Phase Equilibrium between $\text{CaO}\cdot\text{Al}_2\text{O}_3$ Saturated Molten $\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--MnO}$ and $(\text{Ca}, \text{Mn})\text{S}$ Solid Solution

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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 $\text{CaO}\text{--}\text{Al}_2\text{O}_3$ is often used in secondary refining and $\text{Ca}\text{--Mn}\text{--Al}$ complex oxide may form, and it is important to clarify the mechanism of MnS precipitation on oxide inclusions. Therefore, molten $\text{CaO}\text{--MnO}\text{--Al}_2\text{O}_3$ oxide was equilibrated with $(\text{Ca}, \text{Mn})\text{S}$ solid solution in Al_2O_3 crucible in an electric resistance furnace at 1 648, 1 698 and 1 748 K in the present work. Phase relation between $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}\text{--MnO}\text{--Al}_2\text{O}_3$ oxide and $(\text{Ca}, \text{Mn})\text{S}$ 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 has been reported^{1,2)} 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,⁴⁾ MnO–SiO₂–TiO₂–MnS system⁵⁾ and MnO–SiO₂–Al₂O₃–MnS system⁶⁾ have been reported by various researchers.

Flux composed of $\text{CaO}\text{--}\text{Al}_2\text{O}_3$ 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, $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}\text{--MnO}\text{--Al}_2\text{O}_3$ oxide was contacted with $(\text{Ca}, \text{Mn})\text{S}$ solid solution to clarify the phase equilibrium between these phases in the present work.

2. Experimental

In the present work, molten $\text{CaO}\text{--MnO}\text{--Al}_2\text{O}_3$ oxide was contacted with $(\text{Ca}, \text{Mn})\text{S}$ solid solution in an Al_2O_3 crucible at 1 648, 1 698 and 1 748 K by using electric resistance furnace. The equipment consists of high purity alumina reaction chamber (outer diameter: 80 mm, inner diameter: 70 mm, height: 1 000 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 CaCO_3 was heated in Pt crucible at 1 473 K in air to obtain CaO. Then it was mixed with equal amount of reagent Al_2O_3 and was melted in Pt crucible at 1 773 K in air to recover 50 mass%CaO–50 mass% Al_2O_3 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 mm ϕ . Also, 0.6 g of reagent CaS powder was pressed into same tablet shape. Both tablets were placed in an Al_2O_3 crucible (outer diameter: 15 mm, inner diameter: 12 mm, height: 100 mm) and 4 Al_2O_3 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 1 648, 1 698 or 1 748 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

Fig. 1. Photo images of sample vertical section held at 1 648 K.

Fig. 2. Observed SEM images of sample held at 1 698 K.

Table 1. Compositions of oxide and sulfide phases in equilibrium at 1 648 K.

No.	Temp.	Oxide phase (mass%)				Sulfide phase (mass%)		
		CaO	Al ₂ O ₃	MnO	S	Al	Ca	Mn
1	1 648	45.3	50.7	1.4	2.6	0.5	79.6	19.9
2	1 648	43.7	48.5	4.5	3.3	0.9	83.5	15.6
3	1 648	38.1	45.5	13.0	3.4	0.4	82.3	17.3
4	1 648	38.0	45.4	13.3	3.3	1.9	80.6	17.5
5	1 648	37.4	45.4	14.0	3.2	1.1	82.9	16.0
6	1 648	37.0	43.2	15.3	4.5	0.2	74.8	25.0
7	1 648	36.7	43.4	15.6	4.3	0.9	71.7	27.4
8	1 648	36.4	42.7	16.1	4.8	0.4	71.4	28.3
9	1 648	35.9	43.3	16.2	4.6	0.4	63.2	36.5
10	1 648	34.2	40.0	20.1	5.7	0.4	65.1	34.5
11	1 648	33.8	38.3	21.4	6.5	0.5	65.3	34.3
12	1 648	33.5	38.0	22.2	6.3	0.5	65.1	34.4
13	1 648	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 1 698 K.

No.	Temp.	Oxide phase (mass%)				Sulfide phase (mass%)		
		CaO	Al ₂ O ₃	MnO	S	Al	Ca	Mn
14	1 698	47.5	51.3	0.0	1.2	0.7	99.3	0.0
15	1 698	44.8	51.0	1.5	2.7	1.3	93.9	4.8
16	1 698	40.6	51.6	5.6	2.2	0.8	88.3	10.9
17	1 698	42.8	49.3	5.9	2.0	0.7	94.0	5.3
18	1 698	41.3	50.3	6.3	2.1	0.5	91.9	7.6
19	1 698	40.8	50.8	6.4	2.0	0.6	89.0	10.4
20	1 698	42.0	49.6	6.4	2.0	0.5	89.1	10.4
21	1 698	40.5	50.9	6.6	2.0	1.9	87.1	11.0
22	1 698	37.8	49.8	9.7	2.7	0.5	76.7	22.7
23	1 698	37.4	49.5	10.3	2.8	0.3	77.0	22.7
24	1 698	37.6	49.5	10.6	2.4	0.8	77.5	21.7
25	1 698	37.7	48.6	10.8	2.9	0.4	82.8	16.8
26	1 698	36.6	49.6	11.1	2.7	0.7	77.2	22.2
27	1 698	36.9	49.1	11.1	2.9	0.8	77.1	22.1
28	1 698	36.6	49.8	11.5	2.1	0.7	78.0	21.3
29	1 698	37.0	49.3	11.6	2.1	0.7	79.5	19.8
30	1 698	36.6	48.2	12.0	3.2	2.1	76.1	21.7
31	1 698	36.8	48.7	12.2	2.4	1.1	76.6	22.4
32	1 698	34.9	48.8	12.9	3.5	0.5	66.7	32.7
33	1 698	38.3	45.4	13.4	2.9	0.7	76.4	22.9
34	1 698	34.2	47.0	14.5	4.3	0.2	63.1	36.7
35	1 698	33.7	46.3	15.6	4.5	0.1	61.6	38.3
36	1 698	33.5	46.3	15.8	4.5	1.3	57.6	41.1
37	1 698	33.1	46.6	15.8	4.5	0.9	68.0	31.1
38	1 698	33.1	45.8	16.4	4.7	1.1	60.6	38.3
39	1 698	33.3	45.5	16.5	4.7	0.7	56.1	43.2
40	1 698	33.1	45.4	16.7	4.8	0.6	55.0	44.4
41	1 698	32.7	45.5	17.0	4.8	0.5	54.3	45.2
42	1 698	32.9	44.7	17.4	5.1	0.3	55.0	44.6
43	1 698	33.1	44.6	17.4	4.9	1.7	51.2	47.1
44	1 698	32.5	44.6	18.0	4.9	1.0	58.0	41.0
45	1 698	32.2	43.8	18.5	5.5	0.3	53.4	46.3
46	1 698	31.9	43.2	19.0	5.8	0.5	57.3	42.2
47	1 698	30.8	44.3	19.3	5.7	1.1	63.2	35.7
48	1 698	31.4	43.3	19.3	6.0	0.2	49.1	50.8
49	1 698	30.8	43.2	20.3	5.7	0.5	59.7	39.8
50	1 698	29.4	42.2	21.4	7.0	2.6	31.4	66.0
51	1 698	29.9	42.0	21.4	6.7	1.4	62.2	36.5
52	1 698	28.4	39.3	24.4	7.9	0.2	58.1	41.7
53	1 698	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 1 648, 1 698 and 1 748 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. Also, 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.

Fig. 3. Phase diagram of CaS–MnS system.¹⁰⁾

(mass%)				
Area	Al ₂ O ₃	CaO	MnO	S
1	48.98	34.74	12.77	3.51
2	48.48	35.08	12.95	3.49
3	49.08	34.86	12.57	3.48
4	48.47	34.72	13.10	3.70
Ave.	48.75	34.85	12.85	3.54

(mass%)			
Area	Al ₂ S ₃	CaS	MnS
5	1.26	65.47	33.27
6	0.22	68.23	31.55
7	0.19	67.12	32.69
8	0.42	65.01	34.57
9	0.62	67.82	31.57
Ave.	0.54	66.73	32.73

Table 3. Compositions of oxide and sulfide phases in equilibrium at 1 748 K.

No.	Temp.	Oxide phase (mass%)				Sulfide phase (mass%)		
		CaO	Al ₂ O ₃	MnO	S	Al	Ca	Mn
54	1 748	41.8	55.3	0.0	0.9	1.1	98.9	0.0
55	1 748	41.7	57.3	0.0	1.0	0.4	99.6	0.0
56	1 748	36.4	52.4	8.8	2.4	1.3	74.4	24.4
57	1 748	35.4	51.3	10.2	3.1	0.3	68.6	31.1
58	1 748	35.2	51.5	10.2	3.0	0.4	68.6	31.0
59	1 748	35.1	51.7	10.4	2.8	0.8	67.8	31.4
60	1 748	32.5	50.0	13.5	4.0	0.7	48.6	50.6
61	1 748	32.5	49.7	13.6	4.2	0.3	45.2	54.5
62	1 748	32.8	49.3	13.8	4.1	0.9	47.3	51.8
63	1 748	32.0	49.0	14.6	4.4	0.5	44.8	54.7
64	1 748	31.8	49.1	14.7	4.5	0.7	47.4	51.9
65	1 748	29.0	43.2	20.6	7.1	0.5	45.7	53.9

Fig. 4. Example of quantitative analysis (sample No. 32).

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 $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}$ system and that in the upper plane represents $\text{CaS}-\text{Al}_2\text{S}_3-\text{MnS}$ system. Phase diagram reported by Kang *et al.*⁽¹¹⁾ was used for $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}$ system. The phase relations obtained in the present work at 1 648, 1 698 and 1 748 K are shown in **Figs. 5–7**. The composition of oxide and sulfide was projected from upper side to the $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}$ system. Composition of oxide phase agrees with the $\text{CaO}\cdot\text{Al}_2\text{O}_3$ 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 Al_2O_3 content with temperature and $\text{CaO}/\text{Al}_2\text{O}_3$ is not constant in **Fig. 8**.

Solubility of CaS in $\text{CaO}-\text{Al}_2\text{O}_3$ 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 $\text{CaO}-\text{Al}_2\text{O}_3$ binary oxide increase with temperature and also $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. In the present work, $\text{CaO}/\text{Al}_2\text{O}_3$ ratio in oxide phase decreased with temperature increase. It is considered that the effect of temperature increase and $\text{CaO}/\text{Al}_2\text{O}_3$ ratio decrease has nearly cancelled out, and as a result sulfur solubility did not apparently change with temperature. The sulfur solubility in $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}$ oxide was experimentally obtained in the present work and this result will be

Fig. 5. Phase relation between $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}-\text{S}$ phase and $\text{CaS}-\text{MnS}$ solid solution phase at 1 648 K.

Fig. 6. Phase relation between $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}-\text{S}$ phase and $\text{CaS}-\text{MnS}$ solid solution phase at 1 698 K.

Fig. 7. Phase relation between $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}-\text{S}$ phase and $\text{CaS}-\text{MnS}$ solid solution phase at 1 748 K.

Fig. 8. Sulfur solubility in $\text{CaO}\cdot\text{Al}_2\text{O}_3$ saturated molten $\text{CaO}-\text{Al}_2\text{O}_3-\text{MnO}$ oxide.

Fig. 9. Sulfur solubility in molten CaO–Al₂O₃ oxide equilibrated with CaS.

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 1648, 1698 and 1748 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.

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