1. Introduction

Control of oxygen in liquid iron is very important not only to remove impurities such as phosphorus and sulfur but also to improve the yield of valuable alloying elements such as chromium and manganese in the steelmaking process. Chromium is the most typical and valuable alloying element for stainless steel. Since Cr is less noble in nature, oxidation loss of Cr could easily occur from metal to slag. The most important knowledge is the equilibrium between dissolved Cr and O in liquid Fe–Cr alloy was thermodynamically discussed in this paper. Mutual solubility between SiO\(_2\) and (Fe,Mg)O\(_2\)-Cr\(_2\)O\(_3\) solid solution was observed at 1 573 and 1 873 K, in order to know the activity of SiO\(_2\) coexisted with Cr\(_2\)O\(_3\) based oxide solid solution after Si deoxidation of liquid Fe–Cr alloy. It was found that Si deoxidation equilibrium of liquid Fe–Cr alloy could be thermodynamically evaluated based on unit activity of SiO\(_2\) due to negligibly small mutual solubility between SiO\(_2\) and FeO–Cr\(_2\)O\(_3\) based solid solution. As the result, the deoxidation power of Si would not enough high to produce low oxygen high Cr steel because of the attraction between Cr and Si in liquid iron.

KEY WORDS: stainless steel; deoxidation equilibrium; thermodynamics; iron–chromite solid solution; Si deoxidation; solid solubility.

Oxygen control in liquid stainless steel production is extremely important for the removal of impurities and improvement of Cr yield. Precise information on the thermodynamics of oxygen in liquid Fe–Cr alloy is necessary for this purpose. The equilibrium relation between dissolved Cr and O in liquid iron saturated with pure solid Cr\(_2\)O\(_3\) or FeO–Cr\(_2\)O\(_3\) solid solution and thermodynamic behavior of FeO–Cr\(_2\)O\(_3\) solid solution had been established in our previous works. Following these studies, the deoxidation equilibrium of Si in liquid Fe–Cr alloy was thermodynamically discussed in this paper. Mutual solubility between SiO\(_2\) and (Fe,Mg)O\(_2\)-Cr\(_2\)O\(_3\) solid solution was observed at 1 573 and 1 873 K, in order to know the activity of SiO\(_2\) coexisted with Cr\(_2\)O\(_3\) based oxide solid solution after Si deoxidation of liquid Fe–Cr alloy. It was found that Si deoxidation equilibrium of liquid Fe–Cr alloy could be thermodynamically evaluated based on unit activity of SiO\(_2\) due to negligibly small mutual solubility between SiO\(_2\) and FeO–Cr\(_2\)O\(_3\) based solid solution. As the result, the deoxidation power of Si would not enough high to produce low oxygen high Cr steel because of the attraction between Cr and Si in liquid iron.

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1. Introduction

Control of oxygen in liquid iron is very important not only to remove impurities such as phosphorus and sulfur but also to improve the yield of valuable alloying elements such as chromium and manganese in the steelmaking process. Chromium is the most typical and valuable alloying element for stainless steel. Since Cr is less noble in nature, oxidation loss of Cr could easily occur from metal to slag. The most important knowledge is the equilibrium between dissolved Cr and O in steel melt for the precise control of Cr in the stainless steelmaking process. A number of researchers have studied on this subject\(^1\) due to such practical importance. However, the equilibrium between Cr and O in liquid iron has not been well established due to the insufficient thermodynamic consideration on the oxide phase in equilibrium with liquid Fe–Cr alloy\(^1\) as pointed out by the authors. The thermodynamic behavior of oxygen in liquid Fe–Cr alloy was re-assessed in our previous papers,\(^2,3\) and the equilibrium relation between dissolved Cr and O in liquid iron saturated with pure solid Cr\(_2\)O\(_3\) was first studied by using Cr\(_2\)O\(_3\) crucible where the activity of Cr\(_2\)O\(_3\) could be precisely defined as unity.\(^2\) Experiments were conducted at the temperature from 1 723 to 1 923 K in the concentration range of 7 to 46 mass% Cr. As the results, equilibrium constant for the reaction of Cr\(_2\)O\(_3\)(s)=2Cr+3O and the interaction parameter between Cr and O in liquid iron were determined as described in the next section, and the activities of Cr and O were well expressed by the functions of their contents and temperature. The critical Cr concentration, at which the equilibrium oxide phase changed from Cr\(_2\)O\(_3\) to FeO–Cr\(_2\)O\(_3\), [%Cr]\(_{\text{critical}}\) was also theoretically revealed as 6.31, 6.82 and 7.24 mass% in Fe–Cr alloy at 1 823, 1 873 and 1 923 K, respectively. Our second study\(^4\) has dealt with the equilibrium between Cr and O in liquid iron saturated with FeO–Cr\(_2\)O\(_3\) solid solution and phase equilibria between liquid Fe–Cr alloy and Cr\(_2\)O\(_3\) containing oxide for the full understanding of the thermodynamic behavior of oxygen in liquid Fe–Cr alloy. The free energy of formation of FeO–Cr\(_2\)O\(_3\) and the activities of constituents in FeO–Cr\(_2\)O\(_3\) solid solution have also been measured by the chemical equilibrium technique at 1 823 to 1 923 K in our second study. It is found that the activities of FeO(\(/\)) and Cr\(_2\)O\(_3\)(\(/\)) in FeO–Cr\(_2\)O\(_3\) solid solution exhibit negative deviation from ideality. This result indicates that the steelmakers would miss-control oxygen in liquid stainless steel when Cr content in metal is lower than these critical Cr contents if they assumed the unit activity of Cr\(_2\)O\(_3\) or FeO–Cr\(_2\)O\(_3\) for the prediction of oxygen. Contrarily, the experimental results on the relation between dissolved Cr and
O in liquid iron were in good accord with the ones predicted by our proposed thermodynamic parameters as shown in Fig. 1 if appropriate correction for Cr₂O₃ activity in oxide phase had been applied.

Hino et al. reported that FeO · Cr₂O₃, MgO · Cr₂O₃ and MgO · Al₂O₃ formed (Fe,Mg)O · (Cr,Al)₂O₃ solid solution and this spinel structure solid solution was in equilibrium with (Cr,Al)₂O₃ solid solution. (Fe,Mg)O · (Cr,Al)₂O₃ solid solution is industrially important oxide system not only for the ferro-chromium production from Cr ore but also for understanding oxide phase in equilibrium with liquid stainless steel thermodynamically. The Si deoxidation equilibrium of liquid Fe–Cr alloy has been thermodynamically discussed in this paper. In order to know the activity of SiO₂ after Si deoxidation of liquid Fe–Cr alloy coexisted with Cr₂O₃ containing oxide solid solution, solubility of SiO₂ into (Fe,Mg)O · (Cr,Al)₂O₃ solid solution has been measured at 1573 and 1873 K. The present work would also provide an useful information for direct smelting reduction of chromium ore with liquid Fe–C–Si alloy.

2. Experimentals

A diffusion couple technique was employed in the present work. A quartz plate (2 mm × 4 mm × 1 mm) was embedded into the powder mixture of (Fe,Mg)O · (Cr,Al)₂O₃ solid solution (hereinafter designated as Spinel) and (Cr,Al)₂O₃ solid solution (hereinafter designated as Sesquioxide), pressed into tablet shape (φ10 mm × 5 mm) as schematically shown in Fig. 2, heated in a Mo crucible at 1573 or 1873 K for 24 h in CO–3%CO₂ atmosphere, and quenched with impinging He. The mixing ratio of Spinel and Sesquioxide was 3 : 1 in mass.

Spinel and Sesquioxide were preliminary synthesized by sintering the mixture of the aimed composition of each component oxide in a Mo crucible at 1573 K for 24 h. The procedure was repeated at least two times. Finally, the formation of each oxide solid solution was confirmed by X-ray diffraction equipment (XRD). The quenched sample was mounted in a mold and was cut in the longitudinal direction. The concentration profile of Si, Fe, Cr, Al and Mg in the sample was detected by the wavelength dispersion type EPMA. The mutual solubility between Spinel and SiO₂ was determined by assuming the local equilibrium at the interface between SiO₂ and Spinel. Equilibrium oxide phases were also identified by XRD.

3. Experimental Results

It was found from XRD analysis that Spinel saturated with Sesquioxide was in equilibrium with SiO₂ (Tridymite at 1573 K and Cristballite at 1873 K) except for Al₂O₃ saturated MgO · Al₂O₃. Since no peak shift in XRD patterns of Spinel and Sesquioxide was observed in all cases, solubility of SiO₂ into Spinel and Sesquioxide was deduced to be very small. Figure 3 demonstrates some examples of microscopic views near SiO₂ and Spinel:Sesquioxide interface after the experiment. A new phase was formed between diffusion couple of (a), whereas no intermediate phase was observed in the case of (b). Very small particles
of Sesquioxide were homogeneously dispersed in Spinel matrix. Since the solubility of SiO₂ into Sesquioxide was found to be negligibly small at any composition and temperature in the preliminary experiments, line analysis with EP AM was performed on Spinel matrix to determine the solubility of SiO₂ into Spinel. It was found that small amount of SiO₂ diffused into Spinel phase as shown in Fig. 4(b) and SiO₂ content in Spinel phase at SiO₂–(Spinel–Sesquioxide) interface was as high as approximately 1.5 mol% at 1573 K. In the case of SiO₂–(MgO · Al₂O₃–Sesquioxide) diffusion couple, intermediate phase consisted of SiO₂ and Al₂O₃, and SiO₂ content in MgO · Al₂O₃ was negligibly small. This phase was identified as Mullite, 3Al₂O₃ · 2SiO₂, from the composition of the intermediate phase. No solubility of Spinel and Sesquioxide into SiO₂ or Mullite was observed in the present work. Morita et al. investigated the reaction between MgO–Al₂O₃–SiO₂ (mass%SiO₂=45–70) and MgO · Al₂O₃–MgO · Al₂O₃ solid solution at 1873 K in air. They observed no solubility of SiO₂ into solid solution. Their findings support the present experimental results.

Figure 5 summarizes the experimental results on SiO₂ solubility into Spinel phase. It could be realized that the

![Fig. 3. Microscopic views of SiO₂–(Spinel+Sesquioxide) diffusion couple at 1573 K.](image1)

![Fig. 4. Concentration profiles in diffusion couple after the experiment at 1573 K.](image2)

![Fig. 5. Solubility of SiO₂ into (Fe,Mg)O · (Cr,Al)₂O₃ solid solution.](image3)
solubility of SiO$_2$ into Spinel was less than 2.7 mol%. Since almost negligible mutual solubility between SiO$_2$ and Spinel was observed in the present work, the following two major conclusions could be obtained. 1) Spinel phase can be approximated as (Fe,Mg)O·(Cr,Al)$_2$O$_3$ solid solution even if SiO$_2$ coexists with Spinel, so that the activities of constituents in Spinel can be calculated by the thermodynamic model proposed in our previous papers.$^{3,4}$ 2) When liquid Fe–Cr–O alloy is deoxidized by Si, the activity of SiO$_2$ in equilibrium with Spinel would be assumed as unity unless the concentration of FeO or Cr$_2$O$_3$ in the solid solution phase is very low.

4. Deoxidation of Liquid Fe–Cr Alloy with Si

The deoxidation of liquid Fe–Cr alloy with Si is discussed in this paper based on the experimental results obtained in the present work. As it has been discussed in our previous papers, liquid Fe–Cr alloy is in equilibrium with FeO·Cr$_2$O$_3$ solid solution or pure solid Cr$_2$O$_3$. MgO as a general refractory material of steelmaking furnace and SiO$_2$ as the deoxidation product are also taken into account for oxide system in addition to these oxides. Phase relation between metal (Fe–Cr alloy) and oxide (FeO–Cr$_2$O$_3$–MgO–SiO$_2$) systems is schematically illustrated in Fig. 6. This diagram is drawn based on the findings in this study and our previous works.$^{3-5}$ It is seen that liquid Fe–Cr alloy is in equilibrium with pure solid Cr$_2$O$_3$ in the almost entire composition range except for extremely low Cr range, where liquid slag would form under the presence of SiO$_2$ in the system. On the other hand, Healy and Schottmiller$^{5}$ and Xiao and Holappa$^{31}$ suggested that SiO$_2$ and Cr$_2$O$_3$ could form liquid CrO–Cr$_2$O$_3$–SiO$_2$ slag at 1873 K under the presence of metallic Cr. The critical oxygen partial pressure at which liquid slag disappears and only SiO$_2$ becomes stable oxide phase was estimated as 3×10$^{-15}$ atm from the data of Xiao and Holappa.$^{31}$ This critical oxygen partial pressure would become much higher with increasing Fe content in metal phase. Therefore, the assumptions of unit activity of SiO$_2$ and no liquid slag formation would be reasonable when we consider the Si deoxidation of liquid steel which contains less than 20 mass% of Cr.

The initial oxygen content in liquid Fe–Cr alloy before Si addition is given by Eqs. (1) and (2).

$$\log K_{\text{Cr}} = \log(k_{\text{Cr}}^i \cdot k_{\text{O}}^j \cdot a_{\text{Cr}_2O_3}) = \log(f_{\text{Cr}}^i \cdot [\%\text{Cr}]^2 \cdot [\%\text{O}]^3) / a_{\text{Cr}_2O_3}$$

$$= \log K_{\text{Cr}}^i + 2 \log f_{\text{Cr}} + 3 \log f_{\text{O}} - \log a_{\text{Cr}_2O_3}$$

$$= \log K_{\text{Cr}}^i + 2 \varepsilon_{\text{Cr}}^i [\%\text{Cr}] + 2 \varepsilon_{\text{O}}^j [\%\text{O}] + 3 \varepsilon_{\text{Cr}}^i [\%\text{Cr}]$$

$$+ 3 \varepsilon_{\text{O}}^j [\%\text{O}] - \log a_{\text{Cr}_2O_3}$$

Where, $K_{\text{Cr}}$, $a_{\text{Cr}_2O_3}$, $f_{\text{Cr}}$, $f_{\text{O}}$, and $\varepsilon_i^j$ denote the equilibrium constant, the Raoultian activity, the Henrian activity, the activity coefficient, and the interaction parameter between $i$ and $j$, respectively. The standard states of $h_{\text{Cr}}$ and $h_{\text{O}}$ in Eq. (2) are infinite dilute solution for Cr and O in liquid iron, and that of $a_{\text{Cr}_2O_3}$ is pure solid. $\varepsilon_{\text{Cr}}^i$ can be assumed as zero,$^{11}$ and $\varepsilon_{\text{O}}^j$ and $\varepsilon_{\text{Cr}}^i$ are also given by the following equations among the parameters in Eq. (2).

$$\varepsilon_{\text{O}}^j = -1750 / T - 0.76$$

$$\varepsilon_{\text{Cr}}^i = 3.25 \varepsilon_{\text{O}}^j - 0.01$$

The present authors have determined $\log K_{\text{Cr}}$ and $\varepsilon_{\text{Cr}}^i$ in their previous work$^{13}$ as Eqs. (5) and (6).

$$\log K_{\text{Cr}} = -36.200 / T + 16.1 \ (1823 \text{ K} < T < 1923 \text{ K})$$

$$\varepsilon_{\text{Cr}}^i = -123 / T + 0.034 \ (\text{mass} \% \text{Cr} < 46, \ 1823 \text{ K} < T < 1923 \text{ K})$$

Even in the range of $\text{Cr}<\%\text{Cr}_{\text{trunc}}$, where the activity of Cr$_2$O$_3$ in oxide phase is not unity, the equilibrium relation between Cr and O can be predicted by Eq. (2) with $a_{\text{Cr}_2O_3}$ in FeO·Cr$_2$O$_3$ solid solution as revealed in our previous paper.$^{31}$

On the other hand, reaction of Si with oxygen in liquid
Fe–Cr–Si–O alloy can be expressed by the following equations on the condition of unit activity of SiO₂.

\[
\log K_{Si} = \log(h_{Si} \cdot h_{O}^2 / a_{SiO_2}) = \log K'_{Si} + \log f_{Si} + 2 \log f_{O} \tag{7}
\]

Where, \( K'_{Si} \) denotes deoxidation product of Si (= \( \log(\%Si \cdot \%O^2) \)). Rearrangement of Eq. (8) and introduction of interaction parameters give Eq. (9).

\[
\log K'_{Si} = \log K_{Si} - (e^{dSi}_0 + 2e^{dSi}_O)[\%Si] - (e^{dCr}_0 + 2e^{dCr}_O)[\%O] - (e^{dSi}_5 + 2e^{dSi}_5)[\%Cr] \tag{9}
\]

Table 1. Thermodynamic parameters related to Si–O equilibrium in liquid Fe–Cr alloy at 1 873 K.

| parameter | \( \log K_{Si} \) | \( e^{dSi}_0 \) | \( e^{dSi}_O \) | \( e^{dSi}_5 \) | \( e^{dCr}_0 \) | \( e^{dCr}_O \) |
|-----------|------------------|----------------|----------------|----------------|----------------|----------------|
| source    | 1)                | 1)             | 1)             | 1)             | 1)             | 1)             |

The values of \( \log K_{Si} \) and interaction parameters except for \( e^{dSi}_5 \) in Eq. (9) are available in the literatures \(^{1,2}\) as listed in Table 1. The interaction parameter between Si and Cr, \( e^{dSi}_5 \), has not been evaluated directly from the present experimental data. However, Suzuki et al.\(^{9}\) evaluated \( e^{dSi}_5 \) recently by the combination of their own experimental results on the Si deoxidation of liquid Fe–Cr alloy with thermodynamic parameters concerning Cr and O (\( \log K_{Cr} \) and \( e^{dCr}_O \)) determined in our previous work.\(^{23}\) Finally, they have proposed following equation at 1 873 K.

\[
e^{dSi}_5 = -0.021 + 4 \times 10^{-4} [%Cr] \tag{10}
\]

Therefore, we can predict the equilibrium oxygen content in metal at given [%Cr] and [%Si] by solving Eq. (9) numerically.

Figure 7 shows relation between oxygen and Cr contents in metal at 0, 0.02, 0.05, 0.1, 0.5, 1 and 5 mass% Si. Initial oxygen content of Fe–Cr melt before the addition of Si is given by Fe–Cr/Fe₃O₄ or Fe–Cr/FeO·Cr₂O₃ equilibrium as upper solid line of [%Si]=0 in Fig. 7. The addition of Si reduces the oxygen content at constant Cr content. However, the deoxidation power of Si becomes weak at higher Cr content due to the attraction between Cr and Si; e.g. oxygen content in Fe–5mass%Cr and Fe–18mass%Cr are reduced by the addition of 1 mass%Si approximately from 350 to 73 and from 450 to 110 mass-ppm, respectively. In short, Si deoxidation would be insufficient to produce low oxygen Fe–Cr alloy, so that degassing with decarburization should be used first for more deoxidation of crude stainless steel melt.

5. Conclusions

Solubility of SiO₂ into (Fe,Mg)O·(Cr,Al)₂O₃ spinel structure solid solution saturated with (Cr,Al)₂O₃ solid solution has been observed at 1 573 and 1 873 K by the diffusion couple technique. The solubility of SiO₂ into (Fe,Mg)O·(Cr,Al)₂O₃ solid solution was less than 1.5 mol% and 2.7 mol% at 1 573 K and 1 873 K, respectively. For Al₂O₃ saturated MgO·Al₂O₃, equilibrium phase was not SiO₂ but 3Al₂O₃·2SiO₂. No solubility of Spinel and Sesquioxide into SiO₂ was observed in the present work, so that Si deoxidation equilibrium in liquid Fe–Cr alloy can be discussed thermodynamically with the assumption of unit activity of SiO₂ unless Cr content in metal was extremely low. Since the deoxidation power of Si became weak at higher Cr content due to the attraction between Cr and Si, Si deoxidation would be insufficient to produce low oxygen Fe–Cr alloy.

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