Effect of Lanthanum Addition on Formation Behaviors of Inclusions in Q355B Weathering Steel

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1. Introduction

Weathering steel contains up to 2 wt.% of Cu, P, Cr, Ni, and other alloying elements. Compared with plain carbon steel, weathering steel has excellent atmospheric corrosion resistance due to the addition of these alloying elements, which forms a protective rust layer during atmospheric corrosion. The rust layer consists of a loose outer rust layer and a dense inner rust layer. The outer rust layer is usually composed of α-FeOOH, γ-FeOOH, and Fe3O4 phase. The inner rust layer is usually composed of extremely dense amorphous spinel Fe3O4 and α-FeOOH phase. The contact area between the internal rust layer and the matrix is highly smooth, and Cu, P, and Cr are uniformly enriched in the amorphous oxide layer. The amorphous spinel oxide layer adjacent to the matrix reduces the number of anodic sites and hinders the penetration of corrosion particles into the matrix, thus effectively improving the corrosion resistance [1–3]. Therefore, it is widely used in container plates, railway vehicles, bridge engineering, and other fields [4,5]. Nowadays, in addition to excellent corrosion resistance, weathering steel is required to possess outstanding mechanical properties, such as strength and toughness, to meet increasingly stringent application requirements. Consequently, improving comprehensive properties, including the corrosion resistance, strength, and toughness on the basis of cost control, is the future direction of weathering steel.

Nonmetallic inclusions are frequently cited as the cause of steel performance issues. They not only deteriorate the corrosion resistance but adversely affect the mechanical properties. The pitting corrosion is mainly caused by manganese sulfide (MnS), deformed...
siliconanate, and aluminum oxide (Al₂O₃), which are not conducive to the formation of a uniform rust layer on the substrate and reduce the adhesion between the rust layer and the matrix, thus resulting in the rust layer falling off [6–9]. In addition, due to the difference in thermal expansion coefficients and deformation capacity between the inclusions and matrix, stress concentration is prone to occur around the inclusions under load, which leads to the initiation of fatigue cracks [10–12]. The addition of rare earth elements can not only purify molten steel but modify inclusions and act as microalloying elements because of their unique electronic layer structure, variable valence, and large-sized atoms. Therefore, adding an appropriate amount of rare earth to steel can significantly improve its corrosion resistance and mechanical properties (e.g., strength, toughness, and heat ductility) [13–16]. At the same time, it is worth mentioning that, compared with the alloying elements Cr, Ni, and Cu in weathering steel, the price of light rare earth metals is lower. Accordingly, it is undoubtedly an excellent way to improve the comprehensive performance of weathering steel by adding an appropriate amount of light rare earth elements. In recent years, there have been many reports on the research of rare earth weathering steel. Xintong Lian’s [17] research on rare earth weathering steel showed that the grain refinement effect of rare earth (Ce and La) increased the density of the protective rust layers and the formation of RE inclusions also weakened the micro-area electrochemical corrosion caused by MnS inclusions. In addition, the segregation of trace rare earth elements at the interface between the corrosion layers and the matrix enhanced the compactness and adhesion of the rust layers and prevented contact of corrosive ions with the matrix. Therefore, the addition of rare earth obviously improved the corrosion resistance of weathering steel. L J Yue [18] showed that by adding an appropriate amount of rare earth into the weathering steels, the strip-shaped MnS inclusions were modified into the dispersive spherical rare earth inclusions. Moreover, the grain refinement and solid solution strengthening effect of rare earth significantly improved the impact toughness and strength of weathering steel.

Plenty of researchers have reported the effect of rare earth in weathering steel, revealing the effects of inclusion modification, molten steel purification, and microalloying on the mechanical properties and corrosion resistance [16–23]. However, few detailed studies have been performed on the modification mechanism of rare earth on inclusions in weathering steel. Therefore, the modification mechanism of lanthanum on inclusions in Q355B weathering steel was studied by combining laboratory experiments and thermodynamic calculations in this work.

2. Materials and Methods

In the present work, four sets of laboratory-scale experiments with different La contents were carried out in a levitation melting furnace. The Q355B weathering steel ingot was loaded into the water-cooled copper crucible of a 1 kg levitation melting furnace. After vacuuming below 10 Pa, high-purity argon gas was added to 50,000 Pa and then gradually heated to 1600 °C for 10 min. Then, La (>99.99 wt.%) wrapped in iron foil was added into the molten steel and then poured into a 70 × 50 × 40 mm mold after holding for 5 min. The ingot was slowly cooled in the furnace after pouring. The addition of La in the four sets of test steels were 0 wt.%, 0.0075 wt.%, 0.0184 wt.%, and 0.0425 wt.%. The final composition of the test steels were determined using ICP-OES (ICPS-8100; Shimadzu corporation, Kyoto, Japan) with an accuracy of ±0.5 ppm. The accuracy and precision of the component analysis were improved by background subtraction and spectral line selection, and the recovery rate test and accuracy test proved that the method was accurate, sensitive, and reliable. The total oxygen content (T.O) refers to the sum of dissolved oxygen and the oxygen content of the inclusions. It was measured by an ON-3000 oxygen and nitrogen analyzer, which adopted a non-dispersive infrared detection system and was equipped with two independent infrared absorption cells. In addition, the length of the absorption cell and the number of channels could be flexibly adjusted depending on the sample, thus ensuring the sensitivity and reliability of the detection. The chemical compo-
position of each test steel is listed in Table 1. Since the weight fractions of trace non-critical elements, such as Ti, Co, and V, were not included in Table 1, the sum of the weight fractions was less than 100%. To clarify the formation behavior of inclusions in the test steel, four 10 × 10 × 10 mm samples were cut from a 1/2 distance from the center by wire electrode discharge cutting at the same height position of each ingot and then were pre-milled and polished. The chemical composition and morphology of inclusions were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) attached to an SEM (SU-1500; Hitachi, Ltd., Tokyo, Japan). The selection of the acceleration voltage and the identification of overlapping peaks were carefully processed to ensure the reliability of inclusion analysis in EDS analysis. The image analysis software Image-Pro Plus 6.0 was used to evaluate the size distribution, number density, and average size of inclusions, and at least 50 viewing fields at 2000 magnification were randomly selected in each sample. Additionally, the modification mechanism of lanthanum on the inclusions was analyzed using thermodynamic calculation. The transformation process of inclusions in molten steel with different La contents at 1600 °C was calculated using the thermodynamic software FactSage 8.1 with the databases of FSstel, FactPS, Ftoxid, and FTlite. The FToxid FactSage database could realize the thermodynamic calculation of complex solutions, where the solution system mainly adopted the quasi-chemical model. Compared with the traditional Wagner approximation formula, FactSage software used an “association compound” to characterize the interaction between solute elements, thus ensuring the accurate prediction of the precipitation behavior of complex inclusions in molten steel.

| Sample | T.O  | C     | Al   | Si   | Mn   | S    | Cr   | La  |
|--------|------|-------|------|------|------|------|------|-----|
| NO. 1  | 0.0076 | 0.1740 | 0.0179 | 0.1346 | 1.56 | 0.0030 | 0.0549 | -   |
| NO. 2  | 0.0076 | 0.1611 | 0.0203 | 0.1327 | 1.47 | 0.0028 | 0.0566 | 0.0075 |
| NO. 3  | 0.0076 | 0.1657 | 0.0192 | 0.1344 | 1.47 | 0.0023 | 0.0555 | 0.0184 |
| NO. 4  | 0.0076 | 0.1791 | 0.0325 | 0.2079 | 1.59 | 0.0022 | 0.0554 | 0.0425 |

3. Results and Discussion

3.1. Effect of La Treatment on Characteristics of Inclusions

The morphology and chemical composition of typical inclusions in RE-free steel are shown in Figure 1. It can be seen that the inclusions are mainly Al2O3 and MnS. Additionally, some alumina and manganese sulfide complex inclusions were also found. The core of the complex inclusion is Al2O3, surrounded by MnS inclusions, as shown in Figure 1c. This is because the solubility of S2− and Mn2+ in molten steel decreases with the decrease in solidification temperature during the solidification process [24] and the first-principles calculation of S2−, Mn2+, and Al2O3 shows that Al2O3 has a strong attraction to S2− and Mn2+ and can easily form complex inclusions [25]. Therefore, during the solidification process, some small-sized Al2O3 inclusions are inclined to be pushed to the liquid phase and act as the sites of MnS inclusion formation due to the micro-segregation of Mn and S.

Figure 1. SEM images and EDS results of typical inclusions in RE-free steel: (a) Al2O3, (b) MnS, and (c) Al2O3-MnS complex inclusion.
Figure 2 displays the typical inclusions in sample steel containing 0.0075 wt.% La. According to the atom fraction of the elemental composition of inclusion, the inclusions are mainly spherical LaAlO$_3$ and irregular MnS. Additionally, a small number of irregular Al$_2$O$_3$ and LaAlO$_3$ complex inclusions can also be found. As shown in Figure 2c, its main body is still Al$_2$O$_3$ and the outer part is modified by La. Consequently, the harmful Al$_2$O$_3$ and MnS inclusions cannot be completely modified by adding a small amount of La.

As shown in Figure 3, the Al$_2$O$_3$ inclusions are completely absent. The inclusions are mainly LaAlO$_3$, La$_2$O$_3$, MnS, and LaAlO$_3$-La$_2$O$_3$ complex inclusions as the La content in steel increases to 0.0184 wt.%.

As shown in Figure 4, when the La content increases to 0.0425 wt.%, the MnS and Al$_2$O$_3$ inclusions disappear completely and the inclusions are mainly La$_2$O$_2$S and La$_2$O$_3$ and a small amount of La$_2$O$_2$S-La$_2$O$_3$ complex inclusions. As shown in Figure 4c, the morphology of complex inclusion is a La$_2$O$_3$ inclusion wrapped in a La$_2$O$_2$S inclusion. This is because the La$_2$O$_3$ inclusions consume the surrounding oxygen during its formation and the formation condition of La$_2$O$_2$S is first satisfied around La$_2$O$_3$ inclusions.

**Figure 2.** SEM images and EDS results of typical inclusions in steel containing 0.0075 wt.% La: (a) LaAlO$_3$, (b) MnS, and (c) Al$_2$O$_3$-LaAlO$_3$ complex inclusion.

**Figure 3.** SEM images and EDS results of typical inclusions in steel containing 0.0184 wt.% La: (a) LaAlO$_3$, (b) La$_2$O$_3$, and (c) LaAlO$_3$-La$_2$O$_3$ complex inclusion.

**Figure 4.** SEM images and EDS results of typical inclusions in steel containing 0.0425 wt.% La: (a) La$_2$O$_3$, (b) La$_2$O$_2$S, and (c) La$_2$O$_2$S-La$_2$O$_3$ complex inclusion.
To investigate the influence of La treatment on the quantity and size distribution of inclusions, the inclusions were statistically measured using Image-Pro software. The size-distribution statistical data show that the inclusions in RE-free steel are large-sized, which can heavily deteriorate the mechanical performance and corrosion resistance of weathering steel [12,26]. With the increase in La content, the percentage of inclusions larger than 5 \( \mu m \) gradually decreases. However, when the La addition reached 0.0425 wt.\%, the proportion of inclusions larger than 10 \( \mu m \) remarkably increases, and inclusions larger than 5 \( \mu m \) are dominant, reaching 65\%. Meanwhile, it can be seen in Figure 5b that with the increase in La content, the number density of inclusions continuously increases, and the average size of inclusions gradually decreases. The average size of inclusions in the RE-free steel is 5.35 \( \mu m \). As the La content increase from 0.0075 to 0.0184 wt.\%, the average size of inclusions significantly decreases from 3.4 to 2.48 \( \mu m \), which means that the inclusions become finer and more dispersive. This is because, compared with \( \text{Al}_2\text{O}_3 \) and MnS inclusion, rare earth inclusion has lower interfacial energy and better wettabiliy with liquid steel and thus is not easy to agglomerate [27].

![Figure 5](image-url)

**Figure 5.** Size distribution (a) and number density and average size (b) of inclusions in four steels with different La content additions.

However, as the La content reaches up to 0.0425 wt.\%, the average size of inclusions sharply increases to 6.85 \( \mu m \) and even exceeds that of the original ones, which indicated that the inclusions seriously grow and agglomerate. This is because rare earth elements have extremely high surface activity and easily adsorb impurity elements in molten steel. The higher the concentration of rare earth in molten steel, the more impurity elements adsorbed. On the other hand, excessive rare earth promotes mutual attraction between rare earth inclusions and then merges into large-sized inclusions. Therefore, when the addition is excessive, rare earth inclusions are prone to agglomeration and growth. Many investigators also reported this regulation in their work [28–30]. In addition, it is worth mentioning that there is an optimum addition amount in the range of 0.0184–0.0425\% La, which can significantly reduce inclusion size and improve corrosion resistance and mechanical properties.

The above experimental results indicate that the original \( \text{Al}_2\text{O}_3 \) and MnS inclusions can be modified to fine and dispersive rare earth inclusions by adding a suitable amount of La. At the same time, the La content has a great influence on the type of inclusion in steel. The main inclusions in weathering steel without La addition are \( \text{Al}_2\text{O}_3 \) and MnS. As the La content increases from 0.0075 to 0.0184 wt.\%, the main inclusions change from \( \text{LaAlO}_3 \), MnS, and \( \text{Al}_2\text{O}_3-\text{LaAlO}_3 \) complex inclusion to \( \text{LaAlO}_3 \), \( \text{La}_2\text{O}_3 \), MnS, and \( \text{LaAlO}_3-\text{La}_2\text{O}_3 \) complex inclusion. When the La content reaches to 0.0425 wt.\%, the original MnS and \( \text{Al}_2\text{O}_3 \) inclusions are completely modified into \( \text{La}_2\text{O}_2\text{S} \) and \( \text{La}_2\text{O}_3 \) inclusions.

Some similar modification rules have been previously reported in other studies on rare earth steels. Huang Y [31] added Ce into H13 steel and found that with the increase in Ce
content, the inclusions were modified according to the rule of MgAl₂O₄ → CeAlO₃ → Ce₂O₃. Ren et al. [32] found that when Ce was added to ultra-low carbon steel, the inclusions were modified along the route of MgAl₂O₄ → CeAlO₃ → Ce₂O₃ → Ce₂O₄S → CeS.

3.2. Thermodynamic Analysis on the Formation and Modification of Inclusions

In order to analyze the formation and modification mechanism of inclusions in steel, thermodynamic analysis was performed in the present work, which can also provide theoretical guidance for controlling inclusions in rare earth steel.

According to the thermodynamic theory of inclusion, during the cooling process of molten steel, the solubility of inclusion decreases continuously and when the actual solubility product of the inclusion generating elements is larger than the equilibrium solubility product, the reaction can occur. Therefore, by comparing the actual solubility product and equilibrium solubility product, the possibility and condition for the reaction of inclusion can be obtained.

The liquidus temperature ($T_L$) and solidus temperature ($T_S$) of steel can be calculated by Equations (1) and (2) [33]. The calculation results are 1784.4 K and 1733.9 K, respectively.

$$T_L = \frac{1809 - 83 \text{ wt.\% (C)} - 7.8 \text{ wt.\% (Si)} - 5 \text{ wt.\% (Mn)} - 32 \text{ wt.\% (P)} - 31.5 \text{ wt.\% (S)}}{-1.5 \text{ wt.\% (Cr)} - 2 \text{ wt.\% (Mo)} - 2 \text{ wt.\% (V)} - 3.6 \text{ wt.\% (Al)} - 18 \text{ wt.\% (Ti)}}$$

$$T_S = \frac{1809 - 344 \text{ wt.\% (C)} - 12.3 \text{ wt.\% (Si)} - 6.8 \text{ wt.\% (Mn)} - 124.5 \text{ wt.\% (P)}}{-1.4 \text{ wt.\% (Cr)} - 183.5 \text{ wt.\% (S)} - 4.1 \text{ wt.\% (Al)} - 4.3 \text{ wt.\% (Ni)}}$$

The standard Gibbs free energy change for the formation of various inclusions in molten steel are shown in Table 2. It is widely known that Al₂O₃ and MnS have different crystalline types under different pressures, temperatures, and vapor partial pressure conditions. Since the modification behavior of inclusions studied in this work is under the condition of liquid steel at 1600 °C, the crystalline type of Al₂O₃ and MnS at this temperature are α-Al₂O₃ and α-MnS in the calculation. Moreover, the crystalline types of these compounds are not related to the thermodynamic calculation.

| Reaction Equation of Various Inclusions | $\Delta G^0 = A + B \times T$ (J·mol⁻¹) |
|----------------------------------------|-----------------------------------------|
| [Mn] + [S] = MnS(s)                    | -158,365                                 |
| [Al] + 3[O] = Al₂O₃(s)                 | -122,500                                 |
| [La] + 3[O] = La₂O₃(s)                 | -1,443,880                               |
| [La] + 2[O] + [S] = La₂O₂S(s)          | -1,341,200                               |
| [La] + [S] = LaS(s)                    | -445,180                                 |
| [La] + [Al] + 3[O] = LaAlO₃(s)         | -801,616                                 |

The reaction equation for the $A_xB_y$ generated by metal element A and nonmetal element B in molten steel is as follows:

$$xA + yB = A_xB_y$$  \hspace{1cm} (3)

When Equation (3) reaches equilibrium, $\Delta G = 0$. Therefore, the relation between the standard Gibbs free energy ($\Delta G^0$) for the reaction and the equilibrium constant ($K$) can be expressed as Equation (4).

$$\ln K = -\frac{\Delta G^0}{RT} = -C_2 - \frac{C_1}{T}$$  \hspace{1cm} (4)

where $R$ is the gas constant in J·mol⁻¹·K⁻¹, $C_1$ and $C_2$ are constants, and $T$ is the temperature (K).
The equilibrium constant ($K$) can also be expressed as follows:

$$K = \frac{\alpha_{A_xB_y}}{\alpha_A \cdot \alpha_B} = \frac{1}{f_A^x \cdot w(A)^x \cdot f_B^y \cdot w(B)^y}$$  \hspace{1cm} (5)

where $\alpha_A$, $\alpha_B$ and $\alpha_{A_xB_y}$ are the activity of A, B and the precipitate $A_xB_y$, respectively; $f_i$ is the activity coefficient of element $i$; and $w(i)$ is the mass fraction of element $i$ in molten steel (wt.%). If these compounds $A_xB_y$, with a high melting point, are solid in molten steel above 1700 K, assuming pure substance as the standard state, $\alpha_{A_xB_y} = 1$.

Substituting Equation (5) into Equation (4) can result in Equation (6).

$$x \ln f_A + y \ln f_B + \ln(w(A)^x \cdot w(B)^y) = C_2 + \frac{C_1}{T}$$  \hspace{1cm} (6)

Therefore, the equilibrium solubility product of $A_xB_y$ in liquid steel can be expressed as Equation (7).

$$\ln(w(A)^x \cdot w(B)^y) = C_2 + \frac{C_1}{T} - x \ln f_A - y \ln f_B$$  \hspace{1cm} (7)

The activity coefficient $f_i$ in Equation (7) is related to the interaction coefficient of each element in liquid steel temperature. The thermodynamic behavior of molten steel deviates from Raoult’s law and Henry’s law due to the solvent–solute interaction and solute–solute interaction. The Wagner model proposed the general formula of activity and interaction parameters in a multi-component solution, which became a basic method to calculate the activity coefficient of a multi-component solution and has been widely used [36]. The limitation of the Wagner model is that the data of the second-order interaction coefficient are missing but the activity coefficient calculated by the Wagner model is correct in the trend analysis of thermodynamic behavior and has little effect on reliability. In this work, Q355B weathering steel is a low alloy steel, which means that the mass fraction of each solute element approaches 0 and the mass fraction of solvent approaches 1. Therefore, the second-order interaction coefficients have little effect on the activity coefficient of the solute. The activity coefficients of each solute element can be calculated directly using the Wagner model characterized by the first-order interaction coefficient:

$$\ln f_i = 2.303 \sum_{j=1}^n e_i^j w[j]$$  \hspace{1cm} (8)

where $e_i^j$ is the first-order interaction parameter between $i$ and $j$ and $w[j]$ is the mass percentage of element $j$.

The first-order interaction coefficients of various solute elements in liquid steel as shown in Table 3. Substituting the data into Equation (8), the activity coefficients of O, S, Al, Mn, and La in molten steel can be obtained, in which element $j$ contains the main elements of weathering steel Q355, including C, Si, Mn, P, S, O, Cr, Ni, Mo, Cu, Al, and La. The results are listed in Table 4.

**Table 3.** First-order interaction coefficients $e_i^j$ of various elements in liquid steel at 1600 °C [34,35,37].

| $e_i^j$ | C   | Si  | Mn  | P   | S   | O   | Cr  | Ni  | Mo  | Cu  | Al  | La  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| O       | -0.45 | -0.131 | -0.021 | 0.07 | -0.133 | -0.2 | -0.04 | 0.006 | 0.0035 | -0.013 | -3.9 | -12.1 |
| S       | 0.110 | 0.063 | -0.026 | 0.029 | -0.028 | -0.27 | -0.011 | 0 | 0.0027 | -0.0084 | 0.035 | -2.79 |
| Al      | 0.091 | 0.0056 | 0.056 | 0.033 | 0.03 | -6.6 | 0.025 | 0.008 | - | 0.008 | 0.045 | -0.51 |
| Mn      | -0.07 | 0.39 | 0 | -0.0035 | -0.048 | -0.083 | 0.003 | -0.007 | 0.0045 | - | 0.07 | - |
| La      | -0.279 | - | 0.28 | 1.734 | -12.130 | -105 | - | - | - | -2.649 | -0.013 | - |
The activity coefficients of O, S, Al, Mn, and La in molten steel at 1600 °C.

| No. | O      | S      | Al     | Mn     | La    |
|-----|--------|--------|--------|--------|-------|
| 1   | 0.6290 | 0.9668 | 1.140  | 1.0981 | -     |
| 2   | 0.5103 | 0.9214 | 1.131  | 1.098  | 0.3484|
| 3   | 0.3764 | 0.8589 | 1.116  | 1.0982 | 0.3483|
| 4   | 0.1924 | 0.7358 | 1.085  | 1.0982 | 0.3480|

Therefore, the logarithm of the equilibrium solubility product of MnS, Al2O3, La2O3, La2O2S, La2S3, LaS, and LaAlO3 in molten steel can be calculated by introducing the activity coefficient of each element in Table 4 into Equation (7).

$$\ln A_xB_y = \ln \left( \frac{a_x^{A_y} a_y^{B}}{a_{A_y}^{B}} \right) = \ln \left( \frac{(w(A) \times f_A)^x \times (w([B]) \times f_B)^y}{} \right)$$ (9)

Figures 6–12 display the comparison of the equilibrium solubility product and the actual solubility product of each inclusion in liquid steel.

**Figure 6.** Logarithm of the solubility product as a function of temperature for Al2O3 in liquid steel.

**Figure 7.** Logarithm of the solubility product as a function of temperature for MnS in liquid steel.
Figure 7. Logarithm of the solubility product as a function of temperature for MnS in liquid steel.

As shown in Figures 8–12, when La is added, LaAlO$_3$, La$_2$O$_3$, La$_2$O$_2$S, LaS, and La$_2$S$_3$ can form at the liquid-phase temperature, which is because rare earth elements have extremely strong activity and easily react with O and S in molten steel. However, rare earth sulfides are not found in the experimental observations. This is because the formation conditions and sequence of inclusions are also related to the free energy and the mutual transformation between inclusions under actual conditions. Consequently, we further analyzed the stability of various inclusions by calculating the Gibbs formation energy in the molten steel at 1600 °C.

Figure 8. Logarithm of the solubility product as a function of temperature for LaAlO$_3$ in liquid steel.

Figure 9. Logarithm of the solubility product as a function of temperature for La$_2$O$_3$ in liquid steel.

Figure 10. Logarithm of the solubility product as a function of temperature for La$_2$O$_2$S in liquid steel.

Figure 11. Logarithm of the solubility product as a function of temperature for La$_2$S$_3$ in liquid steel.
process, the generating elements of MnS inclusion tend to segregate in the liquid phase at the molten steel at 1600 °C. Analyzed the stability of various inclusions by calculating the Gibbs formation energy in the transformation between inclusions under actual conditions. Consequently, we further discussed the relationship between the free energy and the mutual activity of solid inclusion in molten steel.

Rare earth oxides and oxysulfides, such as LaAlO₃, La₂O₃, La₂O₂S, and LaS, can easily react with O and S in molten steel. However, rare earth oxides and oxysulfides tend to form during the solidification process, rather than in the liquid phase. As shown in Figures 6 and 7, Al₂O₃ can form at the liquid-phase temperature for each experimental steel. However, the actual solubility product of MnS in each experimental steel was smaller than the equilibrium solubility product, which means that MnS cannot form in the liquid phase. Many previous studies have proven that, during the solidification process, the generating elements of MnS inclusion tend to segregate in the liquid phase at the solidification front, resulting in an increase in the actual solubility product. Therefore, MnS is usually formed in the solidification process, rather than in the liquid phase.

As shown in Figures 8–12, when La is added, LaAlO₃, La₂O₃, La₂O₂S, LaS, and La₂S₃ can form at the liquid-phase temperature, which is because rare earth elements have extremely strong activity and easily react with O and S in molten steel. However, rare earth sulfides are not found in the experimental observations. This is because the formation conditions and sequence of inclusions are also related to the free energy and the mutual transformation between inclusions under actual conditions. Consequently, we further analyzed the stability of various inclusions by calculating the Gibbs formation energy in the molten steel at 1600 °C.

![Figure 11](image1.png)

**Figure 11.** Logarithm of the solubility product as a function of temperature for La₂S₃ in liquid steel.

![Figure 12](image2.png)

**Figure 12.** Logarithm of the solubility product as a function of temperature for LaS in liquid steel.
The Gibbs free energy of the inclusion formation reaction (Table 2) in liquid steel can be expressed as:

$$
\Delta G_m = \Delta G^0_m + RT \ln \frac{a_{\text{Me}_2\text{X}_3(s)}}{a_{\text{Me}}^{\text{act}} a_{\text{X}}^{\text{act}}} \tag{10}
$$

where $\Delta G^0_m$ is the standard Gibbs free energy change for the formation of various inclusions, $a_{\text{Me}_2\text{X}_3(s)}$ is the activity of each reactant in molten steel, and $a_{\text{Me}_2\text{X}_3(s)}$ is the activity of solid inclusion in molten steel. If these inclusions with a high melting point are solid in molten steel at 1600 °C, assuming pure substance as the standard state, $a_{\text{Me}_2\text{X}_3(s)} = 1$. The stoichiometric number of La and Al was set to 1 when calculating the actual Gibbs free energy of each inclusion.

Therefore, the Gibbs free energy of the inclusion formation reaction can be simplified as:

$$
\Delta G_m = \Delta G^0_m + RT \ln \frac{1}{a_{\text{Me}_2\text{X}_3(s)}} \tag{11}
$$

The mass concentration of component A in molten steel is $w[A]$ and the activity coefficient is $f_A$. The activity of component A can be expressed as Equation (12).

$$
a_A = f_A w[A] \tag{12}
$$

The actual Gibbs free energy of each inclusion formation at 1600 °C is shown in Figure 13. It can be seen that La$_2$O$_3$ is the most stable, followed by La$_2$O$_3$S and LaAlO$_3$, whose Gibbs generation energy is less than $-300$ kJ. Therefore, La$_2$O$_3$, La$_2$O$_3$S, and LaAlO$_3$ inclusions are easier to generate and more stable. Meanwhile, La$_2$S$_3$, LaS, and Al$_2$O$_3$ can also form but their Gibbs formation energy is much higher than that of rare earth oxides and rare earth oxysulfide. In addition, it is worth mentioning that with the increase in La content, the Gibbs free energy of the Al$_2$O$_3$ formation gradually increases, indicating that its formation is more difficult. This is because the rare earth elements have a strong activity, more easily reacting with oxygen in the molten steel, so with the increase in La content, the formation of Al$_2$O$_3$ is more difficult. Based on the above analysis, it can be determined that with the addition of La, the original Al$_2$O$_3$ inclusions are more inclined to be modified into La$_2$O$_3$, La$_2$O$_3$S, and LaAlO$_3$ inclusions.

![Figure 13](image_url). Diagram of inclusion predominance region in steel with different La contents at 1600 °C.

To further clarify the effect of La content on the inclusion, the evolution process of La on inclusion at 1600 °C was calculated by FactSage 8.1. The optimized parameters for...
the binary systems can be used together with appropriate solution models to predict the thermodynamic properties of multicomponent systems, thus calculating phase diagrams of ternary systems. The ternary phase diagram of LaAlO$_3$ and La$_2$O$_2$S can be accurately calculated by combining the phase diagram of the binary systems Al$_2$O$_3$–La$_2$O$_3$ and La$_2$O$_2$S–La$_2$O$_3$ with the calculation model in FactSage software [38,39]. The result is shown in Figure 14. The inclusion in liquid steel without La is Al$_2$O$_3$. With the increase in La content in liquid steel, Al$_2$O$_3$ inclusion is immediately modified into LaAlO$_3$. When the La content reaches about 0.009 wt.%, the Al$_2$O$_3$ inclusion disappears completely and the mass fraction of LaAlO$_3$ reaches peak value. As the La content increases further, the modified product LaAlO$_3$ is transformed into La$_2$O$_3$. When the La content reaches approximately 0.023 wt.%, LaAlO$_3$ is completely turned into La$_2$O$_3$. Furthermore, it can be seen that, during the formation process of rare earth oxide, the dissolved O in molten steel continuously decreases. Consequently, when the ratio of the oxygen-sulfur concentration reaches a certain amount, La$_2$O$_3$ is further transformed into La$_2$O$_2$S with the increase in La content.

![Figure 14. Stability diagram of inclusion predominance region in steel with different La contents at 1600 °C.](image)

Based on the above FactSage thermodynamic calculation results, with the increase in La content, the modification sequence of inclusions in the steel is Al$_2$O$_3$ → LaAlO$_3$ → La$_2$O$_3$ → La$_2$O$_2$S, which is very consistent with the experimental observations. Meanwhile, combined with the experimental results, it can be determined that with the increase in La content, the generation of La$_2$O$_2$S continuously consumes S in the molten steel, thus inhibiting the formation of MnS at the solidification front. In addition, as can be seen from the dissolved La content in Figure 14, La completely forms inclusions in the molten steel when the La content is low. In contrast, as the La content increases to 0.045 wt.%, the mass fraction of La$_2$O$_2$S inclusions reaches the maximum and the dissolved La content in the molten steel gradually increases, which can act as a microalloying element.

4. Conclusions

Laboratory experiments and thermodynamic analysis were performed to investigate the effect of lanthanum addition on the formation behaviors of inclusions in Q355B weathering steel and the main conclusions obtained are as follows:

1. The original harmful inclusions in Q355B weathering steel could be modified to fine and dispersive rare earth inclusions by adding the appropriate amount of La. The main inclusions in RE-free steel are large-sized irregular Al$_2$O$_3$ and MnS, with an average size of about 5.35 µm. As the La content increases from 0.0075 to 0.0184 wt.%, the main inclusions transform from MnS, LaAlO$_3$, and Al$_2$O$_3$–LaAlO$_3$ complex inclusion into LaAlO$_3$, La$_2$O$_3$, MnS, and LaAlO$_3$–La$_2$O$_3$ complex inclusion. Meanwhile, the average size of inclusions significantly decreases from 3.4 to 2.48 µm and the distribution is...
more dispersive. When the La content increases to 0.0425 wt.%, the original MnS and Al₂O₃ inclusions are completely modified into La₂O₂S and La₂O₃ but the inclusions demonstrate serious agglomeration and growth.

2. The thermodynamic calculations indicate that Al₂O₃ and various lanthanum-containing inclusions are formed in the liquid phase. As the La content in molten steel increases from 0 to 0.0425wt.%, the Al₂O₃ inclusion is inclined to be modified into lanthanum oxide and lanthanum oxysulfide. The modification process is Al₂O₃ → LaAlO₃ → La₂O₃ → La₂O₂S, which is very consistent with the experimental observations.

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