

Sulfur Partitions of CaO-Al₂O₃-ZrO₂ Flux in Equilibrium with Liquid Iron

Jun Tanabe and Kazuhiro Nagata*

Assoc. Prof., Dep. Mech. Engin. Nippon Inst. Techn., Gakuendai, Miyashiro-cho, Minami-saitama-gun, Saitama, 345-0826, Japan NIT, Saitama, Japan

* Prof., Dep. Chemi. & Mater. Sci., Tokyo Inst. Techn., Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

Sulfur distribution ratio between liquid Iron and of CaO-Al₂O₃-ZrO₂ flux in equilibrium at 1873K has been studied using Al₂O₃ or CaO-stabilized ZrO₂ crucible. The flux and liquid iron equilibrated with CaO·2Al₂O₃ in Al₂O₃ crucible and with CaO·ZrO₂ in ZrO₂ crucible. These equilibrium relations are coincided with the phase diagram of CaO-Al₂O₃-ZrO₂. From the concentrations of aluminum and oxygen dissolved in liquid iron, the activity of Al₂O₃ in the flux was determined to be 0.397 in Al₂O₃ crucible and 0.389 in ZrO₂ crucible. The activity was examined in comparison with the data in CaO-Al₂O₃ and CaO-ZrO₂ systems. The sulfur content in liquid iron in ZrO₂ crucible was higher than that in Al₂O₃ crucible and increased with an increasing of aluminum content. The sulfide capacity of fluxes was determined to be 4.43×10^{-6} and 5.9243×10^{-6} in Al₂O₃ and ZrO₂ crucibles, respectively.

1.Introduction

At present, crude natural gas including hydrogen sulfide is transported by sour proof steel pipe. The pipe makes cracking assisted mainly by hydrogen and hydrogen sulfide^[1]. Therefore, the steel with ultra low concentration of sulfur and oxygen is required.

Nagata et al.^[2] found that Al, Ca and Zr can control the composition of inclusions in sour – proof pipe steel. In this case, the primary crystallization of MnS during solidification can be also suppressed.^[3-4] The formation of inclusions can be thermodynamically determined by the activities of Ca, Al, Zr and Mn as well as oxygen and sulfur potentials and temperature in molten steel. Then, knowledge of thermodynamic the properties such as the activities and phase diagram for the CaO-Al₂O₃-ZrO₂ system essentially required at the temperature of molten steel. The activities of oxides in CaO-Al₂O₃-ZrO₂ system were measured only for the CaO-Al₂O₃^[5] and CaO-ZrO₂ system^[6].

The phase diagrams of the CaO-Al₂O₃-ZrO₂ 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]. Nurase et al.^[13] determined the CaO-Al₂O₃ system. The Al₂O₃-ZrO₂ system was summarized in Slag Atlas^[14]. Stubican^[15] and Tanabe Nagata^[6] determined the CaO-ZrO₂ system.

□□ In the present study, the phase equilibration between molten iron, CaO-Al₂O₃-ZrO₂ molten slag and Al₂O₃ crucible or ZrO₂+15%CaO) crucible was cleared. Then, aluminum and oxygen contents molten iron and sulfur partition molten iron and slag in equilibrium at 1873K were measured. Using the activity of aluminum oxide and sulfide capacity of the molten slag obtained.

2.Experimental

2.1. Preparing of the flux sample of the CaO-Al₂O₃-ZrO₂ system

CaO-Al₂O₃-ZrO₂ slag samples were melted from the mixture of CaCO₃, Al₂O₃ and ZrO₂ powders in high purity. The samples were equilibrated in a ZrO₂ (ZrO₂+15%CaO) crucible or an Al₂O₃ crucible for 1.8ks at 1923K and for 10.8ks at 1873K.

2.2. Equilibration between molten iron and slag

□□ Detailed descriptions of the experimental procedure are given in the previous articles.^[16-20] 20g of electrolytic iron (99.9%) with approximately 300~1000 mass-ppm oxygen and 6g of CaO-Al₂O₃-ZrO₂ slag containing 0.001~0.5g of CaS were melted in an Al₂O₃ or ZrO₂ (ZrO₂+15%CaO) crucible under deoxidized Ar atmosphere at 1873K. Fe-0.2~10% Al alloy was added to the molten iron, and the molten iron and slag were stirred 3 times by Al₂O₃ rod for 120s every 1.8ks, and they were kept for 3.6ks in order to float inclusions. After then, the crucible with molten iron and slag was cooled rapidly in the He gas, and quenched into water.

2.3. Chemical analysis

Sulfur in metal and slag was analyzed within 8 ± 2 ppm by combustion-infrared absorptiometry. The total oxygen content of the metal determined within 0.6 ± 0.2 ppm by inert-gas fusion combustion-infrared absorptiometry.^[21] The total aluminum content in the metal was determined by inductively coupled plasma (ICP). The contents of Al, Ca and Zr in the slag were determined by ICP. For ICP analysis, the slag samples saturated with Al₂O₃ and ZrO₂ were melted alkali fusion method using Na₂CO₃ and the mixture of Na₂CO₃ and □Na₂O·2B₂O₃, respectively, and dissolved into HCl solution (1:1). The metal samples were dissolved into the HCl solution.

3. Results and discussion

3.1. Equilibrium relation between slag and crucibles

The composition of slag equilibrated with molten iron including Al in an Al_2O_3 crucible was 36.25CaO-37.50 Al_2O_3 -26.75 ZrO_2 (mass%), which was in equilibrium with $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ produced inside crucible. The composition of slag in a ZrO_2 crucible was 41.19CaO-35.10 Al_2O_3 -23.71 ZrO_2 (mass%), which was in equilibrium with $\text{CaO} \cdot \text{ZrO}_2$. These equilibrium relations are coincided with the phase diagram of $\text{CaO}-\text{Al}_2\text{O}_3-\text{ZrO}_2$ determined by Murakami et al. [12], as shown in Figure 1.

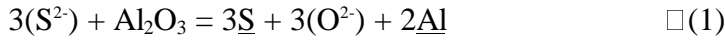
3.2. Activity of aluminum oxide in molten slag

□ The relation between total oxygen content, [mass% O]_{total}, and total Al, [mass% Al]_{total}, are plotted in logarithmic form in Fig.2, in which open circles and squares are data in Al_2O_3 and ZrO_2 crucible, respectively. From the results, the activity of Al_2O_3 in slag equilibrium with molten iron was determined to be 0.397 and 0.389 in Al_2O_3 and ZrO_2 crucible, respectively. For this calculation, ΔG° of the reaction of $2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 (\text{s})$ [22-23] and the interaction coefficients [24] were employed. The solid and dashed lines in Fig.2 are calculated from the activity of Al_2O_3 in slag in Al_2O_3 and ZrO_2 crucibles, respectively and in good agreement with experimental data. In the iron samples, a few Al_2O_3 inclusions were observed, which seem to be secondary inclusions produced during quenching.

3.3. Sulfide capacity of slag

Sulfur distribution ratios, L_S , was as a function of total Al content in molten iron in logarithmic form, as shown in Fig.3. The dotted line in the figure is the experimental result using $\text{CaO}-\text{Al}_2\text{O}_3$ molten slag with Al_2O_3 activity of 0.33 by Tanabe and Suito [20].

The ionic slag-metal reaction with respect to sulfur partition is expressed by Eq. (1).



The logarithm of L_S is expressed by Eq. (2), using the equilibrium constant, K_1 , for the reaction Eq. (1).

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

where L_S is proportional to [mass% Al] to the 2/3 power. The present results in Fig.3 satisfy this relationship. This suggests that the oxygen potentials are controlled by the equilibrium of $2\text{Al} + 3/2\text{O}_2 = \text{Al}_2\text{O}_3 (\text{s})$. The sulfur distribution ratio in ZrO_2 crucible is a little higher than that Al_2O_3 crucible, corresponding to a little smaller Al_2O_3 activity. The result by Tanabe et al. [20] in Fig.3 is not consistent with the present results. Tanabe [24] measured Al_2O_3 activity in $\text{CaO}-\text{Al}_2\text{O}_3$ molten slag to be 0.412.

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

$$\log C_{\text{S}^{2-}} = \log L_S + \log (a_{\text{Al}_2\text{O}_3}^{1/3} / [\text{mass\% Al}]^{2/3}) - \log (K_3^{1/3} / K_S) - \log (f_{\text{Al}}^{2/3} f_{\text{S}}) \square (3)$$

where K_3 is the equilibrium constant of reaction, $2\text{Al} + 3/2\text{O}_2 = \text{Al}_2\text{O}_3 (\text{s})$, which is calculated from ΔG° [23], [26] and K_3 for the dissolution of sulfur [24], $1/2\text{S}_2 = \text{S}$. The calculated results are shown in Fig.4. Sulfide capacity of slags 4.43×10^{-6} and 5.9243×10^{-6} in Al_2O_3 and ZrO_2 crucible, respectively.

4. Summary

Aluminum-oxygen equilibrium and sulfur partitions between molten iron and $\text{CaO}-\text{Al}_2\text{O}_3 - \text{ZrO}_2$ slag in Al_2O_3 and CaO -stabilized ZrO_2 crucible at 1873K has been studied. The following results were obtained;

- (1) $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ molten slag was equilibrated with $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ in Al_2O_3 crucible and with $\text{CaO}\cdot \text{ZrO}_2$ in ZrO_2 crucible. The relations are coincided with the phase diagram of $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ ^[12].
- (2) From the concentrations of aluminum and oxygen dissolved in molten iron, the activity of Al_2O_3 in the slag was determined to be 0.397 in Al_2O_3 crucible and 0.389 in ZrO_2 crucible.
- (3) The sulfur content in molten iron in ZrO_2 crucible was a little higher than that in Al_2O_3 crucible and increased with increasing aluminum content.
- (4) Sulfur distribution ratio between molten iron and $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag was found to linearly related to aluminum contents in molten iron to the power of $2/3$.
- (5) The sulfide capacity of slag is 4.43×10^{-6} and 5.9243×10^{-6} in Al_2O_3 and ZrO_2 crucibles, respectively.

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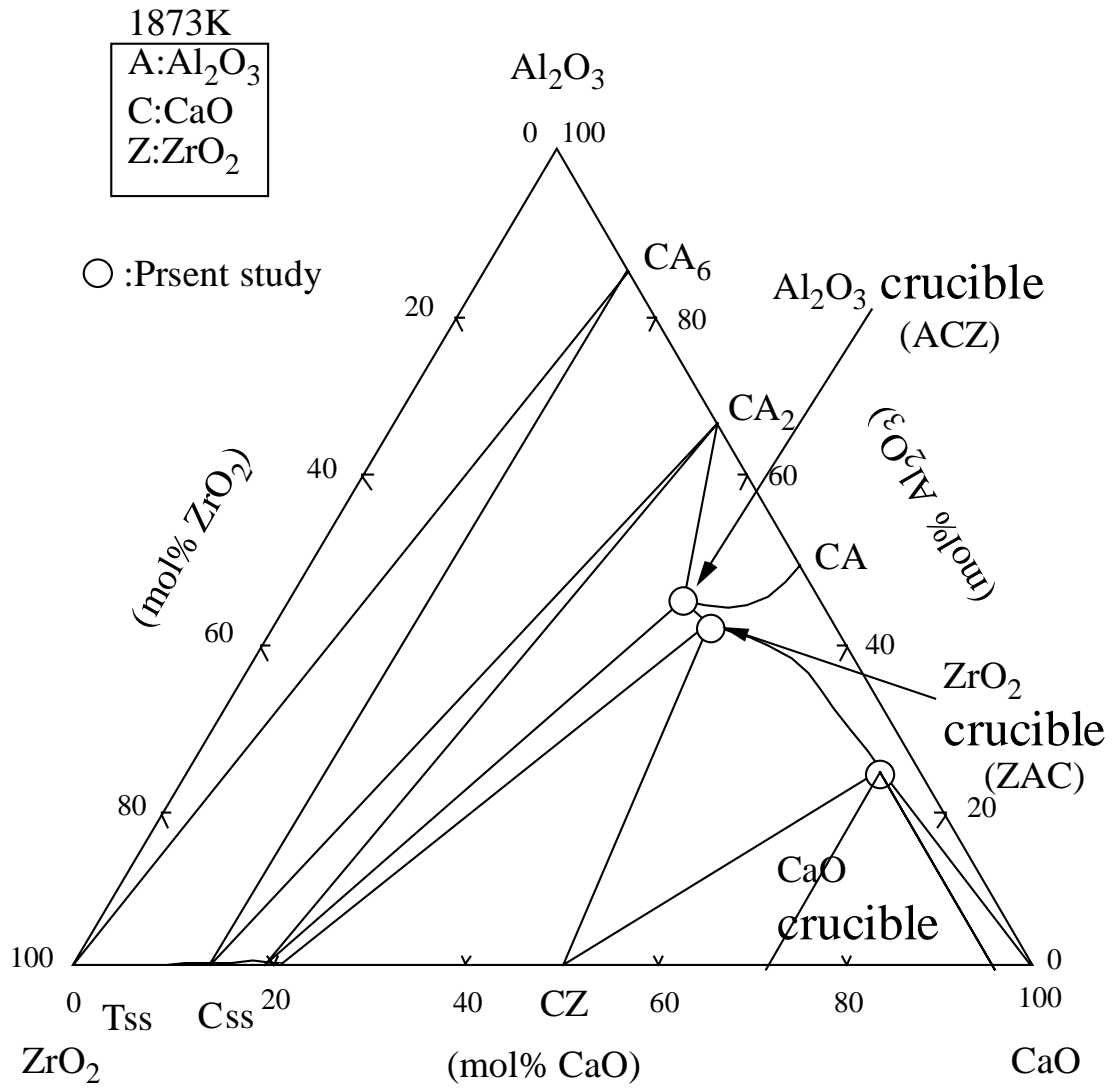


Fig.1 Phase diagram of the $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ molten slag in equilibrium with Al_2O_3 (ACZ) or ZrO_2 (ZAC) crucible at 1873K.

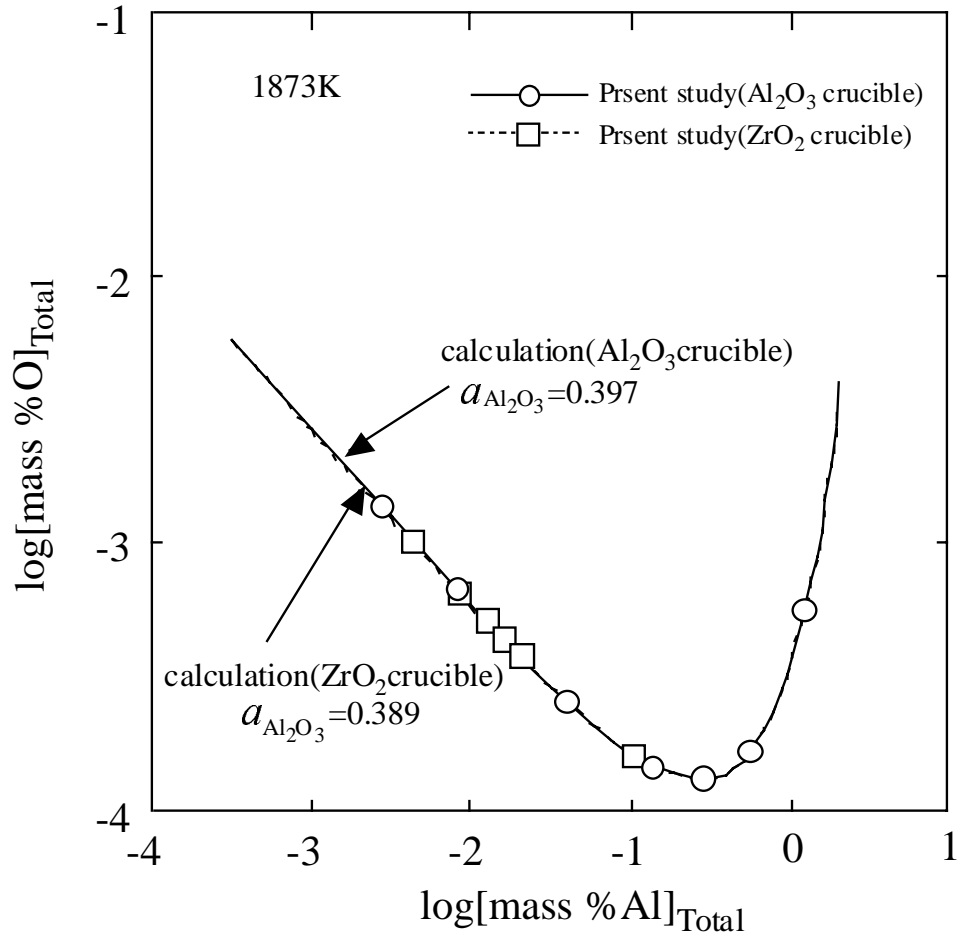


Fig.2 The content of total oxygen in molten iron against that of Al in equilibrium with molten slag in Al_2O_3 or ZrO_2 crucible at 1873K.

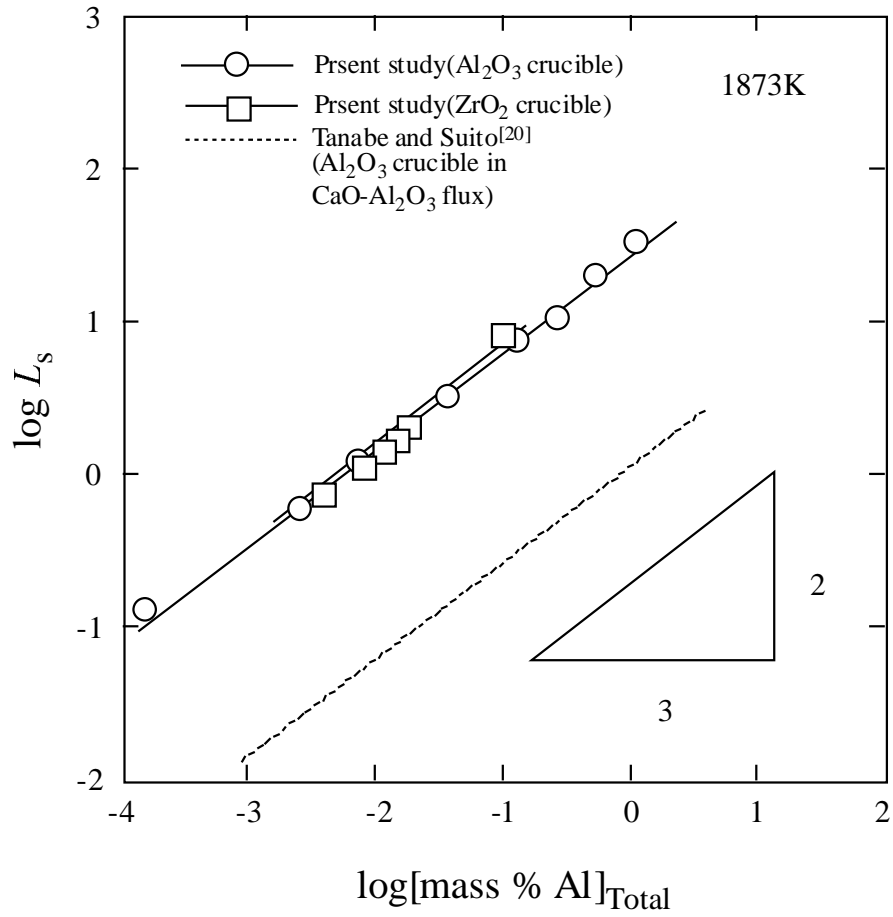


Fig.3 Sulfur distribution ratios between molten iron and $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag in Al_2O_3 or ZrO_2 crucible at 1873K against total Al content in molten iron.

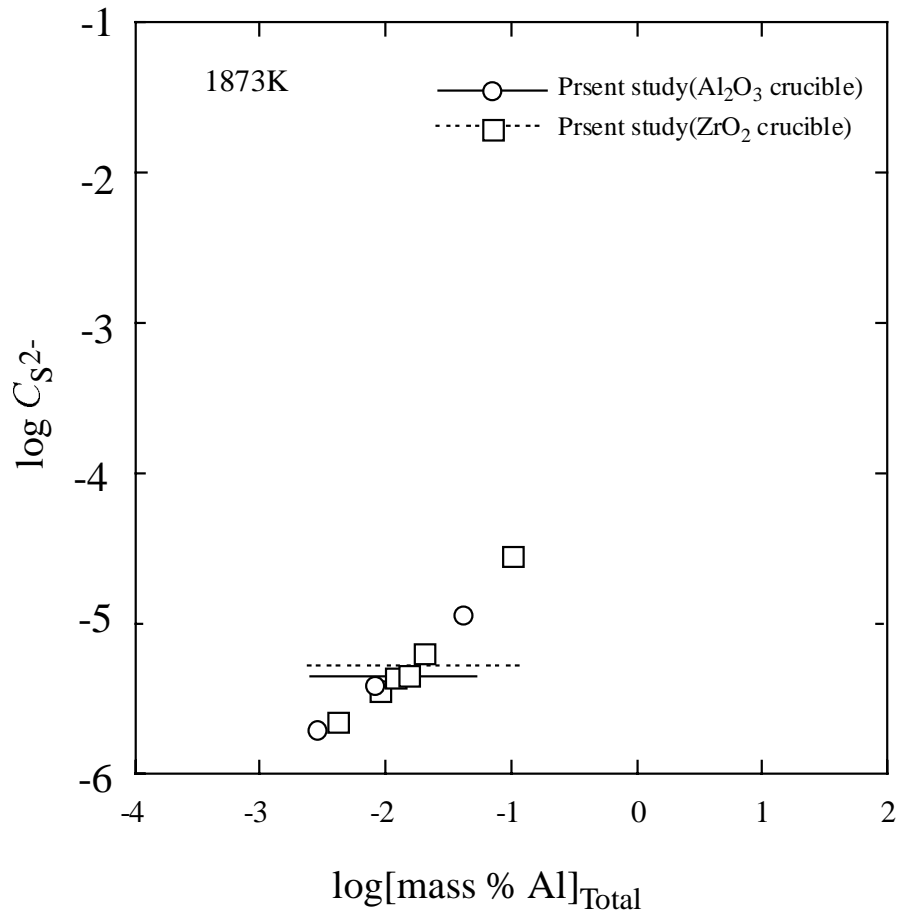


Fig.4 Sulfide capacity $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ slag in Al_2O_3 or ZrO_2 crucible at 1873K against total Al content in molten iron.