Morphology of Solidification Structure and MnS Inclusion in High Carbon Steel Continuously Cast Bloom

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Present study was undertaken to investigate the characteristics of solidification structure and sulfide inclusions in the rail steel U75V continuously cast bloom using various methods, including the metallographic examination, traditional 2D optical microscopy, 3D electrolytic extraction, SEM detection with EDS analysis, and thermodynamic calculation for MnS inclusion precipitation. Metallographic examination shows that the area ratio of chill zone, columnar zone, mixed zone and equiaxed zone in the cast bloom are 5.3%, 43.1%, 21.5% and 30.1%, respectively. 2D/3D investigations on the morphology and distribution of sulfide inclusions reveal that the sulfide inclusions in the subsurface region with smaller equivalent diameter and lower aspect ratio are more fine and rounded compared with those in the bulk, and more complex sulfide inclusions consisting of MnS and TiS with the nuclei of Al2O3 particle are observed in the bloom centre. Moreover, the size and distribution of MnS inclusion precipitation in the rail steel U75V continuously cast bloom was numerical predicted, using the heat transfer model for continuous casting coupled with thermodynamic model for MnS inclusion precipitation, and the parametric study show that sulfide inclusions are much larger in size for the continuously cast bloom with high sulfur content and coarse cast structure.

KEY WORDS: solidification structure; MnS inclusion; thermodynamic calculation; continuously cast bloom.

1. Introduction

Manganese sulfide, as a typical non-metallic inclusion in steels, is known to crystallize and precipitate preferentially in the interdendritic region during steel solidification, due to the microsegregation of manganese and sulfur.1) Usually, soft MnS inclusions are prone to elongate during the hot working process and generally considered to be detrimental to the mechanical properties (such as tensile strength, ductility, fracture toughness, etc.) and corrosion resistance of steel.3) Also, elongated inclusions have a major and superimposing effect on the fatigue anisotropy, because stress concentration at the interface of inclusion and steel matrix becomes a dominating site for fatigue crack initiation.5) But the tiny dispersed MnS inclusions are beneficial for acting as nucleation of intergranular ferrite, resulting in grain refinement and mechanical properties improvement.5) This beneficial effect of non-metallic inclusions is known as “oxide metallurgy” and attracts extensive attentions in recent years. Moreover, sulfur addition are adopted to promote soft MnS inclusions formation and improve the machinability of steel.6) However, no matter what effects of MnS inclusion on the properties of steel are, the morphology, size and distribution of MnS inclusions in steel matrix are key important.

Regarding the important role of MnS inclusions in steel, numerous investigations have been performed over the years. According to the classical work of Sims and Dahle,7) MnS inclusions are roughly classified into three types in the light of inclusion morphology: (i) randomly dispersed globular MnS (Type I); (ii) fine rod-like MnS (Type II) and (iii) angular sulfides (Type III). Moreover, the dendritic MnS inclusion formed in the interdendritic melt at the final stage of solidification process is also regarded as Type II sulfide in some studies.8,9) The theoretical thermodynamic calculation on the role of principal factors controlling the morphology evolution of MnS in sulfur-lean steel performed by Oikawa et al.10) shows that the Type I MnS is formed through a monotectic reaction and subsequent fast solidification, but the formation of Type II and III MnS inclusions are the results of eutectic reaction and irregular eutectic reaction, respectively. By comparison with deformability of Type I and III sulfides, Type II sulfides can deform to a larger extent during the hot working process of steel, resulting in high stress concentrations on sharp edges of the deformed MnS and strong material anisotropy.4,11) Therefore, to achieve an excellent material properties of steels, MnS inclusions must be strictly controlled to be small, uniformly distributed and to have a spherical shape.

In the past few decades, many investigations12) were performed to control the morphology, size and distribution of MnS inclusions in the steel. For instance, elements addition13–15) (such as Al, Mn, Ti, etc.) is utilized to provide various kinds of oxide nuclei for MnS nucleation in molten steel, resulting in fine dispersion of MnS inclusions. Also...
the calcium treatment and Rare-Earth-Metals (REM) treatment are popular ways to modify sulfides in the molten steel before casting and obtain a homogeneous distribution of precipitated sulfides in the solidified steel. Moreover, high cooling intensity is beneficial for the formation of globular Type I MnS in steel during the solidification process through metastable monotectic reaction due to small temperature difference between the eutectic point and the monotectic point. Shape change of MnS inclusion from the Type II and III to Type I can also be accomplished by heat treatments and finally the complete spheroidization of the MnS inclusions is obtained in the steel. Based on the above mentioned works, there are many techniques available for a correction and control of the characteristics of MnS inclusion in the steel. However, new types of non-metallic inclusions introduced by elements additions and Ca/REM treatments in the molten steel may have greatly detrimental effects on the mechanical properties of steel and thus the desired balance between the yielded and sacrificed material properties should be carefully considered in order to achieve satisfied comprehensive properties of steel. Meanwhile, for the spheroidization of MnS inclusions by heat treatment, it remains to be seen what improvement in mechanical properties can be obtained at what cost. Therefore, solidification control is a relative convenient and low-cost method to gain desired morphology of MnS inclusions in the steel.

During the solidification of steel, the dendrites usually grow with excess solutes rejection from solidifying phase into the coexisting liquid phase at the solid/liquid interface, resulting in non-uniform distribution of composition in micro/macrosopic area and precipitation of MnS inclusions. Thus, the dendritic growth significantly affects the solute segregation and sulfides precipitation. Takada et al. investigated the morphology and distribution of sulfides in steel with different sulfur contents and proposed empirical relationships between the average size of Type I/Type II MnS inclusions and solidification variables. Owing to difficulty in comprehensively characterizing the microstructure features of solidifying steel, Ueshima et al. simplified the dendrite morphology with a regular hexagonal transverse cross-section and preliminarily predicted the precipitation behavior of MnS during solidification of low carbon steels with \( \delta' \gamma \) transformation. Imagumbi proposed a novel idea of Solidification-Unit-Cell, primarily taking the relationships between the dendritic structure and morphology of Type II MnS inclusion into account, and quantitatively correlated the diameter of Type II MnS inclusion with solidification parameter. Diederichs and Bleck proposed a model for empirical calculation of MnS inclusion size and investigated the effects of cooling rate on the size of the MnS inclusions after solidification of medium carbon steel. Valdez et al. performed an in-situ observation of MnS precipitation during solidification of high sulphur steels using a confocal scanning laser microscope and developed a model for MnS growth with Mn diffusion as rate controlling step. As mentioned above, many works have been done to predict the precipitation behavior of MnS during the solidification process of steel, based on the empirical or semi-empirical model, but the quantitative relationship between the solidification structure and morphology of MnS inclusion is still unknown.

In order to elucidate the effect of cast features on the MnS inclusion in the high carbon steel continuously cast bloom, the present work involves the following three activities: i) we performed a macroetching technique to reveal the solidification structure and quantitatively evaluate the cast features; ii) both the 2D and 3D investigations on the morphology and distribution of MnS inclusions in different parts of the continuously cast bloom were carried out, and the size and shape of sulfide inclusions were quantitatively characterized. iii) the thermodynamic of MnS inclusion precipitation in the high carbon steel was investigated and the effect of dendrite structure of bloom and sulfur content in steel were numerically analyzed using the heat transfer model for continuous casting coupled with thermodynamic model for MnS inclusion precipitation.

2. Experimental Procedure

2.1. Solidification Structure Examination

In the present study, the rail steel U75V was produced by a vertical bending caster with bloom size of 280 mm×380 mm in a steelmaking plant, and the chemical composition of rail steel U75V is specified in Table 1. The metallurgical length of bloom continuous caster is 20 m, and the secondary cooling zone and radiation zone are respectively 10.36 m and 9.64 m. A bloom sample with 30 mm length was collected under the steady casting conditions, and the operation parameters for sampling are listed in Table 2. The bloom sample was cut into 3 slices with same interval for different examinations, and sampling details are schematically shown in Fig. 1. One slice were firstly macroetched with 1:1 warm hydrochloric acid-water solution to reveal the solidification macrostructure of cast bloom. After the solidification macrostructure examination, the slice are cut into specimens with size of 20 mm×20 mm. Then, specimens were reground, fine polished and etched with picric acid at 25°C for about 5 s to reveal dendrite structure and the primary dendrite arm spacing (PDAS) were measured in combination with an image analyser software. After the metallographic test, different dendritic crystal zones (chill zone, columnar zone, mixed zone, and equiaxed zone) were clearly distinguished and specimens with size of 50 mm×10 mm×5 mm were cut along centerline perpendicular to wide face in different dendritic crystal zones of the second slice for sulfide inclusion test. The surplus slice acts as substitution and only would be used when the sampling or test fails.

<table>
<thead>
<tr>
<th>Table 1. Chemical composition of rail steel U75V.</th>
</tr>
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<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Content(wt%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Casting parameters for sampling.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Items</td>
</tr>
<tr>
<td>Value</td>
</tr>
</tbody>
</table>

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2.2. Sulfides Examination

In order to reveal sulfide morphology more accurately, a 3D investigation method of non-metallic inclusions (NMI) in steel using a non-aqueous electrolytic extraction was employed, and the schematic diagram of experimental set-up for electrolytic extraction is shown in Fig. 2. Specimens were polished and thereafter used as node. For the high efficiency and precision of electrolytic extraction, the extraction solution is of vital importance, and an efficient extraction speed without dissolving the studied inclusions is a prerequisite for the selection of extraction solution. According to the comparison of different extraction methods conducted by Janis et al.,\textsuperscript{27} non-aqueous electrolyte (10 v/v% acetylacetone + 1 w/v% tetramethylammonium chloride methanol) is the most suitable extraction solution to avoid a serious dissolution of MnS and thus it was adopted in the present study. Before the start of electrolysis process, Ar gas was introduced to remove the air at top of electrolytic cell and avoid the oxidation of extraction solution. During the electrolysis process, the power for the electrolytic extraction was provided by a DC power supply, and the voltage was set in the range of 3 V–5 V. The electrolytic cell was located at the thermostatic water bath and the temperature was kept constant in the range of 273 K–278 K. The power was switched off after 8 hours, and then the electrolyte was filtered using a membrane polycarbonate film filter with 0.2 μm diameter open-pores to obtain the non-metallic inclusions. In order to remove the impurities, additional washing works with alcohol were necessary.\textsuperscript{28} Finally, the collected inclusions were transferred directly to conducting graphite tape for SEM observation, and the chemical composition of inclusion was investigated using EDS. Except the above mentioned 3D method, a traditional 2D method were also adopted as a supplement for sulfide test. Samples were taken from different parts of the continuously cast bloom to prepare metallographic specimens for characterizing inclusions, as shown in Fig. 1(b), and standard techniques were used for specimen preparation for optical microscopy and SEM.

3. Model Description

3.1. Heat Transfer Model for Continuous Casting

The bloom continuous casting process is governed by a two-dimensional transient heat conduction equation.

\[ \rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left( k_{\text{eff}} \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left( k_{\text{eff}} \frac{\partial T}{\partial y}\right) + \rho L \frac{\partial f_s}{\partial t} \quad (1) \]

where \( T \) is the temperature (K), \( \rho \) is the mass density (kg/m\(^3\)), \( c_p \) is the specific heat (J/(kg·K)), \( k_{\text{eff}} \) is the effective thermal conductivity (W/(m·K)), \( L \) is the latent heat of fusion (J/kg), \( t \) is the time (s) and \( f_s \) is the solid fraction.

In order to simplify calculation, the effect of the molten steel flow on convective heat transfer in the liquid pool is taken into consideration by multiplying an empirical factor, and the effective thermal conductivity is determined as follows:

\[ k_{\text{eff}} = k_f + mk(1 - f_s) \quad (2) \]

where \( k \) is the thermal conductivity (W/(m·K)), and \( m \) is the empirical factor, which is set to be 2.0 according to Louhenkilpi \textit{et al.}\textsuperscript{29}

In the simulations, the molten steel pours into oscillating mold without temperature decrease and the bulk melt temperature at meniscus is assumed to be casting temperature of the molten steel at the initial time. The initial solidified shell with liquid pool is withdrawn by roller and undergoes three different cooling zones till totally solidified, namely primary mold cooling zone, secondary cooling zone and radiation zone. The heat extraction rates at the primary mold cooling zone, secondary cooling zone and radiation zone are respectively given as followings:\textsuperscript{30}

\[ q = \rho_v c_v W \frac{\Delta T_v}{A_m} \quad (3) \]
\[ q = h(T_{\text{surf}} - T_w) \quad (4) \]
\[ q = \sigma e \left( T_{\text{surf}}^4 - T_{\text{amb}}^4 \right) \quad (5) \]
where \( q \) is the heat flux from the surface (W/m²), \( \rho_c \) is the water mass density (kg/m³), \( c_w \) is the water specific heat (J/(kg·K)), \( W \) is the mould water flow rate (L/min), \( \Delta T_w \) is the effective contact area between the shell and the mould wall (m²), \( \Delta T_m \) is temperature difference between inlet and outlet mould cooling water (K), \( h \) is the heat transfer coefficient (W/(m²·K)), \( \varepsilon \) is emissivity, \( T_{surf} \), \( T_w \) and \( T_{amb} \) are the strand surface, spraying water and environment temperatures (K), respectively.

3.2. Microsegregation and MnS Precipitation Model

During the continuous casting process, dendrites grows from the outer surface inward with excess solutes rejection and the MnS precipitates preferentially in the interdendritic region, when the supersaturation of Mn and S occurs in residual melt. In the present study, Ueshima’s model was adopted to describe the interdendritic microsegregation among hexagonal dendrites and MnS inclusions precipitation. Figure 3 shows the dendritic growth of continuously cast steel and only one-sixth cross section of the dendrite was chosen as calculation domain, and the length of the calculation domain, \( \lambda \), is a half of the primary dendrite arm spacing (PDAS).

Assuming solutes completely mixing in liquid steel, the solute microsegregation in calculation domain is govern by one-dimensional Fick’s second law.

\[
\frac{\partial C_{i,x}}{\partial t} = \frac{\partial}{\partial x} \left( D_{i,x}(T) \frac{\partial C_{i,x}}{\partial x} \right) \tag{6}
\]

where, \( C_{i,x} \) is the concentration of solute element \( i \) in solid phase (wt%), \( D_{i,x}(T) \) is the diffusion coefficient of solute element in solid phase (m²/s), \( T \) is the temperature (K), \( x \) is the horizontal direction of the calculation domain.

The phase occurrence/transformation has a significant effect on the solute diffusion during the solidification process of molten steel, and here the local equilibriums at the \( \delta/L, \gamma/L \) and \( \delta/\gamma \) interfaces are assumed. The key solidification and high temperature transformation temperatures are respectively estimated as followings:

\[
T_{iq} = 1536 - \sum_{i=1}^{N} m_i C_i \tag{7}
\]

\[
T_{Mn} = 1392 - \sum_{i=1}^{N} n_i C_i \tag{8}
\]

where \( m_i \) and \( n_i \) are the slopes of liquidus and \( \delta/\gamma \) transformation line in the Fe-i binary phase diagram, \( C_i \) is the solute concentration of element \( i \) (wt%), \( N \) is the total number of solute elements in the studied steel, but here only 5 solute elements (namely: C, Si, Mn, P, S) are considered. The equilibrium distribution coefficients and diffusion coefficients of elements and other used parameters are listed in Table 3.

With the progress of solidification, the solute elements are enriched in interdendritic liquid and precipitation of MnS occurs, when the product of the local concentrations of Mn and S reaches the equilibrium solubility product, \( K_{MnS} \), calculated by the following equation:

\[
K_{MnS} = \frac{1}{C_{Mn} \cdot f_{Mn} \cdot C_{S} \cdot f_{S}} \tag{9}
\]

where, \( f_{Mn} \) and \( f_S \) are respectively the activity coefficients of Mn ans S, and could be determined by the following equations:

\[
\log f_i = \log e_i - \sum_{i,j} e_i \cdot C_j \tag{10}
\]

\[
e_i = \left( \frac{2.538}{T} - 0.355 \right) e_i(1873K) \tag{11}
\]

![Fig. 3. Schematic diagram of microsegregation model for continuously cast steel: (a) dendritic growth in mushy zone, (b) dendrite array morphology, (c) cross section of dendrites, (d) calculation domain.](image)

**Table 3.** Equilibrium distribution coefficients and diffusion coefficients of elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>( k_i^{eq} )</th>
<th>( k_i / l )</th>
<th>( D_i^{eq}(10^{-9} \text{m}^2/\text{s}) )</th>
<th>( D_i(/10^{-9} \text{m}^2/\text{s}) )</th>
<th>( m_i(% \text{C}) )</th>
<th>( n_i(% \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.19</td>
<td>0.34</td>
<td>0.0127exp(−81 379/RT)</td>
<td>0.0761exp(−143 511/RT)</td>
<td>78.0</td>
<td>−1 122</td>
</tr>
<tr>
<td>Si</td>
<td>0.77</td>
<td>0.52</td>
<td>8.00exp(−248 948/RT)</td>
<td>0.30exp(−251 458/RT)</td>
<td>7.6</td>
<td>60</td>
</tr>
<tr>
<td>Mn</td>
<td>0.76</td>
<td>0.78</td>
<td>0.76exp(−224 430/RT)</td>
<td>0.055exp(−249 366/RT)</td>
<td>4.9</td>
<td>−12</td>
</tr>
<tr>
<td>P</td>
<td>0.23</td>
<td>0.13</td>
<td>2.9exp(−230 120/RT)</td>
<td>0.010exp(−182 841/RT)</td>
<td>34.4</td>
<td>140</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
<td>0.035</td>
<td>4.56exp(−214 639/RT)</td>
<td>2.4exp(−223 425/RT)</td>
<td>38.0</td>
<td>160</td>
</tr>
</tbody>
</table>

Notes: \( R \) is the gas constant, 8.314 J/(kg·K), and \( T \) is temperature, K.

![Image](image)

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where, \(e_i^j\) is the interaction coefficient of element \(j\) to \(i\), and the interaction coefficients of elements in molten steel at 1873 K are listed in Table 4.\(^{3,2}\)

The Gibbs free energy change, \(\Delta G\), associated with the reaction \([\text{Mn}] + [\text{S}] \rightarrow \text{(MnS)}\) is given as follow:\(^{34}\)

\[
\Delta G = -161,436 + 88.33T \quad \text{J/(mol·K)} \quad (12)
\]

Assuming that the MnS precipitates with a globular shape, the shape of MnS inclusion is circle in two-dimensional field and thus the radius of MnS inclusion particles is estimated by:

\[
r = \frac{m_{\text{MnS}}}{\pi \rho_{\text{MnS}}} \quad (13)
\]

where \(\rho_{\text{MnS}}\) is the MnS density, 3990 kg/m\(^3\)\(^{3,5}\) and \(m_{\text{MnS}}\) is the total mass of MnS inclusion precipitated in the calculation domain (kg).

4. Results and Discussion

4.1. Solidification Structure Morphology

Figure 4 shows the macrostructure of continuously cast bloom of rail steel U75V revealed by macroetching techniques. It can be seen that three typical crystal zones, namely chill zone, columnar zone, mixed zone and equiaxed zone, are present in the one-quarter transverse section of bloom. The chill zone is formed at the bloom surface, where highly supercooled liquid adjacent to the mold wall promotes the drastic crystal nucleation with random orientations. With increasing solidification, some crystals with similar orientations with respect to the temperature gradient survive from the competition growth of crystals and thereafter block other crystals growth, resulting in columnar zone development. When the undercooling of bulk liquid is lower than nucleation temperature, equiaxed crystals are produced by nucleation in the highly constitutionally supercooled liquid and block the columnar growth, finally the columnar to equiaxed transition (CET) occurs and equiaxed zone develops in the bloom centre. Usually, the CET can not suddenly occur and thus a mixed zone, where columnar crystal and equiaxed crystal could coexist, appears in the cross section of bloom. Here, the area ratio of each zone in the one-quarter transverse section of bloom is measured and the measurements show that the area ratio of chill zone, columnar zone, mixed zone and equiaxed zone are 5.3%, 43.1%, 21.5% and 30.1%, respectively. Moreover, porosity and cavity are clearly seen in the equiaxed zone, where the shrinkage is hardly compensated by the residual liquid during final stage of solidification.

Figure 5 shows the typical dendritic structure at different position of transverse section of bloom. It is evident that fine dendritic structure appears at the subsurface, while coarse equiaxed dendritic structure locates at the center and columnar dendritic structure sandwiches between them. In order to quantitatively characterize the dendritic structure, the primary dendrite arm spacing (PDAS) were measured in all samples at magnification 10×. At each location, measurements were performed for 10 times and their average values were taken as the PDAS at the given location. The contour plot of measured PDAS in one-quarter cross section of rail steel U75V bloom is shown in Fig. 6, and the results show that although some scatters are apparent in the one-quarter cross section of bloom, generally the PDAS increases towards the interior of the bloom section and reaches stable at the bloom centre. However, a slight decrease of PDAS appears at the bloom centre, which is also mentioned in other research works.\(^{36–38}\) Some reasonable explanation for this phenomenon may be that an extensive undercooling in the bulk liquid ahead of the columnar crystal promotes equiaxed crystal nucleates significantly and leads to the solidification acceleration at the late period of solidification process.

4.2. Manganese Sulfide Morphology

Figure 7 shows both the 2D and 3D morphology of MnS inclusions in different region of rail steel U75V continuously cast bloom. It should be noted that the SA, CA, MA and EA in the left column means the specimens for the MnS inclusions detection are respectively taken from the chill zone, columnar dendrite zone, mixed zone, and equiaxed dendrite zone and the exact locations of specimens are schematically shown in Fig. 1. It is evident that the MnS inclusions have quite different morphologies depending on their locations in the bloom. The MnS inclusions are mainly globular and well rounded in specimens taken from the chill zone of bloom, where the high solidification cooling rate is benefit for the monotectic sulfide formation. While in the specimens taken from the columnar zone, the spindle-shaped MnS inclusions are observed, that may be because the solute enrichment in interdendritic liquid promotes the MnS inclusions nucleation and later the MnS inclusions growth are easily constrained by columnar dendrite growth with <100> direction, resulting in elongated and occasionally branched morphology. Furthermore, angular, spindle-shaped and plate-shaped MnS inclusions are present in the mixed zone and equiaxed dendrite zone, where the lower solidification rate is benefit for the eutectic sulfide formation and the complicated dendrite morphology suppresses the

| Table 4. Interaction coefficient of elements in molten steel at 1873 K.\(^{3,2}\) |
|-----------------|---|---|---|---|---|
| \(e_i^j\) | C | Si | Mn | P | S |
| Mn | -0.0538 | -0.0327 | 0 | -0.06 | -0.048 |
| S | 0.112 | 0.063 | -0.026 | 0.29 | -0.028 |

Fig. 4. Macrostructure of one-quarter continuously cast bloom.
MnS inclusion growth with regular shape.

Figure 8 shows the typical globular MnS inclusion in continuously cast bloom with EDS analysis. This typical globular MnS inclusion precipitates in the remnant liquid in the interdendritic space through monotectic reaction and is well recognized as Type I MnS inclusion. Metallographic observations showed that these precipitations distributed in the whole cross section of rail steel U75V continuously cast bloom and the diameters of MnS inclusions in the subsurface were significantly smaller than those in the bloom centre, that would be rationally explained that the high solidification cooling rates at the bloom subsurface is more easy to build nucleation undercooling in bulk liquid and promotes nucleation of MnS inclusion, resulting in fine globular MnS inclusion. Therefore, the cooling rate has great effects on the size of Type I MnS inclusion, which is in a good agreement with the previous literatures.10,23,39,40)

Figure 9 shows the typical complex inclusions in continuously cast bloom with EDS analysis. The EDS data shown in Fig. 9 indicate both titanium and manganese are present in a single sulfide precipitation with a nuclei of Al₂O₃ particle. It seems reasonable that the endogenous inclusions Al₂O₃ formed during the cooling process of the melt is favorable for acting as heterogeneous nucleating agents for sulfide inclusion, and later the high segregated liquid steel at the very end of solidification process would promote the formation of a eutectic sulfide mixture of MnS and TiS around the Al₂O₃ nuclei following the eutectic reaction: L→MnS + TiS. Moreover, these sulfide mixtures consisted of MnS and TiS are usually observed at the bloom centre, where the residual liquid is full of solute enrichment at the final solidification stage of continuously cast bloom, which is in a good agreement with Xu’s work.41)

In order to quantitatively characterize the sulfide inclusions, the equivalent diameter, which is calculated as the diameter of a circle with the same area as the sulfide inclusion, was considered as the representative value of sulfide inclusion size, and the aspect ratio, which is defined by the ratio of the maximum dimension to the minimum dimension of the sulfide inclusion, was considered as another representative value of sulfide inclusion morphology. Table 5
summarizes the values for the size and aspect ratio of sulfide inclusions in different region of rail steel U75V continuously cast bloom. It can be seen that sulfide inclusions in the subsurface region have smaller equivalent diameter and lower aspect ratio, indicating that sulfide inclusions in the subsurface region are more fine and rounded compared with those in the bulk. Moreover, the ranges of both equivalent diameter and aspect ratio for sulfide inclusions in the bulk are larger, compared with those in the subsurface, that means the shape and morphology of sulfide inclusion in the bulk are more diverse than those in the subsurface region. The present quantitative characterization of the sulfide inclusions in the high carbon steel continuously cast bloom agrees well with the previous works.\textsuperscript{40,42)}

4.3. Thermodynamic Behavior of MnS Precipitation

Figure 10 shows the change of phase fraction and interdendritic solute segregation with the solidification of rail steel U75V. Here, it should be firstly mentioned that microsegregation index was defined by the ratio of interdendritic solute concentration and initial solute concentration, $C_l/C_0$. It can be seen that during the solidification process, the γ-austenite crystal begins to nucleate at the liquidus temperature of 1467°C without consideration of nucleation undercooling, as shown in Fig. 10(a). With the decrease of temperature, the γ-austenite crystal grows with solute rejec-

<table>
<thead>
<tr>
<th>Region</th>
<th>Typical MnS inclusion in 2D view</th>
<th>Typical MnS inclusion in 3D view</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>CA</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>MA</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>EA</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 7. 2D and 3D morphology of MnS inclusions in different zone of rail steel U75V continuously cast bloom.

Fig. 8. Typical complex inclusions with EDS analysis.
tion, resulting in solute enrichment in interdendritic liquid, and thus the microsegregation index increases. Due to the small equilibrium distribution coefficient of S at γ-austenite/liquid interface, the interdendritic solute S shows a strong trend of microsegregation during the solidification process, especially at the final stage of solidification. When the product of the interdendritic solute concentrations of Mn and S reaches the equilibrium solubility product, the MnS inclusion precipitates in the interdendritic liquid with the consumption of excess solute, and the solute microsegregation index of S decreases at the final stage of solidification, as shown in Fig. 10(b). Moreover, the quantitative analysis from Fig. 10 shows that the start precipitation temperature for MnS inclusion in rail steel U75V is 1 355°C, where the solid fraction is 0.96, and the final solidification temperature for rail steel U75V is 1 342°C.

Figure 11 shows the contour of calculated MnS inclusion size in one-quarter cross section of rail steel U75V bloom. It should be firstly emphasized that the measured PDAS in transverse section of continuously cast bloom, as shown in Fig. 6, was adopted as input data in the case of MnS inclusion size prediction, while the local solidification time was calculated using the proposed heat transfer model for continuous casting and shown in Fig. 12. It can be found that the intensive mould cooling makes the molten steel

<table>
<thead>
<tr>
<th>Items</th>
<th>SA</th>
<th>CA</th>
<th>MA</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent diameter, μm</td>
<td>1.0–2.3</td>
<td>1.4–7.2</td>
<td>1.3–8.5</td>
<td>2.1–12.4</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>1.0–1.5</td>
<td>1.0–20.1</td>
<td>1.5–61.6</td>
<td>2.1–109.5</td>
</tr>
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solidify suddenly near the mould copper and thus the local solidification time in bloom subsurface region is very short, as shown in Fig. 12. Correspondingly, the MnS inclusions precipitated in the bloom subsurface region are lack of time to grow up and the crystal structure is also very fine in the bloom subsurface region, leading to tiny MnS inclusion. Thus, the size of most MnS inclusions in the bloom subsurface region is smaller than $3\mu m$, as shown in Fig. 11. With the distance approach the interior of bloom section, the latent heat release in liquid core of strand becomes different and the local solidification time gradually increases, resulting in coarse dendrite structure and large MnS inclusion. Therefore, the size of MnS in the bloom centre is usually larger than that in the bloom subsurface region, as shown in Fig. 11. But some scatters obviously appears in the contour of calculated MnS inclusion size, which may be induced by the scatters of measured PDAS, which were directly used in the calculation without data filtering.

Figure 13 shows the comparison between the measured equivalent diameter and calculated average diameter of sulfide inclusions in different region of continuously cast bloom. It is notable that the calculated diameters of sulfide inclusions increase from the subsurface to the bloom centre and fit the trend of measured equivalent diameter change. Moreover, the calculated diameters of sulfide inclusions are all in the range of measured equivalent diameters at different locations. Therefore, it is reasonable to infer that the present model is capable of predicting the distribution of MnS inclusion in the continuously cast bloom.

Figure 14 shows the effect of sulfur content on MnS inclusion size. It can be seen that when the initial sulfur content is lower than 30 ppm, the predicted diameter of MnS inclusion is zero. That is to say MnS inclusions can not precipitate during the solidification process, due to the product of the interdendritic solute concentrations of Mn and S lower than the equilibrium solubility product. While the initial sulfur content is higher than 30 ppm, the product of the interdendritic solute concentrations of Mn and S would exceed the equilibrium solubility product at the final stage of solidification, resulting in the MnS inclusion precipitation. Also, the size of MnS inclusion increases with the increase of sulfur content in steel.

Figure 15 shows the effect of PDAS and sulfur content on MnS inclusion size. It is evident that for the case with same sulfur content in steel, the coarse dendrite with large PDAS has a strong trend of solute enrichment in interdendritic liquid, leading to the precipitation of coarse MnS inclusion and the MnS inclusion size increases with the increase of PDAS. For the dendrite with same PDAS, the high sulfur content in steel is prone to promote solute enrichment in interdendritic liquid and MnS inclusion precipitation at the final stage of solidification, and the MnS inclusion size increases with the increase of sulfur content in steel. Therefore, reducing sulfur content in steel and refining solidification structure in bloom are both effective methods to achieve tiny MnS inclusion precipitation in continuously cast bloom of rail steel U75V.
5. Conclusion

In the present study, various methods, including the metallographic examination, traditional 2D optical microscopy, 3D electrolytic extraction, SEM detection with EDS analysis, and thermodynamic calculation for MnS inclusion precipitation, were adopted to investigate the characteristics of solidification structure and sulfide inclusions in the high carbon steel continuously cast bloom. Some of the salient findings are summarized below:

(1) Metallographic examination reveals that the rail steel U75V cast bloom consists of chill zone, columnar zone, mixed zone and equiaxed zone and the measurements show that the area ratio of chill zone, columnar zone, mixed zone and equiaxed zone are 5.3%, 43.1%, 21.5% and 30.1%, respectively.

(2) 2D/3D investigations on the MnS inclusion morphology in the rail steel U75V cast bloom show that the high solidification cooling rate in the subsurface region is benefit for the monotectic sulfide formation and thus sulfide inclusions in the subsurface region with smaller equivalent diameter and lower aspect ratio are more fine and rounded compared with those in the bulk. Moreover, sulfide mixtures of MnS and TiS around the Al$_2$O$_3$ nuclei were observed in the bloom centre, because the Al$_2$O$_3$ particles act as heterogeneous nucleation catalysts for sulfide mixtures, promoting the eutectic reaction (L→MnS + TiS) in high segregated liquid steel at the final stage of solidification process.

(3) Thermodynamic calculation for MnS inclusion precipitation shows that the calculated average diameters of sulfide inclusions increase from the subsurface to the bloom centre and fit the trend of measured equivalent diameter change. Moreover, the parametric study reveals that the size of sulfide inclusion increases with the increase of sulfur content in steel and dendrite arm spacing of continuously cast bloom.

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