Research Article

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A thermodynamic assessment of precipitation, growth, and control of MnS inclusion in U75V heavy rail steel

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Abstract: Thermodynamic analysis of the precipitation behavior, growth kinetic, and control mechanism of MnS inclusion in U75V heavy rail steel was conducted in this study. The results showed that solute element S had a much higher segregation ratio than that of Mn, and MnS would only precipitate in the solid–liquid (two-phase) regions at the late stage during the solidification process at the solid fraction of 0.9518. Increasing the cooling rate had no obvious influence on the precipitation time of MnS inclusion; however, its particle size would be decreased greatly. The results also suggested that increasing the concentration of Mn would lead to an earlier precipitation time of MnS, while it had little effect on the final particle size; as to S, it was found that increasing its concentration could not only make the precipitation time earlier but also make the particle size larger. Adding a certain amount of Ti

additive could improve the mechanical properties of U75V heavy rail steel due to the formation of $\text{TiO}_x\text{--MnS}$ or MnS--TiS complex inclusions. The precipitation sequences of $\text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}_2 \rightarrow \text{TiO} \rightarrow \text{MnS} \rightarrow \text{TiS}$ for Ti treatment were determined based on the thermodynamic calculation.

Keywords: U75V heavy rail steel, MnS inclusion, thermodynamic calculation, Ti treatment

1 Introduction

High-carbon heavy rail steel possesses good fatigue resistance, excellent corrosion resistance, high toughness, and strength, and thus, it is widely used for the transportation rails, such as high-speed railways [1,2]. Considering the security and service life, the formation of risky Al_2O_3 inclusion should be avoided, and therefore, the manufacturing process of this type of steel has improved from previous Al deoxidation to the current Si/Si–Mn alloys deoxidation during steelmaking processes. A certain amount of S is usually required in rail steel because the formation of MnS could reduce the detrimental effect of hydrogen induction white dots (MnS could reduce the diffusion velocity of H in steel) [3–5]. Due to the excellent deformability, however, the newly formed MnS particle could be easily elongated into a long strip in the rolling process, which will deteriorate the mechanical properties of steel seriously [6]. During the actual application process, MnS inclusion is frequently observed by the optical microscopy and ultra-sonic inspection; sometimes, its amount and size will be even beyond the ASTM standard [7], which will decrease the fatigue resistance and shorten the service life of steel greatly. Therefore, the control of MnS inclusion in rail steel has drawn increasing attention recently.

Up to date, considerable efforts have been made to reduce the harmful effect of MnS inclusion on the property of steel, such as heating treatment (controlling the heating temperature or holding time) [8–12] and adding a

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certain amount of alloy elements (such as Ca, Mg, Al, Zr, Ti, V and rare earth elements) [13–19]. The main purposes of these methods can be simply summarized as follows: (1) transforming the morphology of MnS inclusion from rod-like (type II) or angular shape (type III) into dispersed globular shape (type I); (2) reducing its particle size from several hundred micrometers to dozens or several micrometers; (3) making the distribution of MnS inclusion uniform; and (4) modifying the composition of single deformed particle into the composite nondeformed compounds, such as CaS and (Mn, Ca)S. Among these aspects, Ti treatment is an effective way for the inclusion modification, and it has been widely used for improving the mechanical properties of steels [20–23]. The mechanism of Ti treatment is mainly to produce TiS inclusion (to surround the MnS particle and restrain its deformation during the rolling process) or TiO_x fine cores, which is similar to the theory of “oxides metallurgy” [24] in which oxide particles in steels were utilized as the nucleation sites of precipitation by controlling its morphology, size, distribution, and composition [25,26]. For example, when the small TiO_x oxides were formed in steels first, the subsequent MnS could precipitate on the surface of these particles and then further restrains the grain growth of steel by the pinning effect on the grain boundaries [25]. In this case, the newly formed fine MnS (usually less than 100 nm) played a beneficial effect on the nucleation of intragranular ferrite and grain refinement [27–29], which will improve the mechanical properties (such as strength, ductility, and toughness) of steels; however, the actual particle size of MnS inclusion in heavy rail steel was sometimes larger, such as 30 μm or more, and in that case, the “pinning” effect may not work, and then, the existence of MnS could deteriorate the mechanical properties of steel.

Larger numbers of experimental studies had been carried out to explore the function of Ti additive on the properties of steels; however, the theoretical study, especially for the U75V heavy rail steel, was relatively rare. To make up for these gaps, the current study was performed. The precipitation behavior and the growth kinetic

of MnS inclusion in heavy rail steel were analyzed based on the thermodynamic calculation, in which the effect of different parameters such as cooling rate and solute concentrations (Mn and S) were considered. Moreover, the influence of Ti addition on the MnS inclusion was also estimated, in which the main target was aimed to clarify the precipitate sequence of Ti-bearing compounds. The obtained results could provide an important guidance role on the precipitation, growth, and control of MnS inclusion in U75V heavy rail steel.

2 Material

U75V heavy rail steel, which was produced by the route of “Hot metal pretreatment $\rightarrow$ BOF steelmaking (with the Si–Mn alloys as the deoxidizing agents) $\rightarrow$ LF refining $\rightarrow$ RH refining $\rightarrow$ continuous casting (CC) $\rightarrow$ rolling process,” was used as the analyzed material. The corresponding chemical composition is presented in Table 1, in which the contents of total oxygen (TO) and N were determined by the O–N–H analyzer (TC500C, LECO Corporation, St. Joseph, MI), C and S were analyzed by the C–S analyzer (Model EMIA-820V), and the other elements were determined by the ICP-AES (IRIS advantage ER/S, Thermo Elemental Corporation, Waltham, MA) technology.

The liquidus temperature (T_L) and solidus temperature (T_S) of the steel can be evaluated by equations (1) and (2), respectively [30,31],

$$T_L = T_0 - \sum_i \Delta\zeta_L \cdot w_{(i)}, \quad (1)$$

$$T_S = T_0 - \sum_i \Delta\zeta_S \cdot w_{(i)}, \quad (2)$$

where T_0 is the melting point of pure iron, 1,811 K; i represents the solute element, and $w_{(i)}$ denotes its concentration, mass%; $\Delta\zeta_L$ and $\Delta\zeta_S$ are the respective temperature coefficients for T_L and T_S , which means the reduced temperature value for element i when its concentration is 1 mass%, and the reference values can be obtained from Table 2 [30,31].

Table 1: Chemical composition of analyzed U75V heavy rail steel (mass%)

Elements	C	Si	Mn	P	S	V	Cr
Composition/(mass%)	0.75	0.61	0.86	0.015	0.013	0.08	0.02
Elements	Als	Ni	Ti	Mo	N	TO	
Composition/(mass%)	0.0035	0.03	0.004	0.0045	0.0041	0.0011	

Table 2: Values of $\Delta\zeta_L$ and $\Delta\zeta_S$ corresponded to the solute elements shown in Table 1 [30,31]

Elements	C	Si	Mn	P	S	V	Cr	Al	Ni	Ti	Mo	N	O
$\Delta\zeta_L$	65	8	5	30	25	2	1.5	3	4	20	2	90	80
$\Delta\zeta_S$	175	20	30	280	575	4	6.5	7.5	4.75	40	5	—	160

Combining equations (1) and (2) (Tables 1 and 2), the values of T_L and T_S could be evaluated, i.e., $T_L = 1,751$ K, $T_S = 1,626$ K.

The formation of MnS inclusion in molten steel during the solidification process could be written as equation (3), whose standard Gibbs free energy can be deduced from equations (4) to (7) [31].

Combining the equilibrium constant and standard Gibbs free energy, one can obtain

$$\begin{aligned} \lg K_3^\theta &= \lg \frac{a_{(\text{MnS})}}{a_{(\text{Mn})}^T \cdot a_{(\text{S})}^T} \\ &= \lg \frac{1}{w_{(\text{Mn})}^T \cdot w_{(\text{S})}^T \cdot f_{(\text{Mn})}^T \cdot f_{(\text{S})}^T} \\ &= 0 - \lg(w_{(\text{Mn})}^T \cdot w_{(\text{S})}^T) - \lg(f_{(\text{Mn})}^T \cdot f_{(\text{S})}^T) \\ &= -\frac{\Delta G_3^\theta}{2.303RT} \end{aligned} \quad (8)$$

where K_3^θ means the equilibrium constant of equation (3); $a_{(\text{MnS})}$, $a_{(\text{Mn})}^T$, and $a_{(\text{S})}^T$ represent the activities of MnS, Mn,

and S in molten steel, respectively; $w_{(\text{Mn})}^T$ and $w_{(\text{S})}^T$ are the instantaneous concentration of solute elements Mn and S at T ; and $f_{(\text{Mn})}^T$ and $f_{(\text{S})}^T$ denote the instantaneous activity coefficients of Mn and S, which can be estimated by equations (9) and (10), respectively.

$$\lg f_{(\text{Mn})}^T = \left(\frac{2538}{T} - 0.355 \right) \sum e_{\text{Mn}(1873\text{K})}^i \cdot w_{(i)}^{1873\text{K}} \quad (9)$$

$$\lg f_{(\text{S})}^T = \left(\frac{2538}{T} - 0.355 \right) \sum e_{\text{S}(1873\text{K})}^i \cdot w_{(i)}^{1873\text{K}}. \quad (10)$$

Since the total iron concentration is more than 90 mass%, the impact of second-order interaction coefficient can be ignored. Thus, the first-order interaction coefficients were only used in the calculation [32,33]. In equations (9) and (10), $e_{\text{Mn}(1873\text{K})}^i$ and $e_{\text{S}(1873\text{K})}^i$ are the respective first-order interaction coefficients of solute element i to Mn and S at 1,873 K, whose values are presented in Table 3 [31]; $w_{(i)}^{1873\text{K}}$ is the concentration of element i at 1,873 K, which can be considered as the initial concentration of solute elements, as presented in Table 1. Therefore, equations (9) and (10) can be switched as follows:

$$\lg f_{(\text{Mn})}^T = \frac{469}{T} - 0.0656, \quad (11)$$

$$\lg f_{(\text{S})}^T = \frac{245}{T} - 0.0343. \quad (12)$$

Considering the equilibrium solubility product of Mn and S at T as $K_{\text{MnS}}^{\text{Equ}}$, i.e., $K_{\text{MnS}}^{\text{Equ}} = w_{(\text{Mn})}^T \cdot w_{(\text{S})}^T$. So, combining equations (11) and (12) with equation (8), the logarithm of $K_{\text{MnS}}^{\text{Equ}}$ can be obtained as follows:

$$\lg K_{\text{MnS}}^{\text{Equ}} = \frac{-8743}{T} + 4.8669 \quad (13)$$

Table 3: First-order interaction coefficients between elements in molten steel at 1,873 K [31]

	C	Si	Mn	P	S	V	Cr	Al	Ni	Ti	Mo	N	O
Mn	-0.07	0.39	0	-0.003	-0.048	0.0056	0.0036	0.07	-0.007	0.019	0.0045	-0.09	-0.08
S	0.11	0.063	-0.026	0.029	-0.028	-0.016	-0.011	0.035	0	-0.07	0.0027	0.01	-0.27
Ti	-0.165	0.05	0.0043	-0.006	-0.11	—	0.055	0.12	—	0.013	—	-1.8	-1.8
O	-0.45	-0.13	-0.021	0.07	-0.133	-0.3	-0.04	-3.9	0.006	-0.6	0.0035	0.057	-0.2

3 Precipitation and growth behaviors of MnS inclusion

3.1 Precipitation behavior

Temperature will be decreased during the solidification process of molten steel, and accordingly, the solubility of Mn and S will be also decreased and differed in solid and liquid phases, and so, the redistribution of solute elements will occur. Due to the small equilibrium distribution coefficient (smaller than 1), the microsegregation will occur, and thus, Mn and S will be accumulated in the liquid region between the secondary dendrite arm spacing. Thereafter, the actual solubility product of Mn and S will increase as the solidification proceeds; the equilibrium value, on the other hand, will decrease. When the actual solubility product reaches the equilibrium value, MnS will precipitate. Up to date, several models [34–37] have been proposed to describe the microsegregation of solute elements. In this study, the modified Ohnaka model [38] (considering the finite diffusion of solute elements in the solid phase, which not only satisfied the inverse diffusion coefficient of ψ in the range of 0–1 but also possessed the actual physical basis) was used. The models can be expressed by the following equations:

$$w_{(i)}^{\text{act}}/w_{(i)}^0 = [1 - g(1 - \psi_i k_i^{y/L})]^{k_i^{y/L-1} / (1 - \psi_i k_i^{y/L})}, \quad (14)$$

$$\psi_i = \frac{\beta_i}{1 + \beta_i}, \quad (15)$$

$$\beta_i = \frac{4D_i^y \tau}{L^2}, \quad (16)$$

$$\tau = \frac{T_L - T_S}{R_c} \quad (17)$$

$$L = 143.9R_c^{-0.3616} \cdot w_{(C)}^{0(0.5501-1.996w_{(C)})}. \quad (18)$$

where ψ_i means the inverse diffusion coefficient of element i , $k_i^{y/L}$ is the equilibrium distribution coefficient of element i between solid (austenite phase) and liquid phases, β_i denotes the Fourier parameter, τ is the local solidification time (s), D_i^y represents the diffusion coefficient (cm^2/s), and R_c is the cooling rate (K/s). The corresponding data of the aforementioned different parameters are listed in Table 4. It is worth noting that the equilibrium partition coefficients of solute elements are varied with temperature and chemical composition, especially for the chemical composition [39–41]. For example, the values of

Table 4: Thermodynamic data used for the calculation of MnS precipitation [42]

Element	$D_i^y (\text{cm}^2/\text{s})$	$D_i^L (\text{cm}^2/\text{s})$	$k_i^{y/L}$
Mn	$0.055 \exp\left(\frac{-249366}{RT}\right)$	$0.0046 \exp\left(\frac{-70300}{RT}\right)$	0.785
S	$2.4 \exp\left(\frac{-223426}{RT}\right)$	$0.027 \exp\left(\frac{-99200}{RT}\right)$	0.035

them between the liquid/ δ are quite different from that between the liquid/ γ ; however, as to the same solid (liquid/ δ or liquid/ γ), the changes are relatively small, especially for Mn and S. The U75V heavy rail steel studied in the article is a kind of high-carbon steel, the main solid is austenite during solidification, i.e., only liquid/ γ is existed. In the case, the change for the equilibrium partition coefficient can be nearly ignored. What is more, the constant equilibrium partition coefficients of Mn and S were also used in inference [42]; as to other solute elements, such as Ti and N, constant equilibrium partition coefficients were also used [32,36]. So, the constant equilibrium partition coefficients of Mn and S were adopted in this study both due to the unobvious changes and convenient calculation.

According to the aforementioned analysis, segregation ratios of solute elements Mn and S at different cooling rates can be calculated, as shown in Figure 1. The results show that segregation ratios of both Mn and S are increased with increasing the solid fraction, especially in the late period. The segregation ratio of S at each cooling rate is much higher than that of Mn. For example, the value of S is above 225 when the solid fraction closes to 1, while for Mn, the value is always below 6, comparing Figure 1(b) with Figure 1(a). From Figure 1, it can be also discovered that cooling rates seem to have no obvious effect on the segregation ratios of both Mn and S; however, based on the amplified section inset in the figure, it is found that the increasing cooling rate is beneficial for the increase of the segregation ratio, and similar results were also obtained in other studies [30,43].

The relationship between the equilibrium solubility product and actual values at different cooling rates is shown in Figure 2. When the microsegregation is not considered, the initial solubility product of Mn and S is fixed at -1.9488 (marked by the red-dot line) and always below the equilibrium value (marked by the green line), which suggests that MnS will not precipitate throughout the solidification process in this case. However, when the microsegregation is considered, the results are quite different. As can be clearly observed, the values of the

Figure 1: Segregation ratios of solute elements Mn and S at different cooling rates.

Figure 2: Comparisons of the equilibrium solubility product with the actual values at different cooling rates (the initial solubility product is also given as reference).

equilibrium solubility product and actual one are monotonously decreased and increased; when the solid fraction is above 0.9518 (as shown in the arrow direction), the actual solubility products are bigger than the equilibrium value, which indicates that MnS will precipitate at this point. The cooling rate, as expected, has no obvious influence on the precipitation time and can be also easily observed.

3.2 Growth kinetic

When MnS nucleus is formed at the solid fraction of 0.9518, the growing process will proceed. To describe

the growth kinetic, it is assumed that the particle is spherical, a stationary diffusion state is reached, and each particle grows independently without interaction with other particles [44]. In this situation, the rate-controlling step for the growth of MnS may be the interfacial (MnS/molten steel) chemical reaction or the diffusion of solute elements (Mn or S) in molten steel. Due to the fact that the temperature during solidification is high (between the solidus and liquidus temperatures, from 1,628 to 1,751 K), the interfacial chemical reaction would be very fast, so the interfacial chemical reaction will not be the rate-controlling step. Besides, since the initial Mn concentration (0.86 mass%) is much higher than that of S (0.013 mass%), and the actual Mn concentration is still bigger than that of S at the MnS/molten steel interface (4.902 mass% vs 2.951 mass%) even if the segregation ratio of S (about 227) is much higher than that of Mn (about 5.7) during solidification. That is, the Mn concentration required at the MnS/molten steel interface is sufficient; thus, the most likely rate-controlling step for the growth of MnS may be the diffusion of S from the bulk steel to the MnS/molten steel interface. According to Fick's first law of diffusion [45], the diffusion flux of solute S toward MnS particle can be given as follows:

$$J_S = \frac{D_S^{\text{liquid}}}{r} \cdot \frac{\rho_{\text{Fe}}}{100M_{\text{Fe}}} (w_{(\text{S})}^T - w_{(\text{S})}^{\text{Equ}}) \quad (19)$$

where J_S is the diffusion flux of S ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$); D_S^{liquid} is the diffusion coefficient (cm^2/s), whose value is listed in Table 4; r is the radius of MnS particle (cm); ρ_{Fe} is the density of molten steel (7.07 g/cm^3); M_{Fe} is the molar weight of iron (56 g/mol); $w_{(\text{S})}^T$ is the instantaneous concentration of S between the secondary dendrite arm

spacing at T (mass%), which can be calculated by equation (14); and $w_{(S)}^{\text{Equ}}$ is the concentration of S in equilibrium with MnS (mass%), which can be deduced by equation (13). Obviously, the values of $(w_{(S)}^T - w_{(S)}^{\text{Equ}})$ is the diffusion driving force.

According to the assumption of spherical particle and the law of mass conservation [46], the relationship between the diffusion flux of S and particle radius of MnS inclusion can be obtained:

$$J_S \cdot 4\pi r^2 \cdot \Delta t \cdot M_{\text{MnS}} = \frac{4}{3} \pi \cdot [(r + \Delta r)^3 - r^3] \cdot \rho_{\text{MnS}}, \quad (20)$$

where M_{MnS} is the molar weight of MnS (87 g/mol), ρ_{MnS} is the density of MnS (3.99 g/cm³), Δt is the time increment (s), and Δr is the radius increment (cm).

Taking the partial derivative with respect to volume,

$$\frac{\partial V_{\text{MnS}}}{\partial t} = \frac{\partial \left(\frac{4}{3} \pi r^3 \right)}{\partial t} = 4\pi r^2 \frac{dr}{dt} \approx \frac{4}{3} \pi \frac{(r + \Delta r)^3 - r^3}{\Delta t} \quad (21)$$

Combining equations (19)–(21), the following equation can be deduced:

$$r \frac{dr}{dt} = \frac{M_{\text{MnS}}}{\rho_{\text{MnS}}} \cdot \frac{\rho_{\text{Fe}}}{100M_{\text{Fe}}} \cdot D_S^{\text{liquid}} \cdot (w_{(S)}^T - w_{(S)}^{\text{Equ}}). \quad (22)$$

Taking the definite integration of equation (22), i.e., r from r_0 to r and t from 0 to t , then,

$$r = \left[\frac{M_{\text{MnS}}}{\rho_{\text{MnS}}} \cdot \frac{\rho_{\text{Fe}}}{50M_{\text{Fe}}} \cdot D_S^{\text{liquid}} \cdot (w_{(S)}^T - w_{(S)}^{\text{Equ}}) \cdot t + r_0^2 \right]^{0.5} \quad (23)$$

where t is the time (s) and r_0 is the initial radius of MnS nucleus (μm). In this study, r_0 is considered to be zero due to the very small value. As for the time t , two proposals have existed, the local solidification time τ [47] (calculated from the solid fraction of zero) and the local growth time t [48] (calculated from the beginning precipitation time). The deviation of the time in the two cases at different cooling rates is presented in Table 5.

Figure 3 shows the relationships between particle size of MnS and solid fraction at different cooling rates for the two cases (the unit of particle size is converted from cm to μm for clarity). It is found that the particle size of MnS is increased with increasing the solid fraction.

Table 5: Time deviation for the calculation at different cooling rates

Cooling rates/(K/s)	0.5	1	2	10
τ /(s)	246	123	61.5	12.3
t /(s)	11.4144	5.7072	2.8536	0.5707

If taking r equals zero as the initial precipitation time, then it can also obtain that the higher the cooling rate is, the earlier the precipitation time will be, which agrees well with the results reported in the previous study [36] (in which TiN inclusion was investigated). The final particle size of MnS decreased with increasing the cooling rate, for example, when time τ is adopted and the cooling rate increased from 0.5 to 10 K/s, the final particle size decreased from 184 to 58 μm , as shown in Figure 3(a). When time t is adopted, the results are similar to the case of time τ , as shown in Figure 3(b). The only difference is that the particle size of MnS is much smaller than those obtained by adopting time τ ; in this case, the final particle size is 40, 30.51, 23.28, and 12.6 μm at the cooling rate of 0.5, 1, 2, and 10 K/s, respectively. Since the actual particle size of MnS in casting slab of U75V heavy rail steel, as reported in the previous studies [10,49,50], are about 30 μm , so the present work concludes that time t is more reasonable for the thermodynamic calculation; in addition, due to the particle size of MnS obtained at 1 K/s is about 30.51 μm , which is closer to the observed values reported in refs. [7–9]; so the cooling rate of 1 K/s and time t were selected for the following thermodynamic and kinetic calculations.

4 Control of MnS inclusion

4.1 Cooling rate

The effect of the cooling rate on the particle size of inclusion has been widely studied in recent years [7,44,51,52]. Zhang et al. [49] investigated this issue experimentally at three different cooling conditions (water cooling, air cooling, and furnace cooling) and concluded that the average diameter of MnS particle decreased with increasing the cooling rate, which was explained by the Ostwald ripening mechanism. As to other inclusions, such as AlN [44,53], TiN [43], NbN [54], and VCN [55] in other steels, the particle size decreased with the increase of cooling rates, which were also drawn by both experimental research and theoretical calculation. In this study, no matter time τ or time t was adopted, and the final particle size of MnS inclusion was both decreased with the increase of cooling rate. So, increasing the cooling rate is considered to be a common and effective strategy for the purpose of decreasing the particle size of MnS inclusion in rail steel.

Figure 3: Relationship between the particle size of MnS and solid fraction at different cooling rates (0.5, 1, 2, and 10 K/s). (a) Obtained with time τ . (b) Obtained with time t .

4.2 Element concentration

The formation of MnS was through the reaction between Mn and S at the MnS/molten steel interface, and then, the effect of solute concentration on the particle size of MnS should be considered, and the corresponding results are shown in Figures 4 and 5, respectively. It can be found that increasing the concentration of Mn could lead to an earlier precipitation time of MnS, as shown in Figure 4. For example, at a fixed S concentration (0.013 mass%) and cooling rate (1 K/s), when Mn concentration is 0.8, 0.86, 0.92, and 0.98 mass% and the solid fraction for the precipitation of MnS is 0.9545, 0.9518, 0.9487, and 0.9458, respectively. However, the final particle size is

nearly kept the same. That is to say, the increase of initial Mn concentration could contribute to an earlier precipitation time, but it has no obvious effect on the final particle size of MnS inclusion.

As to solute element S, however, the results are quite different. Increasing the concentration of S could not only make the precipitation time earlier but also make the particle size bigger, as shown in Figure 5. At a fixed Mn concentration (0.86 mass%) and cooling rate (1 K/s), when the S concentration is 0.0065, 0.013, 0.026, and 0.052 mass%, the solid fraction for the precipitation of MnS is 0.9740, 0.9518, 0.9149, and 0.8565 mass%, respectively, and the final particle size is 20.58, 30.51, 43.85, and 62.67 μm , respectively. Even though the final values

Figure 4: Effect of Mn concentration on the particle size of MnS inclusion.

Figure 5: Effect of S concentration on the particle size of MnS inclusion.

have some deviations, the tendency of the current results are well coincided with those reported in other studies [49,56]. Therefore, decreasing the concentrations of both Mn (even if it has no obvious effect on the final particle size of MnS, but it could make the precipitation time later and reduce the growth time) and S, especially for S, is an effective route for the control of the final particle size of MnS in U75V heavy rail steel.

4.3 Ti additive

As mentioned in the Section 1, adding a certain amount of micro-alloy element could decrease the detrimental effect of MnS on heavy rail steel. In this study, element Ti was selected as the considered object. Due to the microsegregation of the solute element, concentrations of both Ti and O will be increased and accumulated (the needed data are listed in Table 6), as shown in Figure 6, and so Ti–O compounds will be also formed between the secondary dendritic arm spacing. Among those, relatively stable compounds are Ti_3O_5 , Ti_2O_3 , TiO_2 , and TiO , and the corresponding chemical reactions for their formations can be written as follows [57,58]:

Similar to the aforementioned method, the corresponding equilibrium concentration products of Ti_3O_5 , Ti_2O_3 , TiO_2 , and TiO can be obtained:

$$\lg K_{\text{Ti}_3\text{O}_5}^{\text{Equ}} = \lg(w_{\text{Ti}})^3 \cdot w_{\text{O}}^5 = \frac{-85822}{T} + 28.8209, \quad (28)$$

$$\lg K_{\text{Ti}_2\text{O}_3}^{\text{Equ}} = \lg(w_{\text{Ti}})^2 \cdot w_{\text{O}}^3 = \frac{-53380}{T} + 18.0568, \quad (29)$$

$$\lg K_{\text{TiO}_2}^{\text{Equ}} = \lg(w_{\text{Ti}}) \cdot w_{\text{O}}^2 = \frac{-32514}{T} + 11.4897, \quad (30)$$

$$\lg K_{\text{TiO}}^{\text{Equ}} = \lg(w_{\text{Ti}}) \cdot w_{\text{O}} = \frac{-17376}{T} + 6.6301. \quad (31)$$

Due to the microsegregation of Ti and O, the actual concentration of them will increase, and then, the corresponding solubility products can be also obtained:

$$\lg K_{\text{Ti}_3\text{O}_5}^{\text{act}} = \lg(w_{\text{Ti}}^T)^3 \cdot (w_{\text{O}}^T)^5, \quad (32)$$

$$\lg K_{\text{Ti}_2\text{O}_3}^{\text{act}} = \lg(w_{\text{Ti}}^T)^2 \cdot (w_{\text{O}}^T)^3, \quad (33)$$

$$\lg K_{\text{TiO}_2}^{\text{act}} = \lg(w_{\text{Ti}}^T) \cdot (w_{\text{O}}^T)^2, \quad (34)$$

$$\lg K_{\text{TiO}}^{\text{act}} = \lg(w_{\text{Ti}}^T) \cdot w_{\text{O}}^T. \quad (35)$$

By comparing equations (28) to (31) with equations (32) to (35), the precipitation time and sequences of Ti–O compounds can be estimated, as shown in Figure 7. It can be easily found that all of the four kinds of Ti–O compounds could precipitate in the solid–liquid (two-phase) zones with the sequences of Ti_3O_5 , Ti_2O_3 , TiO_2 , and TiO , corresponding to the solid fractions of 0.3443, 0.3809, 0.5449, and 0.8933, respectively. The solid fractions for the precipitation of Ti–O compounds are all much smaller than that of MnS ($g = 0.9518$), which means that Ti–O compounds are priority to precipitate than MnS. So, the priority Ti–O compounds could work as precipitate sites for MnS. In other words, Ti–O compounds could act as a core and MnS will precipitate around them. However, the accurate stoichiometry of Ti–O compounds are difficult to be determined, so the complex inclusions can be defined as $\text{TiO}_x\text{–MnS}$ composite inclusions. Zhang et al. [49] studied the effects of the cooling rate on the characteristics of MnS inclusion in high-carbon heavy rail steel and reported that many oxide inclusions, including TiO_x , were partially or fully covered with MnS. That is, MnS inclusion was precipitated on the surface of these oxides, which acted as the heterogeneous nucleation sites. The current theoretical analysis could give a better explanation of the experimental results [49]. What is more,

Table 6: Thermodynamic data used for the calculation of Ti–O compounds [48]

Elements	$D_f^{\text{I}} (\text{cm}^2/\text{s})$	$D_f^{\text{II}} (\text{cm}^2/\text{s})$	$k_f^{\text{I/II}}$
Ti	$0.15 \exp\left(\frac{-250000}{RT}\right)$	$3.1 \times 10^{-3} \exp\left(\frac{-11500}{RT}\right)$	0.30
O	$5.75 \exp\left(\frac{-40300}{RT}\right)$	$3.34 \times 10^{-3} \exp\left(\frac{-12000}{RT}\right)$	0.025

When adding a certain amount of Ti additive to molten steel, the precipitation time of Ti-O compounds are changed, as shown in Figure 8. The results show that when Ti concentration is increased, the solid fraction for the precipitation of Ti-O compounds is decreased, which means that higher Ti concentration will contribute to an earlier precipitation time of Ti-O compounds. The corresponding precipitation time of Ti-O compounds at different Ti concentrations are displayed in Table 7, from which it can be seen that the precipitation sequence of $\text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}_2 \rightarrow \text{TiO}$ is still kept regardless of added Ti concentration, which is consistent with the

The aforementioned results could also be supported by the thermodynamic phase diagram of the Ti–O binary system, as shown in Figure 9. When analyzing the figure carefully, the relationship between Ti–O compounds and Ti concentration (O concentration is fixed at 0.0011 mass%) can be roughly divided into several sections.

Figure 8: Effects of solute element Ti on the precipitation time of Ti–O compounds at the cooling rate of 1 K/s. (a) Ti_3O_5 , (b) Ti_2O_3 , (c) TiO_2 , and (d) TiO .

Table 7: Solid fraction for the precipitation of different Ti–O compounds with various Ti concentration at the cooling rate of 1 K/s

$w_{(\text{Ti})}^0/\text{mass\%}$	Ti_3O_5	Ti_2O_3	TiO_2	TiO
0.001	0.5774	0.6064	0.6824	0.9513
0.004	0.3518	0.3771	0.5379	0.8901
0.009	0.1658	0.1911	0.4258	0.8341
0.02	Liquid	Liquid	0.2903	0.7581

(I) $w_{(\text{Ti})} < 0.0009$ (point A_1 in Figure 9(d))

In this section, the concentrations are both below the values of liquid and solid phase lines for all the four kinds of Ti–O compounds, which suggest that all the Ti–O compounds will only precipitate in the solid phase or not precipitate without considering the segregation behavior.

(II) $0.0009 < w_{(\text{Ti})} < 0.0012$ (between point A_1 and A_2 in Figure 9(d))

As to Ti_3O_5 , the concentration is bigger than that of the solid phase line but smaller than the liquid phase line, which means that Ti_3O_5 will always precipitate in the solid–liquid (two-phase) zones regardless of whether segregation occurs. However, as to Ti_2O_3 , TiO_2 , and TiO , their concentrations are smaller than both the respective liquid and solid phase lines, which indicate that the three kinds of Ti–O compounds will precipitate in the solid phase or not precipitate without considering the element segregation. However, when segregation is considered, the most possibly precipitate time of them is in the solid–liquid (two-phase) zones, as shown in the calculated results for point P_1 .

Figure 9: Ti–O equilibrium phase diagram at: (a) and (b) 1,751 K; (c) and (d) 1,628 K.

(III) $0.0012 < w_{(\text{Ti})} < 0.0027$ (between point A_2 and A_3 in Figure 9(d))

In this section, Ti_3O_5 and Ti_2O_3 will always precipitate in the solid–liquid (two-phase) zones as their actual concentrations are always between the solid and liquid phase lines. Similarly, in case of TiO_2 and TiO , their initial concentrations are smaller than both the respective solid and liquid phase lines, which suggest that they will only precipitate in the solid phase or not precipitate.

(IV) $0.0027 < w_{(\text{Ti})} < 0.0157$ (between point A_3 (in Figure 9(d)) and A_4 (in Figure 9(b)))

As to Ti_3O_5 , Ti_2O_3 , and TiO_2 , their initial concentrations are bigger than their respective solid phase line but below the liquid phase line, which indicates that all the Ti–O compounds except TiO could precipitate in the solid–liquid phases regardless of whether microsegregation occurs.

(V) $0.0157 < w_{(\text{Ti})} < 0.0170$ (between point A_4 and A_5 in Figure 9(b))

As for Ti_3O_5 , it is found that its actual concentration is bigger than the value of the liquid phase line, which means that Ti_3O_5 will always precipitate in the liquid phase. However, as to Ti_2O_3 , TiO_2 , and TiO , their initial concentrations are between the solid- and liquid phase lines, so it is possible for them to precipitate only in the solid–liquid (two-phase) zones.

(VI) $0.0170 < w_{(\text{Ti})} < 0.0693$ (between point A_5 and A_6 in Figure 9(b))

In this section, the initial concentrations of Ti_3O_5 and Ti_2O_3 are always bigger than their liquid phase lines, which suggests that both Ti_3O_5 and Ti_2O_3 will precipitate in the liquid phases, as supported by point P_4 in Figure 9. While, as to TiO_2 and TiO , their concentrations values are between their

respective solid- and liquid phase lines, indicating that they can only precipitate in the solid–liquid (two-phase) zones.

(VII) $w(\text{Ti}) > 0.0693$ (bigger than point A_6 in Figure 9(b))

When Ti concentration still increased (for example, $w(\text{Ti}) > 0.0693$), all of Ti_3O_5 , Ti_2O_3 , and TiO_2 would precipitate in the liquid phase even if element segregation is not considered. However, for TiO , it is found that it will not precipitate in the liquid phase during the solidification process due to the low O content in molten steel.

After all, the results of the Ti–O thermodynamic phase diagram agree well with those shown in Figure 8. To make a clearer understanding of the effect of Ti additive on the precipitation time of Ti–O compounds, the corresponding results are summarized and listed in Table 8.

What is more, when a certain amount of Ti was added into the steel, TiS will also be formed. The chemical reaction can be described as follows [31]:

Similarly, the equilibrium solubility product of Ti and S can be calculated,

$$\lg K_{\text{TiS}}^{\text{Equ}} = \frac{-8014}{T} + 4.0247. \tag{37}$$

Due to the segregation of Ti and S, as mentioned in the previous section, their actual solubility products will increase and the equilibrium value decrease during solidification, the corresponding relationships between them at various Ti concentrations are shown in Figure 10. The results show that the precipitation time of TiS will be earlier with the increase of initial Ti concentration. At the fixed S concentration (0.013 mass%) and cooling rate (1 K/s), when Ti concentrations are 0.001, 0.004, 0.009, and 0.2 mass%, and the solid fractions for the beginning precipitation of TiS inclusion are 0.9989, 0.9944, 0.9888, and 0.9799, respectively. Comparing with the results of MnS, it is found that the precipitation time of TiS is longer

Figure 10: Relationship between the equilibrium solubility product and the actual values of Ti and S.

than that of MnS (about 0.9518), which means that TiS has the possibility to precipitate on the surface of previously precipitated MnS with a wrapped or a semi-wrapped state, and then, the composite inclusion of MnS–TiS would be formed. The calculated results could explain well the experimental data reported by Chen [20].

In summary, when element Ti as the additive is added into steel, the precipitation sequence of $\text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO}_2 \rightarrow \text{TiO}$ is always tenable regardless of the amount of added Ti. The higher the added Ti concentration is, the earlier precipitation time of Ti–O compounds will be. When Ti concentration is above 0.0157, Ti_3O_5 will precipitate in the liquid phase, which could give a better precipitate site of MnS particle for heterogeneous nucleation due to the decreased nucleation energy. Since Ti–O compounds have the tendency to disperse finely themselves in steel, so the average diameter of MnS could be decreased greatly if appropriate Ti additive is added, which could not only reduce the detrimental effect of MnS on steel but also refine the austenite structure and improve the mechanical property of the steel. Besides, TiS inclusion will be also possible to precipitate in the

Table 8: Precipitation time of Ti–O compounds in steel when without considering the effect of element segregation (S: solid; L: liquid; S–L: solid–liquid phases; 0.082 was the critical Ti concentration of TiO at the solid phase line)

$w(\text{Ti})$	(0, 0.0009)	(0.0009, 0.0012)	(0.0012, 0.0027)	(0.0027, 0.0157)	(0.0157, 0.0170)	(0.0170, 0.0693)	(0.0693, 0.082)	(0.082, 1)
Ti_3O_5	S	S–L	S–L	S–L	L	L	L	L
Ti_2O_3	S	S	S–L	S–L	S–L	L	L	L
TiO_2	S	S	S	S–L	S–L	S–L	L	L
TiO	S	S	S	S	S	S	S	S–L

very later period during the solidification process, which would contribute to the formation of complex inclusion of the MnS–TiS system. Due to the nondeformed properties of TiS, the newly formed MnS–TiS inclusion will not be elongated into long strips during the rolling process, and then, the detrimental effect could be largely decreased. Even though the calculation results are somewhat in agreement with the previous studies [20–23], further experiments are needed to be carried out to verify the results.

5 Conclusions

In this article, the precipitation behavior and growth kinetic as well as the control mechanism of MnS inclusion in U75V heavy rail steel were analyzed based on the theoretical calculation. The following conclusions have been drawn, which could give guidance on improving the properties of steels.

- (1) S has a larger segregation ratio than Mn during the solidification process, which are both increased with increasing the solid fraction and have no obvious relationship with cooling rates.
- (2) MnS inclusion will precipitate in the solid–liquid (two-phase) zones at the solid fraction of 0.9518. Increasing the cooling rate has no obvious effect on its precipitation time, while the particle size will decrease greatly.
- (3) Increasing the initial Mn concentration could make the precipitation time earlier, while it has no obvious effect on the final particle size of MnS inclusion. However, increasing the initial S concentration could not only lead to an earlier precipitation time but also a larger particle size.
- (4) Ti–O compounds are all precipitated earlier than that of MnS, while TiS later. The precipitation sequence of inclusions in steel are as follows: $Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_2 \rightarrow TiO \rightarrow MnS \rightarrow TiS$. Further experimental study and model calculation to deep understand the effect of Ti addition on the characteristic of MnS inclusion should be done in the future study.

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