Effect of Rare Earth Yttrium on Inclusion Characteristics of Grain-Oriented Silicon Steel

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Abstract: To investigate the influence of heavy rare earth element yttrium on the type, morphology, and quantity distribution of inclusions in grain-oriented silicon steel, thermodynamic calculation was carried out on the typical rare earth inclusions in grain-oriented silicon steel containing yttrium. The main inclusions in the experimental steels with and without yttrium were observed and analyzed using field emission scanning electron microscope (FESEM, Zeiss Gemini SEM 300) and energy dispersive spectrometer (EDS, OXFORD Ultim Extreme). The electron backscatter diffraction (EBSD, OXFORD Symmetry) was used to analyze the local average misorientation of the hot-rolled plate. The results show that the inclusions in the Y-free steel are mainly long MnS, irregular Al2O3, and MnS-Al2O3. The inclusions in the Y-bearing steel are spherical rare earth compounds. The number of inclusions in Y-bearing steel decreases and the size increases compared with Y-free steel. The mean value of local average misorientation and the dislocation density of Y-bearing steel are smaller compared with Y-free steel, which could avoid the cracking problem caused by dislocation accumulation during hot rolling. After heating the rough-rolling sample to 1350 °C, there is no obvious difference in the inclusions type between the Y-free steel and Y-bearing steel. However, the area fraction of inclusions in Y-bearing steel increases slightly. According to the thermodynamic calculation results, there are mainly three kinds of rare earth inclusions, YS, Y2S, and Y2O3, in Y-bearing steel, among which YS has the strongest stability and the stability of Y2O3 is the weakest. The rare earth element yttrium can effectively modify the inclusions, transforming the irregular Al2O3 inclusions, formed during the deoxidation of silicon steel into spherical rare earth inclusions, which suppress the precipitation of long MnS inclusions. Thus, the formability of the steel could be improved.

Keywords: rare earth yttrium; grain-oriented silicon steel; inclusion; thermodynamics

1. Introduction

Grain-oriented silicon steel is an important soft magnetic alloy with Si content of 2.9–3.4%, which has excellent magnetic properties such as high magnetic induction, low iron loss, and low magnetostriction. At present, it is mainly used in power, electronics and military industries. It is also used to manufacture iron cores of transformers and large motor stators [1–3]. The prior research showed that the cleanliness of silicon steel has an important influence on its magnetic properties. However, with the current melting process, there must be a certain amount of non-metallic inclusions and other impurities in the finished steel. The number, size, and density distribution of inclusions affect the...
microstructure and formability of grain-oriented silicon steel [4,5]. Reducing the number
and size of inclusions and reasonably controlling the characteristics of inclusions in steel
are important to improve the magnetic properties of silicon steel. In grain-oriented silicon
steel, the inhibitor-forming element Al will form irregular Al₂O₃ inclusions in the deoxy-
dation stage, and the Mn element will also form large-sized plastic MnS inclusions. Rea-
sonable control of the quantity and density distribution of Al₂O₃ and MnS inclusions is
the key factor to ensure the preparation of high-quality grain-oriented silicon steel.

China is rich in rare earth resources. At the same time, China is one of the countries
with a complete industrial chain of rare earth. The electronic structure of rare earth atoms
determines its chemical properties. Generally, there are three electrons in the outermost
or secondary layer of rare earth elements that are most likely to be lost. Therefore, rare
earth metals are very easy to react with oxygen, sulfur, and other elements to generate
compounds with high melting points, thus achieving the role of purifying molten steel.
Moreover, adding rare earth elements to silicon steel can modify inclusions and refine the
primary recrystallization structure, improving the as-cast structure and properties [6–8].
Studies have shown that rare earth cerium and lanthanum can effectively reduce the num-
er of non-metallic inclusions in grain-oriented silicon steel, change the morphology of
inclusions, and make the hot-rolled plate structure and the inhibitor distribution more
uniform [9–11]. Compared with the light rare earth elements cerium and lanthanum, the
heavy rare earth element yttrium has a smaller atomic radius and better solid solution
effect in molten steel. In addition, the rare earth yttrium element and its formed oxygen
sulfides are distributed at grain boundaries, playing a role in pinning grain boundaries
and inhibiting grain growth [12–14]. It is reported that the inclusions in the pipeline steel
and ship plate steel are mainly spherical or ellipsoidal Y₂O₃, Y₂O₃S, Y₂S₃, and YS inclusions
with the addition of yttrium-based rare earth. The Al₂O₃ inclusions in the steel are modi-
ified into rare earth compounds, and the mechanical properties of steel are improved [15–
17]. Studying the influence of rare earth elements on the characteristics of inclusions in
oriented silicon steel is an important basis for determining whether rare earth elements
can be used as alloy elements. At present, there are few articles analyzing the effect of rare
earth yttrium on the inclusion characteristics of oriented silicon steel. The effects of yt-
trium on the type, composition, size, and morphology of inclusions in grain-oriented sili-
con steel were studied in this paper, and the influence mechanism was illustrated by ther-
modynamic calculation. It is beneficial to accelerate the application of rare earth elements
in oriented silicon steel and provide data reference for the development of high-grade
oriented silicon steel.

2. Materials and Methods

The experimental steel was obtained by smelting and casting in a 50 kg vacuum in-
duction furnace, and its basic material is Fe-3wt% silicon steel. The chemical composition
is shown in Table 1; 1 # steel does not contain Y, and the Y content in 2 # steel is 0.078%.
The addition method of rare earth yttrium is to put it into the bottom of the mold in ad-
ance and dissolve it evenly in the molten steel. The yield of Y is 36.5%. The ingot was
heated to 1150 °C and kept for 0.5 h, and then rough rolled 6 times to a size of 1000 mm ×
200 mm × 20 mm steel plate. The rough-rolled plate was then hot rolled with 5 passes to
become a plate with a thickness of 2.5 mm. The normalizing temperature is 920 °C, and
the holding time is 5 min; the test steel was taken out for air cooling to 900 °C, and then
cooled to room temperature by water spraying. The rolling and heat treatment process is
shown in Figure 1.
### Table 1. Chemical composition of 3% Si-oriented silicon steel (mass fraction, %)

<table>
<thead>
<tr>
<th>Number</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Als</th>
<th>N</th>
<th>O</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.050</td>
<td>2.98</td>
<td>0.22</td>
<td>0.01</td>
<td>0.018</td>
<td>0.028</td>
<td>0.0043</td>
<td>0.0021</td>
<td>—</td>
</tr>
<tr>
<td>2#</td>
<td>0.014</td>
<td>2.97</td>
<td>0.22</td>
<td>0.01</td>
<td>0.011</td>
<td>0.035</td>
<td>0.0045</td>
<td>0.0020</td>
<td>0.078</td>
</tr>
</tbody>
</table>

![Figure 1. The schematic diagram of rolling and heat treatment process.](image)

Samples with the size of 10 mm × 8 mm × 2.5 mm were taken from the experimental steels, which were used for inclusions detection and analysis. The samples were mechanically ground and polished, then slightly corroded with 4% nitric acid alcohol to eliminate surface stress, cleaned with deionized water and anhydrous ethanol, then dried by cold air. Field emission scanning electron microscopy (FESEM, Zeiss Gemini SEM 300, Oberkochen, Germany) and its attached energy spectrometer (EDS, OXFORD Ultim Extreme, Oxfordshire, UK) were used to analyze the number and density distribution and chemical composition of large-sized inclusions in the test steel. At the same time, typical inclusions were selected and their morphology and composition were determined [18,19].

Electron backscatter diffraction (EBSD, OXFORD Symmetry, Oxfordshire, UK) was used to analyze the local average orientation difference of hot-rolled plates. When observing texture, sample preparation is usually divided into conventional polishing and electrolytic polishing methods. When observing hot-rolled plates, electrolytic polishing is used, with an electrolyte of 5% perchloric acid, a voltage of 25–30 V, and an electrolytic time of 5-10 s. The EBSD scanning step of a hot-rolled plate is 2 μm. The scanning area is 3 mm, and the data obtained after scanning are analyzed using CHANNEL 5 software. The morphology and quantity of inclusions were observed and statistically analyzed using transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-TWIN, Hillsboro, USA), and the composition of inclusions was qualitatively analyzed using energy dispersive spectroscopy (EDS, FEI Tecnai G2 F20S-TWIN, Hillsboro, USA). TEM samples were prepared by carbon coating method.

### 3. Results and Discussion

#### 3.1. Effect of Rare Earth Y on the Type and Morphology of Inclusions in Hot-Rolled Plates and Normalized Plates

The statistical results of the type and quantity of inclusions in Y-bearing and Y-free hot-rolled and normalized plates are shown in Tables 2 and 3, where N represents the total number of inclusions per unit area, and the dmean is the average size of inclusions in the corresponding silicon steel plate. The analysis shows that the inclusions in the test steel without rare earth Y are mainly MnS, Al2O3 single-phase inclusions, and Al2O3-MnS composite inclusions. With the progress of rough rolling, finishing rolling, and normalizing process, the total number of inclusions in the test steel increases gradually, but the type of inclusions remains the same. With the addition of rare earth Y, the amount of rare earth sulfur oxide inclusions in the test steel increases greatly, the Al2O3-MnS type
inclusions are transformed into Y$_2$S$_x$-Y$_2$O$_2$S rare earth inclusions, and the single-phase MnS inclusion disappears. In addition, there are a small amount of large-sized Al$_2$O$_3$ inclusions.

Table 2. Type and quantity statistics of inclusions in Y-free silicon steel plate.

<table>
<thead>
<tr>
<th>Steel sample</th>
<th>Inclusion type</th>
<th>N/pcs</th>
<th>(d_{\text{mean}}/\mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough rolled plate</td>
<td>MnS, Al$_2$O$_3$-MnS</td>
<td>301</td>
<td>1.59</td>
</tr>
<tr>
<td>Finish rolled plate</td>
<td>MnS, Al$_2$O$_3$-MnS</td>
<td>388</td>
<td>1.36</td>
</tr>
<tr>
<td>Normalized plate</td>
<td>MnS, Al$_2$O$_3$-MnS</td>
<td>397</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Table 3. Type and quantity statistics of inclusions in Y-bearing silicon steel plate.

<table>
<thead>
<tr>
<th>Steel sample</th>
<th>Inclusion type</th>
<th>N/pcs</th>
<th>(d_{\text{mean}}/\mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rough rolled plate</td>
<td>Y$_2$S$_x$-Y$_2$O$_2$S, Al$_2$O$_3$</td>
<td>248</td>
<td>2.17</td>
</tr>
<tr>
<td>Finish rolled plate</td>
<td>Y$_2$S$_x$-Y$_2$O$_2$S, Al$_2$O$_3$</td>
<td>266</td>
<td>1.92</td>
</tr>
<tr>
<td>Normalized plate</td>
<td>Y$_2$S$_x$-Y$_2$O$_2$S, Al$_2$O$_3$</td>
<td>266</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Figure 2 shows the composition and morphology of inclusions in rough-rolled plates without Y. Elliptical MnS inclusions and irregular Al$_2$O$_3$-MnS type inclusions are mainly found in the rough-rolled plates. Due to the high solid solution temperature of MnS, the size of MnS inclusions in the rough-rolling stage is relatively large, with most of the MnS sizes being around 2 \(\mu m\). The solid solution temperature of Al$_2$O$_3$ is very high. Before the steel liquid solidifies, Al$_2$O$_3$ already exists. During the cooling process of the steel liquid, the particles that precipitate later are easy to precipitate and grow with the existing particles as the core. Therefore, a large part of the inclusions in the rough-rolled plate are composite inclusions with Al$_2$O$_3$ as the core; as the size of Al$_2$O$_3$ as the core itself is about 2 \(\mu m\), the generated composite inclusions are larger in size, around 5 \(\mu m\). Due to the small reduction in rough rolling, the deformation of inclusions is also less affected.

Figure 3 shows the composition and morphology of inclusions in the Y-free precision rolled steel plate. Compared with the rough-rolled plate, the main types of inclusions have not changed, mainly consisting of MnS inclusions and Al$_2$O$_3$-MnS composite inclusions. Unlike rough-rolled plates, MnS inclusions change from elliptical to elongated shapes because MnS has high plasticity and extends with deformation under large deformation variables. The Al$_2$O$_3$-MnS composite inclusion is formed by Al$_2$O$_3$ as the core, which has the characteristic of high hardness. Under large reduction, the Al$_2$O$_3$-MnS composite inclusion does not deform and its size does not change.

Figure 4 shows the composition and morphology of inclusions in a normalized plate without Y. The inclusions in the normalized plate after normalization treatment are mainly elliptical MnS and irregular Al$_2$O$_3$-MnS. Unlike rough and finish-rolled plates, MnS inclusions are finer, with a size of around 600 nm. This is because during normalization treatment, as the temperature increases, MnS solidly dissolves into the austenite phase, and as the temperature decreases, fine and dispersed MnS precipitates. However, there are still some large-sized Al$_2$O$_3$-MnS composite inclusions remaining in the normalization plate, which is because the lower normalization temperature did not completely dissolve MnS.
Figure 2. Composition and morphology of inclusions in the rough-rolled steel plate without Y.

Figure 3. Composition and morphology of inclusions in finish-rolled steel plate without Y.
With the addition of rare earth Y, the composition and morphology of inclusions in the steel are shown in Figure 5. The inclusions in rough-rolled plate, finish-rolled plate and normalizing plate are all transformed into spherical or ellipsoidal Y₂S, Y₂O₅S type inclusions. There are no MnS or MnS-Al₂O₃ type inclusions in Y-bearing silicon steel. Rare earth Y is easy to combine with oxygen and sulfur in molten steel to form spherical yttrium sulfide, yttrium sulfur oxide or other type inclusions containing yttrium, which can effectively inhibit the formation of long strip MnS inclusions in the steel. Due to the strong deoxidization ability of rare earth, most of the Al₂O₃ inclusions in steel are also modified into rare earth sulfur oxides. Spherical or ellipsoidal rare earth sulfides are dispersed in the steel matrix and maintain their original morphology during rolling [20–24]. The residual Al₂O₃ inclusions have a larger size and a strip-shaped morphology, with a relatively small quantity, which will not affect the mechanical properties of the steel.

Figure 4. Composition and morphology of inclusions in the normalized steel plate without Y.

Figure 5. Composition and morphology of inclusions in Y-bearing steel.
The morphology and composition of micro inclusions in the hot-rolled plate of the test steel were observed by TEM and EDS. The results are shown in Figures 6 and 7. Spherical MnS-SiO$_2$ composite precipitates with a size less than 200 nm are mainly found in Y-free steel. From the element distribution diagram, it can be seen that the distribution of S element is relatively high, and MnS precipitates with SiO$_2$ as the core composite. In the Y-bearing steel, there are spherical particles with a size of about 20 nm, which are distributed in an aggregated state. The EDS analysis results show that the particles are mainly composed of O, Si, S, Mn, and Y. No Al containing particles and single fine MnS precipitation were found in the experimental steel [25]. From the distribution maps of various elements, it can be seen that small inclusions adhere to the SiO$_2$ matrix, with a relatively low content of Mn element. The aggregated small particles are mostly rare earth oxide sulfides.

Figure 6. Composition distribution of fine precipitates in Y-free steel.
3.2. Effect of Rare Earth Y on Inclusions Composition in The Hot-Rolled Plate and Normalized Plate

Inclusion data in 30 consecutive fields of view were collected using a field emission scanning electron microscope (FE-SEM) with a magnification of 500 times. The density of inclusions is expressed by \( N \), as shown in formula (1), that is, the number of inclusions within a certain size range detected in the unit field of view area of the sample, unit: pieces/mm\(^2\). Among them, the \( N_t \) represents the total number of inclusions in all fields of view, unit: pieces, and \( A_t \) represents the total area of all fields of view, unit: mm\(^2\). The inclusion area fraction is expressed by the percentage of the inclusion area to the total field of view area in a certain size range detected in the steel, % [11,26].

\[
N = \frac{N_t}{A_t}
\]

The quantity density and area fraction of inclusions in different size ranges in the rough-rolled plates are shown in Figure 8. With the addition of rare earth Y, the number of inclusions in the rough-rolled plate decreased as a whole, in which the inclusions in the size range of 0.5~2 μm decreased by 29%. However, the number of larger size inclusions increased significantly, and the inclusions in the size range of 2~4 μm increased by about 1.5 times. Compared with the samples without rare earth Y, the area fraction of inclusions in Y-bearing steel increases generally. The area fraction of inclusions smaller than 4 μm is 0.171%, and the area fraction of inclusions larger than 4 μm is 0.086%.

The quantity density and area fraction of inclusions in different size ranges in the finish-rolled plate are shown in Figure 9. With the addition of rare earth Y, the number of inclusions in the finish-rolled plate is greatly reduced, in which the number of inclusions within the size range of 0.5~2 μm is reduced by 48%, and the number of inclusions within the size range of 2~4 μm is increased by 14%. The area fraction of inclusions smaller than 4 μm in finish-rolled steel plates containing yttrium decreased to some extent. However,
there are many inclusions with a size larger than 4 μm in the Y-bearing finish-rolled plate. The area fraction of inclusions in the Y-bearing finish-rolled plate increased obviously. Compared with the samples without rare earth, the area fraction of inclusions in Y-bearing steel is obviously higher.

Figure 9. Quantity density and area fraction of inclusions in finish-rolled plate.

The quantity density and area fraction of inclusions in different size ranges in the normalized plate are shown in Figure 10. With the addition of rare earth Y, the number of inclusions in the normalized plate is still reduced overall, among which the number of small size inclusions in the range of 0.5–2 μm is reduced by 38%, and the inclusions in the range of 2–4 μm are reduced by 11%. Similar to the hot-rolled plate, there are still many inclusions larger than 4 μm in the Y-containing normalizing plate. These large-sized inclusions lead to a significant increase in the area fraction of inclusions in normalized plates containing yttrium. Compared with the samples without rare earth, the area fraction of inclusions with the size of 0.5–2 μm reduces by 0.069%, with the size of 2–4 μm increases by 0.017%, with the size of 4–6 μm increases by 0.064%, and that of the inclusions larger than 6 μm increases by 0.048%. The addition of rare earth yttrium reduces the area fraction of small-sized inclusions and increases the area fraction of large-sized inclusions.

Figure 10. Quantity density and area fraction of inclusions in the normalized plate.

The addition of rare earth yttrium inhibits the nucleation of small-sized inclusions such as MnS and Al₂O₃, and reduces the number and area fraction of small-sized inclusions in the steel. At the same time, large-sized rare earth containing inclusions are formed in the steel. With rough rolling, finishing rolling, and normalization progress, the number of small-sized inclusions in Y-free steel increases significantly. This is due to the uniform and fine precipitation of MnS during the rolling process, and the number of large-sized inclusions has no obvious change. According to the statistical results of inclusions area fraction, the area fraction of small-sized inclusions in Y-free steel increases obviously with the progress of the rolling and annealing processes. The number of inclusions in Y-bearing
steel increases slightly in the three processes, and the area fraction of small-sized inclusions decreases, while that of large-sized inclusions increases. The author believes that this is due to the heating treatment of different processes, which increases the size of rare earth inclusions within a certain size range. In general, due to the relatively large amount of rare earth in the experimental steel, the number of inclusions larger than 4 μm increases, but the average size of the inclusions only increases about 0.60 μm.

3.3. Morphological Characteristics of Inclusions in Test Steel after Solid Solution Heat Treatment

Samples with the size of 10mm × 8mm × 8mm were taken from two kinds of test steels. Put the sample into a 1350 °C tube furnace, keep it for 20 min, and then put it into cold water to cool to room temperature. The morphology of inclusions is shown in Figures 11 and 12. The inclusions in Y-free steel are mainly irregular Al₂O₃ and strip or spherical MnS-Al₂O₃ inclusions, and no MnS inclusions are detected. This is because the solution temperature of MnS in the steel is about 1320 °C, and the sample is heated to 1350 °C and kept for 20 min in the experiment, which made MnS a solid solution again. The inclusions in the Y-bearing steel are still spherical YₓSᵧ-Y₂O₂S inclusions, and the high-temperature heating does not affect the inclusion types of the Y-bearing steel.

Figure 11. Composition and morphology of inclusions in Y-free steel after high-temperature heating.
Figure 12. Composition and morphology of inclusions in Y-bearing steel after high-temperature heating.

The quantity density and area fraction of inclusions in the rough-rolled plate heated at high temperature are shown in Figure 13. Compared with Y-bearing steel and Y-free steel, the number of small inclusions in the size range of 0.5~2 μm in the Y-free steel is reduced by 41%, and inclusions in the size range of 2~4 μm are reduced by 62%. However, there are still many large-sized inclusions in the Y-bearing steel, which are larger than 4 μm. The inclusions area fraction of Y-free steel is also significantly lower than that of Y-bearing steel. According to Figure 6 and Figure 11, since most MnS inclusions in the steel are redissolved at high temperatures, the number and area fraction of inclusions in the Y-free steel are significantly reduced. However, the area fraction of inclusions in Y-bearing steel increases slightly, which is consistent with the results of the above experiments. The high heating temperature before hot rolling makes the MnS and other inhibitors in the grain-oriented silicon steel dissolve again, and fine particles are precipitated during hot rolling. With the addition of rare earth yttrium, the inclusions in steel are transformed into high melting point rare earth inclusions due to the denaturation effect of rare earth on inclusions. With the high heating temperature at 1350 °C, only the area fraction of inclusions in Y-bearing steel increased slightly.

Figure 13. Quantity density and area fraction of inclusions in experimental steel with high heating temperature.

3.4. Influence of Rare Earth Y on the Formability of Hot-Rolled Plate

Figure 14a,b represent the local average orientation difference (LAM) of hot-rolled plates, Y-free and Y-bearing, respectively. By scanning the orientation difference between adjacent data points in the grain using EBSD, and statistical analysis of LAM, the orientation change inside the grain of plastic deformed metal after deformation is analyzed. The small angle orientation difference between grains can form substructure grain boundaries and dislocations, so although dislocation density cannot be directly measured, the relative size of dislocation density can be measured through statistical LAM [27]. The dislocation density increases with the increase of the deformation variable, so the LAM value is
indirectly positively correlated with the dislocation density, that is, the higher the overall dislocation density, the greater the LAM value.

The LAM values are shown in Figure 15, where the abscissa represents the LAM value and the ordinate represents the relative frequency. The peak values of LAM of hot-rolled plates without and containing Y appeared at 1.05° and 0.75°, respectively, and the average values of local orientation difference were 1.72° and 1.40°, respectively. This shows that the number of data points with higher local misorientation decreases after adding rare earth. There are strip MnS inclusions and irregular Al₂O₃ inclusions in the traditional hot-rolled plate of grain-oriented silicon steel. Due to the presence of these inclusions, when the interface deformation is incompatible with the matrix, dislocation accumulation is easy to occur at the interface, which makes the stress and strain distribution more uneven [28]. Stress concentration areas are easily formed at the interface. In addition, there is an area between the inclusion and the steel matrix where the stress gradient is not obvious. If the inclusion is close enough, that is, the number density of the inclusion is relatively high, the stress fields around the inclusion may interact and cause stress concentration [29,30]. With the addition of rare earth, the inclusions such as MnS and Al₂O₃ in the hot-rolled plate are transformed into spherical rare earth compounds, and the number of small- and medium-sized inclusions in steel is significantly reduced. This improves the mechanical properties of the hot-rolled silicon steel plate and avoids the cracking problem caused by dislocation accumulation during the hot-rolling process.

Figure 14. Distribution diagram of LAM of hot-rolled sheet: (a) Y-free; (b) Y-bearing.

Figure 15. LAM statistical chart of hot-rolled plate: (a) Y-free; (b) Y-bearing.
4. Thermodynamic Calculation Results and Analysis

4.1. Thermodynamic Analysis of Rare Earth Inclusions

Due to the low electronegativity of rare earth elements, they have a strong ability for deoxidation and desulfurization. The addition of rare earth elements in steel will form rare earth compounds containing sulfur and oxygen. Four inclusions of \( \text{Y}_2\text{O}_3, \text{Y}_2\text{O}_2\text{S}, \text{Y}_2\text{S}_3, \) and \( \text{YS} \) may be formed after the addition of rare earth in grain-oriented silicon steel [31–33]. To analyze the formation and change of rare earth inclusions in the test steel, the thermodynamic calculation is used to analyze and discuss them. The formation reaction formulas and standard Gibbs free energies of formation of four rare earth compounds at 1600 °C are shown in Table 4.

Table 4. Formation reaction formulas and standard Gibbs free energies of formation of rare earth compounds

<table>
<thead>
<tr>
<th>Chemical Reaction Formula</th>
<th>( \Delta G^\theta/(\text{J} \cdot \text{mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2[\text{Y}] + 3[\text{O}] = \text{Y}_2\text{O}_3(\text{s}) )</td>
<td>(-1792600 + 658.0T )</td>
</tr>
<tr>
<td>( 2[\text{Y}] + 2[\text{O}] + [\text{S}] = \text{Y}_2\text{O}_2\text{S}(\text{s}) )</td>
<td>(-1521000 + 536.0T )</td>
</tr>
<tr>
<td>( 2[\text{Y}] + 3[\text{S}] = \text{Y}_2\text{S}_3(\text{s}) )</td>
<td>(-1171000 + 441.0T )</td>
</tr>
<tr>
<td>([\text{Y}] + [\text{S}] = \text{YS}(\text{s}) )</td>
<td>(-321080 + 91.0T )</td>
</tr>
</tbody>
</table>

According to equation (2)–(6), the Gibbs free energy of the reaction can be obtained [34]. The reaction of any rare earth element in steel can be expressed by the following general formula:

\[
[\text{RE}] + \frac{M}{N}[F] = \frac{1}{N} \text{RE}_n F_M
\]  

\( [\text{RE}] \) is the rare earth element, \([F] \) is the reactant, \( \text{RE}_n F_M \) is the product, \( N \) and \( M \) are the number of atoms of rare earth elements and reactants in the product. Gibbs free energy of formation can be obtained from the isothermal equation:

\[
\Delta G = \Delta G^\theta + RT \ln J
\]

Among them, \( \Delta G^\theta \) is the standard Gibbs free energy of formation, unit: \( \text{J/mol} \); \( R \) is the gas constant, which is generally taken as 8.314 \( \text{J/(mol·K)} \); \( T \) is the thermodynamic temperature, unit: \( \text{K} \); \( J \) is the activity product, and its calculation formula is:

\[
J = \left( \frac{a_{\text{RE}_n F_M}}{a_{\text{RE}} a_F} \right)^\frac{1}{N}
\]

Since the mass fraction of each solute in the molten steel tends to 0 and the mass fraction of the solvent tends to 1, the mass fraction of 1% is selected as the standard state. The activity \( a_i \) of any component \( i \) in steel is expressed by the following formula:

\[
a_i = f_i \omega [i]
\]

where \( f_i \) is the activity coefficient. The calculation method is the Wagner model. Under isothermal and equal pressure, for Fe-2-3- system, it is considered that the logarithm of the activity coefficient \( f_2 \) of component 2 of the multiple system is a function of the concentration of each component [2%], [3%], and the simplified calculation formula of the model is as follows:

\[
\lg f_i = \sum_{j=1}^{n} e_i^j \omega [j]
\]
In the formula, \( e_i^j \) is the activity interaction coefficient of element \( j \) to solute \( i \). \( \omega[i] \) and \( \omega[j] \) are the mass percentage of \( i \) and \( j \) in molten steel, respectively. The activity interaction coefficient of relevant elements in molten steel at 1600 °C is shown in Table 5 [35,36].

### Table 5. Interaction coefficient of elements in molten steel at 1600 °C.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>N</th>
<th>Al</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-0.450</td>
<td>-0.131</td>
<td>-0.021</td>
<td>0.070</td>
<td>-0.133</td>
<td>-0.20</td>
<td>0.057</td>
<td>-3.900</td>
<td>-16.300</td>
</tr>
<tr>
<td>Si</td>
<td>0.112</td>
<td>0.063</td>
<td>-0.026</td>
<td>0.029</td>
<td>-0.028</td>
<td>-0.27</td>
<td>0.01</td>
<td>0.035</td>
<td>-0.550</td>
</tr>
<tr>
<td>Y</td>
<td>-0.220</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>-7.340</td>
<td>-90.70</td>
<td>-0.875</td>
<td>—</td>
<td>-0.006</td>
</tr>
<tr>
<td>Al</td>
<td>0.091</td>
<td>0.0056</td>
<td>0.035</td>
<td>0.033</td>
<td>0.030</td>
<td>-6.60</td>
<td>-0.058</td>
<td>0.045</td>
<td>—</td>
</tr>
</tbody>
</table>

Henry activity coefficients and Henry activities of O, S, Y and Al in molten steel are calculated according to the above Wagner model. The results are shown in Table 6. The activities of the four rare earth compounds Y₂O₃, Y₂O₅S, Y₃S₃, and YS in the molten steel at 1600 °C are 1. According to formula (3) and formula (4), the Gibbs free energy of the formation of rare earth compounds is obtained, and the results are shown in Table 7.

### Table 6. Activity coefficient and activity of various elements of Y-bearing steel at 1600 °C.

<table>
<thead>
<tr>
<th>Element</th>
<th>( f_{[O]} )</th>
<th>( f_{[S]} )</th>
<th>( f_{[Y]} )</th>
<th>( a_{[O]} )</th>
<th>( a_{[S]} )</th>
<th>( a_{[Y]} )</th>
<th>( a_{[Al]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01553</td>
<td>1.38283</td>
<td>0.01521</td>
<td>0.53749</td>
<td>0.04192</td>
<td>1.03367</td>
<td>0.04651</td>
</tr>
</tbody>
</table>

### Table 7. Gibbs free energy of each reaction formula of Y-bearing steel at 1600 °C.

<table>
<thead>
<tr>
<th>Chemical Reaction Formula</th>
<th>( J )</th>
<th>( \Delta G )</th>
<th>J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [2\text{[Y]} + 3\text{[O]} = \text{Y}_2\text{O}_3(s)] )</td>
<td>( 1.89 \times 10^{12} )</td>
<td>23,456,912</td>
<td></td>
</tr>
<tr>
<td>( [2\text{[Y]} + 2\text{[O]} + [S] = \text{Y}_2\text{O}_5\text{S}(s)] )</td>
<td>( 3.87 \times 10^{12} )</td>
<td>-29,879.46</td>
<td></td>
</tr>
<tr>
<td>( [2\text{[Y]} + 3\text{[S]} = \text{YS}(s)] )</td>
<td>( 1.62 \times 10^{12} )</td>
<td>-50,675.21</td>
<td></td>
</tr>
<tr>
<td>( [\text{Y} + [S] = \text{YS}(s)] )</td>
<td>( 1.57 \times 10^{12} )</td>
<td>-36,062.01</td>
<td></td>
</tr>
</tbody>
</table>

According to the physical meaning of Gibbs free energy, when \( \Delta G > 0 \), the reaction proceeds forward; when \( \Delta G > 0 \), the reaction proceeds backward. It can be found from the calculation results of table 7, \( \Delta G (\text{Y}_2\text{O}_3) = 23,456.92 \text{ J/mol} \), and that \( \text{Y}_2\text{O}_3 \) inclusions cannot be precipitated in molten steel Y-bearing at 1600 °C. \( \Delta G (\text{Y}_2\text{O}_5\text{S}) = -29,879.46 \text{ J/mol} \), \( \Delta G (\text{Y}_3\text{S}_3) = -50,675.21 \text{ J/mol} \), \( \Delta G (\text{YS}) = -36,062.01 \text{ J/mol} \). The Gibbs free energy of formation of \( \text{Y}_2\text{O}_3\text{S}, \text{Y}_3\text{S}_3\), and \( \text{YS} \) is less than 0, so these three kinds of inclusions can be precipitated from the Y-bearing steel.

### 4.2. Mutual Conversion of Rare Earth Inclusions

The rare earth inclusions precipitated from molten steel cannot exist stably all the time, which is related to the actual production environment and the mutual transformation of inclusions. The reaction formula for the experiment’s mutual transformation of the three rare earth inclusions is shown in Table 4.

\[
[Y]+\text{YS}(s) + 2\text{[O]} = \text{Y}_2\text{O}_3\text{S}(s) \quad \Delta G^\theta = -1199920 + 445T \tag{7}
\]

\[
2\text{YS}(s) + [S] = \text{Y}_3\text{S}_3(s) \quad \Delta G^\theta = -528840 + 259T \tag{8}
\]

\[
\text{Y}_3\text{S}_3(s) + 2\text{[O]} = \text{Y}_2\text{O}_3\text{S}(s) + 2[S] \quad \Delta G^\theta = -350000 + 95T \tag{9}
\]

Formula (7) is the conversion reaction between \( \text{YS} \) and \( \text{Y}_2\text{O}_3\text{S} \). Combined with the above relevant data and formulas, it is concluded that the Gibbs free energy of formation of the reaction is 6182.56 J/mol; it can be known that the reaction is carried out in reverse.
the Y₂O₃:S inclusions precipitated in the molten steel will be transformed into YS inclusions, that is, the stability of YS is better. According to the conversion reaction formula between YS and Y₂S₃ in formula (8), it is calculated that the Gibbs free energy of formation of the reaction is 19448.82 J/mol, and the reaction proceeds in the reverse direction. The reaction formula between Y₂S₃ and Y₂O₂S is shown in formula (9). After calculation, the Gibbs free energy of formation of the reaction is 20795.75 J/mol, and the reaction proceeds in reverse. It can be seen that when the Y content is 0.078%, the stability of the three rare earth inclusions in the molten steel at 1600 °C is YS > Y₂S₃ > Y₂O₂S, that is, YS will preferentially precipitate. However, due to the limitation of the reaction balance, the conversion reaction between rare earth inclusions will not proceed completely, so YS, Y₂S₃, and Y₂O₂S will exist in the molten steel at the same time.

4.3. Evolution of Al₂O₃ Inclusions in Y-Bearing Grain-Oriented Silicon Steel

In the smelting process of grain-oriented silicon steel without yttrium, Al will be added to the molten steel for deoxidation, so Al₂O₃ inclusions will inevitably be generated in the steel. The morphology of Al₂O₃ is generally irregular, and its thermal expansion coefficient is significantly different from that of the steel matrix, therefore, it is easy to cause cracks in the steel during the rolling process. The thermal expansion coefficient of rare earth inclusions are similar to that of steel substrates, avoiding the generation of cracks at the interface between rare earth inclusions and steel substrates during steel processing, thereby improving the impact resistance of the steel. With the addition of rare earth yttrium, since the affinity of Y to O and S is stronger than that of Al, rare earth yttrium has a metamorphic effect on Al₂O₃ inclusions [37]. The formation reaction formula and standard Gibbs free energy of the formation of Al₂O₃ are as follows:

\[ 2[\text{Al}] + 3[\text{O}] = \text{Al}_2\text{O}_3(s) \quad \Delta G^\theta = -1205198 + 387.72T \] (10)

The conversion reaction formula between Al₂O₃ and Y₂O₂S is:

\[ 6[\text{Y}] + 2\text{Al}_2\text{O}_3(s) + 3[\text{S}] = 3\text{Y}_2\text{O}_3\text{S}(s) + 4[\text{Al}] \quad \Delta G^\theta = -2152764 + 832.56T \] (11)

From the calculation results, it is known that the Gibbs free energy of formation of the above formula is -292574.63 J/mol, and the reaction is going forward, that is, with the addition of rare earth Y in molten steel, Y can transform Al₂O₃ into Y₂O₂S. However, it is still limited by the reaction equilibrium, and a small amount of Al₂O₃ remains in the steel. According to the influence of rare earth yttrium on the modification effect of inclusion, the diagram of inclusion modification is drawn as shown in Figure 16. To sum up, the inclusions in the steel containing yttrium are mainly yttrium sulfide, yttrium sulfur oxide, and its composite inclusions. In addition, there are residual Al₂O₃ inclusions, which are consistent with the test results.

![Figure 16. Schematic diagram of inclusion modification after adding rare earth yttrium.](image-url)
5. Conclusions

(1) In the Y-free silicon steel, the inclusions are mainly strip MnS, irregular Al_2O_3, and MnS-Al_2O_3. With the addition of rare earth Y, the inclusions in the test steel changed into spherical rare earth compounds, and the average size of the inclusions increased significantly. The addition of rare earth Y effectively improves the morphology of inclusions, especially the large-sized MnS and Al_2O_3 inclusions. The spheronizing modification of inclusions in steel is obvious, which is beneficial for improving the plasticity of steel.

(2) In roughing and finishing hot-rolling and normalizing processes, the number and area fraction of smaller inclusions in Y-free steel gradually increase. There is no obvious change in the number of inclusions in the roughing, finishing, and normalizing samples of Y-bearing steel, but the area fraction of inclusions increases slightly. The addition of rare earth reduces the precipitation amount of irregular large-sized inclusions in the steel. Due to the relatively large addition of rare earth in the experimental steel, the number of inclusions with a size of more than 4 μm increased, but the average size of inclusions increases by only about 0.60 μm. When the rough-rolling sample is heated at 1350°C, the characteristics of rare earth inclusions in Y-bearing steel are relatively stable, and only the area fraction increases slightly.

(3) Through thermodynamic calculation, when the yttrium content is 0.078%, three kinds of rare earth inclusions, YS, Y_2S, and Y_2O_3S, mainly existed in the steel. The stability of YS is the strongest, and that of Y_2O_3S is the weakest. The addition of rare earth yttrium can denature the Al_2O_3 inclusions formed by deoxidation of the silicon steel, and inhibit the precipitation of long strips of MnS. Reasonable controlling of liquid steel composition and rare earth addition can effectively control the characteristics of inclusions in the steel.

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References


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