclusions observed after vacuum degassing.

mass%	CaO	Al ₂ O ₃	SiO ₂	MgO
low SiO ₂	30~38	45~53	2~6	8~10
high SiO ₂	44~48	32~36	11~15	5~7

Table 5. Composition of the steel after vacuum degassing.

mass%	C	Si	Mn	Cr	V	Mo	Al	O
	0.41	1.07	0.39	5.20	0.92	1.29	0.022	0.0002

Table 6. Interaction parameters at 1 873 K used in this study.

i	e_i^j	j						
		O	C	Si	Mn	Cr	V	Al
i	Si ^[13]	-0.23	0.18	0.11	0.002	-0.0003	0.025	0.058
	O ^[14]	-0.17	-0.421	-0.066	-0.021	-0.055	-0.14	-1.17

tents at the end of the ladle treatment a thermodynamic consideration using the present activity data would be helpful. To assist the discussion, the composition range of the liquid inclusions observed after vacuum degassing is presented in **Table 4**.²⁾ The typical steel composition after vacuum degassing is presented in **Table 5**.²⁾

The activity of SiO₂ in equilibrium with the liquid steel can be calculated using the following reaction.

$$\log K_8 = \log \frac{a_{\underline{\text{Si}}} \cdot a_{\underline{\text{O}}}^2}{a_{\text{SiO}_2}} = -\frac{30\,414}{T} + 11.59 \dots\dots\dots(9)$$

$$a_i = f_i [\%i] \quad \log f_i = \sum_j e_i^j [\%j] \dots\dots\dots(10)$$

where $a_{\underline{\text{Si}}}$ and $a_{\underline{\text{O}}}$ are the activities of silicon and oxygen in liquid steel relative to a dilute solution; a_{SiO_2} is the activity of SiO₂ with pure solid as the standard state; $[\%i]$ and f_i are the concentration of element i and its activity coefficient on a weight percent basis with dilute solution as its reference state; and e_i^j is the first order interaction parameter of j on i . The interaction parameters employed in this study are shown in **Table 6**.^{13,14)}

The decrease in the dissolved oxygen level during degassing period may have some influence on the equilibrium between the inclusions and liquid metal. On the basis of the steel composition in Table 5 and the interaction parameter in Table 6, the activities of the dissolved Si and O after vacuum degassing were calculated to be 1.8 and 4.2×10^{-5} , respectively. Correspondingly, the equilibrium activity of SiO₂ after vacuum degassing could be evaluated as 1.4×10^{-4} using Eq. (9).

According to the composition range of the inclusions having low SiO₂ content in Table 4, the activity of SiO₂ in the inclusions is positioned between 0.0001–0.0002 in the iso-SiO₂ activity contour shown in Fig. 2. This is in very good agreement with the value 1.4×10^{-4} , which is evaluated from $a_{\underline{\text{Si}}}$ and $a_{\underline{\text{O}}}$ in the steel. This agreement strongly suggests that the inclusions are in equilibrium, or at least very close to the equilibrium with the steel after vacuum degassing.

In the case of the liquid inclusions having high SiO₂ content found after vacuum degassing, the experimentally determined SiO₂ activities in Table 3 could be used directly for the discussion. While the two values (the last two rows) are somewhat higher than the a_{SiO_2} in the inclusions with low SiO₂ content, they could be considered to be quite similar. As mentioned in the previous section, the main reason

for the coexistence of the two types of inclusions could be the difference in their CaO contents. The inclusions having higher SiO₂ content have considerably higher CaO content. The difference between the measured activities in the last two rows in Table 3 and the value calculated from $a_{\underline{\text{Si}}}$ and $a_{\underline{\text{O}}}$ in the steel could be due to either or both of the following two factors. (i) The EDX analyses to determine the compositions of the inclusions²⁾ were possibly associated with uncertainties. As shown in the last two rows in Table 3, slight change in the composition would results considerable difference in the a_{SiO_2} . (ii) A final equilibrium between the inclusion with steel has not been reached. Nevertheless, the present results would suggest that the SiO₂ activities of the 2 types of inclusions are rather close to each other. Both types of inclusions are very close to the equilibrium with the steel after vacuum treatment.

4. Summary

In order to consider the equilibrium between non-metallic inclusions and liquid steel, the activities of SiO₂ in CaO–Al₂O₃–SiO₂–(MgO) liquid solutions having low SiO₂ contents were measured. The solution was equilibrated with Cu at known oxygen potential at 1 873 K for 18 h. The SiO₂ activities were evaluated using Si content in Cu and oxygen partial pressure. The present measured values were higher than the previously reported data for the CaO–Al₂O₃–SiO₂ system. Addition of 10 mass% MgO was found to reduce the SiO₂ activity substantially. On the basis of the experimental data, iso-activity contours of SiO₂ were drawn at 1 873 K. The results were found to be helpful in discussing the presence of non-metallic inclusion during vacuum degassing.

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