Effect of S Content on the MnS Precipitation in Steel with Oxide Nuclei

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Manganese sulphide formation experiments were carried out by deoxidizing with various elements and by changing S content to clarify the effect of S content on the MnS precipitation with various kinds of oxide nuclei. The behavior of MnS precipitation on oxide particles in the steel with 1 mass% of Mn was characterized according to S content. When S content was below 100 ppm, a lot of MnS precipitated only on some kinds of oxide. It is effective to use an oxide having high sulphide capacity and low melting temperature for uniform dispersion of fine MnS. On the other hand, when S was above 100 ppm, almost all the oxides worked as the precipitation sites of MnS. In that case, for the MnS dispersion, it is better to select the oxide which tends to disperse finely itself in steel. The average diameter of MnS, calculated by using a mathematical model considering the oxide nuclei with changing the precipitation ratio according to S content and to the kind of oxides, agrees well with the experimental data.

KEY WORDS: low carbon steel; inclusions; nucleus; oxide; precipitation; solidification; manganese sulphide; manganese silicate; zirconium; aluminum; inoculant; deoxidation; sulphide capacity.

1. Introduction

It is well known that many efforts have been made to remove nonmetallic inclusions from molten steel because they cause many harmful effects on steel properties. However, the authors presented a new idea called "Oxides Metallurgy", in which oxide particles in steel are utilized as the nucleation sites of precipitates by controlling the size, the distribution and the nature of oxides.^{1,2)} Precipitates in steel exert various effects on steel properties. For example, small MnS restrains the grain growth of steel by a pinning effect on the grain boundaries. MnS also works as the transformation site of fine acicular ferrite and as the precipitation site of cementite. If we control the precipitates by using oxide particles, many steel properties can be improved.

From the standpoint described above, the authors have studied the behavior of MnS precipitation on oxide particles in low S steel in terms of precipitation ratio of MnS on oxide particles defined as the ratio of the number of oxide particles worked as the sites of MnS precipitation to the number of oxide particles in steel. It was observed that the ratio depended on the kind and the composition of oxides and that the ratio was higher in the case of Mn-silicate having a lower melting temperature and a higher sulphide capacity in the steel containing 1 mass% of Mn and 50 ppm of S.^{3,4)} Based on these phenomena,

the authors concluded the precipitation mechanism of MnS on oxide particles is as follows^{3,4)}: In molten steel, S distributes between liquid Mn-complex oxide and molten steel. As the temperature decreases and after the solidification of the steel, a small amount of MnS crystallizes on the surface of the oxide and works as an embryo for MnS precipitation. The MnS grows by Mn and S diffusion in the steel.

However, the investigation was carried out only in the case of low S steel, and a study in a wide range of S content is necessary because S content range of steel now in production is from a few to thousands ppm. In this study, the effects of S content on the MnS precipitation with several kinds of oxide nuclei were investigated during laboratory scale experiments.

2. Experimental Procedures

One kg of pure iron was melted by induction heating in a magnesia crucible under an Ar gas atmosphere. After adjusting the main composition at 1 570°C (1 843 K), 1 g of Fe₂O₃ was added to control initial oxygen content. Then deoxidizing elements were added. The melt was kept for 30 s after deoxidation and cooled in the crucible by switching the power off.

Chemical compositions of specimens are listed in **Table 1**. The amount of S was changed from 13 to 620 ppm

Table 1. Chemical compositions of specimens. (mass%)

	C	Si	Mn	S	Ti	Zr	Al	N	O
MS-1	0.11	0.18	0.91	0.0013	0.0075	0.	0.	0.0023	0.0033
MS-2	0.11	0.18	0.90	0.0013	0.	0.0054	0.	0.0018	0.0042
MS-3	0.09	0.007	1.02	0.0030	0.	0.	0.	0.	0.0040
MS-4	0.09	0.21	1.03	0.0040	0.	0.	0.	0.	0.0030
MT-1	0.10	0.	0.95	0.0040	0.0270	0.	0.	0.	0.0073
MT-2	0.09	0.	0.96	0.0064	0.0270	0.	0.	0.0023	0.0098
MT-3	0.10	0.	0.97	0.0129	0.0280	0.	0.	0.0007	0.0068
MT-4	0.10	0.	0.99	0.0371	0.0290	0.	0.	0.0022	0.0068
AL-1	0.07	0.011	0.99	0.0070	0.	0.	0.0290	0.0023	0.0009
AL-2	0.08	0.011	0.98	0.0110	0.	0.	0.0290	0.0021	0.0016
AL-3	0.08	0.009	1.00	0.0530	0.	0.	0.0280	0.0030	0.0019
AL-4	0.08	0.010	1.01	0.0620	0.	0.	0.0300	0.0027	0.0013
AL-5	0.16	0.	0.90	0.0060	0.	0.	0.0070	<.0005	0.0018
AL-6	0.10	0.	0.90	0.0060	0.	0.	0.0070	<.0005	0.0018
AL-7	0.10	0.19	0.93	0.0040	0.	0.	<0.003	0.	0.0071
ZR-1	0.11	0.	0.98	0.0040	0.	0.0250	0.	0.	0.0085
ZR-2	0.10	0.	0.96	0.0068	0.	0.0250	0.	0.	0.0086
ZR-3	0.11	0.	0.96	0.0388	0.	0.0290	0.	0.	0.0073

and the deoxidation elements were Al, Zr, Mn–Si and Mn–Ti. The samples were analyzed by a computer-aided, two-dimensional X-ray microanalyzer (CMA). The kinds and distributions of particles in the samples were determined from the characteristic X-ray images. The morphologies of the particles were observed by using a SEM with an energy dispersion analyzer.

On the characteristic X-ray image analysis, threshold values for identifying the particles, based on a previous work,⁵⁾ were as follows: For MnS, the threshold value of Mn was the value of X-ray intensity corresponding to the concentration $1.32C_{AV}$ and that of S was $X_{AV} + 5\sigma$ of X-ray intensity (C_{AV} : average concentration of an element; X_{AV} , σ : average and standard deviation of X-ray intensity). For oxide particles, the threshold value was also $X_{AV} + 5\sigma$ of X-ray intensity of each deoxidizing element.

3. Mathematical Model for MnS Formation

The mathematical model used here was developed by Ueshima *et al.*^{5,6)} In the model, a hexagonal dendrite model as shown in Fig. 1 is assumed, and solute distribution between liquid and solid during solidification is calculated at each temperature step taking into consideration the back diffusion of elements in the solid. Delta/gamma transformation is also considered in the model. The precipitation of MnS starts when the concentration product of Mn and S reaches the value of equilibrium solubility product, and the MnS grows spherically under the diffusion control of Mn and S in the solid. The equilibrium solubility product values of Mn and S are calculated by the Eqs. (1) and (2) obtained by attaching the correction term of Si content to the equations derived by Wriedt *et al.*⁷⁾ and Turkdogan *et al.*⁸⁾

$$\log[\text{mass\%Mn}][\text{mass\%S}](\delta) = -10590/T + 4.0302 - 0.07[\text{mass\%Si}] \quad (1)$$

Fig. 1. Schematic drawing of the longitudinal and transverse cross section of dendrites.⁶⁾

$$\log[\text{mass\%Mn}][\text{mass\%S}](\gamma) = -90080 + 2.929 - (-215/T + 0.097)[\text{mass\%Mn}] - 0.07[\text{mass\%Si}] \quad (2)$$

The values of physical properties used for the calculation are listed in Table 2.^{9–12)} In the calculation, Mn concentration was kept at 1 mass% and S content was varied nine times from 10 to 3200 ppm. The distance among the sites for MnS precipitation was 100 μm , which was constant and did not depend on the kind of oxides. The distance among oxides, 100 μm corresponds to that obtained in the case of Al-deoxidation. The condition for the calculation is shown in Table 3. The cooling rate was 35°C/min (0.58°C/s) and the primary dendrite arm spacing was 300 μm ; these corresponded to the values obtained from the 1 kg ingot experiments.

Table 2. Equilibrium distribution coefficients and diffusion coefficients of elements.

Element	$k^{\delta/L}$	$k^{\gamma/L}$	$k^{\gamma/\delta}$	D^{δ} (cm ² /s)	D^{γ} (cm ² /s)
C	0.19	0.34	1.79	0.0127exp (−19450/RT)	0.0761exp (−32160/RT)
Si	0.77	0.52	0.68	8.0exp (−59500/RT)	0.30exp (−60100/RT)
Mn	0.76	0.78	1.03	0.76exp (−53640/RT)	0.055exp (−59600/RT)
P	0.23	0.13	0.57	2.9exp (−55000/RT)	0.010exp (−43700/RT)
S	0.05	0.035	0.70	4.56exp (−51300/RT)	2.4exp (−53400/RT)

Sources: $k^{\delta/L}$ and $k^{\gamma/L}$: Reference 10 for phosphorus and Reference 9 for the other elements.
 D^{δ} and D^{γ} : Reference 12 for carbon and Reference 11 for the other elements.

Table 3. Conditions for the calculation of MnS formation.

Composition (mass%)	C	Si	Mn	P	S
	0.1	0.001	1.0	0.001	0.001–0.320
Cooling rate	35 °C/min (0.58 °C/s)				
Primary dendrite arm spacing	300 μ m

Fig. 2. Distribution of oxides and sulphides. (by CMA/1mass%Mn–0.03mass%Al)

4. Results

4.1. MnS Formation Experiments

Figure 2 shows the distribution of oxide particles and MnS particles in the cases of 70 and 530 ppm S with Al-deoxidation obtained by using the CMA. The red network structure indicates Mn microsegregation, blue spots represent the oxide particles, and yellow spots show MnS. As a result, white spots represent the MnS precipitated on the oxide particles. In the case of 70 ppm of S, in addition to the white spots, many blue spots are seen, which represent the oxide particles without MnS precipitation. In the case of 530 ppm of S, a lot of stringlike MnS are visible, and the white spots that show the MnS precipitated on oxides can also be seen. The black area around the stringlike MnS, resulted from the decrease in Mn concentration in the inter-dendritic region caused by the formation of MnS as reported by Ueshima *et al.*¹³⁾ in the case of the steel containing 1 mass% of Mn and 3 200 ppm of S.

The result of quantitative analysis of the photograph is given in Table 4. The number of oxide and MnS particles were counted in the area of $1.5 \times 1.5 \text{ mm}^2$. The MnS precipitation ratio on oxides is defined as the number of oxide particles with MnS precipitation divided by the total number of oxides observed, which indicates the ratio of oxide particles being as the precipitation sites

Table 4. Number of oxide and MnS particles in the steel having various S content and deoxidized with various deoxidation elements.

Deoxidation elements	S (ppm)	Number of particles (1/1.5mm × 1.5mm)			Precipitation ratio of MnS (%) (*3/*1) × 100
		Oxides *1	MnS *2	MnS on oxide *3	
Mn-Si (1)	13	75	27	26	34.7
Mn-Si (2)	13	278	80	74	26.6
Mn-Si (3)	30	176	228	152	86.4
Mn-Si (4)	40	143	179	110	76.9
Mn-Ti (1)	40	304	197	186	61.2
Mn-Ti (2)	64	354	262	239	67.5
Mn-Ti (3)	129	292	288	255	87.3
Mn-Ti (4)	371	370	461	353	95.4
Al (1)	70	299	223	124	41.5
Al (2)	110	139	219	116	83.5
Al (3)	530	171	1012	142	83.0
Al (4)	620	98	581	83	84.7
Al (10kg-1)	60	374	180	115	30.7
Al (10kg-2)	60	460	245	174	37.8
Al (Ueshima)	40	155	—	37	23.9
Zr (1)	40	677	174	174	25.7
Zr (2)	68	490	292	250	51.0
Zr (3)	388	520	838	511	98.3

of MnS. The table also shows the result of 10 kg ingot experiment carried out by the author and the data for 1 kg ingot experiment obtained by Ueshima *et al.*⁵⁾

The relationship between the precipitation ratio of

MnS and S content obtained from Table 4 is shown in Fig. 3. In the case of Al-deoxidation, the precipitation ratio in low S region was 20 to 40%, which was very low; however, the ratio reached 85% in the S region over 100 ppm. The result of 10 kg ingot experiment and the data from Ueshima *et al.*⁵⁾ were also on the same curve as this study. The same tendency was seen in the case of Zr-deoxidation. In the case of Mn-Si-deoxidation, the precipitation ratio was about 85%, which was higher even in the low S region at 40 ppm, and the ratio fell to 30% in the very low S region at 13 ppm. In the case of Mn-Ti-deoxidation, the value was 60 to 70% when the S content was below 100 ppm and rose when the S was over 100 ppm.

Figure 4 shows typical morphologies of oxide and MnS particles in the cases of Al-deoxidation and Mn-Ti-deoxidation. In the case of 70 ppm S with Al-deoxidation (1), Al_2O_3 with complicated shape was seen, and when the S was 530 ppm (2), the whole particles were MnS, and no oxide was detected. However, it seems that Al-oxides were inside of the MnS as the precipitation sites of the MnS, because a slight signal of Al was observed in the MnS by EDX analysis. In the case of 64 ppm S with Mn-Ti-deoxidation (3), Mn-Ti-oxide particle was seen and MnS was observed partly in the lower part of the oxide in the photograph. The data of

EDX analysis of the MnS included weak signals of Mn and Ti. It is considered that the signals came from the oxide behind and around the MnS. When the S was 371 ppm (4), the black part in the center of the particle

Fig. 3. Change in the precipitation ratio of MnS with S content and with the kind of deoxidation elements.

(1) Al-deoxidation (S=70ppm)

(2) Al-deoxidation (S=530ppm)

(3) Mn-Ti-deoxidation (S=64ppm)

(4) Mn-Ti-deoxidation (S=371ppm)

Fig. 4. SEM images of oxide and MnS particles.

was Mn-Ti-oxide, and MnS surrounded it.

4.2. Calculation of MnS Formation

The relationship between the temperature of the beginning of MnS formation and S content calculated by the mathematical model is shown in Fig. 5. In the calculation, Mn was kept at 1 mass%. Liquidus and solidus temperatures and the starting temperature of the δ/γ transformation are also indicated in Fig. 5. In the low S region, MnS precipitates in γ phase, and the beginning temperature of MnS precipitation increases according to the increase of S content and reaches δ/γ transformation beginning temperature. At 100 ppm of S, MnS precipitates in δ phase before the transformation, and in the region of S above 400 ppm, crystallization of MnS occurs in the inter-dendritic liquid region after the precipitation in δ phase. Figure 6 indicates the amount of MnS formation for various S content. The amount was represented as the S amount of MnS formed by the crystallization from liquid steel having high Mn and S concentration in the inter-dendritic region and by the precipitation from solid steel during cooling. The amount of crystallized MnS and precipitated MnS was derived by the calculation model. The amount of crystallized MnS is large when S content is over 800 ppm. Figure 7 shows the ratio of crystallization amount of MnS to the total amount of MnS. In Fig. 7, the ratio increases with the increase of S content, and its value is 89% at 3 200 ppm of S.

5. Discussion

5.1. Mechanism of MnS Formation with Oxide Nuclei

From Fig. 3, the behavior of MnS precipitation on oxide particles in the case of 1 mass% Mn is characterized according to S content as follows:

- (1) $S < 0.002$ mass%: The number of MnS precipitating on oxides was small in any kinds of oxide.
- (2) $0.002 \leq S < 0.01$ mass%: The precipitation ratio was high in some kinds of oxide.
- (3) $S \geq 0.01$ mass%: The ratio was large in almost all oxides. That means they worked as the precipitation sites of MnS.

Several experimental results and discussion were shown in the Refs. 3), 4) by the authors in the case of (2). The preferable oxides for the MnS precipitation sites were Mn-complex oxides having lower melting temperatures and higher sulphide capacities, such as Mn-silicate and Mn-aluminate in the steel containing 50 to 100 ppm of S. Based on these phenomena, the authors concluded the precipitation mechanism of MnS on oxide particles as follows: In molten steel, S distributes between liquid Mn-complex oxide and the molten steel. As the temperature decreases and after the solidification of the steel, a small amount of MnS crystallizes on the surface of the oxide and works as an embryo of MnS precipitation. The MnS grows by the diffusion of Mn and S in the steel.

Sano¹⁴⁾ and Hasegawa *et al.*¹⁵⁾ reported Mn-silicate had large solubility of MnS. Based on the data, MnS formation from Mn and S diffusion at the surface of

Fig. 5. Starting temperature of precipitation or crystallization of MnS. (estimated)

Fig. 6. Change in the amount of S as MnS. (estimated)

Fig. 7. Ratio of the MnS amount formed by crystallization from molten steel. (estimated)

Mn-silicate oxide particle and dissolution of the MnS in the oxide after solidification of steel seem to be promoted because of low activity of MnS in such liquid oxide particles (the lowest melting temperature of Mn-silicate is about 1 250°C (1 523 K)). As the temperature decreases, the oxide solidifies and MnS crystallizes on the surface of the oxide. Therefore, Al-oxide and Zr-oxide are not suitable as the precipitation sites of MnS because they seem to have no or a little solubility of Mn and S.

In Fig. 3, Mn-Ti-oxide had 60 to 70% of the pre-

precipitation ratio in the range of S content from 20 to 100 ppm. Titanium-oxide in steel is regarded as Ti_3O_5 or Ti_2O_3 ,¹⁶⁾ but phase diagrams and the data of sulphide capacity for $MnO-Ti_3O_5$ and $MnO-Ti_2O_3$ are not available. Mn-Ti-oxides seem to have high sulphide capacity because of their higher precipitation ratio of MnS. Recently, Morita *et al.*¹⁷⁾ reported there was liquid phase in wide range of $MnO-Ti_2O_3$ system at 1873 K. Low melting temperature is one of the conditions for oxides to be better site of MnS precipitation. Therefore, in the case of (2), it is desirable to select the oxides having high sulphide capacities and low melting temperatures as the precipitation sites of MnS for the fine dispersion of MnS.

In the region of (1), the precipitation ratio becomes low even in the case of Mn-Si-deoxidation, because it is difficult to form an embryo for MnS precipitation on oxides for the lack of S amount dissolved in the oxides. Moreover, the growth of MnS is not expected because the precipitation temperature is below 1325°C (1598 K) from Fig. 5, which makes the diffusion of Mn and S rather slow. However, from Table 4, the number of MnS increased when the number of oxides was large even in the case of 13 ppm-S. Therefore, it is possible to promote the diffusion by the dispersion of fine oxide particles having high value of precipitation ratio so that the distance among the precipitation sites is shortened. It is necessary to find the oxides having a higher S capacity than that of Mn-silicate for the fine dispersion of MnS in this S region (1).

In the S region of (3), MnS precipitates on most of the oxide particles in the steel, and the precipitation does not depend on the kind of oxides. From the result of the calculation shown in Fig. 5, the temperature at which MnS precipitation begins reaches the δ/γ transformation temperature and MnS precipitated in δ phase in the S region above 100 ppm. However, it is difficult to explain the MnS behavior in the region (3) by the MnS precipitation in δ phase. It is better to consider that the supersaturation owing to high $[Mn] \times [S]$ product value leads to the heterogeneous nucleation of MnS regardless of the kind of the nuclei.

From the calculation result, crystallization of MnS from liquid steel in the inter-dendritic region occurs when S content is more than 400 ppm as shown in Fig. 7. **Figure 8** presents the number of MnS with oxides and without oxides obtained by CMA analysis in the cases of Al-deoxidation and Mn-Ti-deoxidation. In the figure, the number of the MnS without oxides is large when the S content is over 530 ppm. Though all the MnS without oxides does not represent the sole MnS because of the precision limit of the CMA measurement, it seems to be possible that the solidification front also works as the precipitation site of MnS as do the oxide particles. However, fine MnS dispersion could be obtained if the MnS precipitation in δ phase is promoted by using the oxide particles dispersed with very short distances, before the crystallization of MnS starts from liquid in the inter-dendritic region.

Therefore, in the region (3), the oxide that tends to disperse finely itself in steel should be selected because

Fig. 8. Change in the number of MnS in the steel having various S content and deoxidized with various deoxidation elements.

any kind of oxides could be the precipitation site of MnS, regardless of whether the oxide has high sulphide capacity.

5.2. Calculation of MnS Formation Considering the Precipitation Ratio

Based on the discussion and the experimental data described above, some calculations were made by using the mathematical model for MnS formation considering the nuclei of MnS precipitation. To consider the oxide nuclei, the number of precipitation sites of MnS is determined by the number of oxide particles multiplied by the precipitation ratio, which is determined according to the kind of oxide and the S content.

Two ways of determining the precipitation site of MnS were used in the calculation based on the experimental results: First, the number of the precipitation sites, which is the oxide number, is changed but the precipitation ratio is kept at 100% in the full range of S, and second, the precipitation ratio is changed according to the S content and the number of oxides were kept as 200 ($1/1.5 \times 1.5 \text{ mm}^2$). The former case corresponds to that of Mn-Ti-deoxidation and the latter case corresponds to that of Al-deoxidation. **Table 5** shows the conditions for the calculations.

The relationship between the average diameter of MnS and S content obtained by the calculation is shown in **Fig. 9**. When the oxide number changes as shown in (1),

Table 5. Condition for the calculation of MnS diameter taking into consideration of the oxide nucleus.

Composition (mass%)	C	Si	Mn	P	S
	0.1	0.001	1.0	0.001	0.002–0.080
Cooling rate	35 °C /min (0.58 °C /s)				
Primary dendrite arm spacing	300 μ m				
Number of MnS site : N (1/1.5x1.5mm)	(1) N=50,200,400,800, R=100% (2) N=200, R: changed based on the experimental data				
Precipitation ratio : R					

(1) Mn-Ti-deoxidation

(2) Al-deoxidation

Number of MnS site : N (1/1.5x1.5mm), Precipitation ratio : R

(1)Mn-Ti-deoxidation: N=50, 200, 400, 800, R=100%

(2)Al-deoxidation: N=200, R: changed based on the experimental data

Fig. 9. Change in the average diameter of MnS in various conditions of precipitation sites. (estimated)

the average diameter of MnS increases with the increase of S content and decreases as the number of oxides becomes large. Therefore controlling the number of oxide particles is important for getting the appropriate diameter of MnS.

On the other hand, in the case of varying the precipitation ratio (2), the diameter does not change below 70 ppm of S because of the competition of the

following effects: a) The diameter becomes small according to the increase of S content because the precipitation sites increase. b) The diameter becomes large according to the increase of S content because of the increase of the $[Mn] \times [S]$ value. In the S content range from 70 to 100 ppm, the diameter decreases because of the effect of increasing the number of precipitation sites. On the other hand, in the case of more than 100 ppm S, the diameter increases because the precipitation ratio is kept constant as 100% and the $[Mn] \times [S]$ increases. In Fig. 9 (2), the average diameter of MnS (total MnS or MnS with oxides) obtained by Al-deoxidation experiment is plotted. There is a minimum point at 110 ppm S in the case of the average diameter of the MnS with oxides, and this agrees with the results of the calculation.

6. Conclusions

MnS formation experiments were carried out by deoxidizing with various deoxidation elements and changing S content to clarify the effect of S content on the MnS precipitation with various kinds of oxide nuclei. The experimental data and discussion yielded the following results.

(1) The behavior of MnS precipitation on oxide particles in the case of 1 mass% of Mn was characterized according to S content as follows:

- $S < 0.002$ mass%: The number of MnS precipitating on oxides was small in any kinds of oxide.
- $0.002 \leq S < 0.01$ mass%: The precipitation ratio was high in some kinds of oxides.
- $S \geq 0.01$ mass%: The ratio was high in almost all the oxides. That means they worked as the precipitation sites of MnS.

(2) For the uniform dispersion of fine MnS, it is effective to use an oxide having a high sulphide capacity and a low melting temperature in the case of low S range below 100 ppm, and it is better to select the oxide which tends to disperse finely in steel in the case of higher S region above 100 ppm.

(3) The average diameter of MnS calculated by using a mathematical model considering the oxide nuclei with the precipitation ratio according to S content agrees well with the experimental data.

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