Relationship between the Aluminum and Oxygen and Sulfur Partitions for Molten Iron and a $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ Slag in Equilibrium

Jun TANABE,¹⁾ Ichiro SEKI²⁾ and Kazuhiro NAGATA³⁾

1) Department of Mechanical Engineering, Faculty of Engineering, Nippon Institute of Technology, Gakuendai, Miyashiro-cho, Minamisaitama-gun, Saitama 345-8501 Japan. E-mail: tanabe@nit.ac.jp 2) Formerly Department of Chemistry and Materials Science, Faculty of Engineering, Tokyo Institute of Technology, now at Institute for Materials Research, Tohoku University Works, Katahira 2-1-1, Aoba-ku, Sendai 980-8577 Japan. 3) Department of Chemistry and Materials Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8852 Japan.

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The relationship between the aluminum–oxygen and sulfur distribution ratio for molten iron and a $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag in equilibrium at 1873 K was studied using an Al_2O_3 or CaO -stabilized ZrO_2 crucible. The slag and molten iron equilibrated with $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ and C_{ss} (cubic solid solution in CaO-ZrO_2 system) in the Al_2O_3 crucible, and with $\text{CaO}\cdot\text{ZrO}_2$ and C_{ss} in the ZrO_2 crucible. These equilibrium states coincided with the phase diagram of $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$. From the concentrations of aluminum and oxygen dissolved in molten iron, the Al_2O_3 activity in the slag was determined to be 0.393 in the Al_2O_3 crucible and 0.385 in the ZrO_2 crucible. These activities were compared with the data in the $\text{CaO-Al}_2\text{O}_3$ and CaO-ZrO_2 systems. The sulfur distribution ratio was higher a little in the ZrO_2 crucible than in the Al_2O_3 crucible and increased with aluminum content. The sulfide capacity of the fluxes was determined to be 8.77×10^{-5} and 9.10×10^{-5} in the Al_2O_3 and ZrO_2 crucibles, respectively.

KEY WORDS: $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag; molten iron; aluminum; oxygen; sulfur distribution ratio; sulfide capacity; activity; thermodynamics.

1. Introduction

Nowadays, crude natural gas, including hydrogen sulfide, is transported by rust-proof steel piping. Hydrogen and hydrogen sulfide typically induce crack formation in the piping.¹⁾ Thus, steels with ultra-low sulfur and oxygen content are required. Nagata *et al.*²⁾ found that Al, Ca and Zr can control the composition of inclusions in rust-proof steel piping. In this case, the primary crystallization of MnS during solidification can also be suppressed.^{3,4)} The formation of inclusions can be thermodynamically determined by the activities of Ca, Al, Zr and Mn, as well as the oxygen and sulfur potentials and temperature of molten steel.

Thus, thermodynamic data, such as the activities and phase diagram for the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ system, are essentially required at molten steel temperatures. Oxide activities in the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ system were measured only for the $\text{CaO-Al}_2\text{O}_3$ ⁵⁾ and CaO-ZrO_2 systems.⁶⁾

Phase diagrams of the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ system were reported by Berezhnoi *et al.*,⁷⁾ Espinosa *et al.*,⁸⁾ Bannister,⁹⁾ Kisida *et al.*,¹⁰⁾ Sakai *et al.*¹¹⁾ and Murakami *et al.*¹²⁾ Nurse *et al.*¹³⁾ established the $\text{CaO-Al}_2\text{O}_3$ system. The $\text{Al}_2\text{O}_3\text{-ZrO}_2$ system was summarized in the Slag Atlas.¹⁴⁾ Stubican¹⁵⁾ and Tanabe and Nagata⁶⁾ established the CaO-ZrO_2 system.

The present study establishes the phase equilibria between molten iron and a $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ molten slag inside an Al_2O_3 or ZrO_2 ($\text{ZrO}_2 + 11\text{mol}\%\text{CaO}$) crucible. The aluminum and oxygen contents of molten iron and sulfur partition of molten iron and flux in equilibrium at 1873 K were measured to determine the activity of aluminum oxide and sulfide capacity of the molten slag.

2. Experimental

2.1. Preparation of the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ Slag Sample

Murakami *et al.*¹²⁾ determined ternary phase diagrams for a saturated $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag in an Al_2O_3 or ZrO_2 crucible at 1873 K. According to their data, the Al_2O_3 or ZrO_2 crucible saturation points are shown in Fig. 1 (①, ②).

$\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag samples were prepared by homogeneously mixing high-purity CaCO_3 , Al_2O_3 and ZrO_2 powders (Starting materials: 44.1mass% CaO –45.4mass% Al_2O_3 –10.5mass% ZrO_2 for Al_2O_3 crucible, 40.0mass% CaO –41.0mass% Al_2O_3 –19.0mass% ZrO_2 for ZrO_2 crucible (in Fig. 1)). The slag was melted in an Al_2O_3 or CaO -stabilized ZrO_2 crucible at 1873 K by a vertical resistance furnace with MoSi_2 heating bars. The melt samples were mixed for 60 s and left to stand for 1 h. The furnace hot zone (40 mm) temperature was within ± 2.5 K of 1873 K.

Fig. 1. Phase diagram of the CaO–Al₂O₃–ZrO₂ molten slag in equilibrium with an Al₂O₃ (①) or ZrO₂ (②) crucible at 1873 K.

The temperature was measured by a thermocouple (B-type). They were equilibrated at 1873 K. Then, the sample crucibles were raised above the furnace, and rapidly cooled by He gas and water. Sample compositions were characterized by X-ray diffraction. The slag composition after the experiment were ① in Fig. 1: 40.0mass%CaO–45.1mass% Al₂O₃–14.9mass%ZrO₂ (Al₂O₃ crucible) or ② in Fig. 1: 45.0mass%CaO–41.7mass%Al₂O₃–13.3mass%ZrO₂ (ZrO₂ crucible).

2.2. The Equilibrium between Molten Iron and Slag

Detailed descriptions of the experimental procedure are given in previous reports.^{16–20} Twenty grams of electrolytic iron (99.9%) with approximately 300–1 000 ppm (by weight) oxygen and 6 g of CaO–Al₂O₃–ZrO₂ slag containing 0.001–0.5 g of CaS were melted in an Al₂O₃ or ZrO₂ (ZrO₂+11%molCaO) crucible under a deoxidized Ar atmosphere at 1873 K. A Fe–(0.2–10)mass%Al alloy was added to the molten iron, and the mixture was stirred 3 times by an Al₂O₃ rod for 120 s every 1.8 ks. The mixture was left to stand for 3.6 ks in order to float inclusions. Subsequently, the crucible with the molten iron and slag was cooled rapidly in He gas, and quenched in water.

2.3. Chemical Analysis

The sulfur content of the metal and slag was analyzed by combustion-infrared absorptiometry. The total oxygen content of the metal was determined with inert-gas fusion combustion-infrared absorptiometry.²¹ The total aluminum content, as well as the Al, Ca and Zr contents, were determined by inductively coupled plasma emission spectroscopy (ICP). For ICP analysis, the slag samples saturated with Al₂O₃ and ZrO₂ were melted by the alkali fusion method using Na₂CO₃ and a mixture of Na₂CO₃ and Na₂O·2B₂O₃, respectively, and dissolved by an HCl solution (1:1). The metal samples were dissolved by the HCl solution.

Table 1. Chemical compositions of metal and slag phases in the experiment at 1873 K.

Run Number	Metal					Slag			
	[Al] Total (ppm)	[Ca] Total (ppm)	[Zr] Total (ppm)	[O] Total (ppm)	[S] Total (ppm)	(Al) (Pct)	(Ca) (Pct)	(Zr) (Pct)	(S) (Pct)
Al ₂ O ₃ Crucible									
1	12100	7.3	4.3	5.52	25.0	22.68	30.28	11.20	0.0830
2	5490	3.9	3.4	1.65	42.0	22.65	30.25	11.20	0.0832
3	2830	3.1	2.6	1.28	92.0	22.60	30.19	11.02	0.0958
4	1370	2.3	1.8	1.41	123	22.68	30.17	11.04	0.0942
5	390	0.80	1.3	2.52	303	22.64	30.23	11.09	0.0994
6	79.7	0.60	0.90	6.70	850	22.65	30.28	11.00	0.0993
7	26.9	0.40	1.8	13.7	1250	22.71	30.27	11.03	0.0737
ZrO ₂ Crucible									
8	157	6.8	4.5	4.32	529	21.67	33.40	9.13	0.0862
9	42.6	2.8	2.6	10.0	1740	21.65	33.44	9.08	0.119
10	200	4.5	3.5	3.72	2630	21.63	33.52	9.09	0.502
11	124	3.3	4.1	5.02	2570	21.66	33.42	9.08	0.358
12	84.9	4.4	4.9	6.40	1720	21.61	33.55	9.09	0.186
13	1010	8.5	9.0	1.56	2450	21.60	33.90	9.01	2.03

Fig. 2. X-ray diffraction patterns for the Al₂O₃ crucible slag sample in the CaO–Al₂O₃–ZrO₂ system equilibrated at 1873 K. The data agree with the X-ray spectrums of the compounds.

Fig. 3. X-ray diffraction patterns for the ZrO₂ crucible slag sample in the CaO–Al₂O₃–ZrO₂ system equilibrated at 1873 K. The data agree with the X-ray spectrum of the compounds.

3. Results

The slag and metal phase compositions obtained in the experiments are given in Table 1. Figures 2 and 3 show X-

ray diffraction results for saturated slags equilibrated with an Al_2O_3 or ZrO_2 crucible at 1873 K, and for comparison, the standard spectra (JCPDS) for the $\text{CaO-Al}_2\text{O}_3$ and CaO-ZrO_2 binary systems.

4. Discussion

4.1. Equilibrium between Slag and Crucibles

X-ray diffraction patterns for the saturated slag in the Al_2O_3 crucible are shown in Fig. 2. The data corresponds exactly to $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ in the $\text{CaO-Al}_2\text{O}_3$ system compositions. The result is also consistent with the component in the CaO-ZrO_2 system, which is Css (cubic solid solution) at 1873 K, among the CaO-ZrO_2 system compositions. Thus, the Al_2O_3 crucible saturated slag is equilibrated with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and Css.

Figure 3 shows the X-ray diffraction results for the saturated slag in the ZrO_2 crucible. The data corresponds to $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ in the case of the $\text{CaO-Al}_2\text{O}_3$ system. The result is also consistent with the component in the CaO-ZrO_2 system, which are Css (cubic solid solution) and $\text{CaO} \cdot \text{ZrO}_2$ at 1873 K, among the CaO-ZrO_2 system compositions. But, the spectrum of $\text{CaO-Al}_2\text{O}_3$ compositions is not higher than that of the saturated slag in the Al_2O_3 crucible, and the spectrum of the CaO-ZrO_2 system is found to be higher than that of the CaO-ZrO_2 system in the case of the saturated slag in the Al_2O_3 crucible. Considering the possible formation of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ during cooling after experiments, the saturated slag in the ZrO_2 crucible may form equilibrium phases of $\text{CaO} \cdot \text{ZrO}_2$ and Css in the CaO-ZrO_2 system compositions as is reported by Murakami *et al.*¹²⁾

4.2. Activity of Aluminum Oxide in Molten Slag

Total oxygen content, $[\text{mass}\% \text{O}]_{\text{total}}$, is plotted against total Al content, $[\text{mass}\% \text{Al}]_{\text{total}}$, on a log-log plot in Fig. 4, in which the open circles and squares represent data pertaining to the Al_2O_3 and ZrO_2 crucibles, respectively. On the basis of these results, the activity of Al_2O_3 in slag equilibrium with molten iron was calculated to be 0.393 and 0.385 in the Al_2O_3 and ZrO_2 crucibles, respectively. For this calculation, $\Delta G^\circ (= -1\,202\,000 + 386.3T (\text{J/mol}))$ of the reaction $2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 (\text{s})$ ²²⁻²⁴⁾ and interaction coefficients²⁴⁾ were employed. The solid and dashed lines in Fig. 4 were calculated from the Al_2O_3 activity in the slags in Al_2O_3 and ZrO_2 crucibles, respectively, and were in good agreement with experimental data. In the iron samples, a few Al_2O_3 inclusions were observed, which appear to be secondary inclusions produced during quenching.

Figure 5 shows the relationship between CaO and Al_2O_3 activity in the $\text{CaO-Al}_2\text{O}_3$ system, as reported by Tanabe *et al.*,^{5,23)} who defined the activity of Al_2O_3 in $\text{CaO-Al}_2\text{O}_3$ as $a_{\text{Al}_2\text{O}_3} (\text{Al}_2\text{O}_3 \text{ sat.}) = 0.412$. They reported value is comparable to the activity of Al_2O_3 in the saturated slag in the Al_2O_3 crucible, and the activity of $\text{CaO} \cdot \text{Al}_2\text{O}_3$ is not variously to one.

$a_{\text{Al}_2\text{O}_3}$ in $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ coexistence in $\text{CaO-Al}_2\text{O}_3$ system is 0.412 from Fig. 5. The Al_2O_3 crucible saturated $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag is equilibrated with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and Css. Thus, as for $a_{\text{Al}_2\text{O}_3}$, the Al_2O_3 crucible saturated $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag became smaller than the Al_2O_3 crucible saturated $\text{CaO-Al}_2\text{O}_3$ slag.

Fig. 4. The total oxygen content of molten iron versus the total Al content in equilibrium with the molten slag in an Al_2O_3 or ZrO_2 crucible at 1873 K.

Fig. 5. Activities of Al_2O_3 and CaO in the $\text{CaO-Al}_2\text{O}_3$ system at 1873 K.²⁵⁾

Alternatively, the activity of Al_2O_3 of the saturated slag in equilibrium with the ZrO_2 crucible in the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ system is compared to the activity of Al_2O_3 of the saturated slag in equilibrium with the Al_2O_3 crucible, which reveals that the former is lower than the latter. The Al_2O_3 - and ZrO_2 -crucible saturated slags become almost parallel with the $\text{CaO-Al}_2\text{O}_3$ axis in the phase diagram of the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ system because ZrO_2 content does not change much. Thus, it is possible to estimate the activity of Al_2O_3 in the ZrO_2 -crucible saturated slag. The tendency is that the activity of Al_2O_3 is lower at higher CaO contents between $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and CaO. Therefore, the activity Al_2O_3 of the ZrO_2 -crucible saturated slag will be lower than that of the Al_2O_3 -crucible saturated slag. It typically corresponds to the activity relations as shown in the phase diagram of the $\text{CaO-Al}_2\text{O}_3$ system.

4.3. Sulfide Capacity of Slag

Figure 6 plots the sulfur distribution ratios, L_S , as a function of total Al content of molten iron on a full logarithmic

Fig. 6. Sulfur distribution ratios between the molten iron and CaO–Al₂O₃–ZrO₂ slag in an Al₂O₃ or ZrO₂ crucible at 1873 K versus total Al content of molten iron.

Fig. 7. Sulfide capacity of the CaO–Al₂O₃–ZrO₂ slag in an Al₂O₃ or ZrO₂ crucible at 1873 K against the total Al content in molten iron.

plot. The dotted line in the figure represents experimental results obtained by Tanabe and Suito²⁰⁾ using a CaO–Al₂O₃ molten slag with an Al₂O₃ activity of 0.33.

The ionic slag–metal reaction with respect to the sulfur partition can be expressed by:

The logarithm of L_s can be expressed by Eq. (2) using the equilibrium constant K_1 for the reaction in Eq. (1).

$$\log L_s = 2/3 \log [\text{mass}\% \text{Al}] - 1/3 \log K_1 + \log \{a_{\text{O}^{2-}} / (f_{\text{S}^{2-}} \cdot a_{\text{Al}_2\text{O}_3}^{1/3})\} + \log (f_{\text{Al}}^{2/3} \cdot f_{\text{S}}) \dots \dots \dots (2)$$

where sulfur distribution ratio, L_s ($= (\text{mass}\% \text{S}^{2-}) / [\text{mass}\% \text{S}]$), is proportional to $[\text{mass}\% \text{Al}]$ to the power of 2/3. The present results shown in Fig. 6 satisfy this relationship. This suggests that the oxygen potentials are controlled by the equilibrium $2\text{Al} + 3/2 \text{O}_2(\text{g}) = \text{Al}_2\text{O}_3(\text{s})$. The sulfur distribution ratio in the ZrO₂ crucible is slightly higher than that in the Al₂O₃ crucible, corresponding to a slightly smaller Al₂O₃ activity. The results by Tanabe *et al.*²⁰⁾ in Fig. 6 is not consistent with the present results, although Tanabe²⁵⁾ measured the Al₂O₃ activity in a CaO–Al₂O₃ molten slag to be 0.412.

Sulfide capacity, $C_{\text{S}^{2-}}$, defined by $(\text{mass}\% \text{S}) \cdot P_{\text{O}_2}^{1/2} / P_{\text{S}_2}^{1/2}$ is expressible as:

$$\log C_{\text{S}^{2-}} = \log L_s + \log (a_{\text{Al}_2\text{O}_3}^{1/3} / [\text{mass}\% \text{Al}]^{2/3}) - \log (K_{\text{Al}_2\text{O}_3}^{1/3} / K_{\text{S}}) - \log (f_{\text{Al}}^{2/3} \cdot f_{\text{S}}) \dots \dots \dots (3)$$

where $K_{\text{Al}_2\text{O}_3}$ is the equilibrium constant for the reaction $2\text{Al} + 3/2 \text{O}_2(\text{g}) = \text{Al}_2\text{O}_3(\text{s})$, which is calculated from ΔG° ($= -1\,202\,000 + 386.3T$ (J/mol)) ($= -1\,554\,000 + 337.6T$ (J/mol))^{23,26)} and K_{S} ($= 10^{6.535/T - 0.964}$) for the dissolution of sulfur²⁴⁾ via $1/2 \text{S}_2(\text{g}) = \text{S}$. The calculated results are shown in Fig. 7. Sulfide capacity of the slag was 8.77×10^{-5} and 9.10×10^{-5} in the case of the Al₂O₃ and ZrO₂ crucibles, respectively. In the relationship between sulfide capacity and composition of both slag, sulfide capacity seems to be high a little, because it is abounding, when the CaO concentration is the ZrO₂ crucible, 5%.

5. Summary

Aluminum–oxygen equilibrium and sulfur partitions between molten iron and a CaO–Al₂O₃–ZrO₂ slag in Al₂O₃ and CaO-stabilized ZrO₂ crucibles at 1873 K has been studied. The following results were obtained:

- (1) CaO–Al₂O₃–ZrO₂ molten slag equilibrated with CaO₂₅·2Al₂O₃ in the Al₂O₃ crucible and with CaO·ZrO₂ in the ZrO₂ crucible. The relations coincided with the phase diagram of CaO–Al₂O₃–ZrO₂.
- (2) From the concentrations of aluminum and oxygen dissolved in molten iron, the activity of Al₂O₃ in the slag was determined to be 0.393 and 0.385 in the case of the Al₂O₃ and ZrO₂ crucibles, respectively.
- (3) The sulfur content of molten iron in the ZrO₂ crucible was slightly lower a little than that in the Al₂O₃ crucible and increased with aluminum content.
- (4) Sulfur distribution ratio between the molten iron and CaO–Al₂O₃–ZrO₂ slag was found to be linearly proportional to the aluminum content in molten iron to the power of 2/3.
- (5) The sulfide capacity of the slag is 8.77×10^{-5} and 9.10×10^{-5} in the Al₂O₃ and ZrO₂ crucibles, respectively.

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