Interaction between Silicon and Titanium in Molten Steel

Mitsuhiko OHTA and Kazuki MORITA

School of Engineering, The University of Tokyo, Hongo, Bunkyoku, Tokyo 113-8656 Japan.

(Received on July 12, 2002; accepted in final form on October 2, 2002)

1. Introduction

In order to control the composition of deoxidation product in steel, Gibbs energy of formation for such oxide components, their activities and interaction parameters between alloying elements in steels are required. Especially, complex deoxidation by silicon and titanium is important because that process can be used as the substitution for aluminum deoxidation which forms harmful deoxidation product.

However, interaction parameter between silicon and titanium in steels have been reported only by Batalin et al.\(^1\) Their value is too large to explain the deoxidation equilibrium of the practical process and their method of experiment might have any problems.

Therefore, in this study, interaction parameter between silicon and titanium in steels has been investigated by the measurements of distribution ratio of silicon and titanium between molten iron and silver at 1 873 K.

2. Experiments

Chemical potentials of silicon in molten iron and silver phases are equal when they are in equilibrium and the following equation is obtained.

\[
RT \ln \alpha_{\text{Si in Fe}} = RT \ln \alpha_{\text{Si in Ag}} \quad \text{...............(1)}
\]

Equation (1) can be rewritten as Eq. (2) using the first order interaction parameters.

\[
\ln \gamma^g_{\text{Si in Fe}} + \ln X_{\text{Si in Fe}}^e + \ln \gamma^g_{\text{Si in Ag}} + \ln X_{\text{Si in Ag}}^e + e_{\text{Si in Fe}}^{\text{Ti in Fe}} \cdot X_{\text{Ti in Fe}} = \ln \gamma^g_{\text{Si in Ag}} + \ln X_{\text{Si in Ag}} \quad \text{...............(2)}
\]

Here, \(\gamma^g_{\text{Si in Fe}}\) denotes activity coefficient of \(i\) in regard to infinite dilute solution as a standard state in molten \(j\) and \(e_{\text{Si in Fe}}^{\text{Ti in Fe}}\) is interaction parameter between \(i\) and \(k\) in molten iron. Regarding the activity coefficient of silicon, that with respect to infinite dilute solution in silver is adopted because iron and titanium contents are very low in silver and interaction among silicon and other components can be ignored. Self-interaction of silicon in silver can also be ignored because silicon content is very low, less than 0.05 mol%. Equation (3) is derived from Eq. (2) by transposition of unknown parameters to the right hand side. Although molar fraction of silver in molten iron should be the function of molar fraction of titanium in molten iron, it is assumed that the both molar fractions are independent for the convenience.

\[
\ln X_{\text{Si in Ag}}^e - \ln \gamma^g_{\text{Si in Ag}} - \ln X_{\text{Si in Fe}}^e - \ln \gamma^g_{\text{Si in Fe}} = e_{\text{Si in Fe}}^{\text{Ti in Fe}} \cdot X_{\text{Ti in Fe}} + \ln \gamma^g_{\text{Si in Ag}} - \ln X_{\text{Si in Ag}}^e - \ln \gamma^g_{\text{Si in Ag}} - \ln X_{\text{Si in Fe}}^e - \ln \gamma^g_{\text{Si in Fe}} \quad \text{...............(3)}
\]

When the values of the left hand side of Eq. (3) are plotted against molar fraction of titanium in iron, the slope of linear relations shows interaction parameter between silicon and titanium in iron. Values reported by Sigworth et al.\(^2\), Hultgren\(^3\) and Sakao et al.\(^4\) are adopted as the activity coefficient of silicon with respect to infinite dilute solution in iron, that in silver and self-interaction parameter of silicon in iron, respectively.

Experiments were carried out as follows. A vertical electric resistance furnace with MoSi\(_2\) heating elements was employed in this experiment. Preliminarily, the Fe–Si–Ti alloys of the fixed composition were melted with a mullite crucible at 1 873 K. Ten grams of Fe–Si–Ti alloy and silver in a mullite crucible was loaded with a graphite holder in the furnace controlled at 1 873 K for more than 4 h. Argon gas deoxidized with magnesium chips was flown into the experimental furnace to avoid the specimen from being oxidized. After an achievement of the equilibrium, the sample was taken out of the furnace and rapidly cooled by argon flush. Iron and silver phases were separated and subjected to chemical analysis. Silicon in both phases and titanium in steels were measured by ICP-AES and ICP-MS. Titanium content in silver phase was not measured because that was too small to be measured even by ICP-MS.

3. Results and Discussions

Experimental results are shown in Table 1 and the relationship between the left side of Eq. (3) and molar fraction of titanium in steels is shown in Fig. 1. Although many literatures reported the reciprocal solubility between the Ag–Fe binary system, neither silver in molten iron nor iron in molten silver were detected by chemical analysis in the present study. Which suggests that interaction parameters between silver and silicon or titanium in molten iron and those between iron and silicon or titanium in molten silver are positive and large values.

A linear relation is recognized in experimental data. The slope, 166, corresponds to interaction parameter in molar

| No. | Si in Ag (10\(^{-6}\)) | Si in Fe (mass%) | Ti in Fe (mass%) | \(X_{\text{Si in Ag}}\) (10\(^{-3}\)) | \(X_{\text{Si in Fe}}\) (10\(^{-3}\)) | \(X_{\text{Ti in Fe}}\) (10\(^{-3}\)) |
|-----|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 01  | 2.15           | 3.42            | 0.027           | 0.82            | 6.59            | 0.30            |
| 02  | 4.75           | 3.83            | 0.283           | 1.83            | 7.33            | 3.18            |
| 03  | 13.0           | 3.67            | 0.898           | 5.00            | 7.03            | 10.1            |
| 04  | 9.22           | 3.05            | 0.800           | 3.54            | 5.87            | 9.05            |
| 05  | 2.07           | 1.67            | 0.000           | 5.30            | 3.27            | 0.00            |
| 06  | 5.01           | 3.83            | 0.192           | 1.93            | 7.36            | 2.16            |
| 07  | 4.09           | 4.60            | 0.005           | 1.57            | 8.77            | 0.05            |
| 08  | 2.83           | 3.10            | 0.149           | 1.01            | 6.00            | 1.68            |
| 09  | 3.97           | 4.30            | 0.044           | 1.53            | 8.22            | 0.49            |
| 10  | 3.66           | 3.58            | 0.108           | 1.41            | 6.90            | 1.22            |
| 11  | 2.91           | 3.80            | 0.058           | 1.12            | 7.31            | 0.65            |
fraction between silicon and titanium in steels. The slope drawn by a broken line in the figure shows interaction parameter by Batalin et al. Interaction parameter obtained in this study is 0.68 of that by Batalin et al. Interaction parameters in regard to 1 mass% dilute solution as a standard state between silicon and titanium, $e_{\text{Si}}^{0}$ and $e_{\text{Ti}}^{0}$, were derived from the result as 0.84 and 1.43, respectively.

Complex deoxidation equilibrium by silicon and titanium is investigated with the present result. Deoxidation equilibrium by titanium can be represented as Eq. (4).

$$\text{Ti}_2\text{O}_3 (s) = 2\text{Ti} + 3\text{O} \quad \text{(4)}$$

Standard Gibbs energy change of Eq. (4), $\Delta G^\circ_{\text{Ti}_2\text{O}_3} = 217300 \, \text{[J]}$ (at 1873 K) 

$$\text{(5)}$$

Relationship between oxygen and titanium content in steels equilibrated with pure Ti$_2$O$_3$ is shown in Fig. 2. Broken lines show the relations obtained with $e_{\text{Si}}^{0}$ by Batalin et al. When silicon content is 1 mass%, and oxygen content is 10 mass ppm, titanium content is 0.1 mass% from the present study, while titanium content is as low as 0.01 mass% from the values by Batalin et al. Thus, it is considered that the interaction parameter between silicon and titanium in molten iron would cause the great effect to calculation of the deoxidation equilibrium.

Deoxidation equilibrium between molten steel and the Al$_2$O$_3$–SiO$_2$–TiO$_X$ system is also studied. Activities of each component in the liquidus area of the oxide system were reported by the present authors. Relationship between the compositions of the oxide and the steel is shown in Fig. 3. It shows a considerable change in titanium content of the steel with the change in Al$_2$O$_3$ and SiO$_2$ contents of the oxide although activity of TiO$_{1.5}$ slightly changed from 0.67 to 0.88. Titanium content in the steel changes from 130 to 1.5 mass ppm while silicon content changes from 0.57 to 2.2 mass% when SiO$_2$ content of the oxide increases from 45 to 75 mass%. It is considered that the considerably large value of the interaction parameter between silicon and titanium in the steel has caused such estimation.

Ratio of change in titanium content in the present analysis is remarkably smaller than the previous analysis using the parameter by Batalin et al., which is from 0.024 to 44.6 mass ppm. This phenomenon may be due to difference between the parameter obtained from the present work and that of Batalin et al.

4. Conclusions

Interaction parameters between silicon and titanium in
molten iron at 1 873 K were obtained as follows by the measurement of distribution ratio of silicon and titanium between molten iron and silver.

\[
\begin{align*}
\epsilon_{\text{Si}/\text{Ti}} &= 166 \\
\epsilon_{\text{Si}} &= 0.84, \quad \epsilon_{\text{Ti}/\text{Si}} = 1.43
\end{align*}
\]

Acknowledgement

The authors are grateful to Nippon Steel Corporation for financial support.

REFERENCES

1) G. I. Batalin and V. S. Sudavtsova: Sov. Prog. Chem., 9 (1976), 930.
2) G. K. Sigworth and J. F. Elliott: Met. Sci., 8 (1974), 298.
3) R. Hultgren: Selected Values of the Thermodynamic Properties of Binary Alloys, Amer. Soc. Met., Metals Park, Ohio, (1973), 99.
4) H. Sakao and T. Fujisawa: The 19th Committee on Steelmaking Rept., The Japan Soc. for the Promotion of the Science, 10519 (1983), 1.
5) E. T. Turkdogan: Physical Chemistry of High Temperature Technology, Academic Press, London, (1980), 22.
6) The 19th Committee on Steelmaking: Steelmaking Data Sourcebook, The Japan Soc. for the Promotion of the Science, Gordon and Breach Science Publishers, New York, (1988), 278.
7) M. Ohta and K. Morita: ISIJ Int., 42 (2002), 474.