Effect of ZrO$_2$ Addition to the CaO-SiO$_2$-MgO-CaF$_2$ Slags on the Sulfur Removal from the 16Cr-14Ni Stainless Steel Melts

Joo Hyun Park$^{1,*}$ and Dong Joon Min$^2$

$^1$Stainless Steel Research Group, Technical Research Laboratories, POSCO, Pohang 790-785, Korea
$^2$Department of Metallurgical System Engineering, Yonsei University, Seoul, 120-749, Korea

The equilibrium distribution ratio of sulfur between the 16 mass%Cr-14 mass%Ni stainless steel melts and the CaO-SiO$_2$-MgO-ZrO$_2$-7 mass%CaF$_2$ ($B (= (\text{mass}\%\text{CaO})/(\text{mass}\%\text{SiO}_2) = 2.0)$) slags was measured at 1873 K to clarify the role of ZrO$_2$ in the desulfurization reaction based on the sulfide capacity concept. The sulfur distribution ratio linearly decreases on increasing the oxygen partial pressure with the slope of \( \frac{1}{2} \) in the logarithmic scale at a fixed sulfur potential and temperature. The sulfide capacity of the slags is constant up to about \( (\text{mass}\%\text{ZrO}_2)/(\text{mass}\%\text{SiO}_2) + (\text{mass}\%\text{MgO}) = 0.3 \), followed by a linear decrease on increasing the \( Z/(Z + M) \) ratio. The effect of ZrO$_2$ substitution for MgO on the decrease in the (apparent) sulfide capacity at \( Z/(Z + M) > 0.3 \) could be explained by the decrease in the basicity of the liquid slag phase due to the formation of CaZrO$_3$ from the computational estimations for the phase equilibria and the thermodynamic activities of slag components. Based on the X-ray diffraction patterns of the slags, it was confirmed that the peak intensity for the Ca$_2$SiO$_4$ is strong through the entire composition range, while the intensity of the peaks corresponding to the CaZrO$_3$ is relatively strong in the composition of \( Z/(Z + M) = 0.42 \) and 0.64. The sulfide capacity can be expressed as a linear function of the mass fraction of CaZrO$_3$ in the slags investigated in the present study, while that exhibits a wide distribution at a relatively narrow optical basicity region, resulting from the effect of ZrO$_2$ on the basicity of the liquid slag phase due to the formation of CaZrO$_3$.

\[
\log L_S = \text{constant} - \frac{1}{2} \log P_O
\]

$^*$Corresponding author, E-mail: basicity@posco.co.kr

1. Introduction

The austenitic stainless steels containing ultra low level of sulfur (< 10 mass ppm) have widely been used to the electronic components in the television monitors and several kinds of generators. Hence, the consumption of the desulfurization fluxes such as lime, dolomite, magnesia and fluor spar in an argon oxygen decarburization converter has been increased under restricted operating time. On the other hand, the recycling of the used refractories has recently been issued not only to decrease a disposal cost but also to meet a global standard for the sustainable and environmentally friendly steelmaking technologies.1,2)

Based on these backgrounds, in the present study, the possibility for the use of the spent zirconia (ZrO$_2$) refractories as a desulfurization flux for the 16 mass%Cr-14 mass%Ni stainless steel melts was investigated by employing the sulfide capacity concept, which is defined as given in eq. (2).3)

\[
C_{S_2^-} = \frac{K_1 \times a_{O^2}}{f_{S_2^-}} = (\text{mass}\%S_2^-) \times \left( \frac{p_{O_2}}{p_{S_2^-}} \right)^{\frac{1}{2}}
\]

where \( C_{S_2^-} \), \( K_1 \), \( a_{O^2} \), \( f_{S_2^-} \), and \( p_i \) are, respectively, the sulfide capacity of the slags, the equilibrium constant of eq. (1), the activity of \( O^2^- \) ions and the activity coefficient of \( S_2^- \) ions in the slags, and the partial pressure of gaseous species \( i \).

However, the sulfide capacity of the slags containing ZrO$_2$ has scarcely been found. Recently, Tanabe et al. observed that the sulfur distribution ratio (log L$_S$) between the molten iron equilibrated with the CaO-Al$_2$O$_3$-ZrO$_2$ slags saturated by CaAl$_2$O$_4$ or CaZrO$_3$ phases linearly increased with increasing aluminum content (log [mass%Al]) in iron melt with the slope of 2/3 at 1873 K.4) From this result, they concluded that the oxygen potential between metal and slag was controlled by the [Al]-[O] equilibrium reaction. Although the nitride capacity of the CaO-SiO$_2$-Al$_2$O$_3$-ZrO$_2$ slags was reported by Sasabe et al.,5) the effect of ZrO$_2$ on the sulfide capacity of the calcium silicate slags that were used for sulfur removal from the austenitic stainless steel melts is not available in the literature.

Therefore, the equilibrium distribution ratio of sulfur between the molten stainless steels and the CaO-SiO$_2$-MgO-ZrO$_2$-7 mass%CaF$_2$ ($B (= (\text{mass}\%\text{CaO})/(\text{mass}\%\text{SiO}_2) = 2.0)$) slags was measured at 1873 K to clarify the role of ZrO$_2$ in the desulfurization reaction.

2. Experimental Procedure

The pure iron, chromium, nickel, manganese, and silicon were premelted in a vacuum induction furnace to make a composition of Fe-16 mass%Cr-14 mass%Ni-0.5 mass%Si-1.5 mass%Mn stainless steel. The metal samples of about 240 grams and the CaO-SiO$_2$-MgO-ZrO$_2$-7 mass%CaF$_2$ ($B = 2.0$) slags of about 20 grams were equilibrated in the pure MgO crucibles, which were located in a high frequency induction furnace. The initial content of sulfur in the premelted Fe-16Cr-14Ni-0.5Si-1.5Mn steel was about 0.032 mass%. The equilibrium compositions of the metals and slags investigated in the present study are listed in Table 1.

A schematic diagram of the experimental apparatus is shown in Fig. 1 and the experimental temperature was...
controlled to be 1873 (±3) K using an R-type (Pt-13 mass%Rh/Pt) thermocouple and a proportional integral differential controller. The oxygen as an impurity in an Ar gas was removed by passing the gas through magnesium turnings heated to about 773 K. After the steel samples were melted at 1873 K, the premelted slags were added. Then, the metal and slag were equilibrated during 30 minutes, which was preliminarily determined.

After equilibrating, the power of the furnace was off and the crucible assembly was quenched by Ar gas. The metal and slag samples were prepared for chemical analysis. The content of sulfur was analyzed by combustion and infrared absorption method and that of oxygen in the metal was determined by fusion and infrared absorption method. The composition of the slags was analyzed by an X-ray fluorescence spectrometer (model: Bruker S4 Pioneer, Bruker AXS Inc., Madison, WI, USA) and the crystalline phase in the final slags was determined by an X-ray diffractometer (model: D8 Advance, Bruker AXS Inc., Madison, WI, USA).

Moreover, the phase equilibria and the thermodynamic properties of the slags at 1873 K were calculated using commercial thermodynamic software, FactSage5.4 along with the FToxid53 compound and solution databases, on the basis of the Gibbs energy minimization principles. 6)

3. Results and Discussion

3.1 Effect of oxygen partial pressure on sulfur distribution ratio

The sulfur distribution ratio ($L_S$), which is given in eq. (3), between the 16 mass%Cr-14 mass%Ni melts and CaO-SiO$_2$-MgO-ZrO$_2$-7 mass%CaF$_2$ ($B = 2.0$) slags is shown in Fig. 2 as a function of the oxygen partial pressure at a fixed sulfur potential ($p_{S_2} = 9.02 \times 10^{-7}$ Pa) and temperature (1873 K).

$$L_S = \frac{\text{sulfur in slag}}{\text{sulfur in metal}}$$

Here, the oxygen and sulfur potentials could be calculated not only by the Gibbs free energy change of the dissolution reaction of gaseous oxygen and sulfur into the molten steel as given in eqs. (4) and (5) but also by the activity of oxygen and sulfur in the steel melts estimated from eq. (6) and the interaction parameters ($\varepsilon_{M}^i$, $i = O$ and $S$) listed in Table 2.7,9)
Table 2 Interaction parameters used in the present study.\textsuperscript{7-9}

<table>
<thead>
<tr>
<th>$e'_i$</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-0.032\textsuperscript{9}</td>
<td>0.006</td>
<td>-0.066</td>
<td>-0.037\textsuperscript{9}</td>
<td>-0.174</td>
<td>-0.133</td>
</tr>
<tr>
<td>S</td>
<td>-0.010</td>
<td>0.000</td>
<td>0.075</td>
<td>-0.026</td>
<td>-0.270</td>
<td>-0.046</td>
</tr>
</tbody>
</table>

Fig. 3 Sulfur distribution ratio as a function of $Z/(Z + M)$ at 1873 K.

where the $f_i$ denotes the henrian activity coefficient of component $i$ in molten steel. The sulfur distribution ratio between metal and slag linearly decreases on increasing the oxygen partial pressure with the slope of $-0.58$, which is close to $-1/2$ in the logarithmic scale, indicating that the sulfur distribution reaction between metals and slags are in equilibrium state in the present study based on eq. (7).

$$
\log L_S = - \frac{1}{2} \log p_{O_2} + \log C_{S^{2-}} + \log f_S - \log K(5)
$$

3.2 Substitution effect of ZrO\textsubscript{2} for MgO on sulfide capacity of the slags

The sulfur distribution ratio is shown in Fig. 3 as a function of the ratio $(\text{mass}\%\text{ZrO}_2)/(\text{mass}\%\text{ZrO}_2 + \text{mass}\%\text{MgO})$ (hereafter, $Z/(Z + M)$) at 1873 K. The $L_S$ slightly increases to about 300 with increasing $Z/(Z + M)$ ratio up to about 0.2, followed by the significant decrease as ZrO\textsubscript{2} substitutes for MgO in the slags. This can quantitatively be understood by taking the sulfide capacity into account as shown in Fig. 4. In this study, the sulfide capacity was estimated on the basis of eq. (2) and the oxygen and sulfur potentials calculated as described in section 3.1.

The sulfide capacity of the slags at 1873 K is constant $(\log C_{S^{2-}} \approx -1.7)$ up to about $Z/(Z + M) = 0.3$, followed by a decrease on increasing the $Z/(Z + M)$ ratio with the following correlation.

$$
\log C_{S^{2-}} = -3.18 \times \left( \frac{\text{mass}\%\text{ZrO}_2}{\text{mass}\%\text{ZrO}_2 + \text{mass}\%\text{MgO}} \right) - 0.68 \ (r^2 = 0.89)
$$

These results indicate that the substitution of ZrO\textsubscript{2} for MgO in the highly basic $(B = 2.0)$ slags would not remarkably change the basicity, i.e., the activity of O\textsuperscript{2-} ions, of the slags at $Z/(Z + M) < 0.3$. That is, the ZrO\textsubscript{2} behaves as a weak basic oxide as likely as MgO in this region. However, the substitution of MgO by ZrO\textsubscript{2} at $Z/(Z + M) > 0.3$ reduces the sulfide capacity (eq. (8)), indicating that a decrease in the basicity of the slags, albeit the ratio of $(\text{mass}\%\text{CaO})$ to $(\text{mass}\%\text{SiO}_2)$ is fixed. The effect of ZrO\textsubscript{2} on the basicity of the CaO-SiO\textsubscript{2}-MgO-7 mass%CaF\textsubscript{2} slags $(B = 2.0)$ can be discussed by taking the formation reaction of calcium zirconate (CaZrO\textsubscript{3}) into account as follows.

3.3 Formation of CaZrO\textsubscript{3} and sulfide capacity of the slags containing CaO and ZrO\textsubscript{2}

The calculated phase equilibria, that is the mass fractions of each mineral and liquid phase are shown in Fig. 5 as a function of the $Z/(Z + M)$ ratio in the slags. The relative fraction of liquid slag increases up to about 90% on increasing the $Z/(Z + M)$ ratio, followed by a slight decrease, while the opposite tendency is observed in the case of calcium silicate compounds, viz. Ca\textsubscript{2}SiO\textsubscript{4} (larnite) + Ca\textsubscript{3}SiO\textsubscript{5} (hatrurite). The mass fraction of MgO (periclase) is nearly constant $(\approx 5\%)$ up to about $Z/(Z + M) = 0.45$, followed by a decrease up to about $Z/(Z + M) = 0.65$, where
Effect of ZrO\textsubscript{2} Addition to the Slags on the Sulfur Removal from the Stainless Steels

---

The solid MgO disappeared. The mass fraction of CaZrO\textsubscript{3} is specifically shown in Fig. 6 as a function of the \(Z/(Z + M)\) ratio at 1873 K. The CaZrO\textsubscript{3} is calculated not to form at \(Z/(Z + M) < 0.3\), while its fraction linearly increases with increasing \(Z/(Z + M)\) ratio greater than about 0.3 with the following relationship.

\[
\text{(mass\%CaZrO}_3) = 29.5 \times \left( \frac{\text{mass\%ZrO}_2}{\text{mass\%ZrO}_2 + \text{mass\%MgO}} \right) - 10.7 \quad (r^2 = 0.98) \tag{9}
\]

Therefore, it is computed that the slag system investigated in the present study is saturated by MgO and CaO-rich calcium silicate compounds (mainly larnite) at about \(Z/(Z + M) < 0.3\) and that the additional CaZrO\textsubscript{3} is formed as a saturating phase at about \(Z/(Z + M) > 0.3\). These computational results indicate that the (apparent) sulfide capacity of the multi-phase slags (liquid + solids), which is significantly meaningful in the actual refining converter, could be affected by the formation behavior of the CaZrO\textsubscript{3} and thus the thermodynamic properties of the liquid phase rather than by the changes in the mass fractions of liquid phase and the calcium silicate compounds. This can easily be confirmed from the formation reaction of CaZrO\textsubscript{3} as given in eq. (10) and the computed relationship between the activities of CaO and ZrO\textsubscript{2} in the liquid phase at 1873 K as shown in Fig. 7.

\[
\text{CaO (s)} + \text{ZrO}_2 (s) = \text{CaZrO}_3 (s), \quad \Delta G^o = -78200 + 0.83T \quad (J/mol) \tag{10}
\]

where the \(K_{(10)}\) and \(a_i\) are, respectively, the equilibrium constant of eq. (10) and the activity of component \(i\) in the liquid slag phase. In the composition of “liquid phase + calcium silicates + MgO” coexistence, because the activity of CaO in the liquid phase would not significantly be affected by the activity of ZrO\textsubscript{2}, the activity of SiO\textsubscript{2} in the liquid phase is nearly fixed. However, the higher the activity of ZrO\textsubscript{2} due to further substitution of ZrO\textsubscript{2} for MgO, the lower the activity of CaO in the liquid phase is expected, because of the formation of CaZrO\textsubscript{3} (eq. (11)). This results in the increase of the activity of SiO\textsubscript{2} in the liquid phase. Consequently, it is proposed that the effect of ZrO\textsubscript{2} substitution for MgO on a decrease in the (apparent) sulfide capacity at \(Z/(Z + M) > 0.3\), which is shown in Fig. 4, could be explained by the decrease in the basicity of the liquid slag phase due to the formation of CaZrO\textsubscript{3}.

The X-ray diffraction patterns of the slags are shown in Fig. 8. The peak intensity for the Ca\textsubscript{2}SiO\textsubscript{4} phase is strong through the entire composition range, while the intensity of the peaks corresponding to the CaZrO\textsubscript{3} phase is relatively strong in the samples of \(Z/(Z + M) = 0.42\) and 0.64. This is in good agreement to the calculated results shown in Fig. 5 and Fig. 6.

The sulfur distribution ratio between 16 mass\%Cr-14 mass\%Ni melts and the CaO-SiO\textsubscript{2}-MgO-ZrO\textsubscript{2}-7 mass\%CaF\textsubscript{2} (\(B = 2.0\)) slags is shown in Fig. 9 as a function of the mass fraction of CaZrO\textsubscript{3} phase in the slags at 1873 K. The \(L_S\) continuously decreases on increasing the mass fraction of CaZrO\textsubscript{3} in the slags, while the sulfide capacity linearly decreases on increasing the mass fraction of CaZrO\textsubscript{3} in the slags with the following correlation (Fig. 10).
This linear relationship between the sulfide capacity and the mass fraction of CaZrO$_3$ in the slags could quantitatively be understood by employing the activity of CaO, which is dependent on the formation of CaZrO$_3$ as discussed in Fig. 7.

### 3.4 Sulfide capacity of slags and the relative basicity indices

The sulfide capacity of the slags can be described as a function of the activity of CaO in the liquid phase as shown in eq. (15) by combining eqs. (14) and (2).

\[
\log C_{S^{2-}} = \log a_{CaO} - \log a_{Ca^{2+}} - \log f_{S^{2-}} + \log K_{11}
\]

(12)

Thus, it can be noted that the sulfide capacity (log $C_{S^{2-}}$) of the slags is in proportion to the activity of CaO (log $a_{CaO}$) in the liquid phase with the slope of unity by assuming that the activity of Ca$^{2+}$ and S$^{2-}$ ions would not significantly be affected by the composition of slags at a fixed temperature.$^{11,12}$

The sulfide capacity of the slags is shown in Fig. 11 as a function of the activity of CaO in the liquid slag phase at 1873 K. The log $C_{S^{2-}}$ linearly increases on increasing the log $a_{CaO}$ with the slope of about 2.4, which is greater than the expected value of unity in eq. (15). This means that the activity coefficient of S$^{2-}$ ions would significantly be decreased by increasing the activity of CaO in the liquid phase, while the activity coefficient of Ca$^{2+}$ ions probably increases. Thus, it is qualitatively suggested that the highly basic slags saturated by the magnesia, calcium silicates, and calcium zirconate are effective to increase the stability of S$^{2-}$ ions in the liquid slag phase.

In Fig. 12, the relationship between the sulfide capacity and the theoretical optical basicity of the various CaO-based slags is appeared.$^{13-16}$ Here, the theoretical optical basicity of the slags ($\Lambda$) was calculated from eq. (16).$^{17,19}$

\[
\Lambda = \sum_{t} x_{i} n_{i} A_{i}
\]

(16)
where \( n_i \) and \( \Lambda_i \) are, respectively, the mole fraction and the number of oxygen or fluoride in each component and the theoretical optical basicity of each oxide or fluoride \( i \). The theoretical optical basicity of \( \text{CaF}_2 \) \((\Lambda_{\text{CaF}_2})\) was taken to be about 0.67 from an averaged electron density, and that of \( \text{ZrO}_2 \) \((\Lambda_{\text{ZrO}_2})\) was taken to be about 0.90 from an electronic polarizability.\(^{21}\) The experimental results for the \( \text{CaO-SiO}_2 \)-\( \text{CaF}_2 \) (1773 K), \( \text{CaO-MgO-CaF}_2 \) (1723 K) and the \( \text{CaO-SiO}_2-\text{MgO-CaF}_2 \) (1573 K) slags were extrapolated to 1873 K based on the following equation:\(^{22}\)

\[
\log C_{S^-} = \left( \frac{22690 - 54640A}{T} \right) + 43.6A - 25.2 \quad (17)
\]

The sulfide capacity of the \( \text{CaO-SiO}_2-\text{MgO} \), \( \text{CaO-SiO}_2-\text{CaF}_2 \), and the \( \text{CaO-MgO-CaF}_2 \) slags exhibits a good correspondence to eq. (17), while that of the \( \text{CaO-SiO}_2-\text{MgO-CaF}_2 \) \((-\text{ZrO}_2 \)) slags shows somewhat positive deviation from eq. (17) due to their highly basic characteristics.\(^{23–25}\) Furthermore, it is of interest that the sulfide capacity of the slags containing \( \text{ZrO}_2 \) exhibits a wide distribution at a relatively narrow basicity region, resulting from the effect of \( \text{ZrO}_2 \) on the basicity of the liquid slag phase due to the formation of \( \text{CaZrO}_3 \) as discussed in section 3.3.

In summary, although the large substitution of \( \text{MgO} \) by \( \text{ZrO}_2 \) decreases the sulfide capacity because of a decrease in the basicity of slags due to the formation of \( \text{CaZrO}_3 \), the small amount of \( \text{ZrO}_2 \) could be used as a potential desulfurization flux in view of the saving the consumption of \( \text{MgO} \) with maintaining the high sulfur removal ability.

4. Conclusions

The equilibrium distribution ratio of sulfur between the 16 mass\%\( \text{Cr} \)-14 mass\%\( \text{Ni} \) stainless steel melts and the \( \text{CaO-SiO}_2-\text{MgO-\text{ZrO}_2-7 mass\%\text{CaF}_2} \) \((B(= (\text{mass\%CaO})/(\text{mass\%SiO}_2) = 2.0))\) slags was measured at 1873 K to clarify the role of \( \text{ZrO}_2 \) in the desulfurization reaction based on the sulfide capacity concept. The following conclusions were obtained.

1. The sulfur distribution ratio linearly decreases on increasing the oxygen partial pressure with the slope close to \(-1/2\) in the logarithmic scale at a fixed sulfur potential and temperature.
2. The sulfide capacity of the slags is constant up to about \((\text{mass\%ZrO}_2)/(\text{mass\%CaF}_2) + (\text{mass\%MgO}) = 0.3\), followed by a linear decrease on increasing the \(Z/(Z + M)\) ratio.
3. It is computed that the slag system investigated in the present study is saturated by \( \text{MgO} \) and calcium silicate compounds (mainly \( \text{Ca}_2\text{SiO}_4 \)) at about \(Z/(Z + M) < 0.3\) and that the additional \( \text{CaZrO}_3 \) is formed at about \(Z/(Z + M) > 0.3\). Thus, it is concluded that the effect of \( \text{ZrO}_2 \) substitution for \( \text{MgO} \) on the decrease in the (apparent) sulfide capacity at \(Z/(Z + M) > 0.3\) could be explained by the decrease in the basicity of the liquid slag phase due to the formation of \( \text{CaZrO}_3 \).
4. From the X-ray diffraction patterns of the slags, it was confirmed that the peak intensity for the \( \text{Ca}_2\text{SiO}_4 \) is strong through the entire composition range, while the intensity of the peaks corresponding to the \( \text{CaZrO}_3 \) is relatively strong in the composition of \(Z/(Z + M) = 0.42\) and 0.64.

(5) The sulfide capacity can be expressed as a linear function of the mass fraction of \( \text{CaZrO}_3 \) in the slags investigated in the present study as follows.

\[
\log C_{S^-} = -0.12 \times (\text{mass\%CaZrO}_3) - 1.77 \quad (r^2 = 0.89)
\]

(6) The sulfide capacity of the slags containing \( \text{ZrO}_2 \) exhibits a wide distribution at a relatively narrow optical basicity region, resulting from the effect of \( \text{ZrO}_2 \) on the basicity of the liquid slag phase due to the formation of \( \text{CaZrO}_3 \).

Acknowledgments

The authors express their gratitude to the anonymous reviewer for the fruitful comments.

REFERENCES