Deoxidation Equilibrium of Cr–Ni Stainless Steel with Si at the Temperatures from 1 823 to 1 923 K

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In order to clarify the effects of Ni and Cr on the Si deoxidation of liquid Fe–Cr–Ni alloy, the deoxidation equilibria of Fe–Ni and Fe–Cr–Ni alloys with Si were studied. The experiments were conducted on the conditions up to 20 mass% Ni in the Fe–Ni system and up to 18 mass% Cr and 9 mass% Ni in the Fe–Cr–Ni system at the temperatures of 1 823, 1 873 and 1 923 K. Results obtained were summarized as follows:

The effect of Ni on the interaction coefficient of Si was expressed by

$$\log f_{Si}^{Ni} = -0.009[\%Ni] + 2 \times 10^{-4}[\%Ni]^2, \quad [\text{mass}\%\text{Ni}] \leq 20, \quad 1 823 \leq T \leq 1 923 K$$

The cross product terms concerning Cr and Ni on the interaction coefficients of Si and O dissolved in Fe–Cr–Ni alloy were expressed by

$$f_{Si}^{Cr,Ni} + f_{O}^{Cr,Ni} = -0.001, \quad 1 823 \leq T \leq 1 923 K$$

The deoxidation product $K_9 = [\%Si][\%O]^2$ was numerically expressed by

$$\log K_9 = 8.40 - 24 600/T - (1.40 - 3.500/T)[\%O] + 0.029[\%Si] - (0.047 - 246/T + 4.3 \times 10^{-4}[\%Cr])[\%Cr]$$

$$-(0.003 + 2 \times 10^{-4}[\%Ni]) [\%Ni] + 0.001 [\%Cr][\%Ni]$$

$$[\text{mass}\%\text{Cr}] \leq 25, \quad [\text{mass}\%\text{Ni}] \leq 20, \quad 1 823 \leq T \leq 1 923 K$$

KEY WORDS: chromium–nickel stainless steel; thermodynamics of deoxidation; deoxidation with Si; cross product term of interaction coefficient.

1. Introduction

Cr–Ni stainless steel is used as a high grade corrosion-resisting and high temperature resisting materials. In stainless steel making, deoxidation is conducted with Si in many cases, due to the harmful effect of Al2O3 inclusion on corrosion-resisting property of the materials. However, the industrial grade Fe–Si deoxidizer used in practical operation contains a small amount of Al as impurity. As the result, the complex deoxidation with Si and Al is conducted in practical process. Therefore, the deoxidations with Si and Si–Al are important for the improvement of corrosion-resisting property of stainless steel. Our previous work1) has reported the effect of Cr on the Si deoxidation and limiting Al content of Al2O3 formation in Cr stainless steel, using the experimental results by Suzuki, et al.2) In the present work, the effects of Cr and Ni on the deoxidation of Fe–Cr–Ni alloy with Si were reassessed by using the previous data2) in a series of the studies concerning the deoxidation of stainless steel production.

2. Experimental Method and Results

The experimental method is the same as that of previous work,1) and is briefly mentioned here. Pre-melted iron alloy of about 50 g was melted in a silica crucible with high frequency induction furnace under purified argon flow, and held at a constant temperature. Then the metallic Si was added into the melt, and the melt was kept until an attainment to equilibrium. The equilibrium was reached within 20 min after the Si addition. After an attainment to equilibrium, a sample for chemical analysis was sucked by silica tube, and then quenched into water. The concentration of O in the sample was determined by the vacuum fusion method, and contents of Si, Cr and Ni were determined by the method prescribed in the Japanese Industrial Standard.

Two series of experiments were conducted. One was the Fe–Ni system containing up to 20 mass% Ni, and the other was the Fe–Cr–Ni system containing up to 18 mass% Cr, in which content of Ni was about one half of that of Cr. The Si content was less than 1 mass% in both systems. The experimental temperatures were 1 823, 1 873 and 1 923 K.

The experimental results of the Si deoxidation on Fe–Ni and Fe–Cr–Ni alloys are listed in Tables 1 and 2, respec-
3. Discussion

3.1. The Effect of Ni on the Si Deoxidation in Fe–Ni Alloy

The deoxidation equilibrium of liquid iron with Si can be expressed by following equations;

\[ \text{SiO}_2(s) = \text{Si} + 2\text{O} \] .................(1)

\[ \log K_{\text{SiO}_2} = \log(a_{\text{Si}}a_{\text{O}})/a_{\text{SiO}_2} \] .........(2)

where \( K \), \( K' \) and \( a \) denote the equilibrium constant, deoxidation product of the reaction (1), and activity of component, respectively. The \( a_{\text{Si}} \) and \( a_{\text{O}} \) represent Henrian activity of Si and O based on infinitely dilute solution in liquid iron, and \( a_{\text{SiO}_2} \) is Raoultian activity of \( \text{SiO}_2 \) based on pure solid \( \text{SiO}_2 \). The values of logarithm of the deoxidation product of \( \text{Si} \), \( \log K_{\text{SiO}_2} \), are plotted against mass\% Ni in Fe–Ni alloy at three temperatures in Fig. 1. The deoxidation product of Si slightly decreased with increasing Ni content in the liquid alloy. That is to say, it is recognized that the addition of noble metal like as Ni makes the deoxidation power stronger. The relation between \( \log K_{\text{Si}} \) and \( \log K_{\text{SiO}_2} \) was expressed by Eq. (4) in the Fe–Ni–Si–O system.

\[ \log f_i^j = \log f_i^j \] 

Where \( f_i^j \) denotes the interaction coefficient, which shows the effect of \( j \) component on \( i \) element dissolved in liquid iron. Since the activity of \( \text{SiO}_2 \) is unity, all terms of right hand side in Eq. (4) are calculated from the results of present work and previous data\(^3,4\) by other researchers which were listed in Table 3. The values of logarithm of interaction coefficient, \( \log f_i^j \), are plotted against mass\% Ni in Fe–Ni alloy in Fig. 2. It was found that the \( \log f_i^j \) decreased with increasing Ni content and systematic change of the values with temperature was not observed. The result was expressed by Eq. (5).

\[ \log f_i^j = -0.009[\%\text{Ni}] + \log f_i^j \] 

The values of \( e_{\text{Si}}^\text{Ni} \) and \( r_{\text{Si}}^\text{Ni} \) were obtained to be \(-0.009\) and \(-0.009\) respectively.

| Table 1. Experimental results on deoxidation of Fe–Ni alloy with Si. |
|------------------|------------------|------------------|------------------|------------------|
| Temp. (K) | Heat No. | mass\%Ni | mass\%Si | mass\%O | \( \log K_{\text{Si}} \) | \( \log K_{\text{SiO}_2} \) |
| 1823 | SN22-1 | 4.04 | 0.409 | 0.0046 | -5.066 | -0.653 |
| | SN22-2 | 4.04 | 0.403 | 0.0045 | -5.088 | -0.620 |
| | SN18-1 | 4.13 | 0.421 | 0.0044 | -5.059 | -0.677 |
| | SN18-2 | 4.13 | 0.445 | 0.0045 | -5.148 | -0.629 |
| | SN20-1 | 8.13 | 0.431 | 0.0043 | -5.093 | -0.686 |
| | SN20-2 | 8.31 | 0.444 | 0.0043 | -5.086 | -0.693 |
| | SN26-1 | 15.16 | 0.429 | 0.0042 | -5.121 | -0.660 |
| | SN26-2 | 15.16 | 0.428 | 0.0041 | -5.143 | -0.619 |
| | SN21-2 | 19.88 | 0.439 | 0.0037 | -5.221 | -0.597 |
| 1873 | SN6-4 | 3.98 | 0.465 | 0.0055 | -7.607 | -0.596 |
| | SN6-5 | 3.98 | 0.462 | 0.0069 | -6.969 | -0.689 |
| | SN14-4 | 4.02 | 0.476 | 0.0066 | -6.583 | -0.802 |
| | SN14-5 | 4.02 | 0.469 | 0.0064 | -6.716 | -0.849 |
| | SN22-3 | 4.04 | 0.390 | 0.0070 | -7.119 | -0.749 |
| | SN16-3 | 4.13 | 0.434 | 0.0061 | -6.792 | -0.814 |
| | SN10-5 | 7.95 | 0.461 | 0.0082 | -7.773 | -1.509 |
| | SN10-6 | 7.95 | 0.463 | 0.0084 | -7.082 | -1.560 |
| | SN8-6 | 7.96 | 0.470 | 0.0075 | -8.080 | -0.798 |
| | SN8-5 | 7.96 | 0.465 | 0.0075 | -7.893 | -0.901 |
| | SN13-3 | 9.99 | 0.500 | 0.0056 | -7.086 | -0.849 |
| | SN13-5 | 9.99 | 0.507 | 0.0073 | -7.838 | -0.953 |
| | SN26-5 | 15.16 | 0.421 | 0.0061 | -8.050 | -0.996 |
| | SN21-3 | 19.88 | 0.439 | 0.0057 | -8.496 | -1.111 |
| 1923 | SN15-4 | 2.04 | 0.439 | 0.0097 | -3.843 | -0.016 |
| | SN15-5 | 2.04 | 0.435 | 0.0097 | -3.838 | -0.012 |
| | SN22-4 | 4.04 | 0.393 | 0.0095 | -4.450 | 0.020 |
| | SN22-5 | 4.04 | 0.383 | 0.0109 | -4.342 | -0.083 |
| | SN17-4 | 6.02 | 0.425 | 0.0092 | -4.444 | -0.009 |
| | SN23-3 | 8.09 | 0.397 | 0.0094 | -4.495 | -0.019 |
| | SN18-4 | 8.13 | 0.443 | 0.0098 | -4.371 | -1.302 |
| | SN19-5 | 8.31 | 0.415 | 0.0100 | -4.382 | -0.094 |
| | SN25-2 | 10.11 | 0.541 | 0.0081 | -4.650 | -0.045 |
| | SN19-12 | 10.12 | 0.432 | 0.0087 | -4.485 | -0.081 |
| | SN26-4 | 15.16 | 0.411 | 0.0089 | -4.487 | -0.071 |
| | SN26-5 | 15.16 | 0.403 | 0.0093 | -4.458 | -1.080 |
| | SN21-4 | 19.88 | 0.425 | 0.0087 | -4.493 | -1.123 |
| | SN21-5 | 19.88 | 0.427 | 0.0086 | -4.501 | -1.114 |
| | SN27-4 | 20.27 | 0.384 | 0.0089 | -4.540 | -0.081 |
| | SN27-5 | 20.27 | 0.392 | 0.0087 | -4.562 | -0.059 |

Fig. 1. Relation between \( \log K_{\text{Si}} \) and [mass\%Ni] in Fe–Ni alloy.

Table 3. Interaction parameters and their temperature dependence.

| elements | interaction parameters at 1873K | temperature dependence | references |
|-----------|---------------------------------|-----------------------|------------|
| O         | O                               | -0.200                | 0          | 1750/T+0.76 | 3, 4 |
| Si        | Si                              | 0.066                 | 0          | 1237/T+0.034 | 6 |
| Cr        | Cr                              | -0.033                | 0          | 1237/T+0.034 | 6 |
| Ni        | Ni                              | 0.048                 | 0          | 1237/T+0.034 | 6 |
| Si        | Si                              | 0.119                 | 0          | 1237/T+0.034 | 6 |
| Cr        | Cr                              | 0.021                 | 4.3x10^-1  | 1 |

\[ \log f_i^j = e_{\text{Ni}}^{\text{Si}} [\% j] + r_{\text{Si}}^\text{Ni} [\% j]^2 \]
0.002 and $\pm 1 \times 10^{-4}$, respectively. The recommended value by the 19th Committee on Steelmaking, Japan Society for the Promotion of Science (JSPS), is also represented by dotted line at 1873 K in Fig. 2. The present result showed the opposite tendency to the recommended value by JSPS. According to the phase diagram of the Ni–Si system, many stable inter-metallic compounds exist. It suggests the existence of the attraction force between the Ni and Si atoms in liquid iron. Therefore, it is considered that the decreasing tendency of interaction coefficient $\log K^{5}_{\text{Si}}$ with increasing Ni content is reasonable. This tendency agrees well with that of the effect of Cr on the interaction coefficient, $\log f^{Cr}_{\text{Si}}$, as already mentioned previously by the present authors.

### 3.2. Cross Product Term of Cr and Ni on Si Deoxidation of Fe–Cr–Ni Alloy

The present authors have already determined the effect of Cr on the Si deoxidation of Fe–Cr alloy in our previous paper, and the effect of Ni on the Si deoxidation of Fe–Ni alloy was obtained in the present study. However the cross product term of Cr and Ni on Si deoxidation in Fe–Cr–Ni alloy has not yet determined.

The effect of cross product term of dissolved elements on a interaction coefficient $C$ in high alloy steel were first reported by Matoba and Kawanabe, and Sakao and Sano in the Fe–O–i–j (i,j=Co, Ni, W, Mo) and the Fe–O–i–j systems, respectively. After that, the thermodynamics of multi-component systems have been developed by Lupis et al. and applied to many systems by Itoh et al. and others. According to the same idea as that of Itoh et al., the value of $\log K_{\text{Si}}$ on Fe–Cr–Ni system can be represented by Eq. (6), by applying the cross product term of Cr and Ni on Si and O in the case of $a_{\text{SiO}_2}=1$.

$$\log K_{\text{Si}} = \log K_{\text{Cr}}^{5} + \log f_{\text{CrSi}}^{5} + \log f_{\text{NiSi}}^{5} + \log f_{\text{CrNi}}^{5} + \log f_{\text{CrNi}}^{5}(\%\text{Cr})(\%\text{Ni}) + 2(\log f_{\text{Cr}}^{5} + \log f_{\text{Ni}}^{5} + \log f_{\text{CrNi}}^{5}(\%\text{Cr})(\%\text{Ni})) \quad \text{(6)}$$

Where the terms of $f_{\text{CrSi}}^{5}$ and $f_{\text{CrNi}}^{5}$ represent the cross product term of Cr and Ni on Si and O dissolved in liquid alloy, respectively. One has Eq. (7), from Eq. (6).

$$Y = \log K_{\text{Si}} - \log K_{\text{Cr}}^{5} - \log f_{\text{CrSi}}^{5} - \log f_{\text{NiSi}}^{5} - \log f_{\text{CrNi}}^{5} - 2(\log f_{\text{Cr}}^{5} + \log f_{\text{Ni}}^{5} + \log f_{\text{CrNi}}^{5}(\%\text{Cr})(\%\text{Ni}))$$

$$= (r_{\text{CrSi}}^{5} + 2r_{O}^{5}(\%\text{Cr})(\%\text{Ni})) \quad \text{(7)}$$

Figure 3 shows the effect of Cr and Ni contents on the $K_{\text{Si}}$ at 1823 K and 1 mass% Si. The value of $K_{\text{Si}}^{5}$ markedly increases with increasing Cr content, and slightly decreases with increasing Ni content. The effect of Cr on the deoxidation of $K_{\text{Si}}^{5}$ is very large, and the value of $K_{\text{Si}}^{5}$ becomes larger with two order of magnitude by the addition of 20 mass% Cr. In Fig. 5, the equilibrium O content in Fe–Cr–Ni alloy at 1 mass% Si and 1823 K are shown as a function of Ni and Cr contents. From Fig. 5, it is observed that the deoxidation with Si in Fe–Cr–Ni alloy is very difficult at the range of high Cr content.
deoxidation. The results obtained were summarized as follows:

1. The effect of Ni on the interaction coefficient of Si was expressed by

\[
\log f_{Si}^{Ni} = -0.009\%Ni + 2 \times 10^{-4}\%Ni^2
\]

\[\text{[mass\%Ni]} \leq 20, \ 1823 \leq T \leq 1923 \text{ K}\]

2. The cross product term of Cr and Ni on the interaction coefficients of Si and O were expressed by

\[
r_{Si}(\text{Cr}, \text{Ni}) + 2r_{O}(\text{Cr}, \text{Ni}) = -0.001, \ 1823 \leq T \leq 1923 \text{ K}.
\]

3. The deoxidation product with Si in Fe–Cr-Ni system was numerically expressed by

\[
\log K_{9Si} = 8.40 - 24600/T - (1.40 - 3 \times 500/T)\%O + 0.029\%Si
\]

\[-(0.047 - 246/T + 4.3 \times 10^{-4}\%Cr)\%Cr
\]

\[-(0.003 + 2 \times 10^{-4}\%Ni)\%Ni
\]

\[+ 0.001\%Cr\%Ni\]

\[\text{[mass\%Cr]} \leq 25, \ [\text{mass}\%Ni] \leq 20, \ 1823 \leq T \leq 1923 \text{ K}\]

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