Solubility of Sulfur in the Solid Oxide of the Calcium-Aluminate System

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The formation of CaS around CaO–Al₂O₃ causes pitting corrosion in ferritic stainless steel. To prevent the precipitation of CaS, the solubility of CaS in both the liquid and solid CaO–Al₂O₃ system has to be clarified. In this study, the sulfur content in the CaS-saturated solid CaO–Al₂O₃ system was measured. The results showed that, sulfur was soluble only in 12CaO·7Al₂O₃ at approximately 1.2 mass% while the sulfur content in the other solid compounds was very low. In addition, the sulfur content of 12CaO·7Al₂O₃ was independent of the heating temperature and was higher than that in the liquid oxide of the same composition. Therefore, 12CaO·7Al₂O₃ can dissolve sulfur in the solid state, preventing CaS formation.

KEY WORDS: CaO–Al₂O₃; CaS formation; solid compound; solubility of sulfur.

1. Introduction

The CaO–Al₂O₃ system inclusion is generally formed by Ca addition or slag entrapment in Al-killed steel. Because of its low melting point, this type of inclusion is generally less harmful than Al₂O₃. However, when CaS is precipitated on this inclusion, it can cause pitting corrosion in ferritic stainless steel.

The formation of CaS around CaO–Al₂O₃ oxides was observed in Ca added steel. Karino *et al.*¹⁾ analyzed the relationship between oxide composition and Ca content in the precipitated sulfide and concluded that CaS precipitated after the formation of the oxide. Takenouchi *et al.*²⁾ measured the solubility of CaS in liquid CaO–Al₂O₃ at various temperatures and determined that the formation mechanism of CaS involved the precipitation from the liquid oxide by the decreased solubility of CaS at lower temperature.

On the other hand, in ferritic stainless steel, in some cases, CaS was observed without Ca addition. Kinoshita *et al.*³⁾ and Yano *et al.*⁴⁾ found that the origin of pitting corrosion was the precipitation of CaS and with increasing [Al] content, the degree of corrosion deteriorated despite the improvement of cleanliness. In addition, the authors showed that CaS was formed by the reaction of 2[Al]+3[S]+3(CaO)=(Al₂O₃)+3CaS. Kitamura *et al.*⁵⁾ observed CaS in ultra-low sulfur cold-rolled steel, where CaS was never observed in the molten steel or slab. The

authors determined that CaS was formed after heating the slab, due to the diffusion of sulfur in the solid steel toward the CaO–Al₂O₃ inclusion.

Many studies have focused on the solubility of CaS in liquid CaO–Al₂O₃ system. The liquid composition saturated with CaS from 1 698 K to 1 899 K have been clarified,^{2,6–12)} and the thermodynamic modeling method has been established.¹²⁾ The sulphide capacity of molten CaO–Al₂O₃ oxide has also been well measured.^{6–9,13–17)} However, the solubility of sulfur in the solid oxide of CaO–Al₂O₃ system remains unknown. It is well known that the CaO–Al₂O₃ binary system forms various stoichiometric compounds depending on the composition in solid state. To clarify the mechanism of CaS formation, the solubility of CaS in the solid oxide of the CaO–Al₂O₃ system is important. In this study, the solubility of sulfur in various compounds of the CaO–Al₂O₃ system was determined in the temperature range 1 173 to 1 573 K.

2. Experimental

First, CaO–Al₂O₃–CaS samples with various compositions were prepared. Reagent-grade CaCO₃, Al₂O₃, and CaS were used, and CaO was produced by calcining CaCO₃ at 1 423 K for 24 h or longer. The reagents were mixed to the target composition and loaded in a vertical furnace using an Al₂O₃ or Pt crucible. After melting at 1 723 K for 30 min under an Ar atmosphere, the crucible was removed from the furnace and quenched using He gas blowing. Because CaS was partially evaporated during melting, the sulfur content of the sample was analyzed using the combustion method

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Table 1. The composition of each sample mass%.

	CaO	Al ₂ O ₃	CaS	Crucible
HS-1	46.90	46.90	6.21	Al ₂ O ₃
HS-2	42.54	51.99	5.47	Pt
HS-3	52.35	42.83	4.82	Pt
LS-1	49.03	49.03	1.94	Al ₂ O ₃
LS-2	50.00	50.00	0.00	Pt

Fig. 1. Heating profile of the samples. (Online version in color.)

and the CaS content in the sample was calculated. The contents of CaO and Al₂O₃ were calculated assuming that their mass ratio was equal to the mixing ratio. **Table 1** lists the sample compositions.

The samples were heated at 1 173–1 573 K and monitored by confocal scanning laser microscopy (CSLM). The prepared samples were crashed into a powder with particles smaller than 50 μm , which was then used to form a 1 mm thick tablet approximately 6 mm in diameter. The formed tablet was inserted into the CSLM using a Pt crucible and heated under high purity Ar gas which passed through the glass tube with Mg power to eliminate residual oxygen.

The sample was heated at 473 K initially and kept for 2 min to eliminate moisture and subsequently heated to 1 573 K at rate of 100 K/min, followed by heating to 1 823 K at 30 K/min. The melting of the sample was identified by observation of its surface and when melting was detected, the sample was cooled to the holding temperature immediately and maintained for 10 min or 1 h. In some cases, the sample was quenched after melting. The cooling rate was approximately 100–150 K/s and the heating profile is shown in **Fig. 1**. After heating, the samples were quenched and their cross sections were observed by electron probe micro analyzer (EPMA).

3. Results

Typical mineralogical structures after heating for 1 h at 1 473 K of samples HS-2 and 3 are shown in **Figs. 2** and **3**, respectively. In **Fig. 2**, the 12CaO·7Al₂O₃, CaO·Al₂O₃, CaO·2Al₂O₃, and CaS phases are shown. In **Fig. 3**, the 12CaO·7Al₂O₃, 3CaO·Al₂O₃, and CaS phases were observed. The observed phases corresponded well with the equilibrium phase at the respective temperatures and the observation of CaS indicated that the sample compositions were saturated with CaS. The sulfur content of 12CaO·7Al₂O₃ was approximately 1.3 mass%, significantly higher than those of CaO·Al₂O₃ and 3CaO·Al₂O₃. **Figure 4**

Phase	Ca	Al	O	S
C ₁₂ A ₇	32.7	24.4	33.0	1.2
CA	24.3	30.8	36.0	0.0
CA ₂	13.9	37.7	37.2	0.1
CaS	51.7	1.0	17.3	26.0

Fig. 2. Typical mineralogical structures of sample HS-2 after heating for 1 h at 1 473 K.

Phase	Ca	Al	O	S
C ₁₂ A ₇	34.1	25.3	36.6	1.3
C ₃ A	43.9	19.0	36.3	0.1
CaS	52.2	0.6	2.2	27.3

Fig. 3. Typical mineralogical structures of sample HS-3 after heating for 1 h at 1 473 K.

shows the mineralogical structures after heating for 1 h at 1 473 K for sample LS-1. In this case, the 12CaO·7Al₂O₃ and CaO·Al₂O₃ phases were observed but CaS was absent and the sulfur content of 12CaO·7Al₂O₃ was approximately one-half that observed in **Figs. 2** and **3**. In this sample, as the precipitation of CaS was not observed, it is likely that the oxide was not saturated with CaS.

In **Figs. 5** and **6**, the influence of the holding temperature on the sulfur content in each phase is shown for samples rich in CaO (HS-3) and Al₂O₃ (HS-1 and 2), respectively. It is clear that the sulfur content of 12CaO·7Al₂O₃ was significantly higher than those observed in the other calcium-aluminate phases regardless of holding temperature. **Figure 7** shows the influence of holding time at 1 473 K

Phase	Ca	Al	O	S
C ₁₂ A ₇	32.8	24.9	34.8	0.6
CA	24.2	31.2	37.3	0.0
CA ₂	14.8	38.2	39.0	0.0

Fig. 4. Typical mineralogical structures of sample LS-1 after heating for 1 h at 1 473 K.

Fig. 5. Influence of the holding temperature on the sulfur content in each phase for the samples rich in CaO (HS-3).

Fig. 6. Influence of the holding temperature on the sulfur content in each phase for the samples rich in containing Al₂O₃ (HS-1 and 2).

on the sulfur content in each phase. The sulfur content in the 12CaO·7Al₂O₃ phase gradually increased with increasing holding time, but even though the oxide quenched from 1 823 K, the sulfur content was approximately 0.9 mass%.

Fig. 7. Influence of the holding time at 1 473 K on the sulfur content in each phase.

Fig. 8. Influence of CaS content in the sample on the sulfur content in 12CaO·7Al₂O₃.

As shown in Fig. 8, the sulfur content in the 12CaO·7Al₂O₃ phase was strongly influenced by the CaS content in the sample, but it saturated when the CaS content was increased to 4 mass% or more.

4. Discussion

The solubility of sulfur in liquid CaO–Al₂O₃ oxide has been previously reported. Hino *et al.* measured the sulfide capacity (C_s ; Eq. (1)) of the system at various temperatures^{10,11)} and compared their results to those reported by other researchers. If the ratio of the partial pressure of O₂ and S₂ is fixed, the sulfur content in the oxide can be calculated using Eqs. (2)¹⁸⁾ and (3).¹⁸⁾ For the Al-killed steel, the activity of oxygen can be calculated using Eq. (4).¹⁸⁾

$$C_s = (\text{mass}\%S) \times (P_{O_2} / P_{S_2})^{1/2} \dots\dots\dots (1)$$

$$\frac{1}{2} O_2 (g) = [O] \quad \log K_O = \frac{6120}{T} + 0.18 \dots\dots\dots (2)$$

$$\frac{1}{2} S_2 (g) = [S] \quad \log K_S = \frac{6540}{T} - 0.96 \dots\dots\dots (3)$$

$$2[Al] + 3[O] = Al_2O_3 (s) \quad \log K_{Al} = \frac{64000}{T} - 20.57 \dots\dots\dots (4)$$

Assuming that the activity of aluminum is 0.05 or 0.025 and that of sulfur is 0.005 or 0.0025, the equilibrium sulfur

Fig. 9. Temperature dependence of the equilibrium sulfur content in the molten oxide.

content in the molten oxide was calculated and the results shown in Fig. 9. In this calculation, the sulfide capacity at 1 823, 1 873, and 1 923 K, the measured values were used and those at 1 723 and 1 773 K were estimated using the temperature dependence obtained from the Arrhenius equation. The activity of aluminum and sulfur in molten steel are 0.05 and 0.005 for case 1; 0.025 and 0.005 for case 2; and 0.05 and 0.0025 for case 3, respectively. Considering the normal grade of Al killed steel, the activity of Al was assumed as 0.0025 and 0.05. In the case to suppress the formation of CaS, desulfurization is generally conducted in the secondary refining. Therefore, the activity of sulfur was assumed as 0.005 and 0.0025. From Fig. 9, the sulfur content depends on the activities of aluminum and sulfur, but the observed sulfur content in the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase in the solid oxide is larger than that in the molten oxide of the sample with identical composition.

The $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase is known to be an electrically conductive oxide ceramic.^{19–21} Its crystal has a unique sub-nanoporous structure composed of 12 positively charged cages, including two free oxygen ions which maintain electrical neutrality. The free oxygen ions can be exchanged with an anion, X (*i.e.* fluorine or chlorine), according to the following reactions:

If the exchange reaction with sulfide is considered, the following equation can be written:

From the mass balance calculations, if all free oxygen sites are replaced by sulfur ions, the sulfur content would increase to 2.28 mass%. Therefore, the observed sulfur content in this study is reasonable.

To suppress the formation of CaS from the inclusion of

calcium-aluminate, the phase ratio of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ in the solid state is an important factor to consider. Because when the mass ratio of this oxide to solid steel is enough large, sulfur can be dissolved in this oxide and the formation of CaS can be suppressed.

5. Conclusions

The sulfur content in the CaS-saturated $\text{CaO}-\text{Al}_2\text{O}_3$ system was measured and the results can be summarized as follows:

(1) In the Al_2O_3 -rich oxide, $\text{CaO}\cdot \text{Al}_2\text{O}_3$, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, and CaS phases were observed, whereas the dominant phases in the CaO-rich oxide were $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3$, and CaS.

(2) Sulfur was dissolved only in $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ at approximately 1.2 mass% while the sulfur content in the other oxides was very low.

(3) The sulfur content in $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ was independent of the heating temperature and was higher than that in the liquid oxide of the same composition.

Based on the experimental results, it is clear that $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ can dissolve sulfur in the solid state, preventing CaS formation.

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REFERENCES

- 1) T. Kano and T. Hanyuda: *Denki-Seiko*, **75** (2004), 27 (in Japanese).
- 2) T. Takenouchi and K. Suzuki: *Tetsu-to-Hagane*, **63** (1977), 1653 (in Japanese).
- 3) N. Kinoshita, N. Ohashi and M. Takeda: *Trans. Iron Steel Inst. Jpn.*, **16** (1976), 251.
- 4) S. Yano, K. Nakanishi, H. Ooi, K. Fujimoto and S. Iwaoka: *Trans. Iron Steel Inst. Jpn.*, **16** (1976), 258.
- 5) S. Kitamura: Proc. 7th Int. Symp. on Molten Slags, Fluxes and Salts, The South African Institute of Mining and Metallurgy, Johannesburg, (2004), 769.
- 6) R. A. Sharma and F. D. Richardson: *J. Iron Steel Inst.*, **198** (1961), 386.
- 7) J. Cameron, T. B. Gibbons and J. Taylor: *J. Iron Steel Inst.*, **204** (1966), 1223.
- 8) B. Ozturk and E. T. Turkdogan: *Met. Sci.*, **18** (1984), 299.
- 9) G. J. W. Kor and F. D. Richardson: *J. Iron Steel Inst.*, **206** (1968), 700.
- 10) T. Fujisawa, S. Inoue, S. Takagi, Y. Wanibe and H. Sakao: *Tetsu-to-Hagane*, **71** (1985), 839 (in Japanese).
- 11) H. Fukaya and T. Miki: *ISIJ Int.*, **51** (2011), 2007.
- 12) R. Piao, H. Lee and Y. Kang: *Acta Mater.*, **61** (2013), 683.
- 13) C. J. B. Fincham and F. D. Richardson: *J. Iron Steel Inst.*, **178** (1954), 4.
- 14) P. T. Carter and T. G. Macfarlane: *J. Iron Steel Inst.*, **185** (1957), 54.
- 15) E. Schürmann, R. Bruder, K. Nürnberg and H. Richter: *Arch. Eisenhüttenwes.*, **50** (1979), 139.
- 16) M. Hino, S. Kitagawa and S. Ban-ya: *ISIJ Int.*, **33** (1993), 36.
- 17) S. Ban-ya, M. Hobo, T. Kaji, T. Itoh and M. Hino: *ISIJ Int.*, **44** (2004), 1810.
- 18) *Steelmaking Data Sourcebook*, ed. by The 19th Committee on Steelmaking, The Japan Society for the Promotion of the Science, Gordon and Breach, New York, (1988), 203.
- 19) R. W. Nurse, J. H. Welch and A. J. Majumdar: *Trans. J. Br. Ceram. Soc.*, **64** (1965), 409.
- 20) K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano and H. Hosono: *Nature*, **419** (2002), 462.
- 21) S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka and H. Hosono: *Science*, **301** (2003), 626.