

## Article

# Study on the Causes and Control Measures of Mg–Al Spinel Inclusions in U75V Heavy Rail Steel

Jun Zhu, Lei Ren  and Jichun Yang

School of Materials and Metallurgy, Inner Mongolia University of Science and Technology (IMUST), Baotou 014010, China; zj198706133972@163.com (J.Z.); yangjichun1963@163.com (J.Y.)

\* Correspondence: renlei19890817@163.com

**Abstract:** U75V heavy rail steel production uses an aluminum-free deoxidation process; however, large particles of MgO–Al<sub>2</sub>O<sub>3</sub> inclusions form in the steel, which has a great impact on product quality. In this paper, we try to explain how spinel inclusions, which affect the metallurgical quality of heavy rail steel, are produced by thermodynamic and experimental methods, and then determined measures for avoiding such inclusions. The formation mechanism of spinel inclusions in U75V heavy rail steel was determined through the analysis of nozzle clogging in the pouring process and typical inclusions in steel. The results show that there are two types of spinel inclusions in heavy rail steel: one is pure Mg–Al spinel inclusions and the other is Mg–Al spinel inclusions coated with calcium aluminate. The small, pure Mg–Al spinel inclusions were precipitated during the solidification of the molten steel, and the precipitation temperature was related to the composition of the molten steel. The large spinel inclusions were derived from clogging of the submerged nozzle. Mg–Al spinel inclusions coated with calcium aluminate were transformed from CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO complex inclusions in the steel during cooling, and the formation temperature was related to the content of Al<sub>2</sub>O<sub>3</sub> and MgO in the inclusions. The content of Al<sub>2</sub>O<sub>3</sub> and MgO in the inclusions was the key to the formation of the Mg–Al spinel inclusions. Therefore, in order to control the production of spinel inclusions in steel, it is necessary to strictly control the content of impurity elements such as magnesium and aluminum in the alloy auxiliary materials, to reduce the secondary oxidation of liquid steel and to reduce the erosion of refractory materials.



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**Keywords:** U75V; heavy rail steel; Mg–Al spinel inclusions

## 1. Introduction

Heavy rail steel is the main load-bearing component of railways. The general trend in the rapid development of railways has been toward high speed and heavy loads. Therefore, the quality requirements of heavy rail steel are becoming more and more strict, not only requiring high cleanliness but also needing to have high strength, high toughness and fatigue resistance. Inclusions in heavy rail steel are mainly divided into two categories: non-metallic inclusions and metal inclusions. Non-metallic inclusions include oxides, sulfides, silicates, etc. Metal inclusions are compounds formed by alloying elements in the melting process. The formation mechanism of inclusions in heavy rail steel is mainly affected by the composition of the raw materials, the reaction during melting and the physical and chemical changes during pouring and solidification. For example, elements such as oxygen, sulfur and phosphorus in raw materials easily react with iron in steel to produce their corresponding oxides, sulfides and phosphates. In addition, in the process of pouring and solidification, due to differences in cooling rates and crystallization rates, the formation of inclusions may also occur. Inclusions have a significant influence on the mechanical properties of heavy rail steel. On the one hand, inclusions are concentrated sources of stress, which reduce the fatigue resistance and toughness of the rail. On the other hand, inclusions also affect the hardness and strength of the rail, thus affecting its wear resistance

and brittleness. Therefore, controlling the quantity and distribution of inclusions is very important in improving the performance of heavy rail steel.

In order to improve the cleanliness, strength, toughness and fatigue resistance of heavy rail steel, an aluminum deoxidation process is strictly implemented during the smelting process. However, non-metallic inclusions in steel are still the main factor affecting the cleanliness of the molten steel. Inclusions are also the key factors affecting rail performance [1–7]. In the process of producing U75V heavy rail steel, several domestic steel mills have found that there are large particles of  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions in damaged rail samples of heavy rail steel [8–10], which seriously affect the rail quality.  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions easily react with acids, alkalis and other substances, thus destroying the protective film on the steel surface and making it more susceptible to corrosion. This kind of inclusion produces stress concentration in steel, which leads to decreases in the fatigue strength of the steel and the easy formation of fatigue fractures.  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions form a brittle phase in steel, which reduces the plasticity and toughness of the steel and makes it prone to brittle fractures. Therefore, in order to reduce the harm of  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions, it is necessary to conduct in-depth research on its formation mechanism and take effective control measures to reduce its content and distribution.

$\text{MgO-Al}_2\text{O}_3$  spinel inclusions have a stable, surface-centered cubic structure, with a melting point of 2135 °C and a high hardness. They do not easily deform during rolling, making them type-D point non-deformable inclusions. Most  $\text{MgO-Al}_2\text{O}_3$  inclusions range in size from 2.0  $\mu\text{m}$  to 6.0  $\mu\text{m}$ , and exist in spherical, cubic and irregular shapes. As non-metallic inclusions in steel,  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions have a high melting point and poor deformation ability [11], which seriously harm the plasticity, toughness and fatigue resistance of the steel matrix [12]. As spinel inclusions do great harm to the quality of steel, many researchers have studied the formation mechanisms of such inclusions. Previous research results can be summarized into four models: (1) the carbon reduction model [13,14]; that is, C in the refractory first reduces MgO to generate CO and Mg vapor, which then diffuse into the molten steel and react with  $\text{Al}_2\text{O}_3$  inclusions in the molten steel to generate spinel inclusions. (2) In the direct reaction model [15,16], the  $\text{Al}_2\text{O}_3$  inclusions in the molten steel react directly when they contact the refractories involved in refining slag. (3) In the aluminum replacement model [17], MgO enters the steel slag after the refractory is eroded, and the dissolved aluminum in the molten steel displaces the MgO in the steel slag and then forms spinel inclusions. (4) In the crystallography model [18,19], when the temperature of the molten steel decreases during continuous casting, the magnesium–aluminum spinel inclusion phase will crystallize inside  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  composite oxide inclusions with a low melting point. Such inclusions are more common in aluminum deoxidized steel [20,21]. The formation and control of spinel inclusions in aluminum deoxidized steel have been extensively reported. Harada A et al. [22] and Park J et al. [18,23] pointed out that the formation of spinel inclusions was related to slag basicity and  $w_{\text{CaO}}/w_{\text{Al}_2\text{O}_3}$ . The formation of spinel inclusions could be inhibited by appropriately reducing the slag basicity and  $w_{\text{CaO}}/w_{\text{Al}_2\text{O}_3}$ . Bjorklund J et al. [24] showed that a reduction in MgO content in the slag by a VD refining process could inhibit the formation of spinel inclusions. Chi Y et al. [25] studied the influence of different refractories on steel cleanliness and pointed out that MgO and enamel refractories promote the formation of spinel inclusions in steel. In addition, Shin J et al. [26] also studied the influence of the  $\text{CaF}_2$  content in slag on the formation behavior of spinel inclusions, and pointed out that a  $w_{\text{CaF}_2}$  of less than 10% in the slag is conducive for spinel control.

In this paper, the formation, development and change of spinel inclusions in the actual production process of heavy rail steel are studied. In actual production, the formation of inclusions involves thermodynamics, dynamics, heat transfer and mass transfer. With the progress of metallurgical technologies and innovations in equipment, the formation conditions and process of inclusions are complicated and changeable. In this paper, the causes of spinel inclusions which affect the metallurgical quality of heavy rail steel are

described from both thermodynamic and experimental aspects, and measures for avoiding spinel inclusions are proposed.

## 2. Investigation Methods

The experimental steel used in this paper was heavy rail steel produced by an iron and steel enterprise. The production process was as follows: KR (Kambara Reactor) molten iron pretreatment desulfurization → 150T top and bottom double blowing converter → aluminum-free final deoxidation → 150T LF (Ladle Furnace) refining → VD (Vacuum Degassing) → VD soft blowing →  $280 \times 380 \text{ mm}^2$  square billet continuous casting. During the production process, the mechanical properties of the rail were detected by tensile tests. The morphology and composition of the inclusions were analyzed by scanning electron microscopy. The formation process of spinel inclusions in the steel was systematically studied by Aspex automatic scanning electron microscopy combined with thermodynamic calculations. Factsage7.3 software was used for thermodynamic calculations in this paper.

## 3. Results and Discussion

### 3.1. Analysis of the Tensile Fracturing of the Rail

The chemical composition of the U75V heavy rail is shown in Table 1. The tensile fracture morphology of the rail was observed under an electron microscope, and the existence of large size inclusions was found, as shown in Figure 1. The main composition was  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ , and the inclusion contained large particles of  $\text{MgO-Al}_2\text{O}_3$  spinel. As a brittle inclusion with a high melting point, the  $\text{MgO-Al}_2\text{O}_3$  spinel had poor deformation ability, which seriously reduced the mechanical properties of the steel matrix—which was the main reason for the tensile fracture. However, U75V heavy rail steel implements a strict aluminum-free deoxidation process, so it is necessary to conduct further research on how these  $\text{MgO-Al}_2\text{O}_3$  spinel inclusions are formed.

**Table 1.** Chemical composition of U75V heavy rail steel (%).

|             | C    | Si  | Mn   | P     | S     | Al    | V    |
|-------------|------|-----|------|-------|-------|-------|------|
| Upper limit | 0.71 | 0.5 | 0.75 | 0.025 | 0.025 | 0.004 | 0.04 |
| Lower limit | 0.8  | 0.8 | 1.05 | 0     | 0     | 0     | 0.12 |

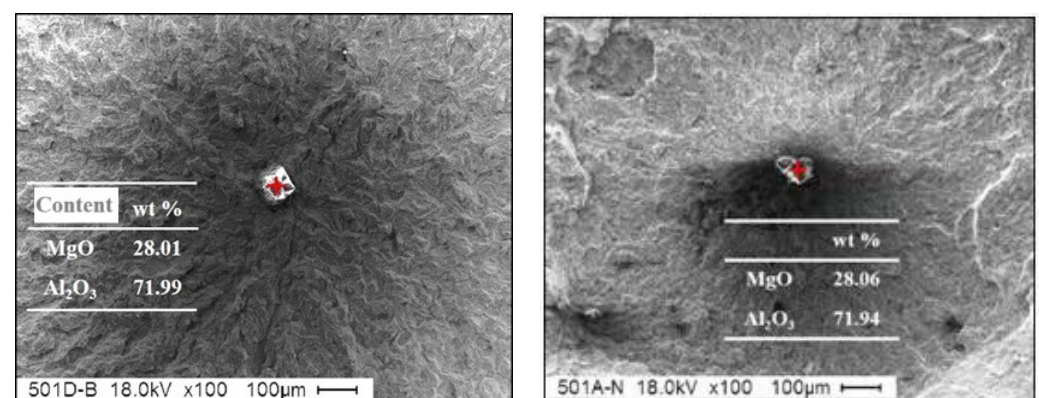


**Figure 1.** Morphology and composition of inclusions at tensile fracture of rail.

### 3.2. Analysis of Nodules in the Nozzle

In order to determine the source of spinel inclusions in U75V heavy rail steel, the immersion nozzle was analyzed after pouring, as shown in Figure 2. Although no obvious orifice blockage was found, a ring nodulation layer about 5 mm thick was found on the inner wall of the orifice. The inner surface and layer structure of nodules were observed and analyzed by Aspex automatic scanning electron microscopy (SEM) after cold inlay and gold spraying. Shown in Figure 3 is the local microscopic morphology of nodules on the

inner wall of the immersed nozzle. The boxes indicate the region of the energy spectrum, and its components are shown in serial numbers 1–4 in Table 2. The nodules are mainly composed of two parts: the pale gray area, whose main components are  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  ( $-\text{MgO}$ ); the dark grayish-black area is mainly composed of spinel inclusions dominated by  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . The results show that nozzle-off is one of the possible sources of spinel inclusions in billet and rail, that the size of spinel inclusions is large and that the potential harm to the steel is very serious. However, there may be more than one source of spinel inclusions, so a more in-depth study of inclusions in steel is necessary. Figure 4 shows the surface scanning results of the element distribution in this area.

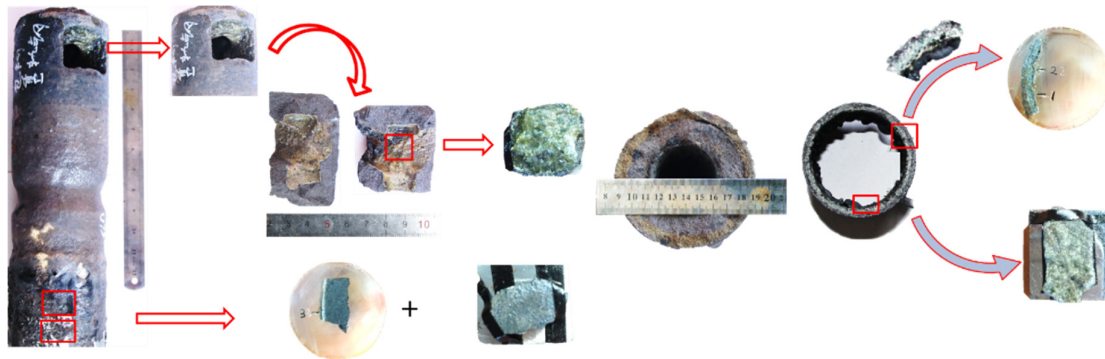


**Figure 2.** Macroscopic morphology and sampling schematic diagram of the immersed nozzle.

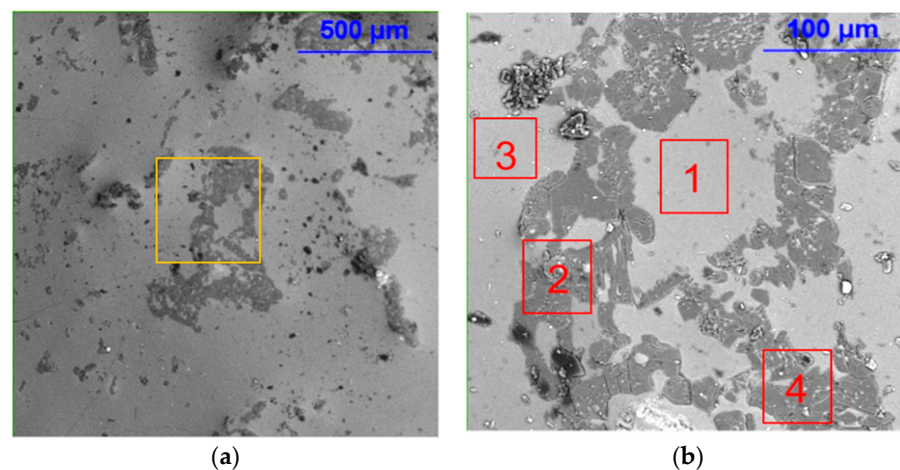


**Figure 3.** Morphology of the nodules on the inner wall of the immersed nozzle 2000 $\times$  (a) and 2500 $\times$  (b). The yellow box indicates the region of the energy spectrum.

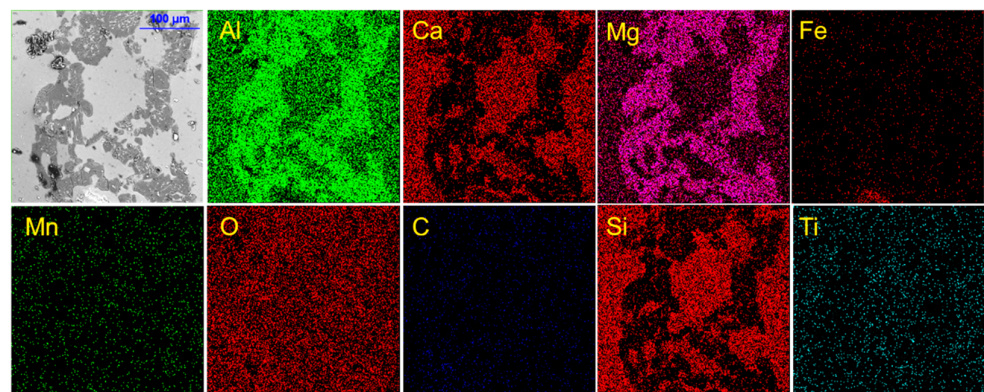


**Figure 4.** Nodular element distribution scanning.

**Table 2.** Components of nodules in each position.

| Area | CaO   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO   | MnO  | C     | Fe   |
|------|-------|------------------|--------------------------------|-------|------|-------|------|
| 1    | 31.86 | 33.24            | 24.60                          | 5.10  | 0.00 | 5.21  | 0.00 |
| 2    | 0.00  | 0.70             | 67.64                          | 28.84 | 0.85 | 1.97  | 0.00 |
| 3    | 31.27 | 30.82            | 24.79                          | 0.00  | 0.00 | 13.12 | 0.00 |
| 4    | 3.18  | 3.10             | 64.93                          | 24.26 | 0.00 | 4.54  | 0.00 |

### 3.3. Formation Analysis of CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO Inclusions

Heavy rail steel adopts aluminum-free deoxidation process. In the steelmaking process, MnSi, FeSi and other alloys are added for deoxidation, and BaCaSi is added for deoxidation in the LF refining process. The smelting process of U75V heavy rail steel is studied here. The composition distribution of inclusions in converter outbound steel is shown in Figure 5, and the average composition of inclusions in the steel is shown in Table 3. In the figure, the position of the black circle represents the proportion of each component of the inclusions, and the size of the black circle represents the size of the inclusions. The main components of the inclusion were SiO<sub>2</sub> and MnO, the content of Al<sub>2</sub>O<sub>3</sub> was low and there was basically no MgO. From the inclusion composition, it can be concluded that it was composed of deoxidized products produced during the process of steel production. The transformation of the liquid steel composition and inclusions in the U75V heavy rail steel smelting process are shown in Figures 6 and 7. Due to the addition of FeSi and other alloy excipients in the refining process, the mass fraction of impurity elements such as Ca and Al in steel increased, and the MnO–SiO<sub>2</sub> inclusions gradually transformed into CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO inclusions. The composition of alloy auxiliary materials is shown in Table 4. The composition of the U75V heavy rail steel refined slag is shown in Table 5. With the smelting process, the mass fraction of Al<sub>2</sub>O<sub>3</sub> and MgO in the refining slag increased continuously. The MgO content increased from 4.61% to 6.69%, indicating that the refractories were eroded into the slag during smelting; this phenomenon was more obvious during the VD vacuum stage. The materials and erosion of the U75V heavy rail steel ladle are shown in Table 6. The slag line was composed of MgO–C, and the Al<sub>2</sub>O<sub>3</sub> content in the furnace lining was very high. Field data show that the weight loss of each ladle after smelting was about 160 kg, and the erosion of the refractory materials was serious. In addition, the results show that VD vacuum refining has a great influence on the composition of liquid steel and the composition of inclusions. The reaction between steel, slag and inclusions–refractories was promoted by the long stirring time of the steel slag under vacuum conditions. The mass fraction of Al and Ca in steel decreased clearly, while the mass fraction of CaO in the inclusions increased. VD refining ended with CaO inclusions exceeding 40%, and finally, the inclusion was completely transformed into a spherical liquid CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO composite inclusion [27].

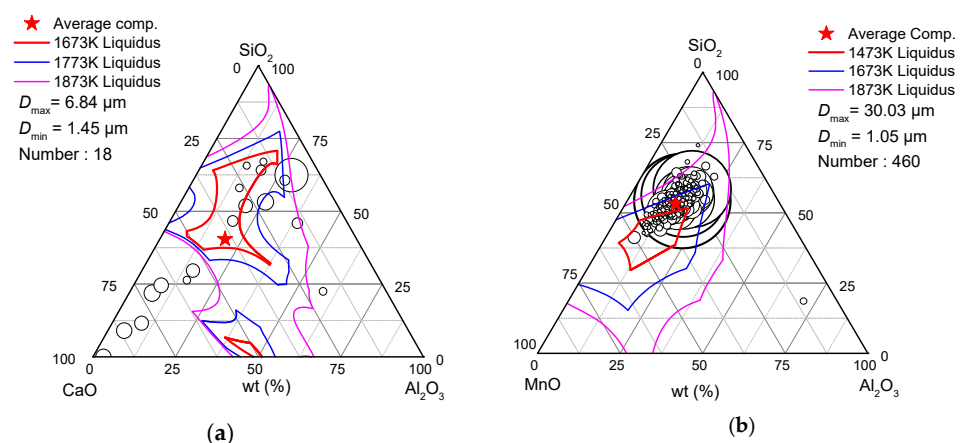


**Figure 5.** Composition distribution of typical inclusions outside converter: SiO<sub>2</sub>–CaO–Al<sub>2</sub>O<sub>3</sub> (a) and SiO<sub>2</sub>–MnO–Al<sub>2</sub>O<sub>3</sub> (b).

Table 3. Average composition of inclusions in converter outbound steel.

| Composition    | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | CaO   | MnO   | MgO  | MnS  | TS (°C) | TL (°C) |
|----------------|--------------------------------|------------------|-------|-------|------|------|---------|---------|
| Real (%)       | 12.92                          | 44.69            | 11.97 | 25.95 | 0.61 | 3.86 | --      | --      |
| Normalized (%) | 13.52                          | 46.78            | 12.53 | 27.17 | --   | --   | 973     | 1082    |

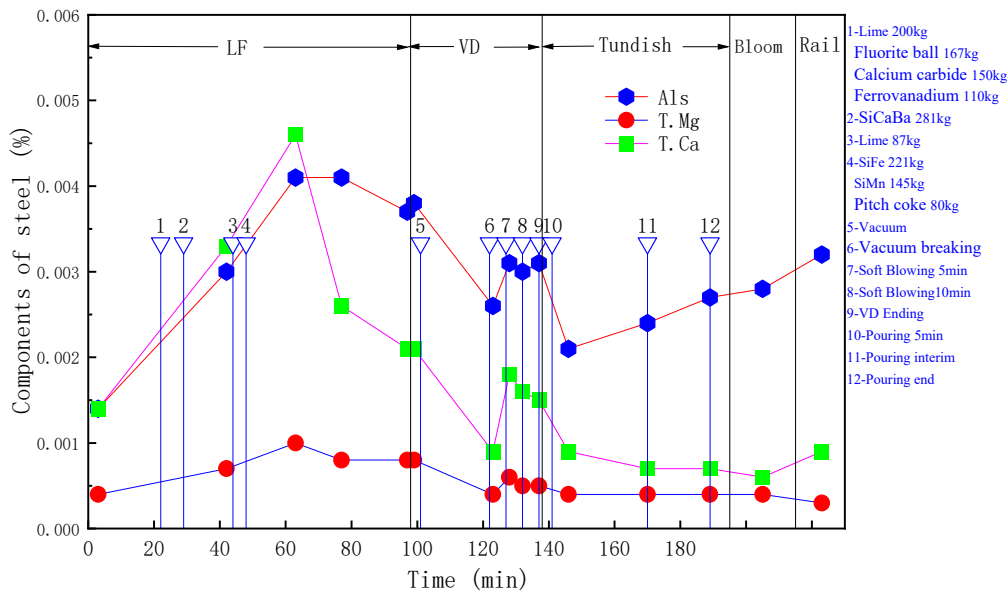


Figure 6. Changes in the composition of the molten steel.

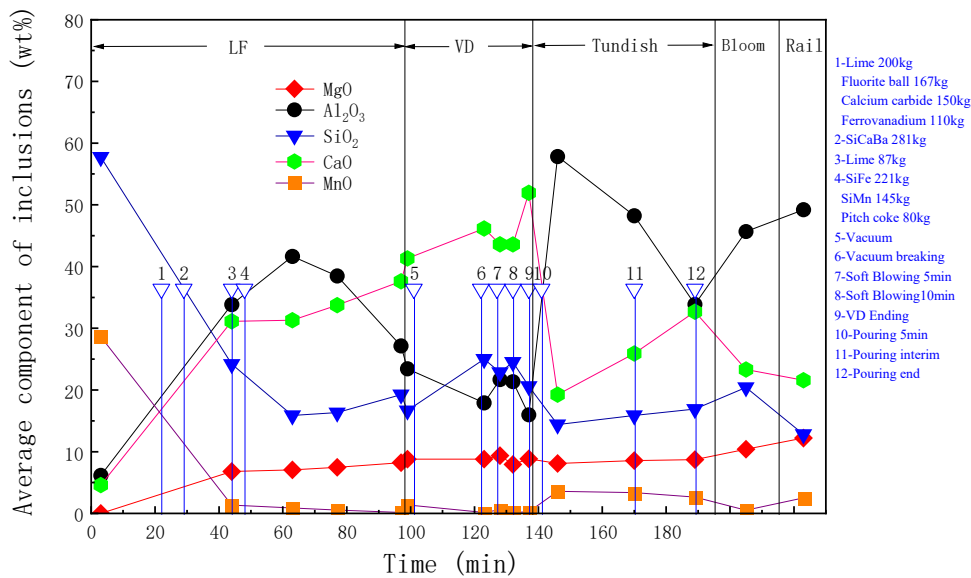


Figure 7. Changes in the composition of the inclusions.

Table 4. Alloy impurity element content.

|                  | Al (wt%) | Mg (wt%) | Ca (wt%) | Ti (wt%) |
|------------------|----------|----------|----------|----------|
| FeSi             | 1.37     | 0.036    | 0.87     | 0.13     |
| FeV              | 0.096    | <0.005   | 0.02     | --       |
| BaCaSi           | 0.20     | 0.036    | 12.68    | 0.11     |
| MnSi             | <0.02    | <0.005   | 0.025    | 0.16     |
| CaC <sub>2</sub> | 0.52     | 0.024    | 55.22    | --       |

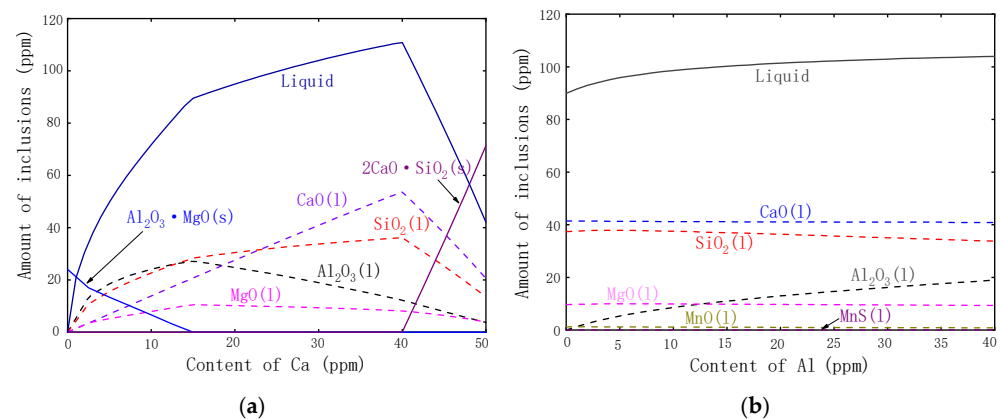
**Table 5.** Refining slag composition (%).

| Process            | CaO   | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | MgO  | MnO  | FeO  | BaO  | CaF <sub>2</sub> | R    |
|--------------------|-------|--------------------------------|------------------|------|------|------|------|------------------|------|
| LF slagging        | 34.36 | 3.52                           | 22.39            | 4.61 | 0.06 | 0.55 | 4.10 | 27.48            | 1.53 |
| LF ending          | 37.03 | 3.56                           | 23.56            | 5.19 | 0.08 | 1.24 | 3.56 | 23.36            | 1.57 |
| VD vacuum breaking | 38.72 | 3.99                           | 24.56            | 6.49 | 0.11 | 0.28 | 3.38 | 20.02            | 1.58 |
| VD ending          | 37.40 | 4.13                           | 25.06            | 6.69 | 0.22 | 0.55 | 3.31 | 20.32            | 1.49 |

**Table 6.** Ladle refractory composition.

| Location              | Chemical Composition/%                                  | Erosion Situation |
|-----------------------|---------------------------------------------------------|-------------------|
| Slag line             | MgO > 78%, C > 13%                                      | 160 kg            |
| Ladle lining          | Al <sub>2</sub> O <sub>3</sub> > 85%, MgO > 3%, C > 3%  |                   |
| The bottom of the bag | Al <sub>2</sub> O <sub>3</sub> > 70%, MgO > 10%, C > 5% |                   |

Figure 8 shows the effects of the Ca and Al content on inclusion formation during the refining process, as calculated by FactSage7.3 thermodynamic software. Figure 8a shows that under the conditions of refining, when the content of Ca in the steel was 15~40 ppm, the inclusions were liquid, and when the mass fraction of Ca was lower than 15 ppm, the solid phase Mg–Al spinel began to form. Figure 8b shows the influence of Al content on the formation of inclusions. With increases in the Al content, the content of Al<sub>2</sub>O<sub>3</sub> in the inclusions gradually increased, and the influence of Al content on the overall composition of the inclusions was small. The calculation results show that the CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO-type inclusions were the main inclusions under the LF refining conditions. The Al content in the steel was certain, and spinel inclusions were formed when the calcium content was low.

**Figure 8.** Effect of Ca (a) and Al (b) content on inclusion formation.

In addition, from the changing trend in the average composition of inclusions in the smelting process of the U75V heavy rail steel, it was also found that the mass fraction of Al<sub>2</sub>O<sub>3</sub> in the inclusions rose sharply at the beginning of pouring. It rose rapidly from around 17% at the end of VD refining to around 58%. The changes in the oxygen and nitrogen mass fractions are shown in Figure 9. The mass fraction of oxygen and nitrogen in the tundish increased significantly at the opening stage, indicating that obvious secondary oxidation occurred at this time. Therefore, it is necessary to improve protective measures to prevent the occurrence of secondary oxidation at the opening stage.

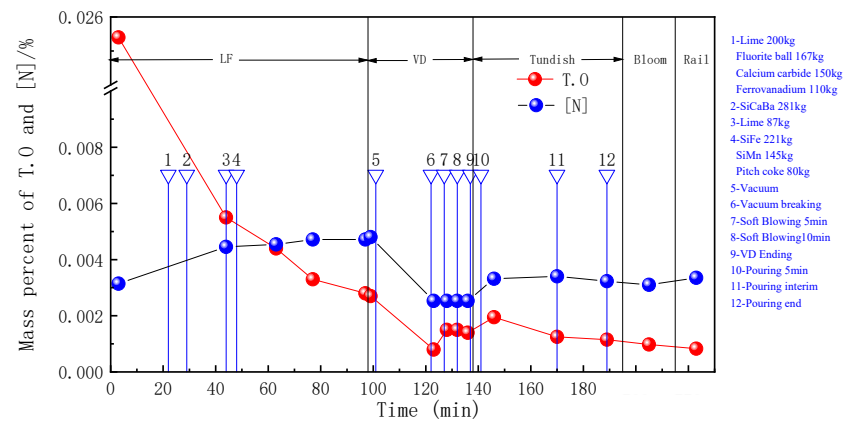


**Figure 9.** Changes in oxygen and nitrogen content.

### 3.4. Precipitation Transition of the Inclusions Themselves

After VD refining, the main components of inclusions in steel were calcium, silicon, aluminum, magnesia and oxygen, and the distribution was uniform, and no spinel inclusions were found. However, Mg–Al spinel was detected in the subsequent molten steel, so the formation of spinel inclusions should be considered from the angle of precipitation and transformation of the inclusion itself. The precipitation transition of the inclusion itself during solidification and cooling was calculated by FactSage7.3 thermodynamic software, considering that the tundish had the closest contact with the water outlet and that the composition of the non-metallic inclusions in the steel in the tundish was closest to the composition of the final inclusions. Therefore, the average composition of non-metallic inclusions in the steel in the tundish under steady-state pouring conditions was calculated (45.70% CaO—22.13% SiO<sub>2</sub>—24.41% Al<sub>2</sub>O<sub>3</sub>—7.15% MgO), selecting the three databases FactPS, FToxide and FSsteel, and the calculation results are shown in Figure 10. At 1600 °C, the component inclusions were a single liquid phase, and as the temperature decreased, the liquid phase gradually decreased; at 1500 °C, a solid phase MgO–Al<sub>2</sub>O<sub>3</sub> spinel precipitated, and then the CaO–SiO<sub>2</sub> phase began to precipitate. The final inclusions were mainly composed of the CaO–SiO<sub>2</sub> phase and spinel phase, additionally containing a small amount of CaO–Al<sub>2</sub>O<sub>3</sub> and CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> phase. This calculation is mainly the transformation of the inclusion phase itself, and does not involve the transformation of the composition of the inclusion. The melting point of U75V heavy rail steel is 1470 °C, and the pouring temperature is about 1500 °C, indicating that the inclusions of this component began to precipitate inside the spinel phase under pouring temperature conditions; this also indicates that the precipitation transformation of the inclusions themselves is one of the reasons for the occurrence of spinel inclusions.

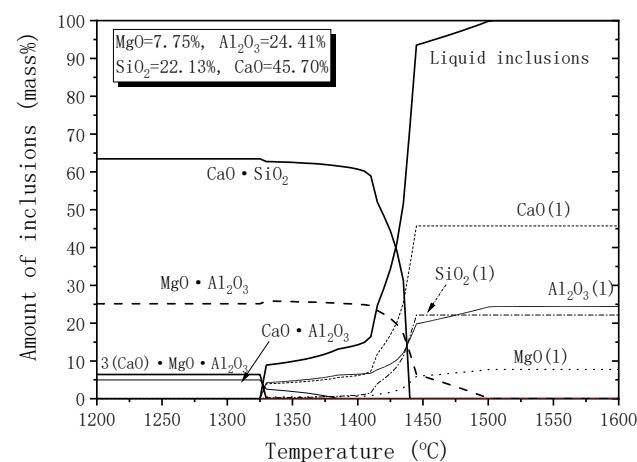


**Figure 10.** Transition of high CaO low Al<sub>2</sub>O<sub>3</sub> inclusions during cooling.

### 3.5. Analysis of Typical Inclusions in Billet and Rail

The morphology and composition of typical inclusions in U75V heavy rail steel billets and rails are shown in Figure 11. The inclusion in the billet was large, it contained spinel and  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  was wrapped outside, as shown in Figure 11a. The  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  phase with its low melting point and high plasticity was prone to deformation in the rolling process, while the  $\text{MgO-Al}_2\text{O}_3$  phase with its high melting point exhibited high hardness and poor deformation performance. This is because of the difference in the properties of the inclusion phases. The non-deformation of the rolling process resulted in the brittle fracture of the inclusions, resulting in bare spinel inclusions in the steel matrix. Figure 11b shows typical inclusions observed along the rolling direction.

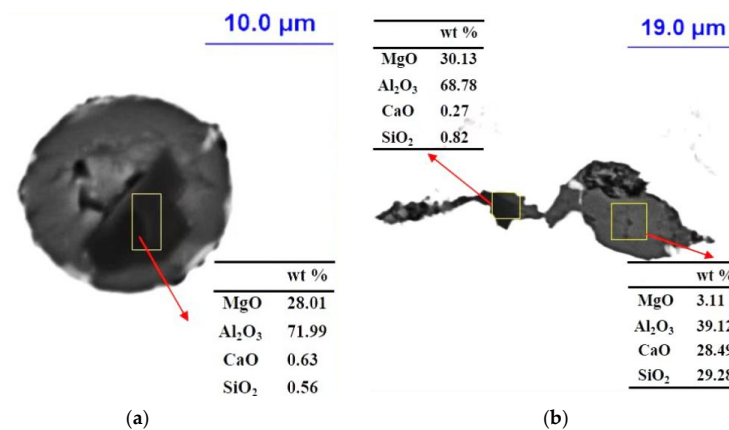


**Figure 11.** Morphology and composition of typical inclusions in billet (a) and rail (b).

FactSage7.3 thermodynamic software was used to calculate the precipitation transformation of inclusions in the cooling process, and the calculation results were shown in Figure 12. The inclusions under this composition precipitated the  $\text{MgO-Al}_2\text{O}_3$  phase in the cooling process, and the precipitation temperature was related to the composition of the initial inclusion. Compared with the results shown in Figure 10, it was found that the precipitation temperature of the spinel phase gradually increased with increases in the  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  content in the inclusion, and some inclusions began to precipitate the  $\text{MgO-Al}_2\text{O}_3$  phase at the temperature of steel making. Therefore, to control the precipitation of  $\text{MgO-Al}_2\text{O}_3$  in the smelting process, the content of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the inclusion should be reduced. Additionally, this is an effective method for controlling the precipitation of spinel inclusions in heavy rail steel to prevent the secondary oxidation of molten steel during smelting and to reduce strong slag reactions and corrosion resistance in VD refining.

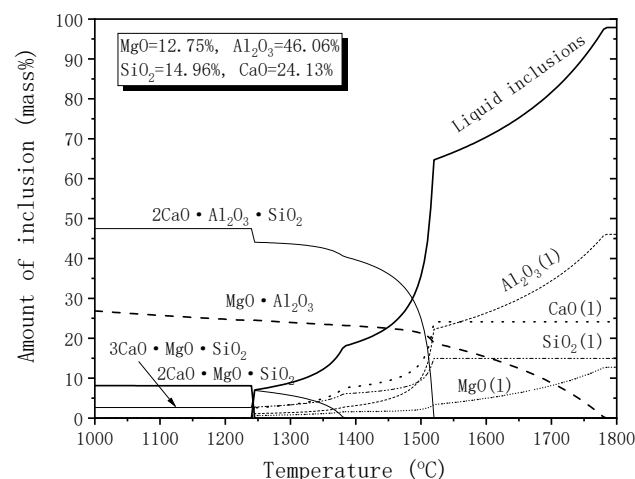


**Figure 12.** Transition of high  $\text{Al}_2\text{O}_3$  low  $\text{CaO}$  inclusions during cooling.

### 3.6. Precipitation of Inclusions during the Solidification of Molten Steel

The precipitation and average composition changes of inclusions in molten steel during the solidification and cooling of U75V heavy rail steel were calculated. The mass fractions of each element were  $w_{[C]} = 0.75\%$ ,  $w_{[Si]} = 0.61\%$ ,  $w_{[Mn]} = 0.95\%$ ,  $w_{[V]} = 0.046\%$ ,  $w_{T[O]} = 0.0013\%$ ,  $w_{[Ca]} = 0.0008\%$ ,  $w_{[Al]} = 0.0040\%$ ,  $w_{[Mg]} = 0.0004\%$  and  $w_{[S]} = 0.0040\%$ . The calculated results are shown in Figure 13, where Figure 13a shows the phase transition of the inclusions and Figure 13b shows the change in the average composition of the corresponding inclusions. T. means Total. This is a habitual expression. The 1600 °C molten steel inclusions were mainly liquid. With decreases in temperature, the contents of CaO and SiO<sub>2</sub> gradually decreased, while the contents of MgO, Al<sub>2</sub>O<sub>3</sub> and CaS gradually increased. When the temperature was lower than 1470 °C, the Mg–Al spinel phase was precipitated from the steel. Furthermore, the average composition of the inclusions showed that the Al<sub>2</sub>O<sub>3</sub> and MgO content gradually increased. When the temperature was approximately 1100 °C, a large number of MnS inclusions were precipitated.

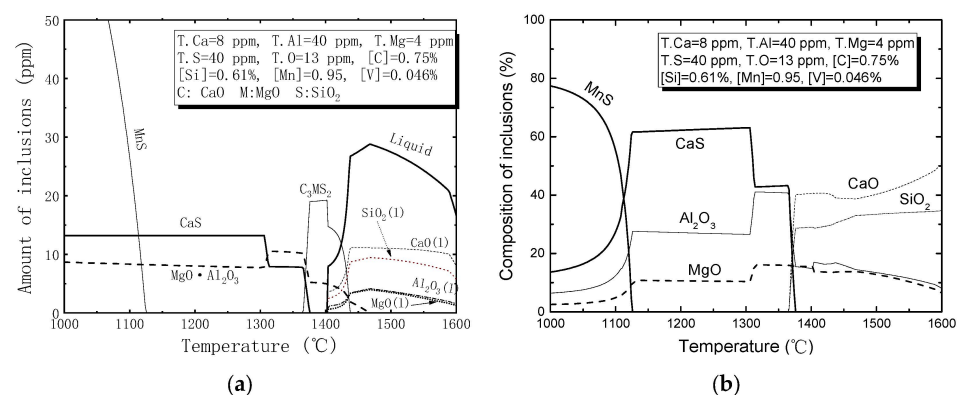


**Figure 13.** Precipitation of inclusions during the solidification and cooling of molten steel: Amount of inclusions (a) and Composition of inclusions (b).

From the above thermodynamic calculation, it can be seen that spinel inclusions will also be produced during the process of liquid cooling of steel. Compared with the transition of inclusions, the temperature required for the precipitation of spinel inclusions during the solidification of liquid steel is relatively low. The spinel inclusions precipitated from molten steel are controlled by two factors: molten steel composition and temperature. Temperature mainly affects the kinetic conditions of spinel inclusion precipitation. The size of spinel inclusions precipitated during the solidification of liquid steel is relatively small, as shown in Figure 14. Inclusion formation can be controlled by controlling the composition of liquid steel [28,29]. Inclusion precipitation can be achieved by controlling the cooling temperature.

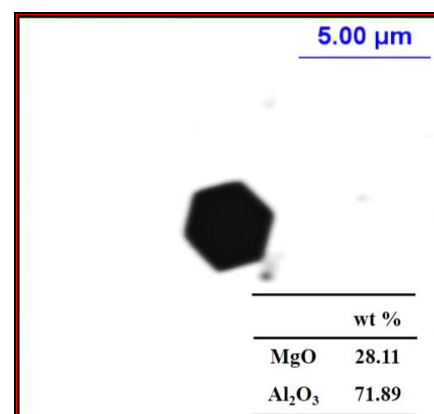


**Figure 14.** Morphology and composition of spinel inclusions in billet.

### 3.7. Formation Mechanism of Spinel Inclusions

Through a systematic study of spinel inclusions in U75V heavy rail steel, it was found that spinel inclusions in heavy rail steel are mainly divided into two categories: spinel alone and spinel inclusions wrapped in calcium aluminate. The results show that the spinel inclusion precipitates in the solidification and cooling process of the liquid steel, and that the precipitation temperature is related to the composition of the liquid steel. This kind of inclusion has little effect on the performance of the heavy rail steel. However, a spinel inclusion of a large size in heavy rail steel may come from the spinel inclusion falling off of the inner wall of the immersed nozzle; its formation mechanism is shown in Figure 15. The initial composition of the inclusion in the ladle before pouring was  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ . During the pouring process, as the temperature decreased, some inclusions were enriched at the nozzle and resulted in nodulation. The temperature near the molten steel side was high, and the solid spinel phase precipitated preferentially. Under the action of molten steel flow, some spinel inclusions with a high melting point accumulate and finally lead to the formation of a spinel layer on the side of the molten steel.

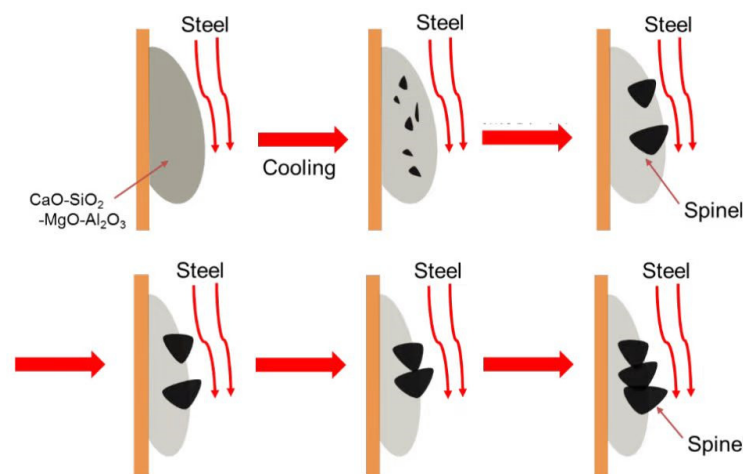


**Figure 15.** Schematic diagram of spinel inclusion formation in the inner wall of the outlet.

Spinel inclusions wrapped with calcium aluminate in heavy rail steel are derived from the precipitation transition of the inclusions themselves. During the process of continuous casting, the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  composite oxide inclusion in steel underwent a phase transformation and began to precipitate the  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  phase, while the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  phase was wrapped on the surface of the spinel phase. If secondary oxidation and corrosion resistance occur during the smelting process, the contents of the  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the inclusions increase, which will accelerate the precipitation of spinel inclusions in the inclusions at steelmaking temperatures. A schematic diagram of spinel inclusion precipitation during the smelting process is shown in Figure 16.

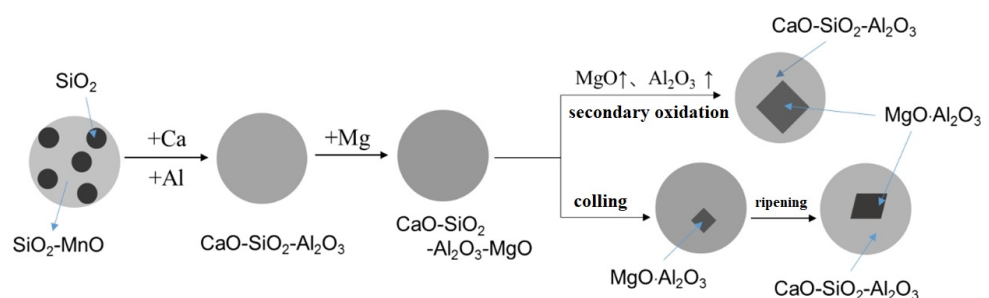


**Figure 16.** Schematic diagram of spinel inclusion formation in heavy rail steel.

#### 4. Conclusions

- (1) Through an immersed nozzle analysis of the U75V heavy rail steel pouring process, spinel inclusions were found in the nozzle nodules, which also existed in the cast billet. The main components were of two types: spinel inclusions existing alone and spinel inclusions wrapped in Ca aluminate.
- (2)  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$  composite inclusions in steel precipitate themselves during cooling. The precipitation temperature is related to the content of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the inclusions. Secondary oxidation and corrosion resistance will accelerate the precipitation of spinel inclusions. The small spinel inclusions in U75V heavy rail steel are precipitated during the solidification and cooling of liquid steel, which is related to the composition of liquid steel, while the large spinel inclusions in steel may come from the shedding of the nodule at the nozzle.
- (3) To improve the cleanliness of U75V heavy rail steel and to reduce the content of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in inclusions, the content of Mg, Al and other impurity elements in the alloy excipients must be strictly controlled to prevent the secondary oxidation of liquid steel and to reduce the corrosion resistance.

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