Sulfide Capacity and Phase Equilibria of MnO–TiO₂–MnS System at 1 723 K

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The sulfide capacity and the activity of MnO in the MnO–TiO₂ system were measured at 1 723 K. Also, the phase equilibria of the MnO–TiO₂–MnS system were estimated by measuring the solubility of MnS in the melts. The thermodynamic behavior of MnO and TiO₂ in the MnO–TiO₂ system exhibits a negative deviation from ideality at 1 723 K. The sulfide capacity increases and the activity coefficient of MnS decreases with increasing MnO content in the MnO–TiO₂ system. The solubility of MnS in the MnO–TiO₂ system increases with increasing MnO content up to about 50 mol%, followed by nearly constant value of about 80 mass% MnS. The solubility of MnS equilibrated with MnO is in good correspondence with the value obtained from the phase diagram of the MnO–MnS binary system. Compared with the phase diagram of the MnO–SiO₂–MnS system, a homogeneous liquid region in the MnO–TiO₂–MnS system is found to be wider at the same temperature. The activity of MnS increases with increasing MnS content at a fixed MnO/TiO₂ ratio in the MnO–TiO₂–MnS system. Also, the activity slightly decreases with increasing TiO₂ content at a fixed MnS/MnO ratio, whilst MnS activity rapidly decreases by increasing the content of MnO at a constant TiO₂/MnS ratio.

KEY WORDS: sulfide capacity; activity; phase equilibria; negative deviation; activity coefficient.

1. Introduction

Because the mechanical properties of steel products have been known to improve by the grain refinement technology, many attempts have been made to decrease the size of ferrite grains by using fine non-metallic inclusions as a heterogeneous nucleation sites during the phase transformation from austenite to ferrite.¹) This technique called “oxides metallurgy” could be enhanced by even dispersion of primary fine (sub-micron) oxides in steel melts and by large precipitation of secondary (sulfides, nitrides, etc.) particles on oxides.

Since the manganese sulfide was reported to act major nucleation sites for the intra-granular ferrites, the thermodynamic studies on the phase equilibria of complex oxides containing MnS have been investigated.²–⁴) Hasegawa et al.⁴) proposed the phase equilibria of the MnO–SiO₂–MnS system from the measurement of MnS solubility in manganese silicates. The solubility of MnS rapidly increased above MnO content of 40 mass%, which could explain the fact that MnS precipitation ratio on the oxide particles increases with increasing MnO content.³) Koyama et al.⁴) concluded that the solubility of MnS in the MnO–SiO₂–TiO₂ system increased by substitution of TiO₂ for SiO₂ at a fixed MnO content in the melts. In addition, Ito et al.⁵) concluded that the activity coefficient of MnS decreases with increasing the ratio of TiO₂ to SiO₂ at a constant MnO content in the MnO–SiO₂–TiO₂ system.

The common results of current studies are that the oxide melts with high sulfide capacity would be preferable to MnS precipitation, that the liquidus temperature of oxide melts containing MnS would be significantly important during solidification and that Mn–Ti deoxidation would qualitatively be more effective for the precipitation of MnS than Mn–Si would be.

Therefore, in the present study, the sulfide capacity and the activity of MnO in the MnO–TiO₂ system were measured at 1 723 K. Furthermore, the phase equilibria of the MnO–TiO₂–MnS system were estimated by measuring the solubility of MnS in the melts.

2. Experimental

2.1. Experimental Principles

The equilibrium reaction between MnO in the slag and Mn in the molten silver is as follows⁶):  

\[
\text{MnO (s)} = \text{Mn (l)} + \frac{1}{2} \text{O}_2 (g) \quad \Delta G^\circ = 401 000 - 84.3T \quad (\text{J/mol})
\]

\[
a_{\text{MnO}} = \frac{Y_{\text{Mn}} \cdot X_{\text{Mn}} \cdot p_{\text{O}_2}^{1/2}}{K(1)} \]

where \(Y_{\text{Mn}}\) is the activity of Mn in the molten silver, \(X_{\text{Mn}}\) is the mole fraction of Mn in the molten silver, \(p_{\text{O}_2}\) is the oxygen partial pressure, and \(K(1)\) is the equilibrium constant of the reaction.
3. Results and Discussion

3.1. Activity of MnO in MnO–TiO₂ System

The relation between the Mn content in molten silver and the MnO content in the MnO–TiO₂ melt at 1 723 K is listed in Table 1. The Mn content in Ag increases from about 1.0 × 10⁻³ to 5.4 × 10⁻² with an increasing content of MnO from 32.6 to 72.4 mol% in the slag.

By combining the activity coefficient of Mn in Ag and the results shown in Table 1, the activity of MnO in the MnO–TiO₂ melt at 1 723 K can be estimated as given in Table 1. The activity of TiO₂ can also be calculated by using Gibbs–Duhem equation as shown in Fig. 1. In Fig. 1, the results at different temperatures available in the literature are shown for comparison. The thermodynamic behavior of MnO and TiO₂ in the MnO–TiO₂ system exhibits a negative deviation from ideality at 1 723 K, and thus the activity of MnO increases with increasing temperature at a fixed MnO content.

The interaction between MnO and other (acidic) oxides should be taken into account to estimate the thermodynamic stability of MnO in homogeneous liquid phase. Recently, the sulfide capacity of molten slags has been defined based on the gas/slag equilibrium reaction by Eq. (3):

\[
C_{S^2-} = \frac{K \cdot a_{O_2}^{\frac{1}{2}}}{f_{S^2-}} \cdot \left(\frac{\text{mass}\% S^2-}{\text{mol} S^2-} \right) \cdot \frac{P_o^{\frac{1}{2}}}{P_{S^2-}^{\frac{1}{2}}} \tag{3}
\]

where \( K \), \( a_{O_2} \), \( f_{S^2-} \) and \( p_i \) are, respectively, the equilibrium constant of the desulfurization reaction, the activity of \( O_2 \) ions, the activity coefficient of \( S^2- \) ions and the partial pressure of \( i \). In Eq. (3), the sulfur potential \( (p_S) \) could be estimated from the Gibbs free energy of dissolution reaction of gaseous sulfur into the silver melt as given in Eq. (4).

\[
\frac{1}{2} \text{S}_2(g) = [\text{S}]_{\text{Ag}}, \quad \Delta G^\circ = -54 800 + 4.267 T \quad (\text{J/mol})
\tag{4}
\]

2.2. Experimental Procedure

A chemical equilibrium technique was employed for the measurement of MnO activity and sulfide capacity of the MnO–TiO₂ system and for the phase equilibria of the MnO–TiO₂–MnS system. The SiC electric resistance furnace combined with an R-type (Pt/Pt–13%Rh) thermocouple was used for all the experiments and the temperature was controlled at 1 723 ± 2 K with a proportional integral differential controller. The metal and slag samples were prepared using reagent-grade chemicals and the schematic diagram of the experimental apparatus is shown in previous articles.

The slag samples of 3 and 8g silver were maintained in a molybdenum crucible under CO/CO₂ atmosphere to control the oxygen partial pressure. Under the present oxygen potential, \( p_{O_2} = 7.23 \times 10^{-13} \text{ atm} \), the oxidation state of titanium in TiO₂ is 4+ from thermodynamic estimation based on the Gibbs free energy of formation of TiO₂ and Ti₂O₃. In the measurement of the phase equilibria of the MnO–TiO₂–MnS system, solid MnO, TiO₂, and MnS sintered pellets, which had been confirmed by XRD analysis, were coexisted with molten slags for the saturation of each component.

The impurities in the gases were removed by passing the gases through CaSO₄, soda lime, and silica gel. The equilibration time was predetermined to be 22 hr. After equilibrating, the samples were quenched by Ar gas and crushed for chemical analysis. The content of manganese in slag and metal samples was determined by atomic absorption spectrometry (Shimadzu, AA-6601 F/G). The content of sulfur in metal and slag samples was determined by infrared absorption analyzer (LECO, CS-300) and by barium sulfate gravimetric method, respectively.

### Table 1

| No. | \( X_{\text{MnO}} \) (mass%) | \( X_{\text{MnO}} \) in Ag | \( a_{\text{MnO}} \) |
|-----|-------------------------------|--------------------------|-----------------|
| 1-1 | 0.326                         | 9.83 × 10⁻⁴              | 2.35 × 10⁻²     |
| 1-2 | 0.326                         | 1.02 × 10⁻³              | 2.85 × 10⁻²     |
| 2-1 | 0.429                         | 2.79 × 10⁻³              | 5.29 × 10⁻²     |
| 2-2 | 0.429                         | 2.83 × 10⁻³              | 6.35 × 10⁻²     |
| 3-1 | 0.530                         | 1.73 × 10⁻²              | 8.21 × 10⁻²     |
| 3-2 | 0.530                         | 1.87 × 10⁻²              | 9.63 × 10⁻²     |
| 4-1 | 0.628                         | 2.09 × 10⁻²              | 3.91 × 10⁻²     |
| 4-2 | 0.628                         | 2.10 × 10⁻²              | 4.11 × 10⁻²     |
| 5-1 | 0.724                         | 5.22 × 10⁻²              | 9.51 × 10⁻²     |
| 5-2 | 0.724                         | 5.52 × 10⁻²              | 9.71 × 10⁻²     |

Fig. 1. Activity of MnO (measured) and TiO₂ (calculated) as a function of MnO content in the MnO–TiO₂ system at 1 723 K. (△: after Ohta and Morita at 1 873 K; ○: after Rao and Gaskell at 1 823 K; □: after Rao and Gaskell at 1 773 K)
Park and Min\(^{12}\) proposed the relative ionic characteristics of various binary compounds (\(\text{MO} \cdot \text{B}_2\text{O}_3\) and \(\text{MO} \cdot \text{Al}_2\text{O}_3\), \(\text{MO} \cdot \text{TiO}_2\) and \(\text{MO} \cdot \text{SiO}_2\), where \(\text{MO}\) represents the basic oxide) based on the differences between the electronegativities of basic and acidic oxides. The order of the relative ionic characteristics was \(\text{MnO} \cdot \text{SiO}_2 > \text{MnO} \cdot \text{TiO}_2 > \text{MnO} \cdot \text{Al}_2\text{O}_3\); thus it could be expected that \(\text{SiO}_2\) exhibits a stronger attraction to \(\text{MnO}\) than \(\text{TiO}_2\) exhibits, followed by \(\text{Al}_2\text{O}_3\).

These trends can be confirmed from the following thermodynamic behavior of \(\text{MnO}\) in the \(\text{MnO–SiO}_2–\text{TiO}_2\) and \(\text{MnO–Al}_2\text{O}_3–\text{TiO}_2\) ternary systems. The activity coefficient of \(\text{MnO}\) decreased with increasing ratio of \(\text{SiO}_2\) to \(\text{TiO}_2\) in the \(\text{MnO–SiO}_2–\text{TiO}_2\) system at a fixed \(\text{MnO}\) content,\(^{5}\) while the activity coefficient decreased by increasing the ratio of \(\text{TiO}_2/\text{Al}_2\text{O}_3\) in the \(\text{MnO–Al}_2\text{O}_3–\text{TiO}_2\) system at 1673 K.\(^{10}\)

3.2. Sulfide Capacity of \(\text{MnO–TiO}_2\) System

The sulfide capacity of the \(\text{MnO–TiO}_2\) system at 1723 K calculated from Eqs. (3) and (4) is shown in Fig. 2 with the results given in the research literature.\(^{5,13,14}\) The experimental results in the present study are listed in Table 2. The sulfide capacity, \(\log C_{\text{S}_2^-}\), commonly increases with increasing \(\text{MnO}\) content in all slag systems. Also, the capacity of the \(\text{MnO–TiO}_2\) system is about 3 times greater than that of the \(\text{MnO–SiO}_2\) system at the same temperature (1773 K), indicating that the \(\text{MnO–TiO}_2\) system would qualitatively be more favorable to the precipitation of \(\text{MnS}\) than the \(\text{MnO–SiO}_2\) would be. However, the \(\text{MnO–SiO}_2–\text{TiO}_2\) (mol\%\(\text{MnO}/\text{mol}\%\text{SiO}_2\geq 2.0\)) system is expected to have the highest sulfide capacity, if the temperature dependence of \(C_{\text{S}_2^-}\) is taken into account. The effect of slag composition on \(C_{\text{S}_2^-}\) can be discussed more quantitatively by considering the relationship between sulfide capacity and \(\text{MnO}\) activity as follows.

The relationship between the sulfide capacity and slag basicity (\(a_{\text{O}_2}\)) can be deduced by Eq. (5) from Eq. (3).

\[
\log C_{\text{S}_2^-} = \log a_{\text{O}_2} - \log f_{\text{S}_2^-} + \text{constant} \quad \ldots (5)
\]

Thus, the \(\log C_{\text{S}_2^-}\) and \(\log a_{\text{MnO}}\) are expected to have a linear correlation with the slope of unity at a fixed temperature, assuming that the activity coefficient of \(\text{S}_2^-\) ions would not be changed significantly by slag composition and that \(a_{\text{O}_2}\) would be in proportion with \(a_{\text{MnO}}\) in \(\text{MnO–RO}\) (RO: acidic oxides) systems.

The sulfide capacities of the \(\text{MnO–TiO}_2\), \(\text{MnO–SiO}_2\), and \(\text{MnO–SiO}_2–\text{TiO}_2\) systems are compared in Fig. 3 as a function of the activity of \(\text{MnO}\). The sulfide capacity, \(\log C_{\text{S}_2^-}\), of each slag system linearly increases with increasing the activity of \(\text{MnO}\), \(\log a_{\text{MnO}}\). However, the slopes of the lines in the \(\text{MnO–TiO}_2\) and \(\text{MnO–SiO}_2\) systems are close to 3/2, while the slope close to 2 is observed in the case of the \(\text{MnO–SiO}_2–\text{TiO}_2\) system. These trends provide that the activity coefficient of sulfide ions would decrease by increasing the content of \(\text{MnO}\), because \(\text{MnO}\) is generally considered as a sulfide former and is the only basic oxide in these slags.

The equilibrium reaction between \(\text{MnO}\) and \(\text{MnS}\) is as follows:\(^{6}\)

\[
\text{MnO} (s) + \frac{1}{2} \text{S}_2 (g) = \text{MnS} (l) + \frac{1}{2} \text{O}_2 (g) \quad \ldots (6)
\]

\[
\Delta G^\circ = 118\,000 - 2827 T \quad (\text{J/mol})
\]

\[
\gamma_{\text{MnS}} = \frac{K_{\text{eq}}^{(6)} a_{\text{MnO}} p_{\text{O}_2}^{1/2}}{X_{\text{MnS}} p_{\text{S}_2}^{1/2}} \quad \ldots (7)
\]

where \(\gamma_{\text{MnS}}, K_{\text{eq}}^{(6)}, a_{\text{MnO}}, X_{\text{MnS}}, p_{\text{S}_2}\), and \(p_{\text{O}_2}\) are, respectively, the ac-

![Fig. 2. Sulfide capacity of the MnO-containing slags as a function of MnO content.](image1)

![Fig. 3. Relationship between the sulfide capacity and the activity of MnO in the MnO-containing slags.](image2)

| No. | MnO (mol%) | TiO₂ (mol%) | MnS (mol%) | \(\log C_{\text{S}_2^-}\) |
|-----|------------|-------------|------------|-----------------|
| 1   | 39.98      | 39.97       | 0.03       | -3.80           |
| 2   | 49.76      | 49.76       | 0.48       | -3.27           |
| 3   | 59.44      | 39.63       | 0.93       | -2.81           |
| 4   | 65.81      | 33.11       | 1.08       | -2.42           |
| 5   | 73.84      | 24.61       | 1.55       | -1.79           |

Table 2. Dependence of sulfide capacity of the MnO–TiO₂ system on slag composition.
tivity coefficient of MnS, the equilibrium constant of Eq. (6), the activity of MnO, the mole fraction of MnS and the partial pressure of $i$. The activity coefficient of MnS calculated from Eq. (7) is shown in Fig. 4 as a function of $X_{\text{MnO}}$ with the results available in the literature for comparison.\(^5\),\(^14\). The activity coefficient of MnS decreases with increasing $X_{\text{MnO}}$ in all MnO-containing slags and the $\gamma_{\text{MnS}}$ decreasing rate in the MnO–SiO$_2$–TiO$_2$ system is larger than that in the MnO–TiO$_2$ and MnO–SiO$_2$ systems. Thus, the deviation from the theoretical expectation observed in Fig. 3 could be explained on the different interaction degree between MnO and MnS in each slag system.

### 3.3. Phase Equilibria of MnO–TiO$_2$–MnS System

The solubility of MnS in the MnO–TiO$_2$ system at 1723 K is shown in Fig. 5 as a function of $X_{\text{MnO}}(X_{\text{MnO}} + X_{\text{TiO}_2})$ with the results of the MnO–SiO$_2$ system given in the literature.\(^2\) In the MnO–TiO$_2$ system, MnS solubility increases with increasing MnO content up to about 50 mol%, followed by nearly constant value of about 80 mass% MnS, while the solubility sharply increases by increasing MnO content from 60 to 80 mol% in the MnO–SiO$_2$ system. In both of slags, the maximum solubility of MnS equilibrated with MnO is in good correspondence with the value obtained from the phase diagram of the MnO–MnS binary system.\(^15\). Therefore, the MnO–TiO$_2$ system could establish the wider homogeneous liquid phase containing MnS than the MnO–SiO$_2$ system. This means that the precipitation ratio of MnS in the MnO–TiO$_2$ system would be larger than that in the MnO–SiO$_2$ system at lower temperatures.

The isothermal phase relations for the MnO–TiO$_2$–MnS system at 1723 K are shown in Fig. 6 with the results for the MnO–SiO$_2$–MnS system.\(^2\) The experimental results in the present study are listed in Table 3. Although the MnO saturated lines in both of slags agree with each other, the TiO$_2$ saturated line shows an opposite trend to that of SiO$_2$ with MnS addition. Also, the MnS saturated line exists from lower MnO/TiO$_2$ ratio in the MnO–TiO$_2$–MnS system than MnO/SiO$_2$ ratio in the MnO–SiO$_2$–MnS system. Compared with the phase diagram of the MnO–SiO$_2$–MnS system, a homogeneous liquid region in the MnO–TiO$_2$–MnS system...
system is found to be wider at the same temperature.

The activity of MnS in the MnO–TiO₂–MnS system is significantly important for predicting the precipitation potential of MnS. The equilibrium reaction between MnS in slags and Mn in the molten silver is as follows:

\[
\begin{align*}
\text{MnS (l)} & \rightarrow \text{Mn (l)} + \frac{1}{2} \text{S}_2 (g) \\
\Delta G^\circ & = 283 000 - 70.27T \quad (J/mol) \\
a_{\text{MnS}} & = \frac{\gamma_{\text{Mn}} X_{\text{Mn}} P_{\text{S_2}}^{1/2}}{K_{(8)}} \\
\end{align*}
\]

where \( K_{(8)} \), \( a_{\text{MnS}} \), \( P_{\text{S_2}} \), \( \gamma_{\text{Mn}} \) and \( X_{\text{Mn}} \) are, respectively, the equilibrium constant of Eq. (8), the activity of MnS, the sulfide potential, the activity coefficient and the mole fraction of Mn in Ag. The activity of MnS in the slag is a function of the activity of Mn in Ag at a fixed sulfur potential and temperature.

The calculated results are listed in Table 4 and the isoactivity curves of MnS in the MnO–TiO₂–MnS system at 1723 K are shown in Fig. 7. The activity of MnS increases with increasing MnS content at a fixed MnO/TiO₂ ratio in the entire compositions. In addition, the activity slightly decreases with increasing TiO₂ content at a fixed MnS/MnO ratio, whilst MnS activity rapidly decreases by increasing the content of MnO at a constant TiO₂/MnS ratio.

4. Conclusions

The sulfide capacity and the activity of MnO in the MnO–TiO₂ system were measured at 1723 K. Also, the phase equilibria of the MnO–TiO₂–MnS system were estimated by measuring the solubility of MnS in the melts. The following conclusions could be summarized.

Table 4. Activity of MnS in the MnO–TiO₂–MnS system at 1723 K.

| No. | MnO (mol%) | TiO₂ (mol%) | MnS (mol%) | \( a_{\text{MnS}} \) |
|-----|------------|-------------|------------|----------------|
| 1   | 28.5       | 3.2         | 68.3       | 0.80          |
| 2   | 40.3       | 2.5         | 57.2       | 0.52          |
| 3   | 44.8       | 2.7         | 52.5       | 0.46          |
| 4   | 50.5       | 2.8         | 46.7       | 0.32          |
| 5   | 54.0       | 14.6        | 51.4       | 0.44          |
| 6   | 52.9       | 23.9        | 50.2       | 0.49          |
| 7   | 39.9       | 17.1        | 43.0       | 0.23          |
| 8   | 37.9       | 25.3        | 36.8       | 0.32          |
| 9   | 23.6       | 35.3        | 41.1       | 0.40          |
| 10  | 35.6       | 33.6        | 30.8       | 0.25          |
| 11  | 30.3       | 45.5        | 24.2       | 0.22          |
| 12  | 39.2       | 37.2        | 23.6       | 0.22          |
| 13  | 47.6       | 31.7        | 20.7       | 0.16          |
| 14  | 47.3       | 45.3        | 7.4        | 0.12          |

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