Phase Equilibrium between CaO·Al2O3 Saturated Molten CaO–Al2O3–MnO and (Ca, Mn)S Solid Solution

Hiroshi FUKAYA1) and Takahiro MIKI2)
1) Formerly Graduate Student, Tohoku University, Japan. Now at The Japan Steel Works, 4, Chatsumachi, Muroran, 051-8505 Japan.  2) Department of Metallurgy, Graduate School of Engineering, Tohoku University, Aoba-yama 6-6-11-1024, Sendai, 980-8579 Japan.

(Received on April 28, 2011; accepted on July 19, 2011)

Refinement of austenite grains by generating intra granular ferrite (IGF) in austenite grains is one of the most effective methods for improving the toughness of the heat-affected zone (HAZ). It is known that MnS precipitated on fine oxides enhance formation of IGF in austenite grains. Flux composed of CaO–Al2O3 is often used in secondary refining and Ca–Mn–Al complex oxide may form, and it is important to clarify the mechanism of MnS precipitation on oxide inclusions. Therefore, molten CaO–MnO–Al2O3 oxide was equilibrated with (Ca, Mn)S solid solution in Al2O3 crucible in an electric resistance furnace at 1648, 1698 and 1748 K in the present work. Phase relation between CaO·Al2O3 saturated molten CaO–MnO–Al2O3 oxide and (Ca, Mn)S solid solution was clarified.

KEY WORDS: inclusion; oxysulfide; phase diagram; deoxidation; desulfurization.

1. Introduction

Non-metallic inclusions often cause defects in steel products and have been considered harmful to steel. On the other hand, small oxides smaller than few micrometers may act as precipitation site for sulfides such as MnS during solidification, and this MnS inclusion is considered useful in the point of view of structural refinement during welding. Refinement of austenite grains by generating plate like intra granular ferrite (IGF) in austenite grains is one of the most effective methods for improving the toughness of the heat-affected zone (HAZ). It is known that MnS precipitated on fine oxides enhance formation of IGF in austenite grains. It has been reported4–7) that MnS and TiN precipitated in fine oxide enhances formation of IGF in austenite grains.

It is important to clarify the mechanism of MnS precipitation on oxide inclusions. Wakoh et al.3) have investigated MnS precipitation behavior on various oxides and concluded that Mn–Si and Mn–Al complex oxides tend to act as precipitation site of MnS, and Mn based oxides with low melting point and high sulfide capacity are advantageous for MnS precipitation. Also, they have reported that MnS precipitates from oxide during cooling and the size of MnS inclusion increase due to diffusion of Mn and S from steel. Therefore, MnS solubility in Mn based oxide is important, and this information for MnO–SiO2–MnS system,5) MnO–SiO2–TiO2–MnS system6) and MnO–SiO2–Al2O3–MnS system8) have been reported by various researchers.

Flux composed of CaO–Al2O3 is often used in secondary refining and Mn–Al complex oxide may change into Ca–Mn–Al complex oxide by Ca treatment. Sulfide solubility in Ca–Al complex oxide has been reported by several researchers.7–9) However, information of sulfide solubility in Ca–Mn–Al complex oxide, important for inclusion control especially for Mn added steel, is unknown. Therefore, CaO·Al2O3 saturated molten CaO–MnO–Al2O3 oxide was contacted with (Ca, Mn)S solid solution to clarify the phase equilibrium between these phases in the present work.

2. Experimental

In the present work, molten CaO–MnO–Al2O3 oxide was contacted with (Ca, Mn)S solid solution in an Al2O3 crucible at 1648, 1698 and 1748 K by using electric resistance furnace. The equipment consists of high purity alumina reaction chamber (outer diameter: 80 mm, inner diameter: 70 mm, height: 1000 mm) and three heating zone type electric resistance furnace. The temperature was monitored by Pt–13 mass%Pt/Rh thermocouple located just below the crucible and controlled by the other three thermocouples which were inserted between heating element and the reaction tube.

Oxide samples were prepared as follows. Reagent CaCO3 was heated in Pt crucible at 1473 K in air to obtain CaO. Then it was mixed with equal amount of reagent Al2O3 and was melted in Pt crucible at 1773 K in air to recover 50 mass%CaO–50 mass%Al2O3 oxide. This oxide was ground by using agate mortar and was mixed with appropriate amount of reagent MnO powder. Mixed oxide powder with weighted amount of 1.2 g was pressed into tablet shape of 10 mmΦ. Also, 0.6 g of reagent CaS powder was pressed into same tablet shape. Both tablets were placed in an Al2O3 crucible (outer diameter: 15 mm, inner diameter: 12 mm, height: 100 mm) and 4 Al2O3 crucibles were placed in MgO outer crucible (outer diameter: 60 mm, inner diameter: 50 mm,
height: 100 mm) and placed in the hot zone of a vertical furnace. The samples were held for 6 hours at 1648, 1698 or 1748 K under dehydrated and deoxidized Ar stream of 100 ml/min. Holding time required for equilibrium was determined from preliminary experiments. The samples were quenched by withdrawing the crucible from the furnace and impinging helium gas on the sample surface.

The quenched samples were mounted and cut in order to

Table 1. Compositions of oxide and sulfide phases in equilibrium at 1648 K.

| No. | Temp. | Oxide phase (mass%) | Sulfide phase (mass%) |
|-----|-------|---------------------|----------------------|
|     |       | CaO Al2O3 MnO S     | Al Ca Mn             |
| 1   | 1648  | 45.3 50.5 1.4 2.6   | 0.5 79.6 19.9        |
| 2   | 1648  | 43.7 48.5 4.5 3.3   | 0.9 83.5 15.6        |
| 3   | 1648  | 38.1 45.5 13.0 3.4  | 0.4 82.3 17.3        |
| 4   | 1648  | 38.0 45.4 13.3 3.3  | 1.9 80.6 17.5        |
| 5   | 1648  | 37.4 45.4 14.0 3.2  | 1.1 82.9 16.0        |
| 6   | 1648  | 37.0 43.2 15.3 4.5  | 0.2 74.8 25.0        |
| 7   | 1648  | 36.7 43.4 15.6 4.3  | 0.9 71.7 27.4        |
| 8   | 1648  | 36.4 42.7 16.1 4.8  | 0.4 71.4 28.3        |
| 9   | 1648  | 35.9 43.3 16.2 4.6  | 0.4 63.2 36.5        |
| 10  | 1648  | 34.2 40.0 20.1 5.7  | 0.4 65.1 34.5        |
| 11  | 1648  | 33.8 38.3 21.4 6.5  | 0.5 65.3 34.3        |
| 12  | 1648  | 33.5 38.0 22.2 6.3  | 0.5 65.1 34.4        |
| 13  | 1648  | 50.9 38.6 26.5 6.2  | 0.4 64.3 35.3        |

Table 2. Compositions of oxide and sulfide phases in equilibrium at 1698 K.

| No. | Temp. | Oxide phase (mass%) | Sulfide phase (mass%) |
|-----|-------|---------------------|----------------------|
|     |       | CaO Al2O3 MnO S     | Al Ca Mn             |
| 14  | 1698  | 47.5 51.3 0.0 1.2   | 0.7 99.3 0.0         |
| 15  | 1698  | 44.8 51.0 1.5 2.7   | 1.3 93.9 4.8         |
| 16  | 1698  | 40.6 51.6 5.6 2.2   | 0.8 88.3 10.9        |
| 17  | 1698  | 42.8 49.3 5.9 2.0   | 0.7 94.0 5.3         |
| 18  | 1698  | 41.3 50.3 6.3 2.1   | 0.5 91.9 7.6         |
| 19  | 1698  | 40.8 50.8 6.4 2.0   | 0.6 89.0 10.4        |
| 20  | 1698  | 42.0 49.6 6.4 2.0   | 0.5 89.1 10.4        |
| 21  | 1698  | 40.5 50.9 6.6 2.0   | 1.9 87.1 11.0        |
| 22  | 1698  | 37.8 49.8 9.7 2.7   | 0.5 76.7 22.7        |
| 23  | 1698  | 37.4 49.5 10.3 2.8  | 0.3 77.0 22.7        |
| 24  | 1698  | 37.6 49.5 10.6 2.4  | 0.8 77.5 21.7        |
| 25  | 1698  | 37.7 48.6 10.8 2.9  | 0.4 82.8 16.8        |
| 26  | 1698  | 36.6 49.6 11.1 2.7  | 0.7 77.2 22.2        |
| 27  | 1698  | 36.9 49.1 11.1 2.9  | 0.8 77.1 22.1        |
| 28  | 1698  | 36.6 49.8 11.5 2.1  | 0.7 78.0 21.3        |
| 29  | 1698  | 37.0 49.3 11.6 2.1  | 0.7 79.5 19.8        |
| 30  | 1698  | 36.6 48.2 12.0 3.2  | 2.1 76.1 21.7        |
| 31  | 1698  | 36.8 48.7 12.2 2.4  | 1.1 76.6 22.4        |
| 32  | 1698  | 34.9 48.8 12.9 3.5  | 0.5 66.7 32.7        |
| 33  | 1698  | 38.3 45.4 13.4 2.9  | 0.7 76.4 22.9        |
| 34  | 1698  | 34.2 47.0 14.5 4.3  | 0.2 63.1 36.7        |
| 35  | 1698  | 33.7 46.3 15.6 4.5  | 0.1 61.6 38.3        |
| 36  | 1698  | 33.5 46.3 15.8 4.5  | 1.3 57.6 41.1        |
| 37  | 1698  | 33.1 46.6 15.8 4.5  | 0.9 68.0 31.1        |
| 38  | 1698  | 33.1 45.8 16.4 4.7  | 1.1 60.6 38.3        |
| 39  | 1698  | 33.3 45.5 16.5 4.7  | 0.7 56.1 43.2        |
| 40  | 1698  | 33.1 45.4 16.7 4.8  | 0.6 55.0 44.4        |
| 41  | 1698  | 32.7 45.5 17.0 4.8  | 0.5 54.3 45.2        |
| 42  | 1698  | 32.9 44.7 17.4 5.1  | 0.3 55.0 44.6        |
| 43  | 1698  | 33.1 44.6 17.4 4.9  | 1.7 51.2 47.1        |
| 44  | 1698  | 32.5 44.6 18.0 4.9  | 1.0 58.0 41.0        |
| 45  | 1698  | 32.2 43.8 18.5 5.5  | 0.3 53.4 46.3        |
| 46  | 1698  | 31.9 43.2 19.0 5.8  | 0.5 57.3 42.2        |
| 47  | 1698  | 30.8 44.3 19.3 5.7  | 1.1 63.2 35.7        |
| 48  | 1698  | 31.4 43.3 19.3 6.0  | 0.2 49.1 50.8        |
| 49  | 1698  | 30.8 43.2 20.3 5.7  | 0.5 59.7 39.8        |
| 50  | 1698  | 29.4 42.2 21.4 7.0  | 2.6 31.4 66.0        |
| 51  | 1698  | 29.9 42.0 21.4 6.7  | 1.4 62.2 36.5        |
| 52  | 1698  | 28.4 39.3 24.4 7.9  | 0.2 58.1 41.7        |
| 53  | 1698  | 27.8 38.5 25.1 8.6  | 0.9 62.8 36.3        |
analyze the molten oxide/sulfide solid solution interface. Mounted sample was polished by abrasive paper of SiC and diamond paste. The compositions of each phases at the interface were analyzed by Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS, SEM: JSM-6510 (JEOL), EDS: Inca Energy 250XT, (Oxford)).

3. Results and Discussion

Molten CaO–MnO–Al₂O₃ oxide was contacted with (Ca, Mn)S solid solution in an Al₂O₃ crucible at 1648, 1698 and 1748 K. The photo images of sample vertical section are shown in Fig. 1. Tablet shape was observed after experiments for all samples. Observed SEM-EDS image for representative samples are shown in Fig. 2. Liquid oxide phase was in contact with solid sulfide tablet for all samples. Also, formation of CaO·Al₂O₃ phase was confirmed by SEM-EDS at the Al₂O₃ crucible/liquid oxide interface for all samples and it was confirmed that oxide was saturated by CaO·Al₂O₃.

Quantitative analysis for Ca, Al, Mn and S and qualitative analysis for O were conducted by SEM-EDS. Elements Ca, Al and Mn were assumed to be in form of CaO, Al₂O₃ and MnO, respectively. Elements observed in sulfide phase were Ca, Mn, S and small amount of Al. Quantitative analysis of O could not be conducted due to lack of intensity and accuracy. The compositions of sulfide and oxide phase after experiment are shown in Tables 1–3. Mass% of CaO, Al₂O₃, MnO, S in oxide and Ca, Mn, Al in sulfide are shown, respectively. Main components of sulfide phase were CaS and MnS and from the CaS–MnS binary phase diagram¹⁰) shown in Fig. 3, sulfide phase in the present work was considered to be (Ca, Mn)S solid solution.

Details of quantitative analysis will be explained using sample No. 32 as an example in Fig. 4. As observed in Fig. 4, liquid oxide phase was not uniform due to precipitation of CaO·Al₂O₃ during sample quench. Quantitative analysis of oxide phase was done by area analysis to obtain the composition at the experimental temperature. Area analysis was conducted for sulfide phase. At least four areas were analyzed for determination of oxide and sulfide phase composition for all samples. The analysis error of SEM-EDS was estimated as +/- 0.5 mass% for oxides and +/- 2.0 mass% for sulfides.

### Table 3. Compositions of oxide and sulfide phases in equilibrium at 1748 K.

| No. | Temp. | Oxide phase (mass%) | Sulfide phase (mass%) |
|-----|-------|---------------------|-----------------------|
|     |       | CaO | Al₂O₃ | MnO | S  | Al  | Ca  | Mn  |
| 54  | 1748  | 41.8 | 55.3  | 0.0 | 0.9 | 1.1 | 98.9 | 0.0 |
| 55  | 1748  | 41.7 | 57.3  | 0.0 | 1.0 | 0.4 | 99.6 | 0.0 |
| 56  | 1748  | 36.4 | 52.4  | 8.8 | 2.4 | 1.3 | 74.4 | 24.4 |
| 57  | 1748  | 35.4 | 51.3  | 10.2| 3.1 | 0.3 | 68.6 | 31.1 |
| 58  | 1748  | 35.2 | 51.5  | 10.2| 3.0 | 0.4 | 68.6 | 31.0 |
| 59  | 1748  | 35.1 | 51.7  | 10.4| 2.8 | 0.8 | 67.8 | 31.4 |
| 60  | 1748  | 32.5 | 50.0  | 13.5| 4.0 | 0.7 | 48.6 | 50.6 |
| 61  | 1748  | 32.5 | 49.7  | 13.6| 4.2 | 0.3 | 45.2 | 54.5 |
| 62  | 1748  | 32.8 | 49.3  | 13.8| 4.1 | 0.9 | 47.3 | 51.8 |
| 63  | 1748  | 32.0 | 49.0  | 14.6| 4.4 | 0.5 | 44.8 | 54.7 |
| 64  | 1748  | 31.8 | 49.1  | 14.7| 4.5 | 0.7 | 47.4 | 51.9 |
| 65  | 1748  | 29.0 | 43.2  | 20.6| 7.1 | 0.5 | 45.7 | 53.9 |

© 2011 ISIJ
In the present work, we will consider a triangle pole to express the phase relation between oxide and sulfide phase. Triangle in the base plane represents CaO–Al₂O₃–MnO system and that in the upper plane represents CaS–Al₂S₃–MnS system. Phase diagram reported by Kang et al.¹¹ was used for CaO–Al₂O₃–MnO system. The phase relations obtained in the present work at 1648, 1698 and 1748 K are shown in Figs. 5–7. The composition of oxide and sulfide was projected from upper side to the CaO–Al₂O₃–MnO system. Composition of oxide phase agrees with the CaO·Al₂O₃ saturated composition reported by Kang et al.¹¹ at low MnO concentration range. However, composition shifts to CaO rich side at high MnO concentration range. This is due to the increase of sulfur content with MnO increase in oxide phase. Also, increase of MnO content in oxide lead to increase of MnS in sulfide phase.

Relationship between sulfur and MnO content in oxide phase is shown in Fig. 8. This sulfur content indicates the sulfur solubility in oxide phase. Sulfur solubility increases with increase of MnO content in oxide phase. However, sulfur solubility did not change with temperature. We have to remember that the oxide composition shifted to high Al₂O₃ content with temperature and CaO/Al₂O₃ is not constant in Fig. 8.

Solubility of CaS in CaO–Al₂O₃ binary oxide obtained from the present work with no MnO addition into oxide phase are shown with the results of other researchers in Fig. 9. Sulfur solubility determined in the present work seems to be slightly larger than the reported values when considering the temperature difference. Solubility of CaS in CaO–Al₂O₃ binary oxide increase with temperature and also CaO/Al₂O₃ ratio. In the present work, CaO/Al₂O₃ ratio in oxide phase decreased with temperature increase. It is considered that the effect of temperature increase and CaO/Al₂O₃ ratio decrease has nearly cancelled out, and as a result sulfur solubility did not apparently change with temperature. The sulfur solubility in CaO–Al₂O₃–MnO oxide was experimentally obtained in the present work and this result will be...
important information to discuss the mechanism of sulfide precipitation on oxide inclusions.

4. Conclusions

Molten CaO–MnO–Al₂O₃ oxide was equilibrated with (Ca, Mn)S solid solution in Al₂O₃ crucible in an electric resistance furnace at 1 648, 1 698 and 1 748 K. Phase relation between CaO·Al₂O₃ saturated molten CaO–MnO–Al₂O₃ oxide and (Ca, Mn)S solid solution was clarified. It was found that sulfur solubility in oxide phase increased with MnO content. However, temperature dependence on sulfur solubility in oxide phase was not found. It is suggested that the effect of temperature increase and CaO/Al₂O₃ ratio decrease was equivalent and apparent sulfur solubility did not change. The present result will be important information to discuss the mechanism of sulfide precipitation on oxide inclusions.

REFERENCES

1) J. Takamura and S. Mizoguchi: Proc. 6th Iron Steel Cong., ISIJ, Tokyo, (1990), 591.
2) K. Yamamoto, S. Aihara, K. Okamoto and S. Funaki: CAMP-ISIJ, 3 (1990), 808.
3) M. Wakah, T. Sawai and S. Mizoguchi: Tetsu-to-Hagané, 78 (1992), 1697.
4) A. Hasegawa, K. Morita and N. Sano: Tetsu-to-Hagané, 81 (1995), 1109.
5) N. Koyama, F. Tsukihashi and N. Sano: Tetsu-to-Hagané, 79 (1993), 1334.
6) D. H. Woo, Y. B. Kang, H. Gaye and H. G. Lee: ISIJ Int., 49 (2009), 1490.
7) G. J. W. Kor and F. D. Richardson: J. Iron Steel Inst., 206 (1968), 700.
8) R. A. Sharma and F. D. Richardson: J. Iron Steel Inst., 198 (1961), 386.
9) B. Ozturk and E. T. Turdogan: Met. Sci., 18 (1984), 299.
10) C. H. Leung and L. H. Van Vlack: J. Am. Ceram. Soc., 62 (1979), 613.
11) Y. B. Kang, I. H. Jung, S. A. Decterov, A. D. Pelton and H. G. Lee: ISIJ Int., 44 (2004), 965.