Effects of cooling rate and Al on MnS formation in medium-carbon non-quenched and tempered steels

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Abstract: The effect of Al on the morphology of MnS in medium-carbon non-quenched and tempered steel was investigated at three different cooling rates of 0.24, 0.43, and 200°C·s⁻¹. The formation mechanisms of three types of MnS were elucidated based on phase diagram information combined with crystal growth models. The morphology of MnS is governed by the precipitation mode and the growth conditions. A monotectic reaction and subsequent fast solidification lead to globular Type I MnS. Type II MnS inclusions with different morphological characteristics form as a result of a eutectic reaction followed by the growth in the Fe matrix. Type III MnS presents a divorced eutectic morphology. At the cooling rate of 0.24°C·s⁻¹, the precipitation of dispersed Type III MnS is significantly enhanced by the addition of 0.044wt% acid-soluble Al (Al_s), while Type II MnS clusters prefer to form in steels with either 0.034wt% or 0.052wt% Al_s. At the relatively higher cooling rates of 200°C·s⁻¹ and 0.43°C·s⁻¹, the formation of Type I and Type II MnS inclusions is promoted, and the influence of Al is negligible. The results of this work are expected to be employed in practice to improve the mechanical properties of non-quenched and tempered steels.

Keywords: medium carbon steels; cooling rate; aluminum content; manganese sulfide; formation mechanisms

1. Introduction

Non-quenched and tempered steel is widely used in the forging parts of automobiles, such as connecting rods and crankshafts, because it has the advantages of energy-savings and high strength. To further reduce costs, the free-cutting element S is usually added to form MnS inclusions for the purpose of improving machinability [1–3]. Since the machinability and mechanical properties of steels are significantly affected by the morphology and distribution of MnS inclusions, numerous studies have focused on the formation mechanism and shape control of MnS for years [4–11]. According to the classic work by Sims and Dahle [8], MnS can be broadly classified by morphology into three types: (1) globular MnS (Type I); (2) fine rod-like MnS (Type II); and (3) angular MnS (Type III). In addition to these types,

sheet-like MnS (Type IIS) and faceted MnS (Type IIF) have been described in later studies [9]. However, the mechanism of morphology evolution and the modification by various added elements still remain controversial. The additions of Al, C, and Si are generally considered to induce a change in MnS from Type II to Type III [8–9]; however, the functional mechanism of Al remains uncertain. To explain the effect of Al, two main theories have been proposed as: (1) Fredriksson and Hillert [9] suggested that the melting point of steel decreased with the addition of Al, promoting the precipitation of Type III MnS; and (2) Oikawa *et al.* [10] reported that Al₂O₃(s), which formed in the melts with increasing aluminum content, acted as the nucleant for rod-like MnS. The discrepancy between these two mechanisms may arise from the different steel compositions. Nevertheless, only a few of the previous studies have taken the

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effect of cooling rate into account. Mohla and Beech [11] reported that high cooling rates gave rise to Type II MnS, although the equilibrium type was either Type I or Type III. Wang *et al.* [12] verified that cooling rate was one of the important factors in determining the free-cutting phase BN, which was similar to MnS. However, these works largely neglect the relationship between cooling rate and alloy elements. In addition, some studies [13–14] have proposed that the morphology of an inclusion depends not only on its crystal structure, but also on the activities in the steel bath.

Although some previous investigations have been carried out, studies on the conditions suitable to control sulfide morphology in non-quenched and tempered steel are still lacking. In non-quenched and tempered steel, MnS may cause the deterioration of transverse impact properties because the MnS inclusions become relatively large and elongated in the hot rolling or forging direction. According to the differences in morphology and distribution among various types of MnS, Type I and Type III MnS are more beneficial compared with Type II MnS due to their appropriate sizes and uniform distributions [15–18]. As a consequence, studies on classifying and controlling MnS in non-quenched and tempered steel are necessary.

In the present work, the effects of cooling rate and Al on the morphology of MnS in medium-carbon non-quenched and tempered steel were investigated to elucidate the formation mechanisms of different types of MnS by phase diagram information for the first time calculated by Thermo-Calc software and experimental techniques. The optimal cooling rate and Al content proposed in this paper were useful for improving both MnS morphology and distribution in steel production.

2. Experimental

The composition of the master alloy is shown in Table 1. The experimental steels were prepared using a vertical resistance furnace equipped with a PtRh30–PtRh6 thermocouple and an FP93 series automatic temperature controller with an accuracy of $\pm 2^\circ\text{C}$. About 310 g of master alloy was melted in an alumina crucible with a diameter of 40 mm and a depth of 125 mm under a purified argon gas atmosphere. After the stabilization of melt at 1600°C , 99.5wt% Al wire was added to adjust the content of acid-soluble Al (Al_s) in the melt. After holding at 1600°C for 10 min, three cooling modes were employed to get samples: (1) the melt in crucible was continuously cooled to room temperature in the furnace by turning off the power (furnace cooling, FC), resulting in an average cooling rate in the solidification range

of $0.24^\circ\text{C}\cdot\text{s}^{-1}$; (2) a portion of the melt was withdrawn into silica tubing by suction with a syringe and immediately quenched in water to form rod-shaped specimens (water cooling, WC); and (3) the crucible with the remaining melt was taken out and cooled to room temperature in air (air cooling, AC). The cooling rates of the WC and AC samples in the solidification range were $200^\circ\text{C}\cdot\text{s}^{-1}$ and $0.43^\circ\text{C}\cdot\text{s}^{-1}$, respectively; these values were calculated by finite element simulation software because it was difficult to measure the cooling rates directly. Table 2 shows the cooling conditions and Al_s contents of the prepared steels.

Table 1. Chemical composition of the master alloy wt%

C	Si	Mn	P	S	Al_s	V	T.O	N	Fe
0.45	0.45	1.36	0.035	0.055	0.019	0.100	0.0011	0.0068	Bal.

Table 2. Cooling conditions and Al_s content in steels

Sample No.	Cooling mode	Al_s content / wt%
1-F	FC	0.034
1-A	AC	0.034
1-W	WC	0.036
2-F	FC	0.044
2-A	AC	0.044
2-W	WC	0.044
3-F	FC	0.052
3-A	AC	0.052
3-W	WC	0.052

Inclusions in the mechanically polished samples were examined by scanning electron microscopy (SEM, JEOL JSM-6480LV) equipped with energy dispersive spectroscopy (EDS, Noran System Six). To measure the size and area fractions of inclusions, 15 images of each sample were processed using the image analysis software ImageJ. In addition, the compositions of over 100 inclusions in each sample were randomly measured by EDS.

The samples were first subjected to electrolytic etching with a 10% AA electrolyte (10vol% acetylacetone + 1wt% tetramethylammonium chloride + methanol solution) [19] to analyze the three-dimensional morphologies of inclusions by SEM. The following parameters of electrolytic etching were set as 0.45–1.00 A electric current, $0\text{--}5^\circ\text{C}$ temperature, and 120 s etching time. Tensile testing was also conducted using MTS 810 servo-hydraulic testing machines to obtain the fracture samples. Subsequently, the fracture surface analysis was carried out by SEM to reveal the morphologies and distributions of inclusions.

3. Results

3.1. Morphology and distribution of MnS inclusions

Fig. 1 shows the typical micrographs related to the mor-

phology and distribution of the inclusions. Hereafter, all inclusions were treated as MnS because about 95% of the total inclusions analyzed by EDS were pure MnS, which could be classified into different types according to the morphology and distribution. Type II MnS colonies with fan-like or chain-like morphologies dominate in all AC and WC samples at the cooling rates of $200^{\circ}\text{C}\cdot\text{s}^{-1}$ and $0.43^{\circ}\text{C}\cdot\text{s}^{-1}$; and the contours of grains are sketched by the dash line in Fig. 1. The similar morphologies and distributions of MnS in these samples indicated that the effect of Al at these two cooling rates was negligible.

However, Al can obviously change the morphology of MnS in FC samples. Figs. 1(a) and (d) indicate that the uniformly distributed Type III MnS inclusions are favored by the contents of 0.034wt% or 0.044wt% Al_s at a lower cooling rate of $0.24^{\circ}\text{C}\cdot\text{s}^{-1}$. When the content of Al_s is increased to 0.052wt%, the sulfides change from Type III to MnS with a well-developed eutectic morphology distributed along the grain boundaries, as shown in Fig. 1(g).

The three-dimensional morphology of MnS was detected in electrolytically etched samples. In Fig. 2, the basic types

of sulfides found in the samples are designated as Type I, Type IIR, or Type III MnS based on the classification of Sims. Due to the different amounts of Al added and the different cooling rates, the morphological changes in the different types of MnS indicated that different formation mechanisms might be involved. In addition, numerous individual MnS grown in the Fe matrix is observed, as shown in Fig. 1.

3.2. Size and number of MnS inclusions

Fig. 3 shows the effects of Al addition and cooling rate on the number and size of MnS inclusions in different samples. With increasing cooling rate the average diameter of MnS inclusions decreases considerably, while the number fraction of small MnS inclusions with diameters $\leq 2.5\text{ }\mu\text{m}$ increases. At the cooling rates of $200^{\circ}\text{C}\cdot\text{s}^{-1}$ and $0.43^{\circ}\text{C}\cdot\text{s}^{-1}$, the average size and diameter distribution hardly change with varying Al_s content. However, at a lower cooling rate of $0.24^{\circ}\text{C}\cdot\text{s}^{-1}$, the average size of MnS inclusions decreases sharply when the content of Al_s is increased to 0.052wt% (sample 3-F). This tendency was in good agreement with the SEM micrographs shown in Fig. 1.

Fig. 1. Typical SEM morphologies and distributions of inclusions (GB indicates the grain boundary): (a) 1-F; (b) 1-A; (c) 1-W; (d) 2-F; (e) 2-A; (f) 2-W; (g) 3-F; (h) 3-A; (i) 3-W.

Fig. 2. Typical three-dimensional SEM morphologies of electrolytically etched MnS: (a) globular Type I; (b) rod-like Type IIR; (c) angular Type III.

Fig. 3. Effects of cooling rate and Al_s content on the size of MnS inclusions in the samples.

In this paper, Type III MnS was characterized by a width of $\geq 3 \mu\text{m}$ and an aspect ratio of ≤ 3 based on the SEM observation and the fact that Type III MnS typically had a large size and equiaxial morphology. Fig. 4 shows that the number of Type III MnS inclusions decreases with increasing cooling rate, and no Type III MnS is found in WC samples at the cooling rate of $200^\circ\text{C}\cdot\text{s}^{-1}$. The number density of Type III MnS peaks in sample 2-F with 0.044wt% Al_s at the lowest cooling rate ($0.24^\circ\text{C}\cdot\text{s}^{-1}$), and this value is decreased in samples with 0.034wt% and 0.052wt% Al_s . In addition, the number density of Type III MnS decreases when the cooling rate is increased from $0.24^\circ\text{C}\cdot\text{s}^{-1}$ to $0.43^\circ\text{C}\cdot\text{s}^{-1}$.

Fig. 4. Effects of cooling rate and Al_s content on the number of Type III MnS inclusions in the samples.

4. Discussion

4.1. Thermodynamic analysis of MnS precipitation and the Fe–Mn–S system

Using the composition given in Table 1, the equilibrium phase diagram showing the relationships between the precipitated phases and temperature was calculated in Thermo-Calc, and the results are shown in Fig. 5. MnS starts to precipitate once the equilibrium activity product is reached with the gradual enrichment of Mn and S in the remaining liquid. Fig. 5 shows that MnS precipitates at an initial temperature of 1421°C , and 87% of the MnS inclusions

precipitate when the liquid phase disappears at 1412°C. Consequently, it was necessary to investigate the characteristics of Fe–Mn–S system related to the residual liquid; for simplicity, the effects of other elements were ignored.

The Fe–Mn–S ternary system was assessed to draw the actual phase diagram of Fe–MnS pseudo-binary system based on Thermo-Calc calculations, and the results are

shown in Fig. 6, which is more accurate than the schematic graphs used by other researchers [8–11]. As illustrated in Fig. 6, the eutectic reaction ($L1 \rightarrow \delta\text{-Fe} + \text{MnS(s)}$) exists on the Fe-rich side, and the eutectic point (point *e*) is located at about 98.5wt% Fe. It is also noteworthy that a widely extended miscibility gap ($L1+L2$) exists in the pseudo-binary phase diagram.

Fig. 5. Equilibrium phase diagram showing the relationships between equilibrium phases and temperature (a) and a magnified area of the diagram showing MnS precipitation (b).

Fig. 6. Fe–MnS pseudo-binary phase diagram (a) and a magnified region showing the Fe corner (b), where L1 is the Fe-rich melt and L2 is the MnS-rich melt.

Fig. 6 shows that, by cooling from the liquid state, the melt is expected to follow a solidification path through the line *ex*. This results in the solidification of the primary Fe matrix phase followed by eutectic precipitation according to the eutectic reaction ($L1 \rightarrow \delta\text{-Fe} + \text{MnS(s)}$). As a conse-

quence, the MnS inclusions grow up with Fe in a eutectic way and distribute mainly along the grain boundaries (Fig. 2(b)), because the residual liquid L1 is pushed to the interdendritic spaces before the precipitation of MnS at the end of solidification. This precludes the formation of any globu-

lar-type MnS since the globular MnS forms only when the solidification path involves the monotectic reaction ($L1 \rightarrow Fe(s) + L2(MnS\text{-rich})$) according to its droplet-like morphology (Fig. 2(a)). In addition, the angular Type III MnS (Fig. 2(c)) is considered as a primary precipitate based on its angular or polyhedral morphology. Therefore, primary MnS forms only when the line ey (Fig. 6(b)) is traversed by the solidification path. Considering the very high content of Fe in the melt, these two cases are highly unlikely in equilibrium solidification according to the Fe-MnS phase diagram. However, in the present work, globular and angular types of MnS were observed in the samples cooled at different cooling rates with the addition of Al. Thus, the effects of cooling rate and Al on the formation of various types of MnS were now discussed.

4.2. Effect of cooling rate on the formation of monotectic MnS

As shown in Fig. 7, a large number of MnS inclusions with Fe-containing cores are observed in AC and WC samples at the cooling rates of $200^{\circ}\text{C}\cdot\text{s}^{-1}$ and $0.43^{\circ}\text{C}\cdot\text{s}^{-1}$, respectively. These inclusions present the globular morphologies after electrolytic etching and are consequently classified as Type I MnS. It has been reported that Type I MnS usually exists in high-oxygen- and high-sulfur-containing steels, and

some previous studies have reported that this type of MnS forms as the result of lowering the melting point of MnS below the eutectic temperature due to oxygen contamination [9,20]. However, the explanation was invalid in this study since the oxygen content was quite low in the experimental steels herein. Oikawa *et al.* [10] proposed a metastable phase diagram for Fe-MnS. According to their calculation, the difference between the eutectic point and the monotectic point was so small (3°C) that a metastable monotectic reaction resulting in the formation of globular Type I MnS was very likely to occur. As a consequence, for non-equilibrium cooling at the high cooling rates in this work, liquid MnS droplets formed first due to the existence of a miscibility gap and the metastable monotectic reaction; subsequently, the direct solidification retained the globular morphology of MnS. As shown in Fig. 7(a), the solid globular MnS usually contains some amount of Fe, since there is not enough time for the dissolved Fe in liquid MnS to precipitate during the solidification due to the significantly high cooling rates. Thus, after the erosion of Fe by electrolytic etching, the cavities in globular MnS are observed in Figs. 7(b) and (c). This type of MnS usually has a diameter larger than $5\text{ }\mu\text{m}$ and accounts for the main proportion of large inclusions in AC and WC samples.

Fig. 7. Globular monotectic MnS inclusions with Fe-containing cores after electrolytic etching: (a) EDS element mapping of MnS inclusions; (b,c) SEM of cavities in MnS.

4.3. Effects of cooling rate and Al on the formation of eutectic and divorced eutectic MnS

Fig. 8 shows the SEM micrographs related to the morphology and distribution of several types of MnS on the

fracture surface, where Type IIR MnS shows a rod-like morphology, Type IIF MnS is faceted at the top of rod, Type IIS indicates a complete sheet-like morphology, and Type III MnS presents a polyhedral morphology. All the Type II and Type III MnS inclusions precipitated in a solid

state because of their typical eutectic morphologies. According to the Fe–MnS pseudo-binary phase diagram, these MnS inclusions could be the products of eutectic reaction. The final morphology of a MnS inclusion observed by SEM

was determined by the growth conditions from nucleation until the end of solidification. Thus, cooling rate and Al could affect the precipitation reaction as well as the growth conditions of MnS inclusions to alter their morphologies.

Fig. 8. Morphologies of various types of MnS on the fracture surface: (a) Type IIR in sample 2-W; (b) Type IIR in sample 2-A; (c) Type IIR + IIF in sample 3-A; (d) Type IIR + IIF in sample 1-F; (e) Type III in sample 2-F; and (f) Type IIS in sample 3-F.

At high cooling rates, the formation of MnS deviated dramatically from equilibrium. Moreover, high cooling rates could significantly affect the growth conditions of inclusions, such as the concentrations or activities of the components, during their precipitation in the melt; these factors were thought to be important in determining the final morphology of inclusions [13–14]. A mechanism that explains the morphological transformation of inclusions well has been proposed based on the crystal growth theory of Sunagawa [21], and this model was adopted herein to elucidate the formation mechanisms of different types of MnS. In this theory, the supersaturation (σ) is thought to play an important role in MnS growth and can be defined as Eq. (1) [21].

$$\sigma = \frac{-RT \ln(a_{\text{Mn}} \cdot a_{\text{S}}) + \Delta G_{\text{MnS}}^{\ominus}}{\Delta G_{\text{MnS}}^{\ominus}} \quad (1)$$

where a_{Mn} and a_{S} refer to the activities of Mn and S in the steel bath, respectively, $\Delta G_{\text{MnS}}^{\ominus}$ the standard formation free energy of MnS, R the gas constant, and T the absolute temperature.

Considering the different growth mechanisms related to σ , a schematic diagram depicting the changes in inclusion morphology that fits well with the MnS morphologies observed in this study is shown in Fig. 9. In this study, the Volmer–Kossel–Stranski (VKS) model was employed for

two-dimensional nucleation, while the Burton–Cabrera–Frank (BCF) model was applied for spiral growth. As shown in Fig. 9, the MnS growth may occur at very low supersaturation according to the BCF model, while VKS growth is dominant at relatively high supersaturation [21]. If the supersaturation is very high, these two models are no longer appropriate and the growth of inclusions depends on the aggregation of single MnS. The morphologies of MnS depend on the growth mechanisms. With increasing supersaturation, the morphology of MnS changes from angular to dendritic due to the different growth mechanisms. It is also noteworthy that different mechanisms may even occur in different parts of a single inclusion, resulting in the irregular MnS inclusions.

Fig. 9. Schematic diagram showing the relationship between supersaturation and growth rate for different growth mechanisms, resulting in the different morphologies of inclusions in steels.

When the cooling rates were raised to very high levels such as $200^{\circ}\text{C}\cdot\text{s}^{-1}$, the time for eutectic reactions to produce MnS in the solidification process was limited. As a result, the activities of Mn and S in the residual melt must be high because of the increased concentration resulting from the segregation of these two elements. Thus, a very high supersaturation would be reached, resulting in the growth by the aggregation of MnS. Consequently, dendritic MnS clusters consisting of large numbers of rod-like Type IIR MnS inclusions formed in the steels (Figs. 8(a) and (b)). The supersaturation around the tips of rod-like MnS decreased as the melt components were consumed, leading to the formation of facets at the tips of the rod-like MnS inclusions [22]. This homologue of rod-like MnS usually coexisted with Type IIR MnS in the samples and was designated as Type IIF MnS according to its faceted morphology (Figs. 8(c) and (d)). The average diameter of these Type II MnS inclusions was relatively fine ($1.1\text{--}1.9\text{ }\mu\text{m}$) due to the insufficient time for their growth.

When the cooling rate was decreased to $0.24^{\circ}\text{C}\cdot\text{s}^{-1}$, the effect of Al was more obvious than that at high cooling rates to affect the near-equilibrium precipitation and the growth of MnS inclusions. Some previous studies [10,23–24] reported that Al_2O_3 could serve as an effective nucleus for the heterogeneous nucleation of MnS, thus changing the sulfide morphology. However, this effect could not be the dominant one in this study because less than 5% of MnS inclusions were found to nucleate on Al_2O_3 nuclei herein. Consequently, the changes in MnS morphology could instead be ascribed to the modification of the precipitation reaction by the added Al. With increasing Al content, the melting point of iron was lowered, and the eutectic point (point *e* in Fig. 6) moved closer to the Fe side of the phase diagram. As a result, the solidification path traversed the liquidus line (line *ey* in Fig. 6), and the primary MnS precipitated at an earlier period of the solidification process. In this early period, the segregation of Mn and S elements was insufficient, so the supersaturation would be relatively low. Moreover, the two growing phases of MnS and Fe might cooperate to a certain degree. The Type III MnS grew separately from the Fe matrix and exhibited a completely divorced eutectic morphology; this type was found primarily in the samples with 0.044wt% Al_s at the cooling rate of $0.24^{\circ}\text{C}\cdot\text{s}^{-1}$ (Fig. 8(e)). In the samples containing 0.052wt% Al_s , the MnS inclusions exhibited the well-developed eutectic morphologies, indicating that they grew cooperatively with the Fe matrix (Fig. 8(f)). This type of sulfide was classified as Type IIS MnS based on the sheet-like morphology and the aggregated distribution along grain boundaries. The change from Type III

to Type IIS might be explained by the instability of supersaturation caused by increasing Al content, leading to the spread of MnS along the supersaturation gradient according to the VKS model.

5. Conclusions

The types of MnS inclusions found in medium-carbon non-quenched and tempered steels were classified, and their formation mechanisms were explained on the basis of phase diagrams calculated by Thermo-Calc along with growth models related to supersaturation. The effects of cooling rate and Al_s content on the changes in MnS morphologies were also illustrated. Finally, the appropriate cooling rate and Al_s content for the control of MnS morphology in medium-carbon non-quenched and tempered steel were identified.

(1) Globular Type I MnS forms via a monotectic reaction followed by the rapid solidification. Various kinds of Type II MnS inclusions with different morphological characteristics form as a result of eutectic reactions and grow cooperatively with the Fe matrix; these processes are explained by the VKS model and the aggregation of single MnS under the relatively high supersaturation due to the enrichment of solutes. The formation of Type III MnS as the primary precipitate with a divorced eutectic morphology is explained based on the BCF growth model under very low supersaturation.

(2) High cooling rates promote the formation of Type I and Type II MnS inclusions. At a lower cooling rate of $0.24^{\circ}\text{C}\cdot\text{s}^{-1}$, the precipitation of Type III MnS is significantly enhanced by the addition of 0.044wt% Al_s in the experimental steel.

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