Precipitation and Dispersion Control of MnS by Deoxidation Products of ZrO_2 , Al_2O_3 , MgO and MnO– SiO_2 Particles in Fe–10mass%Ni Alloy

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An Fe–10 mass%Ni–1 mass%Mn alloy was deoxidized with Zr, Al, Mg and Si and the effect of these deoxidation particles on MnS crystallization and/or precipitation has been studied as a function of S content with focussing on the particle dispersion in microsegregation domain. MnS cannot be uniformly dispersed in microsegregation domain since the crystallization and/or precipitation of MnS occur only on ZrO_2 or Al_2O_3 particles located at the region of final solidification. MnS-containing MnO– SiO_2 particles can be uniformly dispersed in microsegregation domain, if the S level is low enough for particles not to be pushed. MgS and/or (Mg, Mn)S crystallize on MgO particles in Mg deoxidation. In the case of high S level, the MgO, MgS/MgO and (Mg, Mn)S/MgO particles are pushed to the region of final solidification and then MnS crystallizes and/or precipitates on the pushed particles.

KEY WORDS: crystallization; precipitation; MnS; pushing; ZrO_2 ; Al_2O_3 ; MgO; MnO– SiO_2 ; deoxidation particles; microsegregation; solidification; heterogeneous nucleation; misfit parameter.

1. Introduction

It has been known that the nucleation rate of intergranular acicular ferrite might be enhanced by utilizing the primary deoxidation products for the precipitation of MnS. In the production of high-strength and toughness non-thermal tempering forging steel, fine MgO and/or $\text{MgO} \cdot \text{Al}_2\text{O}_3$ particles which are produced by Mg deoxidation are utilized as inoculants for the heterogeneous nucleation of MnS. In recent years a shape-controlled-sulfide free-machining structure steel with duplex structure has been developed by crystallizing complex sulfide (Ca, Mg, Mn)S on deoxidation particles with Ca or Ca/Mg.^{1–5)} These steels are characterized not only in high machinability, but also in improved charpy impact value due to less deformability of duplex sulfides. Furthermore, in view of no lead hazardous to the environment, these steels will be one of the major free-machining structure steels in future.

Ueshima *et al.*⁶⁾ studied the effect of deoxidation products with Ti, Al, Zr, Hf, Y and Ce on MnS precipitation and found that the number of complex sulfide and oxide particles tends to increase with deoxidant potency. Sawai *et al.*⁷⁾ studied the effect of ZrO_2 particles on precipitation of MnS and found that ZrO_2 –Mn silicate–MnS particles were uniformly dispersed by reducing MnO– SiO_2 particles with Zr. Since partitioning of dissolved S occurs between molten steel and the deoxidation products of liquid MnO– SiO_2 , CaO– SiO_2 and CaO– SiO_2 – Al_2O_3 particles, these S-containing oxides can be dispersed uniformly. However, MnS does

not crystallize and/or precipitate on the uniformly dispersed deoxidation particles, because MnS crystallizes and/or precipitates on only oxide particles located in the region of final solidification, such as the interdendritic region.

During the cooling to lower temperature at slow cooling rate and high sulfur content, the precipitation of MnS occurs on all the deoxidation particles dispersed uniformly. In the case of desulfurized steels, the complex oxysulfide (Mg, Mn)(S, O) particles crystallize by Mg deoxidation. These particles result in nonuniform dispersion as a result of particle pushing to the region of final solidification, if the dissolved S content is high such as above a few 100 ppm.⁸⁾

In most of the published studies^{6,7)} on the precipitation of MnS by using oxide particles, the S content is low and the dispersion behavior of MnS particles in matrix has not been examined. The present investigation was undertaken with the purpose of studying the possibility of uniform dispersion of MnS by utilizing primary deoxidation particles. An Fe–10mass%Ni alloy containing 1 mass%Mn was deoxidized with Zr, Al, Mg and Si at 1873 K and the effect of these deoxidation products on MnS crystallization and/or precipitation was studied as a function of S content with particular emphasis on the particle dispersion in microsegregation domain in nondendritic solidification.

2. Experimental

2.1. Procedure

An Fe–10 mass%Ni–1 mass%Mn alloy (70 g) containing

the initial oxygen content of 100 to 120 mass ppm was melted at 1873 K in an alumina crucible using an induction furnace (100 kHz) with a graphite susceptor. (% and ppm represent mass% and mass ppm, respectively, hereinafter.) A melt was deoxidized with an Fe–10%Zr, Fe–10%Al or Fe–40%Mn–20%Si alloy, followed by the addition of an Fe–1 to 10%S alloy in an appropriate proportion and then a sample was cooled from 1873 to 1673 K at the average cooling rate of $50 \text{ K} \cdot \text{min}^{-1}$, followed by rapid quenching. The solidification velocity, V , at this cooling rate was estimated as $5.50 \mu\text{m} \cdot \text{s}^{-1}$ from the equation: $V = d_2 / (2\theta)$, where d_2 and θ are the secondary dendrite arm spacing and local solidification time, respectively. In the case of Mg deoxidation experiments, an Fe–10%Ni (70 g) or Fe–10%Ni–1%Mn (70 g) alloy was deoxidized at 1873 K with a Ni–10%Mg alloy, followed by cooling to 1673 K at $50 \text{ K} \cdot \text{min}^{-1}$.

In the experiments without addition of deoxidant, which is denoted by without oxide experiment in this paper, an Fe–10%Ni–1%Mn alloy containing the initial O content of 100 to 120 ppm was deoxidized at 1873 K with an Fe–10%Al alloy so that the Al content is 0.1 %. Then, an alloy was held at 1873 K for 30 minutes to remove deoxidation particles by flotation as much as possible. After the addition of an Fe–1 to 10%S alloy to control the S level, a melt was cooled to 1673 K at $50 \text{ K} \cdot \text{min}^{-1}$.

The effect of holding time at 1673 K on the precipitation of MnS was studied in the experiment where an Fe–10%Ni–1%Mn alloy deoxidized with an Fe–10%Zr alloy at 1873 K was cooled to 1673 K at $50 \text{ K} \cdot \text{min}^{-1}$ and then held for 1 h, followed by rapid quenching. For the purpose of comparison, the effect of holding time at 1673 K was also studied in the experiment without deoxidant addition. The shape of a quenched sample was the frustum with the top (28 mm) and bottom diameters (16 mm) and the height (20 mm). The quenched sample was sliced vertically with 2–3 mm thickness and these sliced samples in the region of 7 mm away from the crucible side were used for chemical analysis and observation of inclusion. The final solidification part which was located about 3 mm from the top was not used for the chemical analysis.

2.2. Chemical Analysis

The content of soluble and insoluble M (M=Mg, Al, Zr, Si and Mn) was determined by the method described elsewhere.⁹⁾ Total oxygen was analyzed by the method described elsewhere¹⁰⁾ and total sulfur was analyzed by oxygen gas fusion-infrared absorptiometry.

2.3. Measurement of Particle Size and Number

Particle size and number in a cross section was observed by a SEM at a magnification of 1000. In this method the particles above $0.5 \mu\text{m}$ can be estimated. The areas from 7 and 5 mm from top and bottom of samples, respectively were observed for inclusion characteristics. The observed area of each position was 0.25 mm^2 which corresponds to the 24 observation areas consisting of the continuous 6 observation areas to the horizontal direction and the continuous 4 observation areas to the vertical direction. Further details of this method can be found elsewhere.⁹⁾ Morphologies of oxide, MnS, (Mn, Mg)S and the mixture

of sulfide and oxide particles are observed in three dimensions by slightly etching the sample surface with 10 % iodine-methanol for 1 to 3 min.

2.4. Measurement of Particle Dispersion in Microsegregation Domain

The solidification microstructure in a polished cross section was observed by etching with an Oberhoffer solution. Then four corners in the region of $500 \times 400 \mu\text{m}$ square were marked by a Vickers hardness tester and after polishing again particles are observed by a SEM, followed by etching in an Oberhoffer solution to reveal solidification structure. The correlation between particle dispersion and solidification microstructure was studied by superimposing the photomicrographs taken before and after etching in the marked region of a cross section. The fraction of solid in microsegregation of domain nondendritic solidification was determined by the method described elsewhere.⁸⁾

3. Results and Discussion

3.1. Crystallization of MnS during Solidification

Crystallization and precipitation of MnS during solidification and subsequent cooling is discussed based on microsegregation of Mn and S below. The concentrations of Mn and S in liquid and solid (γ) phases at solidification interface are estimated by the microsegregation model proposed by Brody and Flemings¹¹⁾ as follows:

$$C_L = C_0 [1 - (2\alpha k) f_S]^{(k-1)/(1-2\alpha k)} \dots\dots\dots (1)$$

and

$$C_S^* = k C_L \dots\dots\dots (2)$$

where C_L is the solute concentration in liquid phase, C_S^* is the solute concentration in solid (γ) phase at solid/liquid interface, C_0 is the initial solute concentration, k is the equilibrium partition coefficient ($k_{\text{Mn}} = 0.85^{12)}$ and $k_S = 0.05^{12)}$, f_S is the fraction of solid, $\alpha = D_S \cdot \theta_S / L^2$ (D_S : the diffusion constant in solid Fe(γ), $D_{\text{Mn}} = 0.35 \mu\text{m}^2 \cdot \text{s}^{-1}$ ¹³⁾ and $D_S = 81 \text{ mm}^2 \cdot \text{s}^{-1}$ ¹³⁾), θ_S is the local solidification time (10 s) and L is the half of the solidification domain ($50 \mu\text{m}$).

The solubility products of $[\% \text{Mn}]_L \cdot [\% \text{S}]_L$ at 1773 K obtained from Eq. (1) by using the initial content of 1 % Mn and the initial content of 0.01, 0.05 and 0.1 % are plotted against fraction of solid in the upper diagram of **Fig. 1**. The equilibrium solubility product of MnS in liquid Fe, $K_{\text{eq},(L)}$, at 1773 K which is the starting temperature of solidification is calculated from Eq. (3) and given by the broken line.

$$\text{MnS} = \underline{\text{Mn}}_{\text{in Fe}(l)} + \underline{\text{S}}_{\text{in Fe}(l)} \dots\dots\dots (3)$$

$$\log K_{\text{eq},(L)} = - \frac{6890}{T} + 4.16^{14)}$$

In the case of the initial content of 1 % Mn and the initial content of 0.1 %, MnS crystallizes in the range of $f_S > 0.85$. It should be pointed out based on the calculated result that oxide particles dispersed in the range of $f_S < 0.85$ are not utilized as heterogeneous nucleus for the crystallization of MnS.

The solubility product of $[\% \text{Mn}]_\gamma \cdot [\% \text{S}]_\gamma$ at 1773 K ob-

Fig. 1. Relationship between solubility product of MnS and fraction of solid calculated at 1773 K from the Brody and Flemings model.¹¹⁾

tained from Eq. (4) are plotted against fraction of solid in the lower diagram of Fig. 1, as a function of the initial contents of 0.1, 0.05 and 0.01 S%. The equilibrium solubility products, $K_{eq(\gamma)}$, in γ phase calculated from Eq. (4) are shown by the broken lines at 1773 K.

$$\text{MnS} = \underline{\text{Mn}}_{\text{in Fe}(\gamma)} + \underline{\text{S}}_{\text{in Fe}(\gamma)} \dots \dots \dots (4)$$

$$\log K_{eq(\gamma)} = -\frac{9230}{T} + 3.02^{15)}$$

In the case of the initial contents of 1% Mn and 0.1% S which are used in the present study, the precipitation of MnS occurs in the range of $f_s > 0.3$. However, it was found experimentally that MnS does not precipitate in such a low value of f_s in the presence of ZrO_2 or Al_2O_3 particles, as explained in Sec. 3.2. This suggests that high degree of supersaturation is necessary for the precipitation of MnS.

Relationship between dissolved S and dissolved Mn contents is shown in **Fig. 2**, along with the line of the equilibrium solubility product given in Eq. (4). The experimental data were obtained in the experiments where an Fe–10%Ni–1%Mn alloy containing 100 to 120 ppm O was deoxidized with Zr, Al or Mn/Si and cooled to 1673 K, followed by rapid quenching (the open marks) or followed by holding one hour (the half-filled marks). The chemical compositions are summarized in **Table 1**. The dissolved S content ([sol. S]) was determined from Eq. (5) by using the chemically analyzed values for total S content ([T. S]) and insoluble Mn content ([insol. Mn]), provided that only MnS is produced as a sulfide.

$$[\text{sol. S}] = [\text{T. S}] - [\text{insol. Mn}] \cdot M_S / M_{\text{Mn}} \dots \dots \dots (5)$$

where M_S and M_{Mn} are the atomic weight of S and Mn, respectively.

Based on the results shown in Fig. 2, in which the present experimental solubility products are higher than the equilibrium one, it can be concluded that the precipitation of MnS does not proceed unless the enrichment of Mn and S

Fig. 2. Relationship between dissolved S and dissolved Mn contents in Zr, Al and Si/Mn deoxidation experiments.

Table 1. Chemical compositions of metal phase in Zr, Al and Si/Mn deoxidation experiments for Fe–10mass%Ni alloy.

Cooling rate : 50K·min ⁻¹						
Deoxidant	[T. S]	[T. O]	[M]		[Mn]	
			Sol.	Insol.	Sol.	Insol.
(Mass ppm)			(Mass ppm)			
(M = Al)						
—	106	21	811	9.0	9120	16.0
	248	21	857	15.1	9060	147
	342	20	904	14.0	8620	453
	* 332	18	948	8.0	8920	462
	* 375	21	809	20.3	8740	548
(M = Zr)						
0.05% Zr	19	79	80.6	412	8990	11.4
	71	67	68.3	334	9800	30.9
	165	87	89.7	337	9000	133
	345	96	78.6	270	9510	424
	* 112	89	45.5	452	9390	81.9
	* 433	94	57.8	322	8890	651
(M = Al)						
0.05% Al	7	60	328	94.6	9276	2.5
	79	66	348	73.8	9356	11.4
	157	77	376	76.0	8819	88.0
	298	74	374	69.2	9636	278
(M = Si)						
0.5% Si + 1% Mn	13	95	4220	27.7	9880	37.3
	96	83	4610	15.9	9610	81.3
	186	77	4710	23.2	9786	102
	304	63	4580	27.1	9310	345

* ; 1 hour holding experiments at 1673K

as a result of solute microsegregation is taken into consideration. The data for the solubility products obtained at one hour holding time at 1673 K approach the equilibrium line.

When the oxide particles are used as nucleus of crystallization and/or precipitation of MnS, to understand the effect of chemical composition of oxide on the precipitation is of crucial importance. The lattice misfit parameters (misfit) obtained from Eq. (6) are shown in **Fig. 3** for the misfit between MnS and oxides (nitrides, carbides and sulfides).

The lattice misfit parameter is defined by the following

Fig. 3. Misfit parameters for the precipitation of MnS particles.

relation.¹⁶⁾

$$\text{Misfit} = 2 \frac{|X_{\text{MnS}} - X_{\text{Oxide}}|}{(X_{\text{MnS}} + X_{\text{Oxide}})} \dots\dots\dots (6)$$

where X_{MnS} and X_{Oxide} are the lattice distance and the lattice diagonal distance of MnS and oxide, respectively.

The misfit parameters shown in Fig. 3 correspond to the minimum value among various combinations of X_{MnS} and X_{Oxide} in Eq. (6). The calculated results of monoclinic and tetragonal ZrO_2 and that of cubic and hexagonal AlN are shown in Fig. 3. It follows that the misfit parameter of ZrO_2 is significantly smaller than those of MgO and Al_2O_3 .

3.2. Effect of ZrO_2 and Al_2O_3 Particles on Crystallization and Precipitation of MnS

An Fe-10%Ni-1%Mn alloy containing 70 to 100 or 300 to 350 ppm S was deoxidized with Zr or Al at 1873 K and cooled to 1673 K at $50 \text{ K} \cdot \text{min}^{-1}$. On the basis of the microscopic observation in a polished cross section, the effect of ZrO_2 and Al_2O_3 particles on the crystallization and precipitation of MnS has been studied by comparing with the results without deoxidant addition. It cannot be clarified whether the observed MnS is formed by the crystallization and/or precipitation. Therefore, the precipitation used in this text denotes the crystallization and/or precipitation, hereinafter, unless otherwise stated. It was observed that MnS and MnS precipitated on ZrO_2 or Al_2O_3 particles are present at the region of final solidification, i.e., the interglobular region, together with the deoxidation particles dispersed uniformly in microsegregation domain. The N_A values for MnS and MnS/oxide particles are shown in Fig. 4 at low (70 to 100 ppm) and high (300 to 350 ppm) S levels. The N_A value for MnS/ ZrO_2 particles is significantly higher than that for MnS/ Al_2O_3 particles, which is clear from the misfit parameters shown in Fig. 3. The N_A value for MnS particles increases with an increase of S from 70–100 to 300–350 ppm. In the case of ZrO_2 particles, however, the N_A value for MnS particles is about twice greater than that for without deoxidant. The reason for this is not clear, but it is considered that fine ZrO_2 particles located in the interglobular region act as a nuclei for the precipitation of MnS.

The size distributions of ZrO_2 and MnS/ ZrO_2 particles

Fig. 4. Number of MnS and MnS/oxide particles per unit area for Zr and Al deoxidations at low and high S contents.

Fig. 5. Size distribution of oxide and MnS/oxide particles for Zr and Al deoxidations.

and those of Al_2O_3 and MnS/ Al_2O_3 particles are shown in the upper and lower diagrams of Fig. 5, respectively, along with the size distribution of ZrO_2 or Al_2O_3 particles obtained in the experiments without S addition represented by the line. It is apparent from the upper diagram that the size distributions of ZrO_2 and MnS/ ZrO_2 particles at [ppm S]=71 and 165 are in good agreement with that of ZrO_2 particles obtained without S which are represented by the line. This finding suggests that almost all ZrO_2 particles are utilized as a nuclei for the precipitation of MnS during cooling to 1673 K.

As explained later in this section, the ZrO_2 particles are pushed to the interglobular region at high S level and subsequently coagulated, as is apparent from the size distribution observed at [ppm S]=345 represented by the triangles. These coagulated large particles are also used for a nuclei for the precipitation of MnS. As a result of this, the number of particles decreases and their size increases in the case of high S level. The results shown in the lower diagram for

Fig. 6. Relationship between number of MnS and MnS/oxide particles per unit area and fraction of solid in Zr, Al and Mn/Si deoxidations.

Al_2O_3 particles indicate that Al_2O_3 particles with high misfit parameter do not act as a nuclei for the precipitation of MnS. The Al_2O_3 particles are pushed to the region of final solidification even at low S level and then coagulated. In previous study,⁸⁾ it was shown that the Al_2O_3 particles are more easily pushed at lower S level in comparison with the ZrO_2 particles. These coagulated particles are not utilized as a nuclei for the precipitation of MnS, as is clear from the N_A value for MnS/ Al_2O_3 particles in Fig. 4.

The dispersion of MnS and MnS/oxide (ZrO_2 , Al_2O_3 and MnO-SiO_2) particles in microsegregation domain has been studied and the numbers of MnS and MnS/oxide particles are plotted against fraction of solid at low and high S levels in the upper and lower diagrams of **Fig. 6**, respectively. As reported in a separate paper,⁸⁾ oxide particles except for Al_2O_3 particles are not pushed in low S content of 70 to 100 ppm and hence oxide particles are dispersed homogeneously in solidification domain. The crystallization and/or precipitation of MnS occurs at the region of final solidification and the ZrO_2 particles are effectively utilized as a nuclei. The results for MnO-SiO_2 particles show a different trend; that is, the N_A values for MnS and MnS/ MnO-SiO_2 particles are independent of fraction of solid. The reason for this is explained in Sec. 3.4.

In the case of high S level shown in the lower diagram, the oxide particles are pushed to the interglobular region and the number of oxides decreases due to the coagulation. Therefore, the values for N_A of (MnS and MnS/Oxide) particles are nearly the same for ZrO_2 , Al_2O_3 and MnO-SiO_2 particles and equal to that for the without oxide experiments. A large amount of MnO-SiO_2 particles containing MnS is present in the range of $f_s < 0.8$, which implies that the MnO-SiO_2 particles are not completely pushed to the interglobular region compared with other oxides due to low dissolved S content.

On the basis of the size distribution of ZrO_2 and MnS/ ZrO_2 particles shown in the upper diagram of Fig. 5,

Fig. 7. Number of oxide (total ZrO_2 and MnS/ ZrO_2) and MnS (total MnS and MnS/ ZrO_2) particles per unit area at different total S contents in Zr deoxidation.

the N_A values for these particles are plotted at three different S levels in the upper diagram of **Fig. 7**. As a result of particle pushing at high S level (345 ppm), the N_A value for ZrO_2 and MnS/ ZrO_2 particles decreases markedly, but the N_A value for MnS/ ZrO_2 particles does not depend on the S content.

As is clear in the lower diagram, the N_A value for MnS and MnS/ ZrO_2 particles increases with an increase in S content, but the N_A value for MnS/ ZrO_2 particles remains constant. The N_A value for MnS particles in the experiments without deoxidant addition in which the sulfur content is 100 ppm and 250 ppm are 4 and 270 mm^{-2} , respectively. When comparison is made for a given S level, the N_A value for MnS particles are considerably higher than that for MnS particles in the experiment without oxide addition. This can be explained by the following two reasons:

- It was found that MnS particles are located mostly at the region of final solidification which coincides with the initial austenite grain boundary. This coincidence is found in the case that the austenite grain growth is inhibited by ZrO_2 particles. The precipitation of MnS at grain boundaries seems to be favorable in the case that grain boundaries coincide with the interglobular region where solutes of Mn and S are enriched due to microsegregation.
- Fine ZrO_2 particles located in the interglobular region, which could not be detected in this study, act effectively as a nuclei for the precipitation of MnS, since ZrO_2 particle has a low lattice misfit with respect to MnS.

It is well known that the morphology of MnS can be classified into a spherical (Type I), rod-like (Type II) and polyhedral (Type III) shape. The morphology of MnS has been studied by etching the cross section with 10% iodine-methanol to dissolve Fe matrix preferentially around the MnS precipitates, thus resulting in the three-dimensional observation by a SEM. The rod-like MnS was observed

Fig. 8. Change of morphology of MnS obtained 1 h holding at 1 673 K, (a) MnS precipitated in cluster at interglobular region (S=370 ppm), (b) MnS precipitated around ZrO_2 particles which are pushed to the interglobular region (S=433 ppm).

without respect to S content for the samples deoxidized with Al and Zr, which was quenched at 1 673 K. The morphology of MnS in Mg deoxidation experiment is also rod-like, but that in Si/Mn deoxidation is spherical. These results are consistent with the previous results¹⁷⁾ in which the morphology of MnS is influenced by the oxygen content. This was confirmed in the experiment where Fe_2O_3 was added after Al deoxidation in an Fe–10%Ni–1%Mn–266 to 298ppmS alloy, that is, rod-like MnS changes to spherical MnS by increasing the dissolved O contents from 1 to about 100 ppm.

An Fe–10%Ni–1%Mn–370 to 430ppmS alloy deoxidized with Zr or without deoxidation was cooled from 1 873 to 1 673 K and then held for one hour, followed by rapid quenching. The dispersion and morphology of particles were studied in a polished cross section and by etching with 10% iodine-methanol which are shown on the right-hand side and left-hand side of **Fig. 8**, respectively. It can be seen from the upper diagram obtained without deoxidant addition that rod-like MnS precipitated in the interglobular region during cooling to 1 673 K changes to polyhedral MnS with 1 to 2 μm size during holding for one hour at 1 673 K. Similarly, as shown in the lower diagram obtained in Zr deoxidation during cooling to 1 673 K, rod-like MnS and rod-like MnS precipitated around ZrO_2 particles, which are located in the interglobular region, change to spherical MnS. This spherical MnS with the size of 5 to 10 μm are formed around the clustered ZrO_2 particles which are pushed to the region of final solidification, as shown on the

Table 2. Chemical compositions of metal phase in Mg deoxidation experiment for Fe–10mass%Ni(–1 mass%Mn) alloy.

Cooling rate : 50K min ⁻¹						
Deoxidant	[T. S]	[T. O]	[Mg]		[Mn]	
			Sol.	Insol.	Sol.	Insol.
			(Mass ppm)		(Mass ppm)	
0.1% Mg	8	86	139	129	—	—
	58	74	124	153	—	—
	125	67	101	195	—	—
	293	72	3.1	273	—	—
	565	86	1.4	350	—	—
	64	71	57.1	189	9140	33.0
	320	73	6.7	343	8990	46.0
	328	77	3.0	287	8530	67.0

right-hand side of lower diagram of **Fig. 8**. It is of interest to note that in the presence of clustered ZrO_2 particles, the isolated rod-like MnS dissolves and the precipitation of MnS occurs around the clustered ZrO_2 particles. The growth of spherical MnS particles in the presence of ZrO_2 particles was found to be faster than that of MnS particles in the absence of oxide particles.

3.3. Influence of Mg Deoxidation on Crystallization of MnS

It has been well established that a large amount of fine MgO particles can be produced by Mg deoxidation.^{18,19)} The chemical compositions of metal phase in Mg deoxidation are summarized in **Table 2**. If a steel containing S is deoxidized with Mg, magnesium sulfide as well as MgO particles are formed. Therefore, the crystallization behavior of MnS in Mg deoxidation is basically different from that in Zr and Al deoxidations, as described in Sec. 3.2.

The lattice misfit parameter between MnS and MgO is considerably higher than that of ZrO_2 and slightly higher than that of Al_2O_3 , as shown in **Fig. 3**. The MgS, MgO and mixture of MgS/MgO particles are formed depending on the contents of Mg, S and O during Mg deoxidation. In the presence of Mn in steel, MnS, (Mg, Mn)S and (Mg, Mn)S/MgO are formed in addition to MgO, MgS and MgS/MgO particles.

An Fe–10%Ni alloy containing different S contents was deoxidized with Mg at 1 873 K and cooled to 1 673 K at 50 K · min⁻¹, followed by rapid quenching. The results for N_A and $\bar{d}_A$ for MgO particles and the sum of MgS and MgS/MgO particles are plotted against total S content in **Fig. 9**. It should be noted that the classification of MgS and MgS/MgO particles could not be made by a microprobe analysis in this study. In the range of total S below about 100 ppm, the N_A values for MgO particles decrease rapidly and those for the mixture of MgS and MgS/MgO particles increase rapidly. In the range of total S above about 100 ppm, the N_A values for both particles decrease gradually and the $\bar{d}_A$ values for both particles increase with an increase in total S content. This observed behavior can be explained by the particle pushing phenomenon in which MgO, MgS and MgS/MgO particles are pushed to the region of final solidification in the range of above a certain

Fig. 9. Effect of total S content on N_A and $\bar{d}_A$ for MgO and mixture of MgS and MgS/MgO particles.

Fig. 10. Size distribution of total and mixture of MgS and MgS/MgO particles at low and high total S levels.

S level and subsequently coagulated. This phenomenon is already described in detail elsewhere.⁸⁾ The sulfur level for particle engulfment and pushing transition could not be determined in the Mg deoxidation experiments, because the amount of magnesium sulfide increased with increasing sulfur content.

The size distributions of total particles of MgO, MgS and MgS/MgO and the mixture of MgS and MgS/MgO particles are shown in Fig. 10 at low (58 ppm) and high (565 ppm) total S levels. It can be seen that at high total S level the MgO, MgS and MgS/MgO particles with a large size of 2 to 6 μm increase due to the particle coagulation as a result of particle pushing. At low total S level in which no particle pushing occurs, the N_A values for MgO particles below 1 μm are large and the N_A values for MgS and

Fig. 11. Dispersion of MgO and mixture of MgS and MgS/MgO particles in microsegregation domain at 75 (upper diagram) and 565 (lower diagram) ppm total S levels.

MgS/MgO particles above 1.5 μm are large.

The numbers of MgO and the mixture of MgS and MgS/MgO particles in microsegregation domain are plotted against fraction of solid in Fig. 11 at low (58 ppm) and high (565 ppm) total S levels. At low total S level shown in the upper diagram which corresponds to no particle pushing, the numbers of MgO and the mixture of MgS and MgS/MgO particles in the range of $f_s=0.8$ to 1.0 are slightly higher than those in the range of $f_s<0.8$. At high total S level shown in the lower diagram which corresponds to the particle pushing, the N_A values for MgO and the mixture of MgS and MgS/MgO particles, in particular, those for the mixture of MgS and MgS/MgO particles are high at $f_s=0.8$ to 1.0, but very low in the range of $f_s<0.8$ to 1.0. Total number of particles at $f_s=0.8$ to 1.0 are nearly the same for low and high total S levels, but that in the range of $f_s<0.8$ to 1.0 for high total S level is considerably smaller than that for low total S level. This finding indicates that the particle pushing occurs at high total S level and then the particle coagulation occurs during pushing and/or at the region of final solidification.

An Fe-10%Ni-1%Mn alloy containing different S contents was deoxidized with Mg at 1873 K and cooled to 1673 K at 50 K·min⁻¹, followed by rapid quenching. The numbers of MgO, the mixture of MgS and MgS/MgO, the mixture of (Mg, Mn)S and (Mg, Mn)S/Mg and MnS particles are shown in Fig. 12 at three total S levels (12, 64 and 320 ppm). The classification of (Mg, Mn)S and (Mg, Mn)S/MgO particles was difficult to make by a microprobe analysis in this study. At the level of 64 ppm total S, the crystallization of MgS on MgO particles occurs. Since this results in the decrease in dissolved S content, MnS does not crystallize and/or precipitate in the interglobular region. At high total S level (320 ppm), the MgS particles crystallized on MgO particles are pushed to the region of final solidification where MnS precipitates independently and/or preferentially around the pushed particles. When an Fe-10%Ni alloy containing high contents of Mn and S is deoxidized with Mg, the (Mg, Mn)S particles crystallize on MgO particles because the chemical potential of MnS decreases by the formation of solid solution of MgS-MnS system.

Fig. 12. Number of MgO, sulfide, mixture of MgO and sulfide and MnS particles per unit area for different total S contents in Mg deoxidation experiment.

Fig. 13. Dispersion of MgO, sulfide, mixture of sulfide and MgO, and MnS particles per unit area in microsegregation domain at 64 and 320 ppm total S levels.

The number of MgO, sulfide and mixture of sulfide and MgO, and MnS particles in microsegregation domain are shown as a function of fraction of solid in **Fig. 13** at low (64 ppm) and high total S (320 ppm) contents. The dispersion behavior shown in the upper diagram has a similar trend observed in the dispersion behavior in the experiments without Mn shown in the upper diagram of **Fig. 11**. The MgO and the mixture of MgS and MgS/MgO particles are dispersed homogeneously in microsegregation domain. From the results of high total S level shown in the lower diagram, the MgO and the mixture of MgS and MgS/MgO particles are pushed to the region of final solidification where MnS precipitates. The fact that the (Mg, Mn)S and (Mg, Mn)S/MgO particles are observed in the range of $0.4 < f_s < 0.8$ indicates that the (Mg, Mn)S particles in addition to MgS particles crystallize on MgO particles immediately after the Mg addition.

3.4. Influence of Mn/Si Deoxidation on Crystallization of MnS

An Fe–10%Ni–1%Mn alloy containing different S con-

Fig. 14. SEM micrograph of MnO–SiO₂/MnS complex particles: (a) 96 and (b) 304 ppm total S levels.

tents is deoxidized with Si/Mn at 1873 K and cooled to 1673 K at $50 \text{ K} \cdot \text{min}^{-1}$, followed by rapid quenching. The chemical composition of metal phase are summarized in Table 1.

It can be seen from the MnO–SiO₂–MnS phase diagram²⁰⁾ that the wide region of liquid state is present even at lower temperature and the solubility of MnS in this liquid region is high. Sulfide capacity which increases with increasing MnO content, low oxygen content and high sulfur content in steel are necessary to have high solubility of MnS in liquid MnO–SiO₂ particles.

According to SEM micrograph observation, the MnS, MnO–SiO₂ and MnO–SiO₂/MnS particles are observed at low total S level (96 ppm), as shown in **Fig. 14(a)**. At high total S level (304 ppm), the MnS and MnO–SiO₂/MnS particles are observed, as shown in **Fig. 14(b)**. It is considered that the MnS on the surface of a MnO–SiO₂ particle arises from the crystallization of MnS during cooling and the precipitation of MnS during cooling to 1673 K and rapid quenching. As shown in **Fig. 6**, the particle pushing occurs at high S level, but the coagulation of MnS and MnO–SiO₂ particles in the region of final solidification does not occur due to lower interfacial energy between liquid Fe and MnO–SiO₂/MnS oxide, thus leading to the presence of small MnS particles.

The N_A values for MnO–SiO₂ and MnO–SiO₂/MnS oxide particles are plotted against total S content in the upper diagram of **Fig. 15**. It is seen that with increasing total S content the number of total oxides remains constant, which is completely different behavior, compared with that for Zr, Mg and Al deoxidations. This is because no coagulation of MnO–SiO₂/MnS particles takes place although the particles are pushed to the region of final solidification at high S level. This different behavior can be interpreted by the fact that the interfacial energy between solid Al₂O₃, ZrO₂ or MgO oxide and liquid Fe is higher than that between liquid MnO–SiO₂ oxide and liquid Fe.

A plot of the N_A values for MnS and MnO–SiO₂/MnS sulfide particles versus total S content is shown in the lower diagram of **Fig. 15**. The number of MnO–SiO₂/MnS particles is independent of S content, but the number of MnS precipitated at interglobular region increases with S content. The MnS precipitates during cooling to 1673 K and/or

Fig. 15. Number of oxide (MnO-SiO₂ and MnO-SiO₂/MnS) and number of MnS (MnS and MnO-SiO₂/MnS) particles per unit area at different total S contents in Si/Mn deoxidation.

rapid cooling due to low solubility of MnS in solid MnO-SiO₂ particles. This is observed on the pushed MnO-SiO₂ particles, as shown in Fig. 14(b). However, in addition to these particles the MnS particles with the size of 0.3–0.5 μm precipitate at the interglobular region with increasing S content.

The N_A value for MnO-SiO₂ and MnO-SiO₂/MnS particles is plotted against total S content in the upper diagram of Fig. 16, along with the results for ZrO₂ and Al₂O₃ particles. The N_A value for MnO-SiO₂ particles does not depend on total S level, but the N_A values for ZrO₂ and Al₂O₃ particles decrease in the range of above a certain level of total S. The results for Al₂O₃ and ZrO₂ particles are already explained by the coagulation of particles as a result of particle pushing. Although the increase in $\bar{d}_A$ for Al₂O₃ particles cannot be clearly observed in the range between 10 and 100 ppm S, the sudden increase in N_A are observed in this range.

The $\bar{d}_A$ value for MnO-SiO₂ and MnO-SiO₂/MnS oxide particles is shown in the lower diagram of Fig. 16, together with the results for Al₂O₃ and ZrO₂ particles. The gradual increase of $\bar{d}_A$ with total S content for MnO-SiO₂ particles is different from the slight increase of $\bar{d}_A$ observed for Al₂O₃ and ZrO₂ particles. The reason for the gradual increase in $\bar{d}_A$ with total sulfur content can be explained as follows; the sulfur contents in MnO-SiO₂ increase with increasing total S content, followed by the precipitation of MnS on MnO-SiO₂ particles during cooling. In the case of Al₂O₃ and ZrO₂ particles, the MnS particles precipitate on oxide in the region of final solidification during cooling, thus resulting in the increase of $\bar{d}_A$.

The N_A values for MnO-SiO₂ and MnO-SiO₂/MnS particles in microsegregation domain are plotted against fraction of solid as a function of S content in Fig. 17. The result for total S of 304 ppm in which the N_A value is high at $f_s=0.8$ to 1.0 indicates that the particles are not coagulated despite of the particle pushing to interglobular region. The N_A

Fig. 16. Effect of total S content on N_A (upper diagram) and $\bar{d}_A$ (lower diagram) for ZrO₂, Al₂O₃ and MnO-SiO₂ particles.

Fig. 17. Dispersion of MnO-SiO₂ and MnO-SiO₂/MnS particles in microsegregation domain at different total S content in Si/Mn deoxidation.

value for MnS and MnO-SiO₂/MnS particles in microsegregation domain is shown in Fig. 6. At low total S level shown in the upper diagram of Fig. 6, the MnO-SiO₂ particles are dispersed uniformly in microsegregation domain. However, at high total S level of 300 to 350 ppm shown in the lower diagram, the MnS with $N_A=300 \text{ mm}^{-2}$ is obtained in Si-Mn deoxidation, whereas that with $N_A=500 \text{ mm}^{-2}$ is obtained in the experiment without deoxidants.

It can be concluded that only MnO-SiO₂ particles containing MnS can be dispersed uniformly in microsegregation domain when the S level is below the critical S level at which no particle pushing occurs. In this case, however, the particle number cannot be increased and the particle size

cannot be decreased due to the characteristic of Mn/Si de-oxidation.

4. Conclusions

The uniform dispersion of MnS has been studied by using the deoxidation products of ZrO_2 , MgO , Al_2O_3 and $MnO-SiO_2$ particles in an Fe-10%Ni alloy and the results are summarized as follows:

(1) Since the crystallization and/or precipitation of MnS occur only on ZrO_2 or Al_2O_3 particles located in the region of final solidification, MnS cannot be uniformly dispersed in microsegregation domain even if the dissolved S level is low enough for particles not to be pushed.

(2) Since the partition of the dissolved S between steel and liquid $MnO-SiO_2$ particles occurs and the precipitation of MnS occurs during cooling, MnS-containing $MnO-SiO_2$ particles can be uniformly dispersed in microsegregation domain if the dissolved S level is low enough for particles not to be pushed.

(3) In the case of Mg deoxidation, MgS and/or (Mg, Mn)S crystallize on MgO particles. If the dissolved S content is high, the MgO, MgS/MgO and (Mg, Mn)S/MgO particles are pushed to the region of final solidification where MnS crystallizes and/or precipitates.

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