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Effects of Rare Earth La–Ce Alloying Treatment on Modification of Inclusions and Magnetic Properties of W350 Non-Oriented Silicon Steel

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Abstract: In order to study the effects of rare earth La–Ce alloying treatment on the characteristics of inclusions in non-oriented silicon steels, industrial experiments were conducted studying the composition, morphology, size and quantity of inclusions in W350 non-oriented silicon steel during the RH (Ruhrstahl-Heraeus) refining process and tundish process, after rare earth treatment. The products were analyzed by means of ICP-MS (inductively coupled plasma mass spectrometry), SEM/EDS (scanning electron microscope-energy dispersive spectrometry), and ASPEX (automated SEM/EDS inclusion analysis). The research results showed that the types of inclusions in experimental steel changed significantly after rare earth treatment. The types of inclusions after RE (rare earth) treatment are typically rare earth composite inclusions that are mainly composed of (La, Ce)Al₂O₃, and conventional inclusions. The addition of rare earth promotes the agglomeration of inclusions; the morphologies of the inclusions are mostly blocky, and some are distributed in long strips. After rare earth treatment during the RH refining process, the number of inclusions with sizes of 1.0–3.5 µm in the experimental steel is increased, and the average size of the inclusions is 2.66 µm. In addition, the number of inclusions larger than 4 µm in the specimens increases due to the collision and growth of inclusions caused by the RH circulation. After rare earth treatment during the tundish process, the number of micro inclusions with sizes of 1.0–2.5 µm in the specimen steels decreases, while the number of inclusions larger than 5 µm increases. The size distribution of micro inclusions in hot-rolled sheets after rare earth treatment was studied using TEM (transmission electron microscopy). In the specimens without rare earth, the content of micro inclusions (≤ 1 µm) is 51,458.2/mm² and the average size is 0.388 µm. In the specimens with rare earth added, the content of micro inclusions (≤ 1 µm) is 24,230.2/mm² and the average size is 0.427 µm. Compared to sheet produced by the original process, the iron loss of the 0.35 mm finished experimental sheet is reduced by 0.068 W/kg, and the magnetic induction is increased by 0.007 T. The iron loss of the 0.50 mm finished experimental sheet is reduced by 0.008 W/kg, and the magnetic induction is increased by 0.004 T. After rare earth treatment, the average size of micro inclusions increases and the magnetic properties are obviously improved.



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Keywords: rare earth La–Ce; inclusions; modification; non-oriented silicon steel; magnetic property

1. Introduction

High-grade non-oriented silicon steel, as the functional material for high-end power equipment [1,2], is widely used in the cores of large generators and high-efficiency energy-

saving motors, in high-efficiency energy-saving appliances, and in electric vehicle manufacturing, due to its magnetic characteristics of low iron loss and high magnetic induction [3–5]. With the implementation and promotion of frequency conversion technologies in the home appliance industry, the rise of the new energy automobile industry and the development of energy-saving and high-efficiency motors, there is an increased demand for the low iron loss and high magnetic induction properties of high-grade non-oriented silicon steel [6]. Inclusions in steel are one of the many factors affecting its magnetic properties, in particular, the size of the inclusions. Since coercivity is inversely proportional to the size of inclusions, when the size of the inclusions is close to the thickness of the domain wall, the ability of inclusions to pin magnetic domains is usually at its strongest, and the deterioration of magnetic properties is typically at its most serious [7,8]. Relevant production enterprises and research institutes have carried out research on the modification and purification of inclusions in silicon steels, with the mechanisms and production applications of rare earth modified inclusions attracting a large number of researchers. Rare earth elements have unique metallurgical and physical properties, and can change the inherent types and morphologies of inclusions, reduce the harm of inclusions in the steel, and improve the related properties of steel products [9–14]. Takashima et al. [15,16] proposed the addition of composite rare earth and Al to non-oriented silicon steel. Their results showed that after adding rare earth alloys and Al, the inclusion sizes increased, the grain growth rate was significantly improved, the residual stress after annealing was reduced, and the product performance was significantly improved. Li [17], Kong [18], Qiao [19], and Wan [20–22] have studied the applications of rare earth elements in silicon steels. With the addition of rare earth elements, the magnetic properties of silicon steel products are obviously improved. The modification mechanism of rare earth elements on inclusions is relatively clear. However, there is a lack of relevant research on how the type and size distributions of inclusions formed in each process change after the addition of rare earth, especially the type transformations and size changes of micro inclusions in liquid steel.

In this work, industrial trials were carried out using La and Ce rare earth alloys during the production of silicon steels. The effects of rare earth La and Ce alloys on the evolution characteristics and metamorphism of inclusions, and the magnetic properties of products from different processes were investigated, which was conducive to realizing the stable application of rare earth elements in industrial production.

2. Materials and Methods

Slag was completely removed before the hot metal entered the desulfurization station, and slag was removed twice after the deep desulfurization treatment, to achieve $[S] \leq 0.0010\%$ and minimize the amounts of high-sulfur slag entering the converter. The scrap steel was self-produced high-quality scrap steel, of which about 50% was silicon steel scrap. During the tapping of the converter, the slide plate and the slag stopper were used to control the slag, and the thickness of the top slag in the ladle was required to be less than 60 mm. Lime was added to the top slag during the tapping process, and the argon flow rate was controlled to prevent the top slag of the ladle from agglomerating. During the RH refining process, it was forbidden to add aluminum to the liquid steel to melt it after the liquid steel had arrived at the RH refining station. After decarburization, the oxygen content of the liquid steel was less than 300 ppm, before alloying. After adding the desulfurizer and bauxite, rare earth alloys were added to liquid steel. The vacuum was broken after 8 min of net circulation and the sedation time was not less than 15 min.

The chemical composition of La and Ce alloys used in the experiment is listed in Table 1. Spectrography and inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher Scientific (China) Co., Ltd., China) were used to determine the steel composition. The chemical composition of the experimental steel is shown in Table 2.

Table 1. Chemical composition of rare earth La–Ce alloys (wt%).

Element	C	Mg	Si	Ca	La	Ce
Content	0.002	0.001	0.2	0.001	37.32	61.67

Table 2. Chemical composition of experiment steel (wt%).

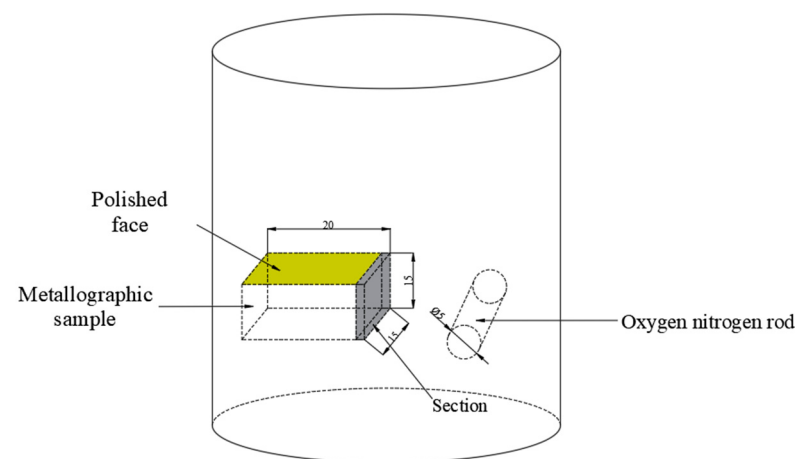
Element	C	Mn	S	P	Si	Als	N	Ti	Cu	La	Ce
RE-free (Rare earth-free)	0.0024	0.32	0.0022	0.016	2.69	0.53	0.001	0.0018	0.038	/	/
RE-added (Rare earth-added)	0.0026	0.36	0.0028	0.015	2.62	0.54	0.001	0.0019	0.040	0.0012	0.0013

During the experiment, steel samples were taken during the RH refining process and from the tundish. The specific sampling plan is shown in Table 3. Metallographic specimens (20 mm × 15 mm × 15 mm) were taken from the edges of the steel samples after removing the oxide scales on their surfaces, as shown in Figure 1. After grinding and polishing, the morphology, quantity, size and composition of inclusions with sizes >1 µm in the steel were analyzed by automated SEM/EDS inclusion analysis (ASPEX, FEI, USA), scanning electron microscopy (SEM, JSM-6490LV, JEOL Ltd., Tokyo, Japan), and energy dispersive spectroscopy (EDS, Oxford Instruments, High Wycombe, UK). The contents of total oxygen (T.O.) and nitrogen in the steel were detected by inert gas fusion pulse-infrared absorption spectroscopy.

Table 3. Sampling plan.

No.	Process	Sampling Location	Sampling Method
1	RH refining	Rare earth alloying	Cylindrical sample (Φ70 mm × 100 mm)
2		Carrying out station	Cylindrical sample (Φ70 mm × 100 mm)
3	Tundish	Impact zone	Cylindrical sample (Φ70 mm × 100 mm)
4		Pouring zone	Cylindrical sample (Φ70 mm × 100 mm)

Φ represents the diameter of cylindrical sample.

**Figure 1.** Diagram depicting sampling of the experimental steel.

The magnetic flux density, B_{50} , was determined at a magnetic field strength of $H = 5000$ A/m, and the core losses, $P_{15/50}$, at an induction of 1.5 T and 50 Hz. Magnetic measurements were carried out for final-annealed sheets of 30 mm in width and 100 mm in length, in both rolling and transverse directions. The measured values were averaged to align with the Epstein method, using MPG100D equipment (Dr. Brockhaus Messtechnik GmbH & Co. KG, Lüdenscheid, Germany).

3. Results

The morphologies and compositions of inclusions in the steel were analyzed by SEM and EDS. Figures 2 and 3 show the typical morphologies, compositions and surface scanning results for inclusions in the steel during the RH refining process, with rare earth treatment. The main types of inclusions in the steel are $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaS} - (\text{CaO} - \text{Al}_2\text{O}_3)$, and $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$. Inclusions with $(\text{La, Ce})\text{Al}_2\text{O}_3$ as the core are surrounded by a $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$ or $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$ composite phase, and their morphologies are spherical or ellipsoidal. Among the inclusions, the $(\text{La, Ce})\text{Al}_2\text{O}_3$ inclusions are distributed in light, white blocks, and $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$ inclusions are spherical or approximately spherical.

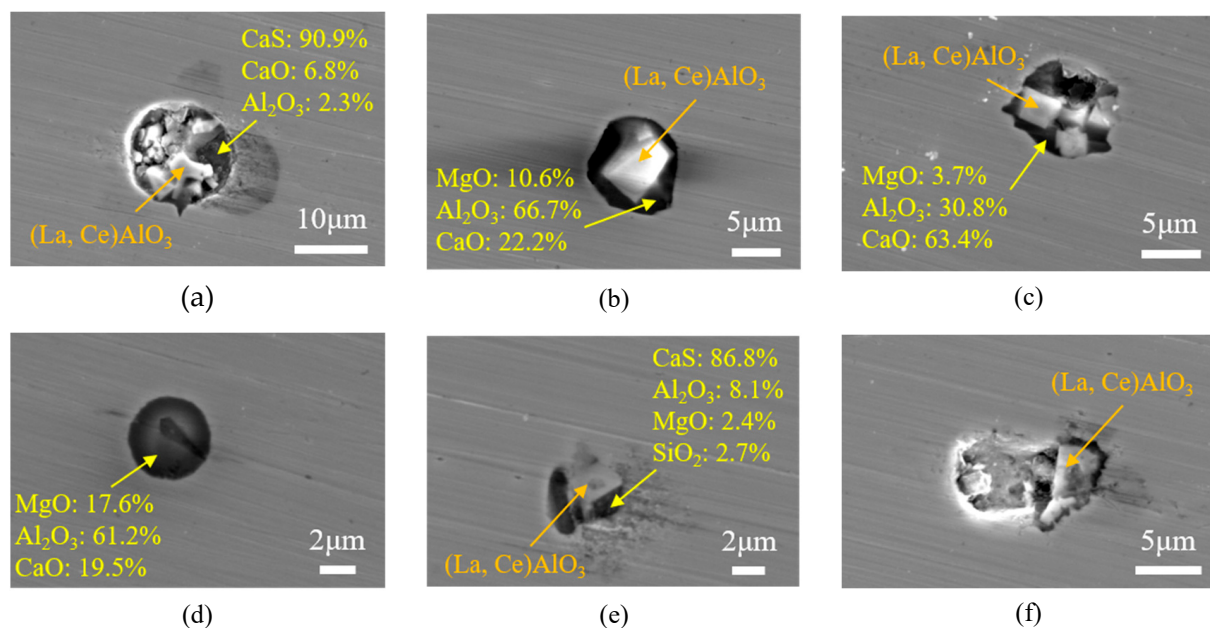


Figure 2. Typical morphologies and compositions of inclusions, with rare earth treatment. (a) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 - \text{CaO} - \text{CaS}$; (b) Inner layer: $(\text{La, Ce})\text{AlO}_3$, Outer layer: $\text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$; (c) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$; (d) $\text{Al}_2\text{O}_3 - \text{CaO} - \text{MgO}$; (e) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 - \text{MgO} - \text{CaS}$; (f) $(\text{La, Ce})\text{AlO}_3$.

Figures 4 and 5 show the typical morphologies, compositions and surface scanning results for inclusions in the steel at the end of the RH refining process. It was found that the types of inclusions are still $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaS} + \text{oxides}$, and $\text{CaO} - \text{Al}_2\text{O}_3 - \text{MgO}$. $(\text{La, Ce})\text{Al}_2\text{O}_3$ inclusions are distributed in long strips at the edge of the composite phase. In addition, some inclusions contain a small amount of SiO_2 .

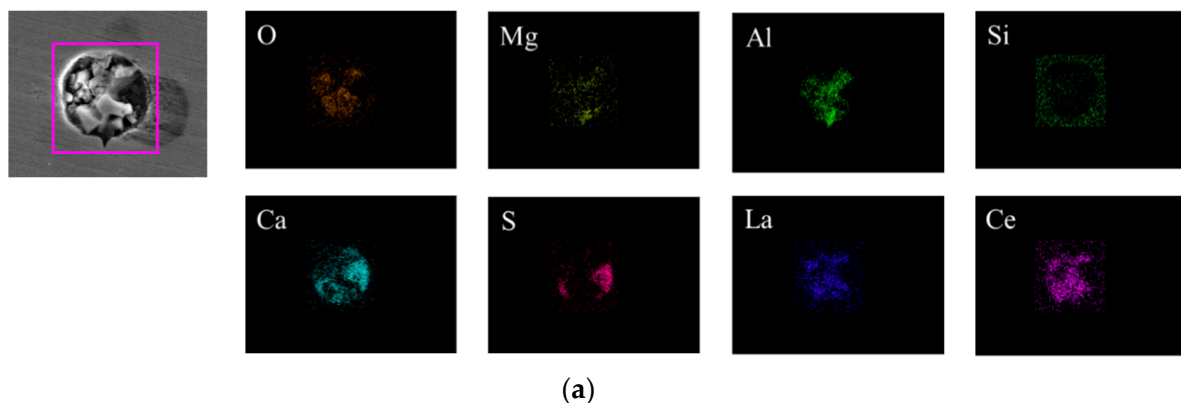


Figure 3. Cont.

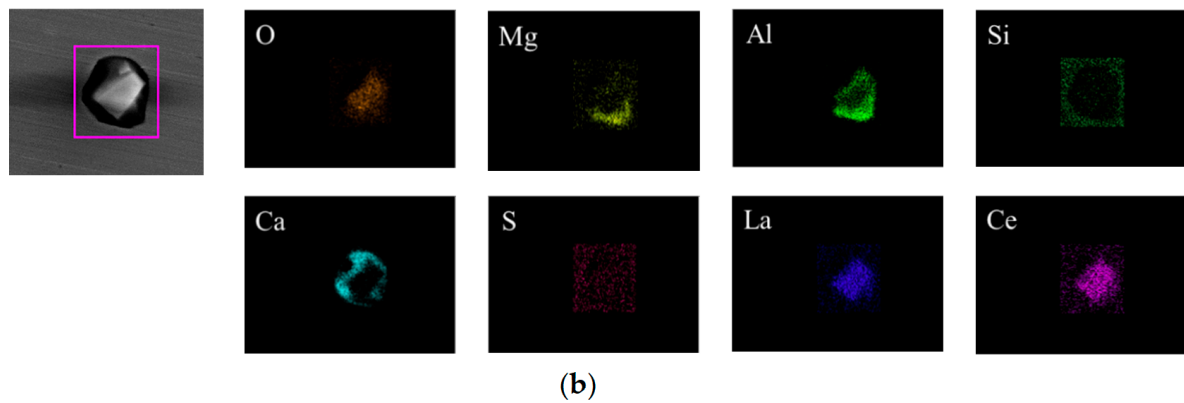


Figure 3. Surface scanning results for inclusions, with rare earth treatment. (a) $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaS}-\text{CaO}-\text{Al}_2\text{O}_3$, (b) $(\text{La, Ce})\text{Al}_2\text{O}_3 + \text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$.

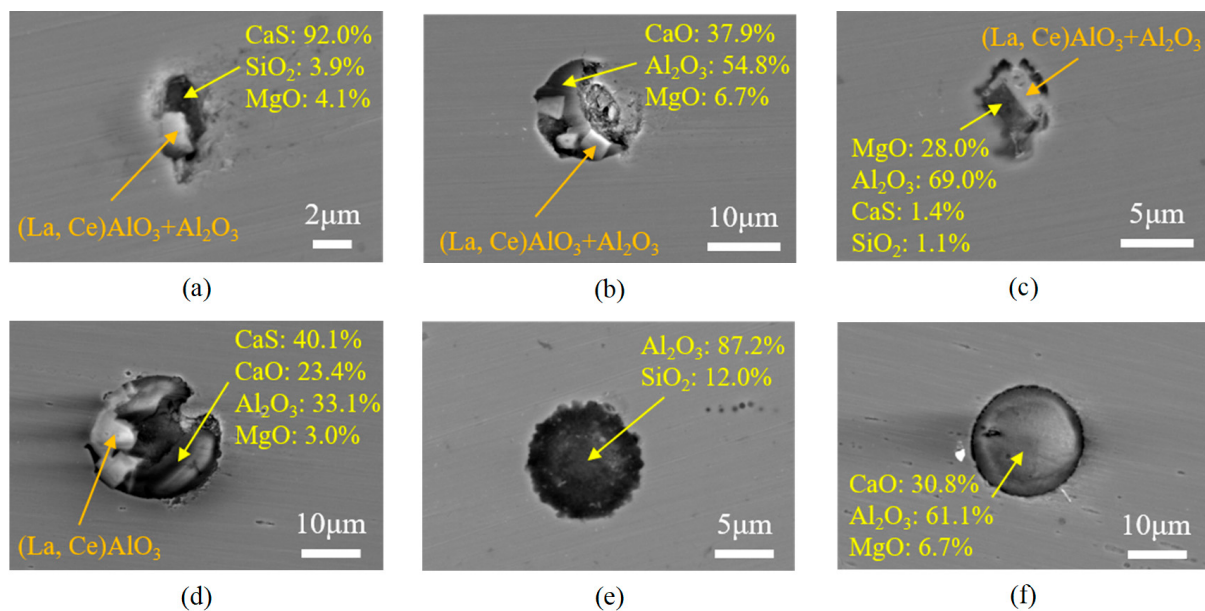


Figure 4. Typical morphologies and compositions of inclusions in the steel at the end of the RH refining process. (a) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 + \text{MgO}-\text{CaS}-\text{SiO}_2$; (b) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}$; (c) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3 + \text{Al}_2\text{O}_3-\text{MgO}-\text{CaS}-\text{SiO}_2$; (d) $(\text{La, Ce})\text{AlO}_3 + \text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{CaS}$; (e) $\text{Al}_2\text{O}_3-\text{SiO}_2$; (f) $\text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}$.

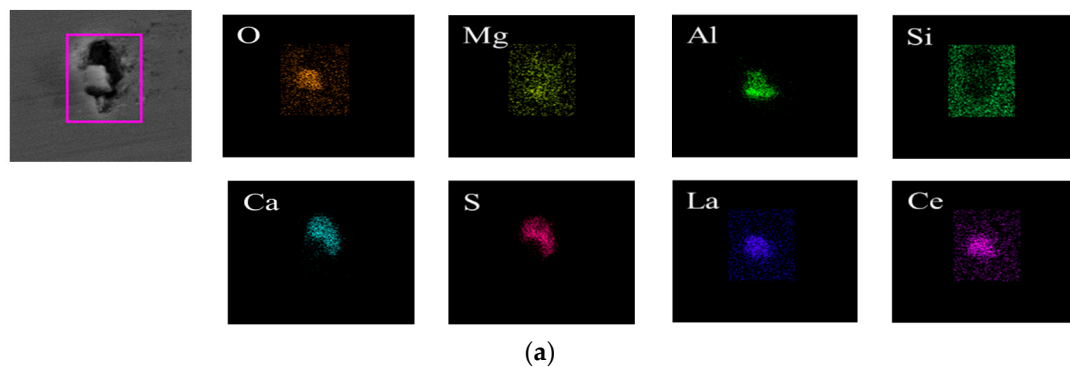


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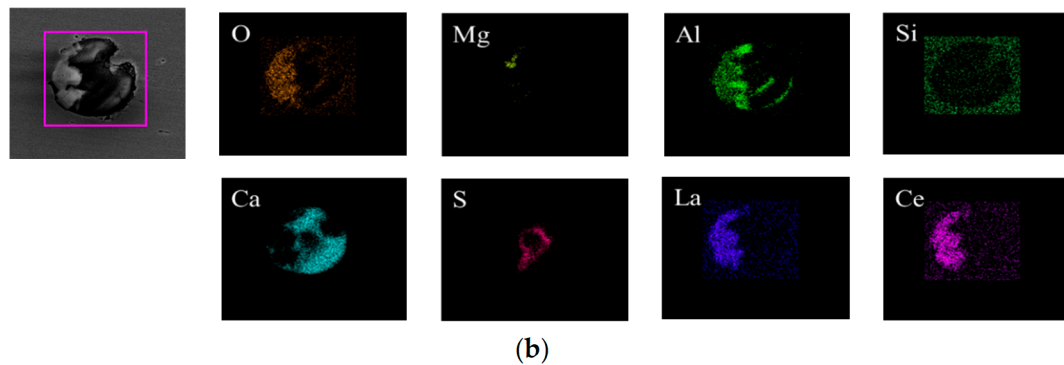


Figure 5. Surface scanning results for inclusions in the steel at the end of the RH refining process. (a) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaS-MgO-Al}_2\text{O}_3$, (b) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaS-MgO-Al}_2\text{O}_3\text{-CaO}$.

The main types of inclusions in the tundish impact zone are $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaO-Al}_2\text{O}_3\text{-MgO}$, $(\text{La,Ce})\text{Al}_2\text{O}_3+\text{CaS+oxides}$ and $\text{CaO-Al}_2\text{O}_3\text{-MgO-(CaS)}$; the typical morphologies and compositions are shown in Figure 6. Compared to the inclusions found after the RH refining process, the morphologies of inclusions in the tundish impact zone are mainly spherical. Figure 7 shows surface scanning results for typical inclusions. The $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions are composed of two composite phases with $(\text{La, Ce})\text{Al}_2\text{O}_3$ as the core, surrounded by $\text{CaO-Al}_2\text{O}_3\text{-MgO}$.

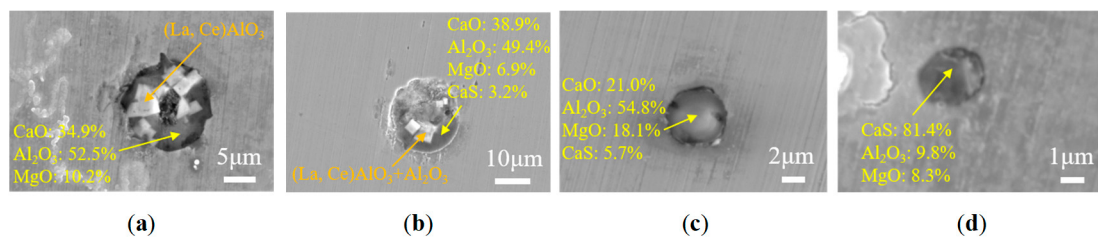


Figure 6. Typical morphologies and compositions of inclusions in the tundish impact zone. (a) $(\text{La,Ce})\text{AlO}_3+\text{Al}_2\text{O}_3\text{-MgO-CaO}$; (b) $(\text{La,Ce})\text{AlO}_3\text{-Al}_2\text{O}_3+\text{Al}_2\text{O}_3\text{-CaO-MgO-CaS}$; (c) $\text{Al}_2\text{O}_3\text{-MgO-CaS-CaO}$; (d) $\text{Al}_2\text{O}_3\text{-MgO-CaS}$.

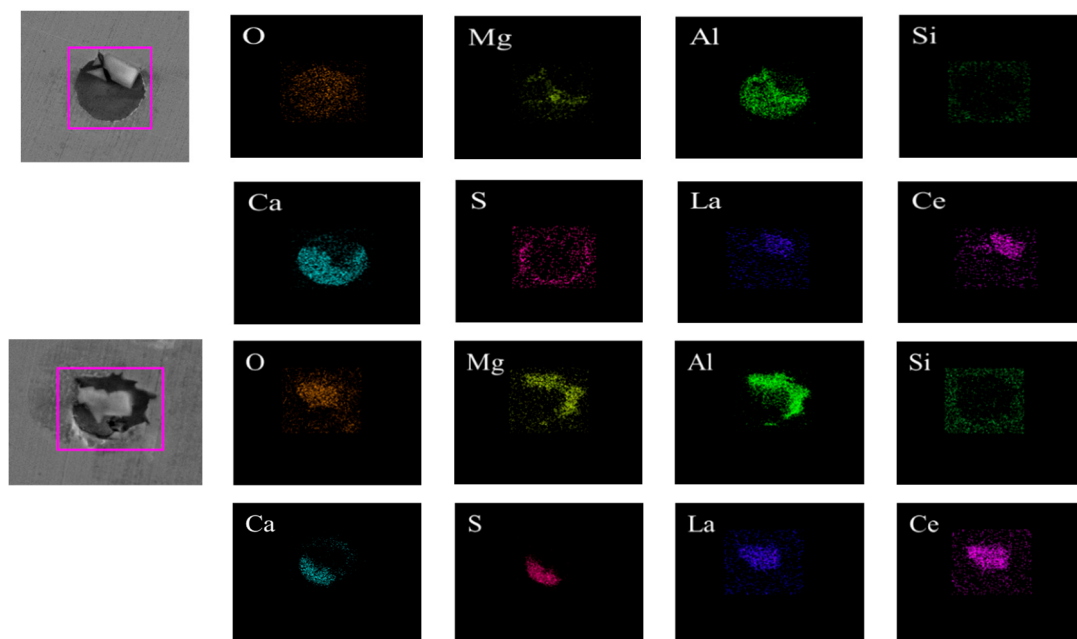


Figure 7. Surface scanning results for $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaO-Al}_2\text{O}_3\text{-MgO}$ in the tundish impact zone.

Figures 8 and 9 show the typical morphologies, compositions and surface scanning results for inclusions in the tundish pouring zone. The types of inclusions in the tundish pouring zone are mainly $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaS}+\text{oxides}$, and $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaS}$. The $(\text{La, Ce})\text{Al}_2\text{O}_3$ inclusions are distributed in light, white blocks.

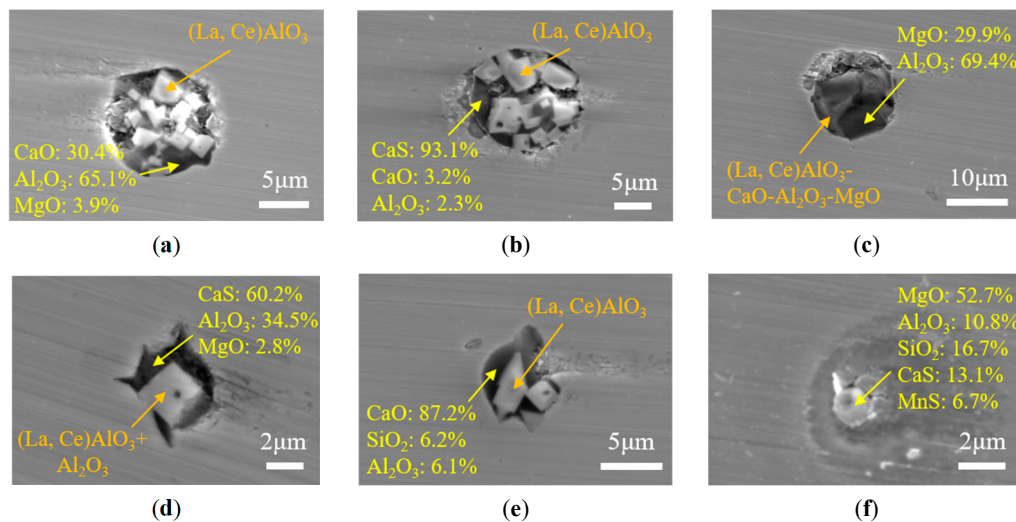


Figure 8. Typical morphologies and compositions of inclusions in the tundish pouring zone. (a) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{Al}_2\text{O}_3-\text{MgO}-\text{CaO}$; (b) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{Al}_2\text{O}_3-\text{CaO}-\text{CaS}$; (c) $(\text{La, Ce})\text{Al}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{MgO}-\text{CaO}+\text{Al}_2\text{O}_3-\text{MgO}$; (d) $(\text{La, Ce})\text{Al}_2\text{O}_3-\text{Al}_2\text{O}_3+\text{Al}_2\text{O}_3-\text{MgO}-\text{CaS}$; (e) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{Al}_2\text{O}_3-\text{CaO}-\text{SiO}_2$; (f) $\text{Al}_2\text{O}_3-\text{CaS}-\text{MgO}-\text{SiO}_2-\text{MnS}$.

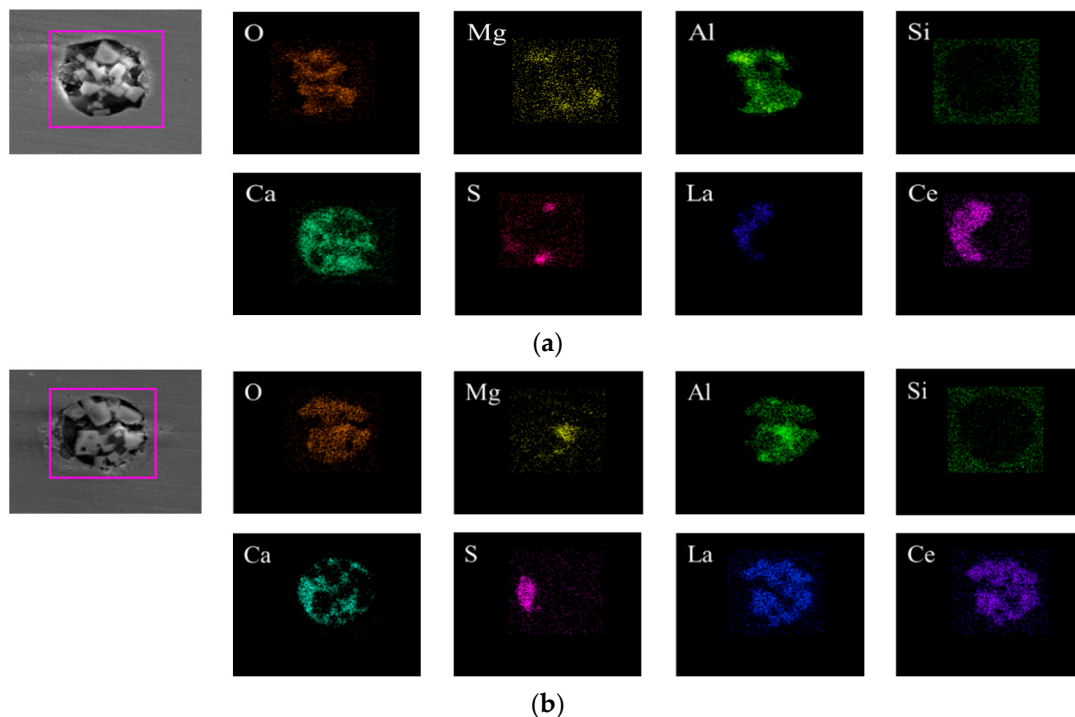


Figure 9. Surface scanning results for inclusions in the tundish pouring zone. (a) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{MgO}-\text{Al}_2\text{O}_3-\text{CaO}$, (b) $(\text{La, Ce})\text{Al}_2\text{O}_3+\text{CaS}-\text{Al}_2\text{O}_3-\text{CaO}$.

4. Discussion

4.1. Changes to Inclusion Types after Rare Earth Treatment

Figure 10 shows the morphologies and compositions of typical inclusions after alloying in the RH refining process, with and without rare earth treatment. It can be seen that without rare earth treatment, the types of inclusions in the steel after RH alloying are mainly $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-(MnO)}$ and $\text{Al}_2\text{O}_3\text{-(MgO)}$, and some inclusions contain a small amount of CaS and MnS. The $\text{Al}_2\text{O}_3\text{-(MgO)}$ inclusions are mostly spherical, while those including CaS and MnS have square or angular shapes. In addition, some Al_2O_3 inclusions aggregate in clusters. After adding rare earth La–Ce alloys during the RH refining process, the main types of inclusions are $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaO-Al}_2\text{O}_3\text{-MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaS-(CaO-Al}_2\text{O}_3)$, and $\text{CaO-Al}_2\text{O}_3\text{-MgO}$, a finding which is similar to that of Ren et al. [23,24]. Inclusions with $(\text{La, Ce})\text{Al}_2\text{O}_3$ as the core are surrounded by a $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ or $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ composite phase, and the morphologies are spherical or ellipsoidal.

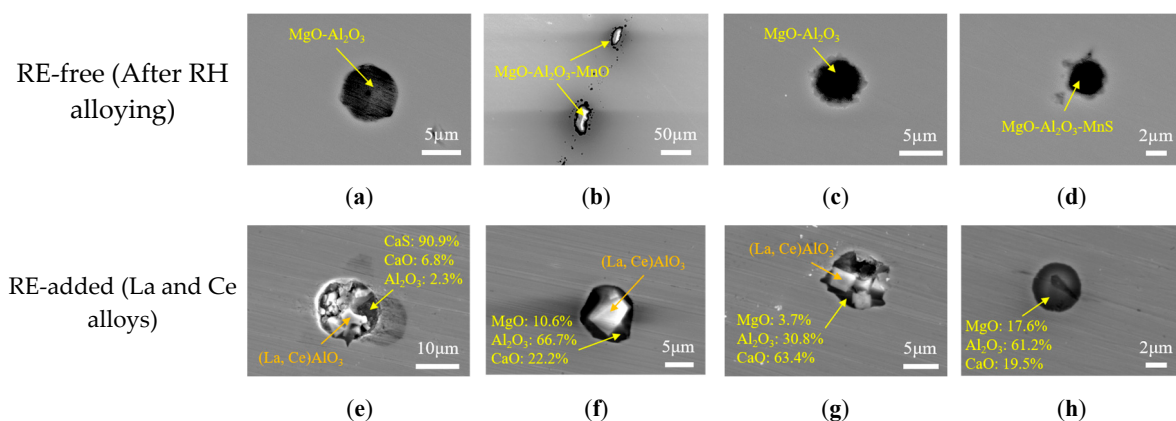


Figure 10. Morphologies and compositions of inclusions, before and after rare earth treatment, after RH alloying. (a) $\text{Al}_2\text{O}_3\text{-MgO}$; (b) $\text{MgO-Al}_2\text{O}_3\text{-MnO}$; (c) $\text{Al}_2\text{O}_3\text{-MgO}$; (d) $\text{Al}_2\text{O}_3\text{-MgO-MnS}$; (e) $(\text{La,Ce})\text{AlO}_3\text{+Al}_2\text{O}_3\text{-CaO-CaS}$; (f) $(\text{La,Ce})\text{AlO}_3\text{+Al}_2\text{O}_3\text{-MgO-CaO}$; (g) $(\text{La,Ce})\text{AlO}_3\text{+Al}_2\text{O}_3\text{-MgO-CaO}$; (h) $\text{Al}_2\text{O}_3\text{-MgO-CaO}$.

Figure 11 shows the morphologies and compositions of typical inclusions in the steel before and after rare earth treatment, after the RH refining station. The majority of inclusions at the RH station are composed of $\text{Al}_2\text{O}_3\text{-CaO}$, with some inclusions containing a small amount of MnS and CaS. The content of Al_2O_3 in the inclusions is high, and their morphologies are spherical or irregular. After rare earth treatment, the main types of inclusions in the steel after the RH refining station are $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaO-Al}_2\text{O}_3\text{-MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaS+oxides}$, and $\text{CaO-Al}_2\text{O}_3\text{-MgO}$. The $(\text{La, Ce})\text{Al}_2\text{O}_3$ inclusions are distributed at the edge of the composite phase. In addition, some of the inclusions contain a small amount of SiO_2 .

Figure 12 shows the typical morphologies and compositions of inclusions in the tundish pouring zone, before and after rare earth treatment. The results show that without rare earth treatment, the inclusions in the tundish pouring zone are composed of $\text{Al}_2\text{O}_3\text{-CaO-MgO-(SiO}_2)$, and their morphologies are spherical or oval. After adding rare earth, the main types of inclusions in the steel are $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaO-Al}_2\text{O}_3\text{-MgO}$, $(\text{La, Ce})\text{Al}_2\text{O}_3\text{+CaS+oxides}$, and $\text{MgO-Al}_2\text{O}_3\text{-CaS}$.

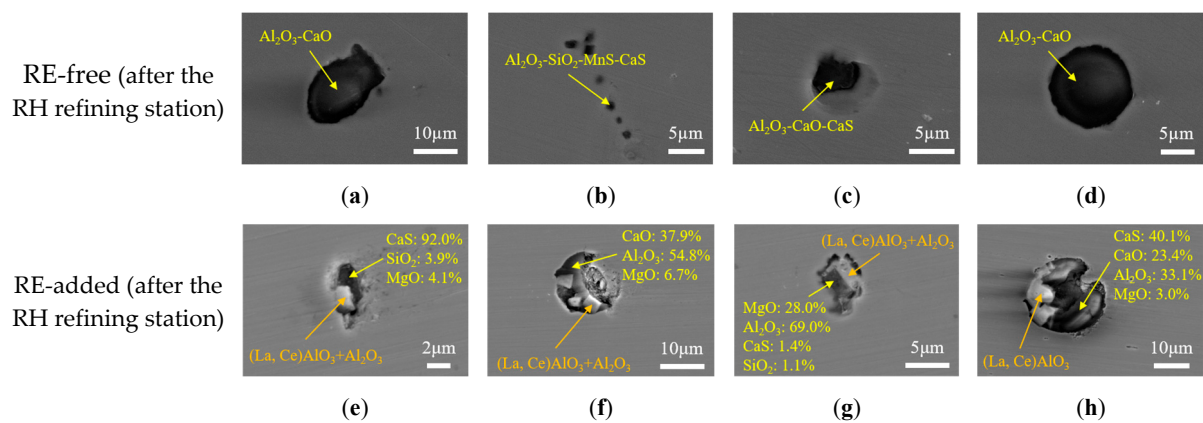


Figure 11. Morphologies and compositions of typical inclusions in the steel, before and after rare earth treatment, after the RH refining station. (a) $\text{Al}_2\text{O}_3\text{-CaO}$; (b) $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MnS-CaS}$; (c) $\text{Al}_2\text{O}_3\text{-CaO-CaS}$; (d) $\text{Al}_2\text{O}_3\text{-CaO}$; (e) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaS-SiO}_2$; (f) $\text{(La, Ce)AlO}_3\text{-Al}_2\text{O}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaO}$; (g) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaS-SiO}_2$; (h) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaS-CaO}$.

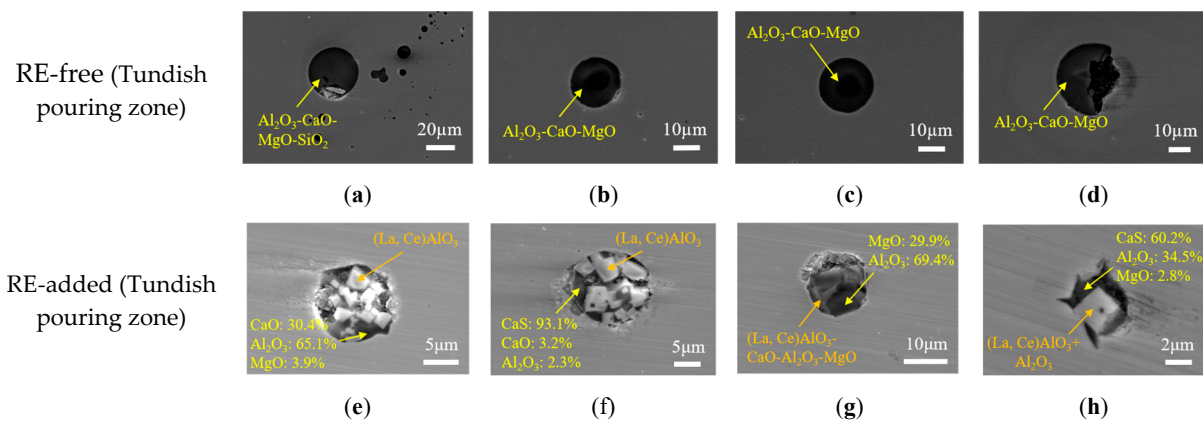
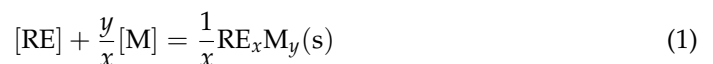


Figure 12. Morphologies and compositions of typical inclusions in the steel, before and after rare earth treatment, in the tundish pouring zone. (a) $\text{Al}_2\text{O}_3\text{-CaO-MgO-SiO}_2$; (b) $\text{Al}_2\text{O}_3\text{-CaO-MgO}$; (c) $\text{Al}_2\text{O}_3\text{-CaO-MgO}$; (d) $\text{Al}_2\text{O}_3\text{-CaO-MgO}$; (e) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaO}$; (f) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-CaS-CaO}$; (g) $\text{(La, Ce)AlO}_3 + \text{Al}_2\text{O}_3\text{-MgO}$; (h) $\text{(La, Ce)AlO}_3\text{-Al}_2\text{O}_3 + \text{Al}_2\text{O}_3\text{-MgO-CaS}$.

Through the analysis of the experimental results before and after rare earth treatment in different processes, it can be seen that rare earth treatment transforms the typical $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ inclusions with rectangular, acicular, or irregular shapes, into spherical or ellipsoidal rare earth inclusions. According to the investigations of Li et al. [17], rare earth elements added to liquid steel at a certain temperature will first react with the non-metallic elements O, S, etc., to form inclusions. The general formula of the chemical reaction is as follows:



where [RE] represents various rare earth elements dissolved in liquid steel, [M] represents various impurity elements dissolved in liquid steel, and (s) refers to the solid phase, with an activity of 1. According to the change of Gibbs free energy, the different types of inclusions can be determined. In addition to the formation sequence of inclusions in liquid steel, rare earth inclusions can also be converted to each other, which is closely related to the amounts of rare earth elements added. In the previous study, the author introduced the modification of inclusions in W350 non-oriented silicon steel by rare earth Ce [25].

Furthermore, it is generally accepted that rare earth inclusions have high melting points, that is, higher than 1690 °C. The temperature of liquid steel during the RH refining process and the continuous casting process is lower than the melting point of rare earth inclusions. Therefore, the physical properties of rare earth inclusions essentially determine that they can be used as the basic conditions for heterogeneous nucleation in liquid steel [26]. Whether during the RH refining process or the tundish process, the types of inclusions in the steel changed significantly before and after rare earth treatment. With the ability of rare earth oxides (sulfides) to form heterogeneous nuclei, the types of inclusions with rare earth treatment are mainly rare earth composite inclusions, and most of them are (La, Ce)Al₂O₃+conventional inclusions [27]. In addition, the inclusions detected after rare earth treatment are usually composed of more than two composite phases, indicating that the addition of rare earth elements promotes the agglomeration of inclusions.

4.2. Size Distribution of Inclusions before and after Rare Earth Treatment

Figure 13 shows the size distributions of inclusions, the proportions of inclusions with different sizes, and the changes in average size during the production processes of RH refining→after RH station→tundish. The morphologies, quantities and sizes of inclusions with a size of >1 µm in the steel were analyzed by an automatic scanning electron microscope (ASPEX). It can be seen that the number of inclusions with a size of 1.0~3.5 µm in the steel during the RH refining process, after rare earth treatment, is increased and their proportion is 11.11~24.07%. The average size of inclusions in the steel is 2.66 µm. The number of inclusions in the steel increases after the RH station, and the number of inclusions larger than 5 µm in the steel increases due to the collision of inclusions during the RH refining process. As the pouring casting proceeds, the number of micro inclusions with sizes of 1.0~2.5 µm in the steel decreases, while the number of inclusions with sizes of >5 µm increases, especially in the tundish impact zone. The number density of inclusions in the tundish pouring zone is 8.50/mm² and their proportion is 28.57%. The size distribution of inclusions is relatively stable.

Inclusions of less than 1 µm were difficult to observe due to their small size. Therefore, high-magnification TEM (backscattered, JEM-2100, JEOL Ltd, Japan) observation was used to assist in the identification of typical inclusions, through energy spectrum observation statistics.

The carbon extraction replica test samples for TEM were prepared as samples with sizes of 8 mm (TD) × 10 mm (RD) by wire cutting, and then roughly and finely ground. The samples were prepared by electro-polishing at 90 mA in 10% AA (acid alcohol) electrolyte for 120 s. The electrolyzed samples were coated with a layer of carbon film with a thickness of approximately 30 nm, using a vacuum carbon spray instrument. After dividing the carbon film into sizes of approximately 2 mm × 2 mm, they were placed in a 10% perchloric acid alcohol solution for electrolytic release, and then molybdenum nets with a 3 mm diameter were used to extract the carbon film. The samples were also prepared for TEM, and then electropolishing and observations, with 30 fields in each sample, were performed at different magnifications under TEM. The sizes and numbers of precipitates were analyzed using Image-Pro Plus.

The inclusions in hot-rolled sheet were observed and counted, and 30 fields of view were randomly selected, as shown in Figure 14.

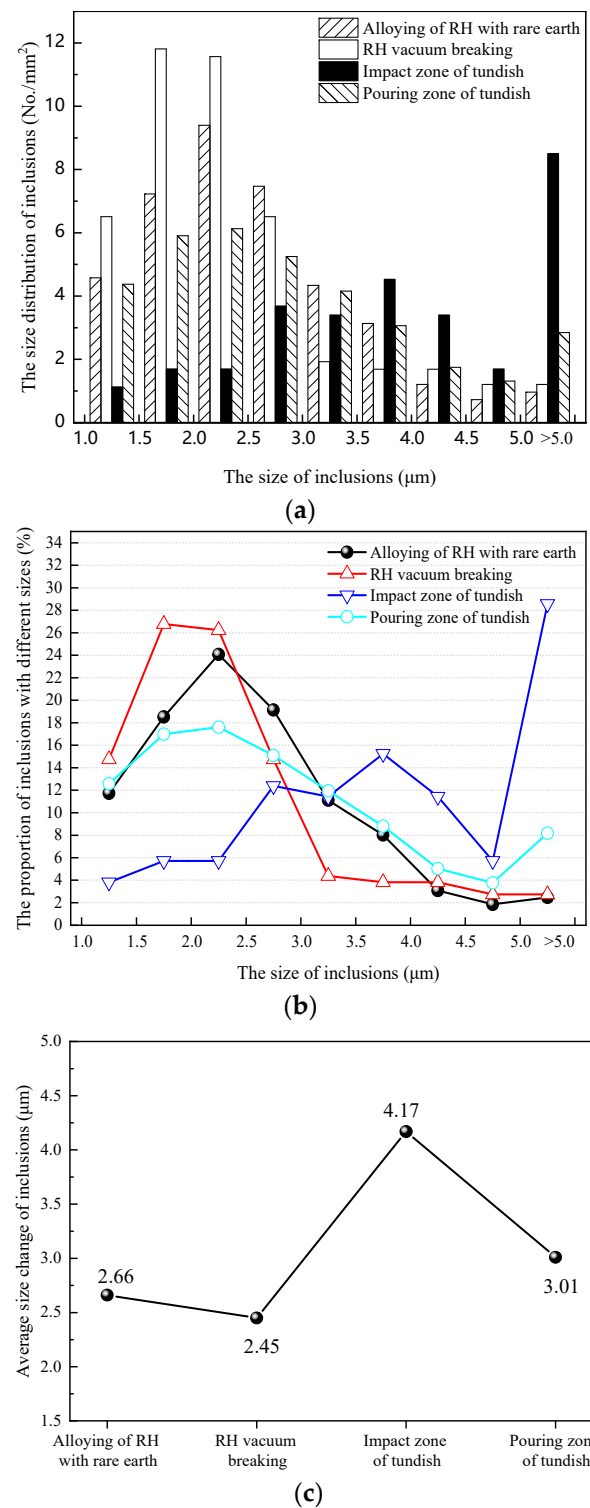


Figure 13. Size distributions and changes to inclusions in the steel. (a) The size distribution of inclusions, (b) The proportion of inclusions with different sizes, (c) Average size change of inclusions.

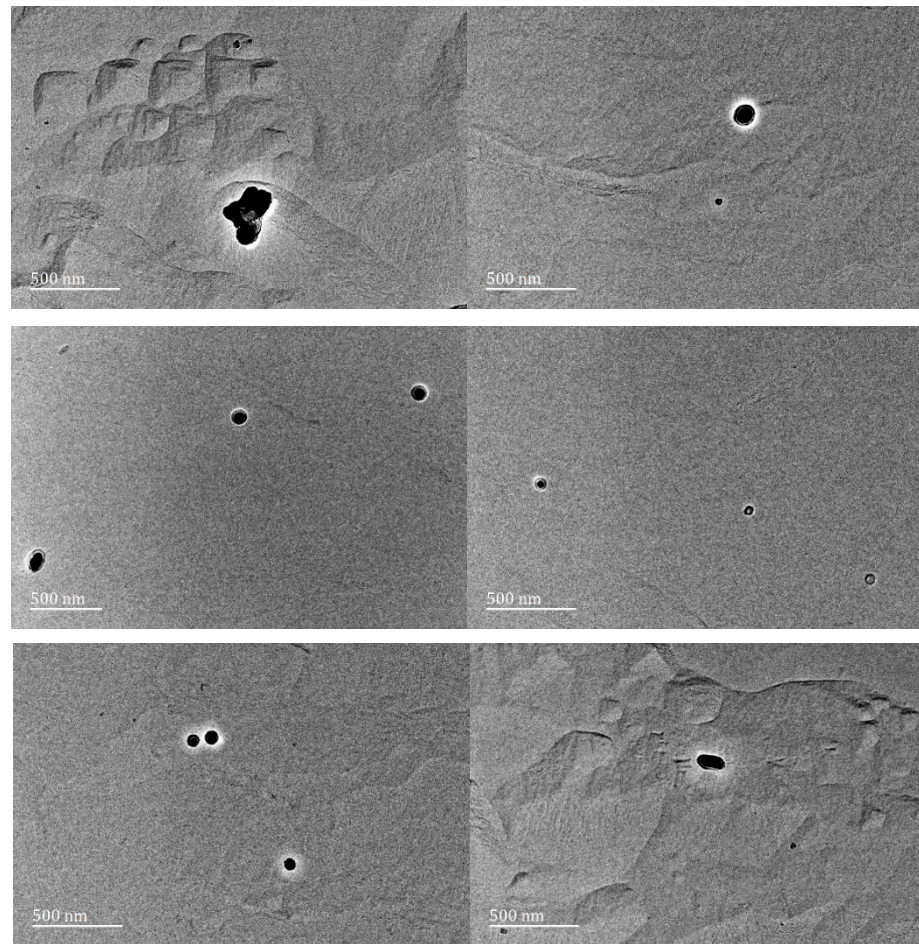


Figure 14. TEM morphology of micro inclusions in hot-rolled sheet, after rare earth treatment.

As illustrated in Figure 15, the content of micro inclusions ($\leq 1 \mu\text{m}$) in hot-rolled sheets is $51,458.2/\text{mm}^2$ and their average size is $0.388 \mu\text{m}$, before rare earth treatment. After rare earth treatment, the content of micro inclusions ($\leq 1 \mu\text{m}$) in hot-rolled sheets is $24,230.2/\text{mm}^2$ and their average size is $0.427 \mu\text{m}$. According to previous investigations, when the size of micro inclusions in non-oriented silicon steel is $0.1\sim 0.5 \mu\text{m}$, the magnetic properties of non-oriented silicon steel seriously deteriorate because the sizes of the micro inclusions are close to the thickness of the magnetic domain wall. In the current study, the number of micro inclusions in hot-rolled sheets after rare earth treatment is greatly reduced, and the average size of the micro inclusions is also increased. The magnetic properties of the steel with rare earth treatment are improved, which is consistent with previous investigations [28–30]. Compared to sheet produced through the original process, the iron loss of the 0.35 mm finished experimental sheet is reduced by 0.068 W/kg , and the magnetic induction is increased by 0.007 T , as shown in Table 4. The iron loss of the 0.50 mm finished experimental sheet is reduced by 0.008 W/kg , and the magnetic induction is increased by 0.004 T .

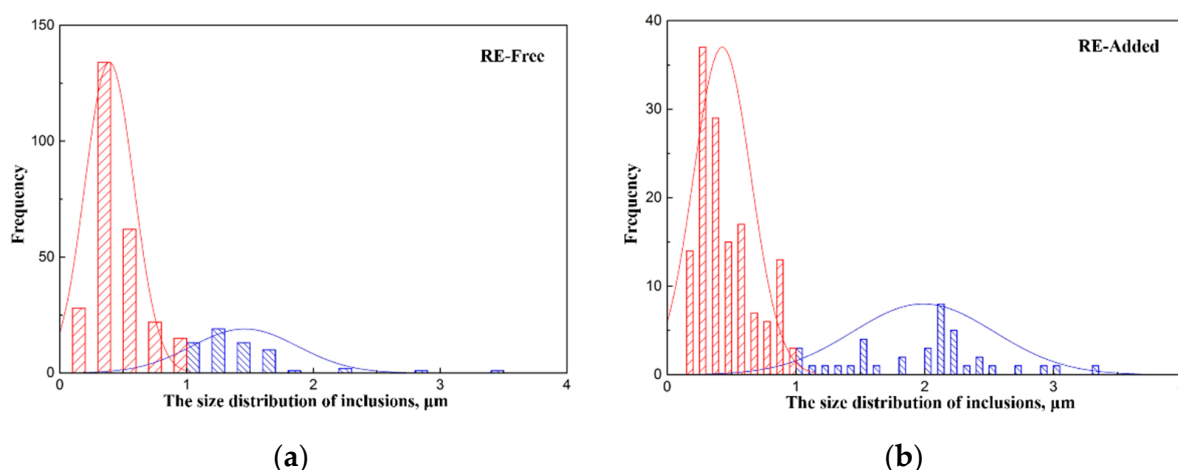


Figure 15. Size distribution of inclusions before and after rare earth treatment. (a) RE-free (b) RE-added.

Table 4. Electromagnetic properties of the steel.

Grade	Project	$P_{1.5/50}$, W/kg	Δ Value ($P_{1.5/50}$, W/kg)	B_{50} , T	Δ Value, (B_{50} , T)
0.35 mm	Experiment roll after rare earth treatment	2.370	−0.068	1.679	+0.007
	Original process sheet	2.438		1.672	
0.50 mm	Experiment roll after rare earth treatment	2.730	−0.008	1.695	+0.004
	Original process sheet	2.738		1.691	

5. Conclusions

(1) The types of inclusions in the steel significantly change after rare earth treatment. They are mainly composed of (La, Ce) Al_2O_3 and conventional inclusions. The morphologies are mostly blocky and partially chain-shaped.

(2) Adding rare earth La–Ce alloys during the RH refining process results in inclusions that are mainly (La, Ce) Al_2O_3 +CaO- Al_2O_3 -MgO, (La, Ce) Al_2O_3 +CaS+oxides, and CaO- Al_2O_3 -MgO. At the end of RH refining, the inclusions are mainly (La, Ce) Al_2O_3 +CaO- Al_2O_3 -MgO, (La,Ce) Al_2O_3 +CaS+oxides, and CaO- Al_2O_3 -MgO. The inclusions in the tundish impact zone are mainly (La, Ce) Al_2O_3 +CaO- Al_2O_3 -MgO, (La, Ce) Al_2O_3 +CaS+oxides, and CaO- Al_2O_3 -MgO-(CaS). The inclusions in the tundish pouring zone are mainly (La, Ce) Al_2O_3 +CaO- Al_2O_3 -MgO, (La, Ce) Al_2O_3 +CaS+oxides, MgO- Al_2O_3 -SiO₂-CaS, and Al_2O_3 -SiO₂-CaO. After rare earth treatment during the RH refining process, the number of inclusions in the steel with sizes of 1.0~3.5 μm is increased and their average size is 2.66 μm . Due to collisions and growth, the number of inclusions with sizes greater than 4 μm in the steel increases after the RH refining station. The number of micro inclusions with sizes of 1.0~2.5 μm in the tundish decreases, while the number of inclusions with sizes larger than 5 μm increases.

(3) Before rare earth treatment, the content of micro inclusions ($\leq 1 \mu m$) in hot-rolled sheets is 51,458.2/mm² and their average size is 0.388 μm . The content of micro inclusions ($\leq 1 \mu m$) in hot-rolled sheets with rare earth treatment is 24,230.2/mm² and their average size is 0.427 μm . Compared to sheets produced by the original process, the magnetic properties of the experimental sheets show that the iron loss of the 0.35 mm finished product is decreased by 0.068 W/kg, and the magnetic induction is increased by 0.007 T. The iron loss of the 0.5 mm finished product is decreased by 0.008 W/kg, and the magnetic induction is increased by 0.004 T.

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