The Deoxidation Ability of Silicon in the Molten Stainless Steel*

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Synopsis

Si is a prime deoxidizing element for stainless steel deoxidation practice. It is considered that the deoxidizing ability of Si may be increased by reducing a_{SiO_2} . This effect, however, has not been understood clearly.

From this viewpoint, the authors have investigated the Si-O equilibrium for 18Cr-8Ni melt, and furthermore measured the effect of crucible materials and that of slag composition on the deoxidation power of Si.

The results are summarized as follows:

(1) The experimental equations for Si-O deoxidation equilibrium for 18Cr-8Ni stainless melt are given as follows;

$$\log K_{\text{Si}} = -19\,690/T + 5.914 \pm 0.041 \quad (1)$$

$$\log K_{\text{Si}} = -31\,740/T + 12.347 \pm 0.041 \quad (2)$$

using the following interaction coefficients:

$$e_{\text{Si}}^{\text{C}} = 0.25, \quad e_{\text{Si}}^{\text{Si}} = 3\,910/T - 1.77, \quad e_{\text{Si}}^{\text{Ni}} = 0.007,$$

$$e_{\text{Si}}^{\text{Cr}} = 0, \quad e_{\text{Si}}^{\text{O}} = -0.24, \quad e_{\text{O}}^{\text{C}} = -0.421, \quad e_{\text{O}}^{\text{Si}} = -0.137,$$

$$e_{\text{O}}^{\text{Ni}} = 0.005, \quad e_{\text{O}}^{\text{O}} = -1\,750/T + 0.76, \quad \log f_{\text{O}}^{\text{Cr}} = -0.040[\% \text{Cr}]$$

(for Eq. (1))

$$\log f_{\text{O}}^{\text{Cr}} = -(369/T - 0.137)[\% \text{Cr}] + 0.0024[\% \text{Cr}]^{1.75}$$

(for Eq. (2))

The value of $\log K_{\text{Si}}$ at 1 600°C agrees well with that of the equation for Fe-Si-O system recommended by the 19th Committee of Japan Society for the Promotion of Science.

(2) As to the effect of crucible materials on the deoxidation power of Si, it increases when using CaO and CaO-SiO₂ crucible, and the effect of Al₂O₃ crucible is considerably small.

The effect of MgO and ZrO₂ crucibles is intermediate.

(3) The deoxidation equilibrium of Si with CaO-SiO₂-Al₂O₃ (sat.) slag has been measured at 1 600°C, and the relation between the (%CaO)/(%SiO₂) and a_{SiO_2} was determined. The result shows that the oxygen concentration on silicon deoxidation is greatly influenced by the basicity of co-existing slag and that the observed values of a_{SiO_2} are larger than the estimation from the slag composition.

(4) The above mentioned results lead to the conclusion that the deoxidation power of Si in actual stainless steel melt is enhanced by using basic slag. However, it seems to be difficult to attain the equilibrium oxygen concentration expected from the slag composition.

I. Introduction

In the stainless steel making operation, such elements as Si, Al, Ti, Ca, etc. are generally used for deoxidation alone or in combination. Being most generally used, Si is known for its characteristic of increasing its deoxidation power in combination with basic slag. In general, the stainless steel making practice uses basic furnaces and the deoxidation process at the final stage of refining is also accomplished in basic slag. Upon tapping, the molten steel is transferred to a ladle together with basic slag. Because of favorable mixing effect of slag and molten metal, the influence of the slag on the deoxidation power of Si cannot be ignored. However, little quantitative

information is available about this effect. Ramachandran and co-workers¹⁾ consider that slag work only as a protective barrier against the oxidation by atmosphere, and rather attach importance to the deoxidation equilibrium with impure silica precipitated from the melt.

In this study, the authors first determined the deoxidation equilibrium of Si in stainless steel and further confirmed the influence of crucible materials and slag composition on this equilibrium.

II. Apparatus and Method of Experiment

1. Apparatus

Schematic drawing of the experimental apparatus is shown in Fig. 1. The Mo-resistance furnace is composed of a 80 mm furnace core (alumina tube) around which 2 mm ϕ Mo wire with the length of about 18 m is wound. The load power source is single phase 200 V, and the electrical capacity of the furnace is 8 kVA. An alumina tube (50 mmID $\times$ 60 mmOD $\times$ 700 mmH, supplied by Degussa) was used as the reaction tube. Temperature of the furnace was controlled with SCR voltage regulator by monitoring with an output type PID meter. By this system, the fine adjustment of furnace temperature, for example 1 580 $\pm$ 1°C, is possible.

A PR18 (Pt-Pt-13% Rh) thermocouple was inserted from the furnace bottom into the reaction tube, being in contact with the crucible bottom, as shown in Fig. 2. The thermocouples were corrected every

Fig. 1. Schematic diagram of the apparatus

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Fig. 2. Temperature distribution in the Mo-furnace

five heat against the Pd melting point. Figure 2 shows the temperature distribution in the reaction tube and Table 1 does the material and dimensions of the crucibles used.

2. Experimental Method

A mother alloy of 18Cr-8Ni was prepared by vacuum induction melting, using electrolytic chromium, electrolytic nickel and electrolytic iron. Its typical chemical is the following:

C	Si	Mn	P	Ni	Cr	N	H	Al
0.03	0.10	0.05	0.010	8.00	18.00	0.010	3 ppm	0.010

The mother alloy and ferric oxide were melted in Ar gas atmosphere, using various crucibles, and after being kept for 15 min at the designated temperature, Ferro-Si (commercial grade: 64.1%Si) was added and the experiment started. After being maintained for the designated period, the specimen was sucked up with a silica tube, the inside of which had been substituted by Ar in advance, and rapidly cooled in water for chemical analysis.

The equilibration time was set 1 to 1½ hr longer than that taken for the oxygen concentration and the value of $[Si] \cdot [O]^2$ to become constant. The weight of melts was 100 to 200 g, taking the crucible dimensions into consideration.

The method of chemical analysis and its accuracy for each element are shown in Table 2.

III. Results and Discussions

1. Theoretical Consideration

The deoxidation equilibrium of Si for stainless steel

Table 1. Crucible dimension

Kind of material	Dimension (mm) (OD) × (ID) × (H)	Remark
SiO ₂	33 × 30 × 60	Fused silica
Al ₂ O ₃	30 × 23 × 150	Corundum
MgO	30 × 24 × 50	Periclase
ZrO ₂	34 × 28 × 120	Zirconia
CaO	27 × 16 × 28	Laboratory made

Table 2. Methods and accuracy of analysis

	Accuracy (1σ)	Method of analysis (JIS)
Si	0.02%	Gravimetric method as Si dioxide
O	8 ppm	Vacuum fusion method
Ni	0.06~0.08%	EDTA titration after Ni dimethylglyoxime separation
Cr	0.06~0.10	K permanganate titration after ammonium persulfate oxidation
Al	0.002	Chromazurol-S absorption method

Table 3. Thermochemical data of interaction coefficients

	C	-Si	Ni	Cr	O
e_{Si}^j	0.25 ⁷⁾	$(3910/T - 1.77)^{4)}$	0.007 ⁷⁾	0 ²⁾	-0.24 ⁴⁾
e_O^j	-0.421 ⁴⁾	-0.137 ⁴⁾	0.005 ³⁾	*	$(-1750/T + 0.76)^{4)}$

* $\log f_O^{Cr} = -0.040[\%Cr]^3$

$\log f_O^{Cr} = -(369/T - 0.137)[\%Cr] + 0.0024[\%Cr]^{1.75 \ 2)}$

melt can be expressed by the following equations:

$$SiO_2(S) = \underline{Si} + 2\underline{O} \dots\dots\dots(1)$$

$$\log K_{Si} = a_{Si} \cdot a_O^2 / a_{SiO_2} \dots\dots\dots(2)$$

where, a_{Si} and a_O : the Henrian activities of $\underline{Si}$ and $\underline{O}$, respectively in wt%

a_{SiO_2} : the activity with reference to solid silica.

a_{Si} and a_O are expressed by the following equations according to Wagner,

$$a_{Si} = f_{Si}^C \cdot f_{Si}^{Si} \cdot f_{Si}^{Ni} \cdot f_{Si}^{Cr} \cdot f_{Si}^O \cdot [\%Si] \dots\dots\dots(3)$$

$$a_O = f_O^C \cdot f_O^{Si} \cdot f_O^{Ni} \cdot f_O^{Cr} \cdot f_O^O \cdot [\%O] \dots\dots\dots(4)$$

In Table 3, the interaction parameters used for the present study are summarized. Equation (2) may be rearranged as follows using the values in Table 3.

$$\begin{aligned} \log K_{Si} &= \log a_{Si} \cdot a_O^2 / a_{SiO_2} \\ &= (3910/T - 2.044)[\%Si] - 0.602[\%C] \\ &\quad + 0.015\%Ni - 0.08\%Cr \\ &\quad + (-3500/T + 1.28)[\%O] + \log[\%Si][\%O]^2 \end{aligned} \dots\dots\dots(5)$$

(here $e_O^{Cr} = -0.040$ is used.)

In this equation, K_{Si} denotes the equilibrium con-

stant of Eq. (1). Many researches have been made for the Fe-Si-O ternary system, and the 19th Committee of Japan Society for the Promotion of Science (JSPS) recommends the following equation.⁴⁾

$$\log K_{\text{Si}} = -3.072/T + 11.76 \quad \text{.....(6)}$$

If Eqs. (3) and (4) hold for the stainless composition, 18Cr-8Ni, K_{Si} value obtained by Eq. (5) must agree with that from Eq. (6). Suzuki, Ban-ya and Fuwa³⁾ report that Eqs. (3) and (4) is applicable to 10%Cr and 5%Ni, while Chino, Nakamura, Tsunetomi and Segawa⁵⁾ report that they hold up to 18%Cr and 8%Ni.

Firstly in this experiment, the deoxidation equilibrium equation of Si for 18Cr-8Ni composition was measured using silica crucible and on this basis, a_{SiO_2} was investigated in equilibrium with the melt of this composition in various crucibles, such as lime, alumina, magnesia, etc., or in coexistence of slag of various basicity.

2. Deoxidation Equilibrium in Silica Crucible

First of all, the experiment to determine the deoxidation equilibrium equation of Si for 18Cr-8Ni melt was carried out using silica crucible without slag. 200 g of mother alloy and 0.3 g Fe_2O_3 were melted in silica crucible, and after reaching designated temperatures (1 510°, 1 550°, 1 575° and 1 600°C), ferro-Si was added (Si: 0.2, 0.4, 0.6, 0.8 and 1.0%). Although the equilibrium was reached in about 3 hr after addition of ferro-Si as shown in Fig. 3, the melts were held 5 hr for safety.

Figure 4 shows the values of $\log K_{\text{Si}}$ given by Eq. (5) and $\log K'_{\text{Si}}$ for 18Cr-8Ni melts. They are constant in the Si range of 0.3 to 1.6%.

The relation between $\log K_{\text{Si}}$ and $1/T$ is shown in Fig. 5. As the stainless steel melt has higher concentration of Cr, $\log K_{\text{Si}}$ greatly depends on the value of $\log f_{\text{O}}^{\text{Cr}}$. So our calculation was made using the data of Kojima and Sano²⁾ who measured the temperature dependency and the data of Suzuki, Ban-ya and Fuwa.³⁾

The $\log K_{\text{Si}}$ obtained in this experiment was plotted against $1/T$ which can be expressed by using the

Fig. 3. Deoxidation curves with Si in silica crucibles for 18Cr-8Ni melts at 1 550°C

method of least squares as follows:

When

$$\log f_{\text{O}}^{\text{Cr}} = (-369/T + 0.137)[\% \text{Cr}] + 0.0024[\% \text{Cr}]^{1.75}$$

(the data of Kojima and Sano²⁾ is used,

$$\log K_{\text{Si}} = -31\,740/T + 12.347 \pm 0.0412 \quad \text{.....(7)}$$

$$r^{**} = -0.9906$$

and by use of $\log f_{\text{O}}^{\text{Cr}} = -0.040[\% \text{Cr}]$ (the data of Suzuki, Ban-ya and Fuwa³⁾),

$$\log K_{\text{Si}} = -19\,690/T + 5.914 \pm 0.0412 \quad \text{.....(8)}$$

$$r^{**} = -0.9724$$

At 1 600°C, either of Eq. (7) or (8) gives the same value for K_{Si} , but at higher temperatures, greater becomes the difference between the values of equilibrium constant by Eqs. (7) and (8). The $\log K_{\text{Si}}$ values thus obtained are compared with the results of other investigators in Fig. 6. When the value of $\log f_{\text{O}}^{\text{Cr}} = -0.040[\% \text{Cr}]$ is used, $\log K_{\text{Si}}$ agrees very well with the data of Suzuki, Ban-ya and Fuwa.³⁾ On the other hand, with $\log f_{\text{O}}^{\text{Cr}}$ of Kojima and Sano²⁾ the value agrees with the JSPS recommended value.⁴⁾

Fig. 4. The effect of Si content on the equilibrium constant, K_{Si} and the product, K'_{Si} for 16.5~17.5Cr-8Ni melt with silica crucibles

*Japan Society for the Promotion of Science

Fig. 5. Comparison of the results for $\log K_{\text{Si}}$ ($=a_{\text{Si}} \cdot a_{\text{O}}^2$) calculated with various thermochemical data and Japan Society for the Promotion of Science's data

*Japan Society for the Promotion of Science

Fig. 6. The effect of temperature on the equilibrium constant, $K_{Si} = a_{Si} \cdot a_O^2$

Since the stainless steel melt has higher Cr content than other alloying elements, $\log f_O^{Cr}$ has greater influence on the equilibrium constant than other elements do. Therefore, many researches have been made for determining e_O^{Cr} . The values of $\log K_{Si}$ of 18Cr-8Ni melt at 1 600°C were calculated by using e_O^{Cr} of various investigators. In Table 4, the calculated values of $\log K_{Si}$ including the one obtained in this experiment are compared. It is noticeable that the all values almost agree at 1 600°C. Further $\log K_{Si}$ obtained in our experiment agrees with the JSPS recommended value⁴⁾ at 1 600°C within allowable error. Therefore, it can be mentioned with safety that the Wagner equation is applicable up to this composition.

Values of $\log f_O^{Cr}$ are almost consistent among the investigators at 1 600°C, but not at other temperatures. This is because $\log f_O^{Cr}$ has temperature dependency. For example, Chipman⁷⁾ reports the temperature dependency at temperatures from 1 550° to 1 650°C for high chromium concentration (25 to 40%). Chino, Nakamura, Tsunetomi and Sagarawa⁸⁾ reported e_O^{Cr} having temperature dependency, i.e., -0.047 (at 1 600°C), -0.043 (at 1 700°C) and -0.038 (at 1 800°C) with e_O^{Cr} . The $\log K_{Si}$ of present work agrees well with the JSPS recommended value when Kojima and Sano's temperature dependency for $\log f_O^{Cr}$ is used. However, it is hardly possible to judge what of these values is the most appropriate.

Since in the stainless steel refining, the temperature of bath after O blowing sometimes exceeds 2 000°C, the melt is refined in the temperature range of 1 500° to 2 000°C. Accurate data of $\log f_O^{Cr}$ for the entire temperature range are desirable.

3. The Influence of Crucible Materials on the Deoxidation Equilibrium

The effect of crucible materials on the deoxidation

Table 4. Comparison of $\log K_{Si}$ at 1 600°C

Researcher	e_O^{Cr} or $\log f_O^{Cr}$ used	$\log K_{Si}$	Composition
Present work	$e_O^{Cr} = -0.040^{5)}$	$-4.627_2 \pm 0.014_8$	(17~17.5Cr-8Ni)
	$\log f_O^{Cr}$ of Sano, <i>et al.</i>	$-4.625_3 \pm 0.014_8$	
Chino, <i>et al.</i> ⁵⁾	$e_O^{Cr} = -0.039^{6)}$	-4.64 ± 0.02	18Cr-8Ni
Kojima, <i>et al.</i> ²⁾	$\log f_O^{Cr}$ of Sano, <i>et al.</i>	$-4.80_6^{4)*}$	18Cr-9Ni
Suzuki, <i>et al.</i> ³⁾	$e_O^{Cr} = -0.040$	-4.55^{**}	17Cr-8Ni
JSPS value ⁴⁾	—	-4.64	Fe-Si-O system

* Calculated from the equation $\log K_{Si} = -25\,400/T + 8.757$, which is obtained from Table 4 in Ref. 2) by the method of least squares.

** Plot of Fig. 10, Ref. 3)

Table 5. Influence of crucible materials on activity of silica at 1 600°C for Fe-Si-O melts

Researcher	Crucible material	a_{SiO_2}
Suzuki, Ban-ya and Fuwa ³⁾	Al ₂ O ₃	0.31
	MgO	0.07
Yokoyama and Oi ⁹⁾	CaO	0.25, 0.16 ₇
Kawawa and Okubo ¹⁰⁾	Al ₂ O ₃	0.29
	CaO-CaF ₂ (20%)	0.015

by Si is known for the Fe-Si-O ternary system, an example of which is shown in Table 5. In our experiment, the effect of crucible materials was demonstrated with 18Cr-8Ni composition melt. Crucible materials are the following: lime-silica (80/20), lime-fluorspar (10 to 15% fluorspar), zirconia, alumina and magnesia.

The experimental method was the same as that for silica crucible. The holding time was 5 to 6 hr since the constant oxygen concentration was attained in 4 to 4.5 hr after Si addition. The deoxidation equilibrium run was carried out at temperatures of 1 510°, 1 550° and 1 600°C, and the activity of silica was obtained from the following equation.

$$\log a_{SiO_2} = \log a_{Si} \cdot a_O^2 - \log K_{Si} \dots\dots\dots(9)$$

Here, $\log K_{Si}$ given by Eq. (8) was used.

The experimental results in this series are summarized in Table 6. As noted therein, a_{SiO_2} is the lowest with lime and lime containing crucibles, while it is the highest with alumina crucible. Magnesia and zirconia stay in the middle.

From these results, it is noted that the deoxidation ability of Si is greatly influenced by crucible materials. This phenomenon is generally explained by that silica formed on deoxidation reaches the crucible wall and is absorbed therein which causes the reduction in activity of silica, eventually increasing the deoxidation capability of Si. The difference in the deoxidation capability of Si for various crucible materials

Table 6. Activities of silica for various crucibles

Crucible materials	a_{SiO_2} (%Si in melt)		
	1 600°C	1 550°C	1 510°C
CaO	0.002 ₀ (0.42) 0.004 ₀ (0.55)	0.005 ₅ (0.63)	0.008 ₆ (0.26) 0.007 ₅ (0.77)
CaO-SiO ₂ CaO/SiO ₂ =80/20	0.005 ₅ (0.23) 0.008 ₅ (0.23)	0.003 ₆ (0.20) 0.022 ₄ (0.47) 0.016 ₁ (0.69)	0.008 ₀ (0.36)
CaO-CaF ₂ (85CaO-10CaF ₂)		0.007 ₂ (0.14) 0.010 ₉ (0.36) 0.019 ₈ (0.37)	
CaO-CaF ₂ (77CaO-15CaF ₂)		0.027 ₇ (0.60)	
Al ₂ O ₃	0.12 ₄ (0.42) 0.41 ₆ (1.26)	0.24 ₁ (0.42) 0.24 ₁ (0.51) 0.55 ₇ (1.05) 0.20 ₄ (1.29)	0.25 ₀ (0.49) 0.51 ₄ (1.40)
MgO	0.027 ₈ (0.38) 0.17 ₅ (1.02)	0.022 ₂ (0.37) 0.038 ₂ (0.41)	0.085 ₈ (0.33) 0.11 ₄ (0.92)
ZrO ₂	0.051 ₂ (1.03)	0.041 ₆ (0.43) 0.088 ₆ (1.09)	0.033 ₅ (0.54)

shown in Table 6 could be interpreted by this concept.

As noted in Table 6, even with the same crucible material, a_{SiO_2} depends on temperature and silicon concentration of melt. The lower is temperature, the greater becomes a_{SiO_2} , and the higher is the concentration of Si, the greater becomes a_{SiO_2} as seen in Fig. 7. This is explained by that at lower temperatures, more silica precipitate remain in metal due to its slow reaction with the crucible material.

4. The Influence of Slag Composition on Deoxidation Equilibrium

To make clear the influence of slag compositions on deoxidation equilibrium of the stainless steel melt, firstly the 50%CaO-50%SiO₂ slag was chosen for the preliminary experiment. This slag was fused together with the mother alloy in a zirconia crucible and a magnesia crucible. However, this experiment failed as both crucibles were attacked by the slag and did not hold even for 1 hr. Then replacing this slag with the CaO-SiO₂-Al₂O₃ ternary system (Al₂O₃ saturated), and using an alumina crucible, the deoxidation power of Si was examined in the existence of slags with different CaO/SiO₂ ratio. The synthetic slag was made from commercial grade CaCO₃, Al₂O₃ and SiO₂ reagents using a graphite crucible.

The experiment procedure is as follows: 75 g of the synthetic slag, 200 g of mother alloy and 0.3 g of Fe₂O₃ were inserted in an alumina crucible and melted in Ar atmosphere and after being held for 5 to 10 min at 1 600°C, ferro-Si was added and then the melt was stirred for about 30 sec with a quartz rod. The viscosity of slag was extremely great at

Fig. 7. Influence of Si content in the liquid stainless steel on the activity of silica for various crucibles

Fig. 8. Deoxidation curves with Si in alumina crucible covered with CaO-SiO₂-Al₂O₃ (sat.) slag at 1 600°C

this time, and the quartz rod did not dissolve into slag. To determine the equilibration time, the change in oxygen concentration with time was measured for two types of slag, which showed O value becoming constant in about 3 hr, indicating that the equilibrium is presumably established by this time. According to this information, the experiments thereafter were carried out with the holding time of 5 hr. Ferro-Si was added to each slag at three Si levels of 0.2, 0.5 and 0.8% to approach the equilibrium from another direction. The results of these experiments are shown in Fig. 8. The a_{SiO_2} values calculated by Eq. (9) and standard deviations for each composition of slags are shown in Table 7. The log K_{Si} value from Eq. (8) is used in this calculation.

In this consideration, the influence of small amount of FeO and Cr₂O₃ on a_{SiO_2} has been ignored.

Figure 9 shows the relation between a_{SiO_2} and %CaO/%SiO₂, a_{SiO_2} decreases with increasing %CaO/%SiO₂ and levels off beyond %CaO/%SiO₂=3.0. Any further increase in basicity is not considered to increase the deoxidation ability of Si and the limit of a_{SiO_2} with the slag of this series appears to be around

Table 7. Activities of silica for various composition of CaO-SiO₂-Al₂O₃ slag at 1600°C

Heat No.	$V = \frac{\% \text{CaO}}{\% \text{SiO}_2}$	%SiO ₂ as presumed ($\frac{\% \text{CaO} + \% \text{SiO}_2}{\% \text{SiO}_2} = 100$)	a_{SiO_2}		n
			X	σ	
B-3	3.54	22.02%	0.038 ₆		1
B-4, B-6	2.09	32.32	0.057 ₉	0.009 ₅	3
B-7, B-9	1.37	42.25	0.118 ₅	0.019 ₀	3
B-11, 12	0.93	51.70	0.180 ₆	0.020 ₄	2
B-13, B-15	0.66	60.15	0.199 ₀	0.024 ₀	3
B-16, B-18	0.38	72.33	0.487 ₃	0.058 ₆	3

Fig. 9. The effect of the basicity of CaO-SiO₂-Al₂O₃ (sat.) slag equilibrated with liquid stainless steel on the activity of silica

0.03 to 0.04.

The above-mentioned experiment was conducted by such procedures that the mother alloy, slag and Fe₂O₃ were mixed together and melted, and, upon reaching 1600°C, ferro-Si was added to the top of the slag. The equilibrium condition was approached using oxygen saturated melt. As the next step, ferro-Si was initially charged with the mother alloy, slag and Fe₂O₃. The results are shown in Fig. 9 together with the results of the previous work. As noted in this figure, the data show somewhat higher a_{SiO_2} value, but it still remains within the standard deviation, indicating its fairly good agreement with the previous works.

The relation between a_{SiO_2} values in CaO-SiO₂-Al₂O₃ ternary system and those obtained from Fe-Cr-Si-O equilibrium is considered as follows. As to the a_{SiO_2} in this slag system, Sambongi and Omori¹¹⁾ determined a_{SiO_2} from the measurement of electromotive force for a double cell and Chipman¹²⁾ from the distribution equilibrium of Si between slag and carbon saturated iron. Both values do not agree for the Al₂O₃ saturated composition range in which the present work was conducted. Figure 10 shows iso-activity lines of silica by Sambongi and Omori¹¹⁾ together with our results obtained from Eq. (9) in the stainless steel melts. In this figure, it can be seen that the a_{SiO_2} values of present work are higher than those of Sambongi and Omori¹¹⁾ as (%SiO₂) increases. When compared with Chipman's values, even more discrepancy is observed.

Though the purpose of this study is not to determine a_{SiO_2} , this phenomenon is interesting to evaluate the role of slag in silicon deoxidation.

Iso-activities line: Sambongi and Omori at 1630°C
▲ Present work, at 1600°C
(1) B-1-B-3 0.039
(2) B-4-B-6 0.058
(3) B-7-B-9 0.119
(4) B-10-B-12 0.181
(5) B-13-B-15 0.199
(6) B-16-B-18 0.487
(7) B-20 0.0038

Fig. 10. SiO₂ activities on the system CaO-SiO₂-Al₂O₃

Kojima and Sano¹³⁾ have investigated the Fe-Cr-Si-O equilibrium under acidic slag, a , in silica crucible. Their log K_{Si} agrees with that for Fe-Si-O system in which a_{SiO_2} is defined as unity. Hilty, Rasbach and Crafts¹⁴⁾ also investigated the equilibrium between Si and Cr in Fe-Cr melt using a silica crucible. Though they did not discuss the relation between O content and slag composition, the oxygen concentration is presumably controlled by Eq. (1). According to the authors' calculation, using their data for Si-Cr equilibrium and the oxygen solubility of Fe-Cr melt,¹⁵⁾ the oxygen concentration in the melt with 17%Cr in equilibrium with chromium oxide containing slag saturated with silica is approximately 300 ppm. This value roughly agrees with that given by Eq. (1).

This means that the equilibrium defined by a_{SiO_2} in slag was not established in this work. The phenomenon can be explained that the deoxidation reaction between the melt and slag might be so sluggish after the oxygen concentration in the melt drops to a certain constant level that the equilibrium given by Eq. (1) on the basis of the activity in slag is hardly attainable.

From these considerations, Eq. (1) might be applied to define the equilibrium of the melt with basic slag as a function of silica activity. In our study, however, the a_{SiO_2} values calculated from Si-O equilibrium did not agree with that in the coexisting slag. This means that the equilibrium was not established in this work.

Usage of an Al₂O₃ crucible in the present work may be a main reason why the equilibrium state was not attained. As made clear previously, the Si-O equi-

Fig. 11. Relation between O and Si content of 18Cr-8Ni melt in ladle (10 t basic arc furnace Slag composition: CaO 40~50%, SiO₂ 20%)

rium is greatly influenced by crucible materials. For instance, the precipitation of chromium oxide at refractory wall may make it impossible kinetically to attain the equilibrium state which is determined by a_{SiO_2} in coexisting slag.

It is concluded, however, that slag coexisting with melt has great influence on the deoxidation power of Si and the basic slag improves the deoxidation power of Si.

Figure 11 shows the relation between Si and O contents in 18Cr-8Ni melts on tapped from a 10 t basic electric furnace lined by MgO. In this figure, the equilibrium lines of Fe-Cr-Si-O of $a_{\text{SiO}_2}=1$ and $a_{\text{SiO}_2}=0.08$ at 1600°C are shown together with the observed oxygen values. To this case, (%CaO)/(%SiO₂) is greater than 2, and a_{SiO_2} of slag is less than 0.02.

Thereby it is easily understood that in the actual operation the deoxidation power is greatly improved by basic slag and that the mixing of slag and melt is favorable for reducing the oxygen concentration in silicon deoxidation practice.

IV. Conclusion

The authors measured the deoxidation equilibrium of Si for 18Cr-8Ni melt using a silica crucible, including the experiments to examine the influence of crucible materials and that of CaO-SiO₂-Al₂O₃ ternary slag on the deoxidation equilibrium of Si and have obtained the following results:

(1) The deoxidation equilibrium of Si in the stainless steel melt can be expressed by the following experimental equations:

$$\log K_{\text{Si}} = 31\,740/T + 12.347 \pm 0.041 \quad \text{.....(a)}$$

Herein,

$$\log f_{\text{O}}^{\text{Cr}} = (-369/T + 0.137)[\% \text{Cr}] + 0.0024[\% \text{Cr}]^{1.75}$$

$$\log K_{\text{Si}} = -19\,690/T + 5.914 \pm 0.041 \quad \text{.....(b)}$$

Herein,

$$\log f_{\text{O}}^{\text{Cr}} = -0.040[\% \text{Cr}]$$

At 1600°C, both of Eqs. (a) and (b) give completely the same value for $\log K_{\text{Si}}$, which also agrees with

the value recommended by the Japan Society for the Promotion of Science for the Fe-Si-O ternary system within allowable error of the experiment. Therefore, Eqs. (c) and (d) are considered to be applicable up to the stainless steel composition.

$$a_{\text{Si}} = f_{\text{Si}}^{\text{C}} \cdot f_{\text{Si}}^{\text{Si}} \cdot f_{\text{Si}}^{\text{Ni}} \cdot f_{\text{Si}}^{\text{Cr}} \cdot f_{\text{Si}}^{\text{O}} [\% \text{Si}] \quad \text{.....(c)}$$

$$a_{\text{O}} = f_{\text{O}}^{\text{C}} \cdot f_{\text{O}}^{\text{Si}} \cdot f_{\text{O}}^{\text{Ni}} \cdot f_{\text{O}}^{\text{Cr}} \cdot f_{\text{O}}^{\text{O}} [\% \text{O}] \quad \text{.....(d)}$$

(2) The deoxidation ability of Si was studied using various crucible materials including lime, lime-silica, lime-magnesia, zirconia, etc. Lime and lime-containing crucibles reduce a_{SiO_2} mostly, while the effect of alumina crucible is comparatively small. Magnesia and zirconia crucibles affect intermediately. The influence of crucibles of the same material on deoxidation depends on temperature and the amount of Si added. This can be considered that the equilibrium state was not established even when 5 to 7 hr of equilibrium time was given.

(3) The deoxidation equilibrium of Si under CaO-SiO₂-Al₂O₃ (Sat.) slag was measured using an Al₂O₃ crucible at 1600°C, and a_{SiO_2} was determined. From this result, it was found that O by silicon deoxidation is greatly influenced by basicity of coexisting slag and that the observed a_{SiO_2} was larger than the estimation from the slag composition.

(4) From the above-mentioned results, it is concluded that the deoxidation power of Si in actual stainless steel melt is enhanced by using basic slag. However, it seems to be difficult to attain the equilibrium oxygen content expected from the slag composition.

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Discussions

D. C. Hilty (Ferroalloy Division, Union Carbide Corporation)

(1) During my investigations of oxygen solubility and oxide phase relations in the Fe–Cr–O system, I made some experiments in SiO₂ crucibles so that the system was saturated with both chromium oxides and SiO₂. If you consider my data in conjunction with the chromium oxide phases that were established in my Fe–Cr–O paper, you can see that Cr and Si interact rather strongly; *i.e.*, Cr seems to have a strong effect on the activity of Si. At one time, John Chipman and I planned to use these data to derive the activity coefficients for Si and Cr, but we never got around to doing it.

(2) I am not surprised that your results for a_{SiO_2} were higher than those you calculated from slag composition. In fact, I suspected that this would be the case, which is why I suggested checking the experimental melts for actual concentrations of Ca and Al.

Our own investigations have led us to the conclusion that in experimental work of this kind, once one goes beyond a simple ternary system of Fe, O and a deoxidizer, the metal does not necessarily come into equilibrium with the refractories and/or slag unless you happen to hit the exact slag or refractory composition required for true equilibrium according to the phase rule.

I have found it more advantageous to determine the equilibrium oxide phase by analyzing (metallographically, X-ray and the microprobe) the inclusions precipitated in the melt when it freezes. These inclusions are the true equilibrium phase and may bear only an artificial or indirect relation to any slag unless the slag is permitted to form from the melt.

Ca will lower the a_{SiO_2} , but the amount of lowering is a function of the amount of Ca or a_{Ca} dissolved in the metal. This can be quite different from what one would calculate from the basicity of a slag which is made up outside of the metal and then brought in contact with it.

One way of estimating the composition of the oxide phase is to run microprobe analysis on the surface of the crucible that was in contact with the metal. Usually, a film of the equilibrium oxide will precipitate on the surface of the crucible. Analysis of the inclusions, however, is the best way. This is something that has not been fully understood by many investigators, including Chipman, who were accustomed to thinking in terms of simple ternary deoxidation systems. Ramachandran, however, learned this from us and tried to apply it.

Incidentally, it was through study of the precipitated oxide inclusions that we discovered that the oxide phase in equilibrium with O-saturated high-Cr FeCr alloys is Cr₃O₄ containing up to about 10% Fe not Cr₂O₃ as had been previously always assumed.

As a further matter of interest, we always find the presence of Ca (and frequently Mg) by microprobe analysis of inclusions in stainless steel heats made by standard 2-slag practice in the arc furnace. The strong reducing conditions present under the second slag is sufficient to introduce a little Ca and/or Mg into the metal. This, in turn, slightly lowers a_{SiO_2} in equilibrium with the metal.

The Authors

It is clear that you are pointing out the following concerning our study.

(1) Because of the strong interaction between Si and Cr, Si is not much of a deoxidizer for stainless steel in the amounts normally employed.

(2) This has been identified in your studies on the oxygen solubility in Fe–Cr–O and Fe–Cr–Si–O (in silica crucible, saturated with silica and chromium oxide slag) systems.

(3) You suggested that we examine the melts for evidence of Ca pick up. In order to improve deoxidation of stainless steel by lowering a_{SiO_2} , it is necessary that the element responsible for the activity lowering (by precipitating the impure silica) should also be dissolved in the steel.

As to the value of $e_{\text{Si}}^{\text{Cr}}$, I have calculated the value of $\log K_{\text{Si}}$ in Fe–Cr–Si–O equilibrium of 18–8 melt from our experimental values and other works (Dr. Fuwa and Dr. Sano's studies on the deoxidation by Si in high alloy steel melt). In my study, I used the value of $f_{\text{Si}}^{\text{Cr}}=1$. (Dr. Fuwa³⁾ and Dr. Sano²⁾ used the values of $\log f_{\text{Si}}^{\text{Cr}}=0$, $\log f_{\text{Si}}^{\text{Cr}}=-0.003$ [%Cr], respectively.) The values of $\log K_{\text{Si}}$ calculated from the results in Fe–Cr–Si–O system were well accorded to the authorized value in Fe–Si–O system. It means that it is not wrong to regard the value of $f_{\text{Si}}^{\text{Cr}}$ as unity and that the interaction between Si and Cr is negligible.

I agree with you that O in the stainless steel melt should be equilibrium with a_{SiO_2} given by the impure silica precipitated from the melt. Through my study, the oxygen concentration might coincide with the one determined from the composition of the precipitated inclusion. In this concept, I do not conclude that the equilibrium state should be considered on the basis of a_{SiO_2} in slag. It should be, however, recognized through my present work that the deoxidation is greatly influenced by co-existing slag. This indicates that even at the stage that the oxygen concentration drops to apparently constant level (in this stage the motion of inclusions in the melt may be considered to be ruled by Brownian motion), the sluggish deoxidation (or oxidation) proceeds on the slag–melt interface. In short, this is the problem on the kinetic view.

In our study, the pick up of Al is also identified as

you suggested, but in this case, this reaction has been also governed by the slag basicity of co-existing slag and can be explained on the basis of silica activity. The oxygen value in the actual stainless steel melting practice only by silicon deoxidation also indicated that the oxygen was reduced roughly in proportion to Si content and that this value was apparently influenced by a_{SiO_2} in the slag after the favorable slag-melt mixing by tapping.

As mentioned above, it may be right to evaluate

the oxygen value thermochemically from the solute elements which are responsible to lower a_{SiO_2} as you pointed out, it is, however, difficult to determine the equilibrium state because of lack of the thermochemical values and the difficulties in the chemical analysis of minor element such as Ca or Al. So, we considered the effects of slag or refractory conveniently for the evaluation of the equilibrium state and could explain the phenomenon of the deoxidation by Si in stainless melt fairly well.