

Article

Distribution of Arsenic Inclusions in Rare Earth Steel Ingots

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Abstract: Trace element arsenic is detrimental to the quality and properties of steel products. We used lanthanum to modify the distribution of arsenic by the formation of arsenic rare earth inclusions and investigated all inclusions on the full profile of the ingots prepared in the laboratory. The results show that the addition of lanthanum has dramatically influenced the distribution of arsenic in the ingots by the formation of arsenic inclusions. The arsenic inclusions turn out to be mainly the cluster-shaped La-S-As, as well as its composite inclusions combined with LaS and La-As. La-S-As can be considered a solid solution of LaS and LaAs. They distribute mainly at the top surface of the ingots within 3 mm, at the side and bottom surfaces within 1.5 mm, leading to a dramatic decrease of arsenic concentration at the inner part of the ingots. This distribution characteristic of La-S-As can be used to manufacture steel ingots with very low arsenic concentration by peeling off these (La-S-As)-containing layers. On the contrary, the distribution of composite inclusions (La-S-As)-(La-As) and single-phase La-As, is uniform. Except for the reaction with arsenic, lanthanum can also react with phosphorous and antimony to modify the existing state of these trace elements.

Keywords: rare earth; inclusion; distribution; trace element; arsenic

1. Introduction

Trace elements, such as arsenic, antimony, and copper, are detrimental to the quality and mechanical properties of steel products [1,2]. These elements are very hard to remove during the mainstream steelmaking process. Arsenic is easy to segregate to phase and grain boundaries in the solidification, heat treatment, oxidation, and cooling process [3–6]. These arsenic-rich grain boundaries are potential crack sources under high temperatures because of the low melting point of arsenic, and the segregation of arsenic significantly reduces the binding force of grain boundaries. However, to reduce the production costs, low-price arsenic ores have been used in some iron and steel companies in China. The reuse of steel scrap also increases the concentration of arsenic in steel. To make these trace elements less harmful has been a matter of concern.

Many methods have been tried to remove arsenic from iron and steel. Reduction roasting can be used to remove arsenic from iron concentrate, as well as the microwave heating and roasting, especially when the additions of reductants are high [7–9]. It is theoretically feasible to use slags to remove arsenic from molten steel. Attempts have been made to remove arsenic from molten steel using CaO-CaF₂, Ca-Si alloy plus CaF₂, and CaC₂-CaF₂ slags, and in the best case, the arsenic can be reduced to about 0.019% [10–12]. However, these methods have disadvantages such as high iron loss and fluoride pollution. Adding various metals and alloys to molten steel (iron) to remove arsenic

has also been investigated, such as silicon, barium, aluminum, calcium, zirconium, boron, rare earth elements (REs), and their alloys [13,14]. Among them, rare earths and calcium have proved to be relatively effective, but the required addition amount is high (for example, the initial addition of cerium is 2.5%) [14]. According to the difference in the saturated vapor pressures between iron and arsenic at high temperatures, vacuum treatment can achieve partial dearsenication, although the iron loss is large [15]. Currently, there is no feasible way to remove arsenic from steel in industrial production. Therefore, changing the existing state of arsenic is another possible way to reduce or avoid its hazard to steel products.

Rare earth elements have been widely used in the steelmaking process to improve the quality of steel or slag [16–18]. Purifying molten steel, modifying inclusions, and micro-alloying are generally considered the essential function of REs for their applications in steel [19–23]. Due to the unique electronic shell structures, REs can react with trace element arsenic to modify its existing state in steel, so as to decrease its hazard to steel products [24]. It is noted that REs will not react with arsenic until oxygen and sulfur are consumed to a specific low concentration because they have strong affinities with oxygen and sulfur. REs, therefore, were used mainly in steels with low content of oxygen and sulfur. However, according to the heterogeneous nucleation theory, the oxides, sulfides, and oxysulfides of REs may have a significant effect on the formation and distribution of the arsenic inclusions. It is reported that $\text{La}_2\text{O}_2\text{S}$ can be used as the heterogeneous nucleation sites of LaAsO_4 [25]. Besides, the ratio of the initial concentration of oxygen to sulfur also plays a vital role in the formation of arsenic inclusions. A high oxygen concentration results in the formation of RE oxides; a high sulfur concentration results in the formation of oxysulfides or sulfides instead [26,27]. These RE inclusions have a different influence on the formation and distribution of the arsenic ones.

To figure out the effect of adding REs on the existing state of arsenic in steel, the RE-O-S-As inclusion system is one of the key issues that need to clarify. RE_2O_3 , $\text{RE}_2\text{O}_2\text{S}$, and RES are possible oxides, sulfides, and oxysulfides, respectively. For the arsenic ones, CeAs and LaAsO_4 were identified [3,25,28]. The remaining ones, however, have not been identified yet. Further, the evolution of RE-O-S-As with different conditions is usually very complicated, determined by the initial concentrations and ratios of oxygen and sulfur, macro- and micro-segregation, as well as the nucleation process [29]. The purpose of this work is mainly to clarify the formation process of arsenic RE inclusions and their distribution in steel ingots, to guide to reduce the harm of arsenic.

2. Materials and Methods

We used industrial billets of high carbon steel as the raw material, manufactured by an iron and steel company from Chongqing, China. In order to make the chemical compositions uniform, the billets with a cross-section size of 150 mm × 150 mm were forged to rods with a diameter of 65 mm before sample preparation. The chemical compositions of the rods are shown in Table 1. The sample preparation was carried out in an induction furnace with argon protection. We gradually increased the output voltage to control the heating process of the induction furnace and used a thermocouple to measure the temperature at the crucible bottom. The time required to reach 1600 °C from room temperature was about 50 min. After vacuuming to a pressure lower than 100 Pa, argon gas was used to fill the furnace tube. Two times of the above process were carried out before heating. About 500 g steel rod without rust was used for each sample. After it melted totally and being held under 1600 °C for 10 min, arsenic with a purity of 99.9% was added. After another 10 min, lanthanum metal was added. The furnace power was turned off after another 20 min, and the alloy was furnace cooled to room temperature. Ingots with a size around Φ 45 mm × 45 mm were obtained.

Table 1. Chemical compositions of the raw material (mass%).

Elements	C	Si	Mn	P	S	Al	O	As
Concentrations	0.79	0.21	0.61	0.011	0.015	0.001	0.0024	0.010

The initial concentrations of arsenic were set to 0.010%, 0.030%, 0.050%, and 0.078%. Lanthanum with the addition of 0.15% was set when prepared La-containing samples. Because of its strong reactivity, lanthanum needs to consume most of the oxygen and sulfur before it reacts with arsenic in steel. According to the ideal stoichiometric ratio, the amount of lanthanum consumed by oxygen and sulfur as the form of La_2O_3 and LaS is 0.086% in total in this work. Considering its yield, we chose 0.15% as the initial added amount of lanthanum. Since the average As content in steel is around 0.030% when using As-containing iron ores for the iron and steel company mentioned above, a blank La-free sample with 0.030% As was also prepared under the same experimental conditions. Figure 1 shows the process of sample preparation.

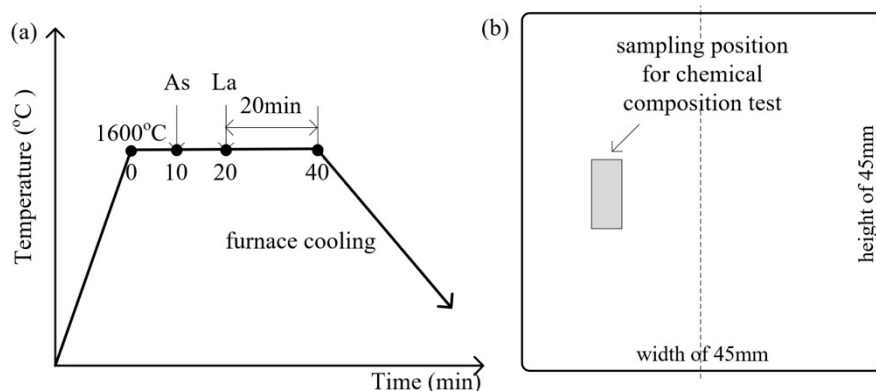


Figure 1. The process of sample preparation: (a) the steelmaking process; (b) the sampling position on the profile of the ingots.

Samples used to measure chemical compositions of the alloys were taken at the 1/2 height and 1/2 radius of the steel ingots, shown in Figure 1b. The concentrations of oxygen and nitrogen were measured with an oxygen-nitrogen analyzer. The concentrations of lanthanum, arsenic, and acid-soluble aluminum were measured with an inductively coupled plasma optical emission spectrometer (Optima 8000, Waltham, MA, USA). Carbon and sulfur were examined with a carbon-sulfur spectrometer (HCS-801S, Deyang, Sichuan, China). The total concentration of aluminum was detected with a direct reading spectrometer (Foundry-master Xpert, Oxford, UK). The phosphorus concentration was measured by the colorimetric method.

Inclusions were observed by an optical microscope (Sunny XD30M, Ningbo, Zhejiang, China) and a scanning electron microscope (SEM, JEOL 7800F, Tokyo, Japan). Besides, their chemical compositions were identified with an energy dispersive spectrometer (EDS, 80 mm² X-Max^N Silicon Drift Detector, Oxford, UK). We also identified the phase of La-S-As inclusions by electron backscattered diffraction (EBSD, NordlysMax², Oxford, UK). After confirming the sample contains La-S-As inclusions, it was polished with an argon ion polishing machine (Gatan 697 Ilion II, Pleasanton, CA, USA). The voltage was set to 6.5 keV for 30 min, then to 2.0 keV for 30 min, finally to 1.0 keV for 10 min, and the total polishing time was 70 min.

3. Results and Discussion

3.1. Types and Distribution of Inclusions

Based on the observation results with OM and SEM, types of inclusions in all La-containing samples are similar, and five primary types were discovered, which are La_2O_3 , $\text{La}_2\text{O}_2\text{S}$, LaS , La-S-As and La-As . Composite inclusions, consisting of these primary inclusions, were also found, such as LaS-(La-S-As) and (La-S-As)-(La-As) . The inclusions in the sample with an initial arsenic concentration of 0.030% were chosen to illustrate their morphologies and compositions.

Figure 2 shows the morphologies and distribution of La_2O_3 and $\text{La}_2\text{O}_2\text{S}$ inclusions. It can be seen that La_2O_3 inclusions distribute on the top surface of the ingot, and some $\text{La}_2\text{O}_2\text{S}$ inclusions distribute

at the sub-top surface except for the ones on top. It means that La_2O_3 forms ahead of $\text{La}_2\text{O}_2\text{S}$ and the former forms mainly in molten steel [5]. Both of them float up to the surface of molten steel in the steelmaking process. The thickness of this $\text{La}_2\text{O}_2\text{S}$ -containing layer turns out to be less than 100 μm .

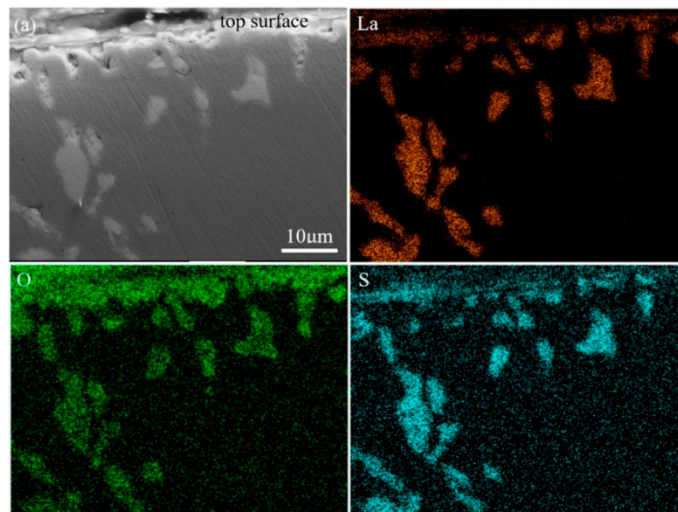


Figure 2. Morphologies and distribution of La_2O_3 and $\text{La}_2\text{O}_2\text{S}$ inclusions. (a) Morphologies of the top surface of the ingot.

Plenty of cluster-shaped La-S-As inclusions were found at the top surface of the ingots within 3 mm, together with a few LaS with a size of bigger than 10 μm , as shown in Figure 3. It can be inferred that LaS forms ahead of La-S-As, and the former can act as heterogeneous nucleation sites for the formation of the latter, illustrated in Figure 3b. The oxygen concentration is very low in these inclusions, resulting from the strong deoxidization effect of lanthanum, listed in Figure 3c. Besides, similar (La-S-As)-containing layers were also found at the side and bottom surfaces near crucibles within 1.5 mm.

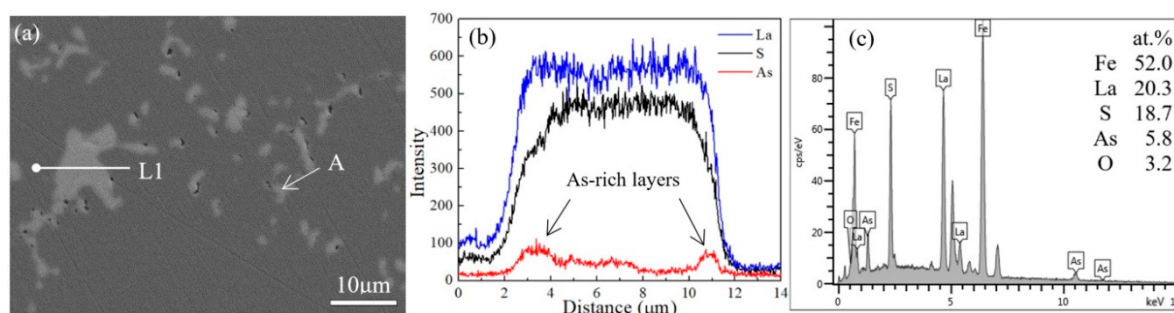


Figure 3. Morphologies and chemical compositions of LaS and La-S-As inclusions at the top surface. (a) Morphologies of inclusions; (b) line scanning of position L1; (c) energy dispersive spectrometer (EDS) of position A.

Inside the ingot, a few (La-S-As)-(La-As) inclusions were discovered, as shown in Figure 4. They distribute uniformly, and the inner La-S-As cores are now tiny, and the main part proves to be La-As. Sometimes only La-As part was discovered and they are considered as La-As binary compounds, as shown in Figure 5. A few fine BN precipitates form around these inclusions, as illustrated in Figure 4d. Except for La-As, a few La-P and La-Sb form together because of the similar shell electron structures of P, As, and Sb (Figure 5c).

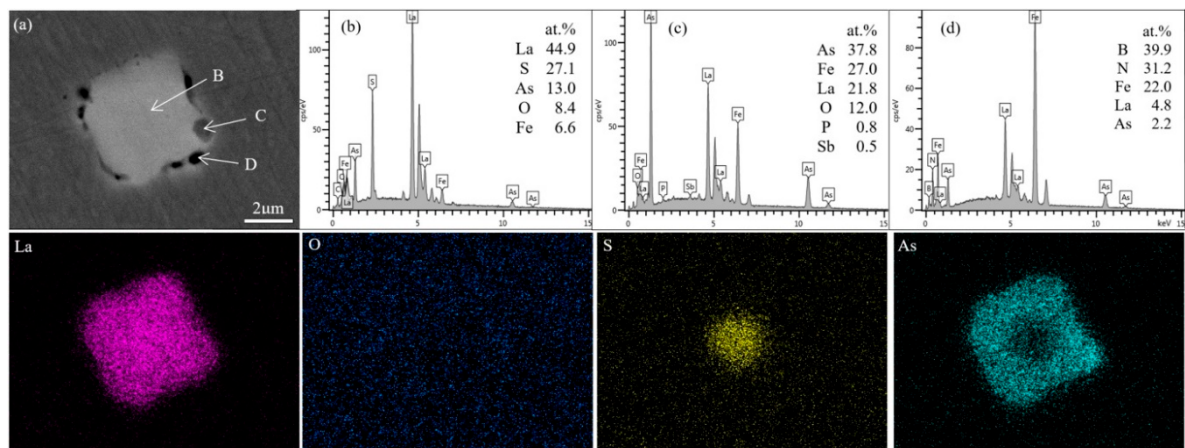


Figure 4. Morphologies and chemical compositions of (La-S-As)-(La-As) inclusions. (a) Morphologies of inclusions; (b) EDS of position B; (c) EDS of position C; (d) EDS of position D.

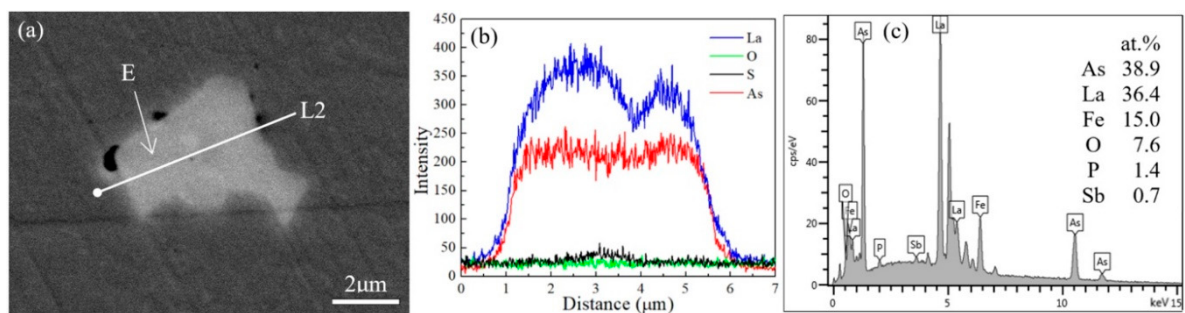


Figure 5. Morphologies and chemical compositions of La-As inclusions. (a) Morphologies of inclusions; (b) line scanning of position L2; (c) EDS of position E.

For the most important inclusions La-S-As that can remove arsenic from steel in this work, we identified their crystal structure by EBSD combined with EDS and mapping, and the details are shown in Figure 6. It shows that these inclusions are a homogeneous phase consisting of La, S, and As, based on mapping results. They proved to be cubic by EBSD patterns (Figure 6f). According to the crystal structure data in the online database of SpringerMaterials, LaS and LaAs are cubic (space group 225), whereas LaAsS and AsS are monoclinic (space group 14) [30]. Based on EDS results, which are only semi-quantitative though, the percentage of La equals to the sum of S and As. Therefore, La-S-As inclusions are possibly a solid solution of LaS and LaAs, just like Nb(C,N) as a solid solution of NbC and NbN in micro-alloyed steels. They have different orientations in the steel matrix and distribute mostly at grain boundaries (Figure 6b–e). Further, we have been trying using a transmission electron microscope to identify these arsenic inclusions and the results will be published in the future.

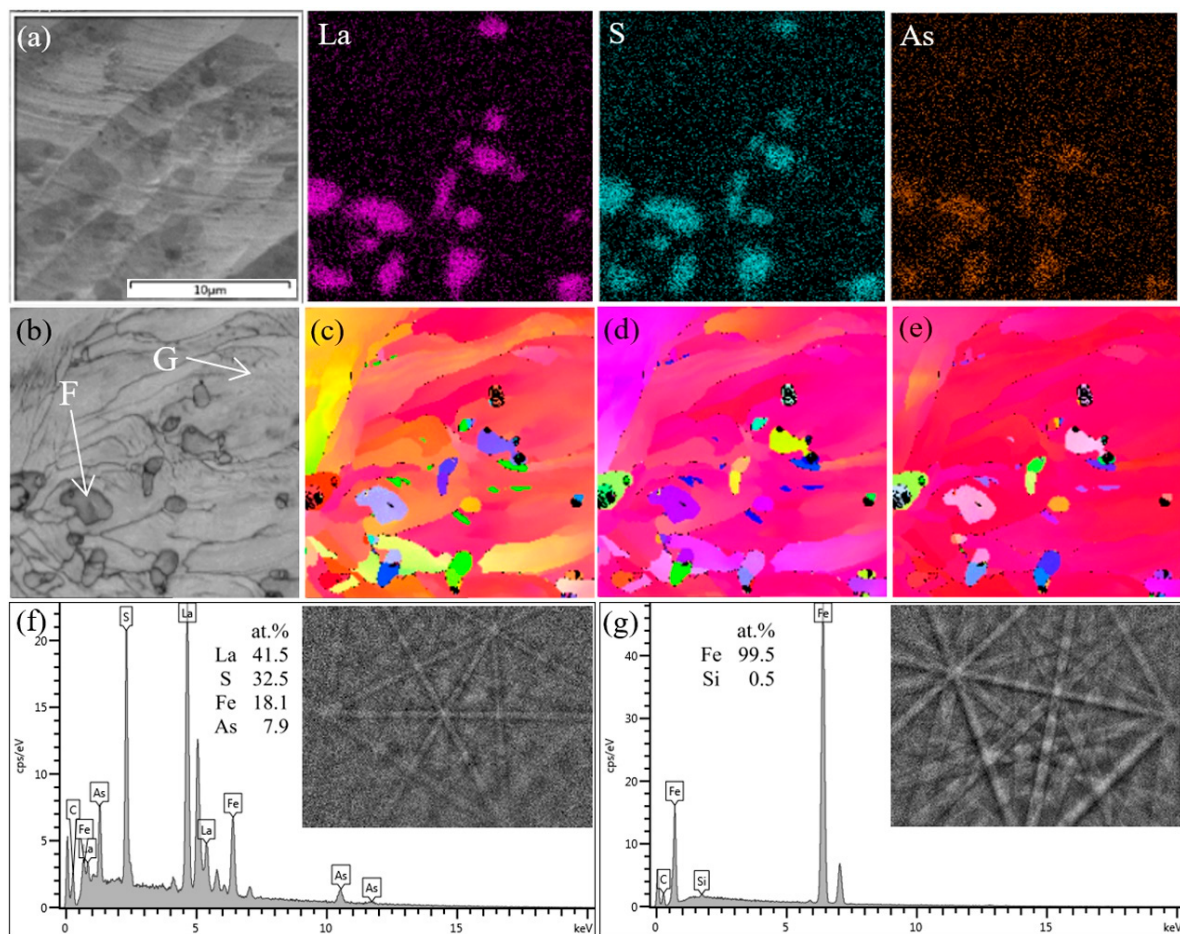


Figure 6. Morphologies, chemical compositions, and phase identification of La-S-As inclusions. (a) Morphologies of the argon ion polished sample; (b) contrast chart; (c) to (e) orientation in X, Y, Z directions; (f) EDS and EBSD patterns of L-S-As inclusions (point F); (g) EDS and EBSD patterns of the steel matrix (point G).

The distribution of inclusions on the full profile of the ingots is illustrated in Figure 7. It shows that the inclusions distribute extremely nonuniform. Only (La-S-As)-(La-As) and La-As inclusions exist inside the ingots; the other types of inclusions distribute on and near the surfaces. To figure out the effect of lanthanum addition on the formation and distribution of arsenic inclusions, we combined the chemical compositions of the ingots and the distribution of inclusions to clarify this issue.

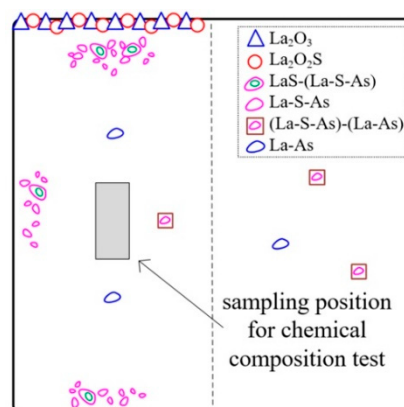


Figure 7. Distribution of inclusions at the profile of the ingot.

3.2. Chemical Composition Changes with La Addition

We added 0.15% La to molten steel during the preparation for each heat of La-containing steel. The addition of La has dramatically influenced the final concentrations of As, S, O and Al, as shown in Figure 8. A significant decrease in arsenic content was caused by the addition of La (Figure 8a). Two factors are accounting for this. On the one hand, a large part of arsenic exists as La-S-As and distributes at the top, side and bottom surfaces. The floating up caused by the difference in densities between the inclusions and molten steel is the key reason that the inclusions distribute at the top surface of the ingot. The densities of possible inclusions LaS and LaAs are 5.66 and 6.08 g/cm³, respectively, which are lower than that of molten steel [30]. Besides, the flow of molten steel also drove the inclusions to move until they were captured by crucibles and the solidified shell at the side and bottom. Therefore, the most amount of these cluster-shaped La-S-As inclusions distributed at the top surface. This dramatically decreases the residual arsenic inside the ingots. On the other hand, the evaporation effect results in the removal of a small part of arsenic, which is around 13% for the sample with 0.030% As. It indicates that about 50% arsenic in total moves away from the inner part of molten steel. Further, this decrease percentage reaches 86% for the sample with 0.010% As.

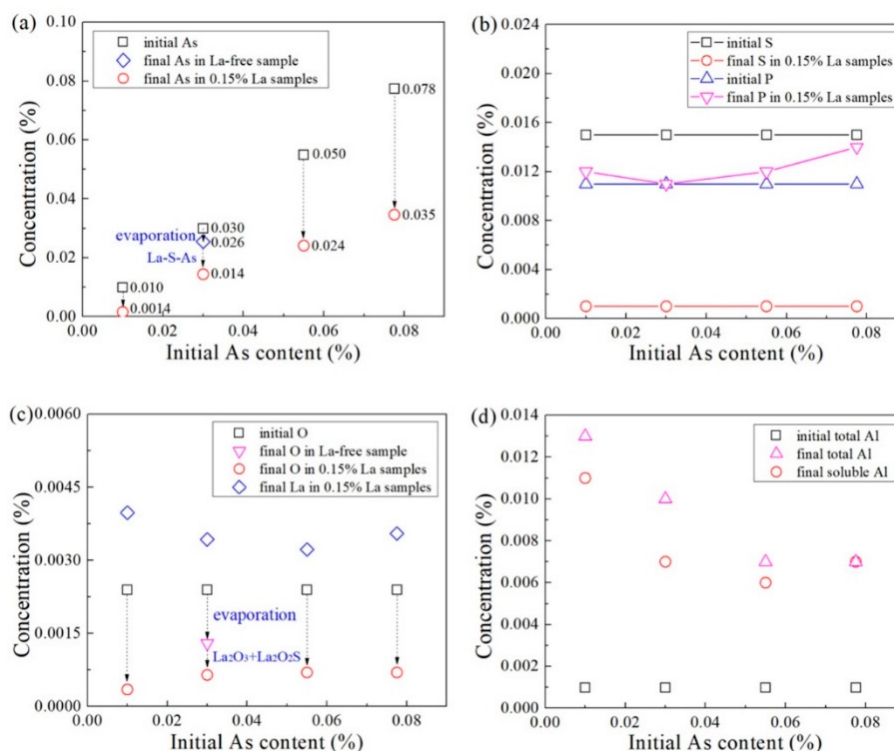


Figure 8. Chemical composition changes of alloys with La addition. (a) Arsenic concentrations; (b) concentrations of sulfur and phosphorus; (c) concentrations of oxygen and lanthanum; (d) concentrations of total and acid-soluble aluminum.

Figure 8b shows that the addition of 0.15% La makes the final sulfur concentration decrease from 0.015% to less than 0.001%. This is caused by the formation of La₂O₂S, LaS, and La-S-As inclusions. However, since the inclusions at the surfaces contain little phosphorous, phosphorous concentrations inside the ingots stay much stable, with only a little fluctuation owing to the solute segregation [29].

Except for sulfur, La addition also dramatically decreases the concentration of oxygen, as shown in Figure 8c. Two factors mainly determine the change in oxygen concentration. First, argon gas protection reduces the partial pressure of CO and enhances the reaction between carbon and oxygen in molten steel, leading to a decrease in oxygen concentration. Second, the formation of La₂O₃ and La₂O₂S, floating up to the top surface of molten steel, takes oxygen away from the inner part of molten

steel. Besides, lanthanum may react with the alumina crucibles during the steelmaking process to form more La_2O_3 or $\text{La}_2\text{O}_2\text{S}$, which is similar to the conditions when melting Ce-containing steels in alumina crucibles [31,32]. However, this process does not have a dramatic influence on the oxygen inside the ingots because of the floating up of these inclusions. The increased concentrations of aluminum and very low concentrations of residual lanthanum in the samples prove that lanthanum did react with alumina crucibles in this work, as shown in Figure 8d.

3.3. Formation Process and Distribution Mechanism of Inclusions

The distribution of inclusions is determined mainly by the formation temperature, flow behavior of molten steel, and segregation of solutes. The following three steps can thoroughly explain the formation and distribution of the inclusions.

- (i) During the steelmaking process, La_2O_3 and $\text{La}_2\text{O}_2\text{S}$ formed and floated up to the top surface of molten steel in the temperature range from 1600 °C to the liquidus, illustrated in Figure 9a. The formation of these inclusions took away most of the oxygen, including the part offered by alumina crucibles, as well as a part of the sulfur.
- (ii) As the consumption of soluble oxygen, lanthanum started to react mainly with sulfur and arsenic, and then LaS and La-S-As inclusions formed. As the temperature decreases, the first solidified part of the molten steel will be the surface, because the surface has the worst thermal insulation conditions. On the one hand, these inclusions floated up to the surface of molten steel and are easy to be captured. On the other hand, the unsolidified molten steel still flows, driven by the temperature gradient, as shown in Figure 9b. The overall solidification structures of the profile of the ingots can well explain this. As shown in Figure 9c, a hole exists at the center of the ingots, and some porous zones with strong columnar crystals exist below that can be seen even directly with the naked eyes. It is inferred that these porous zones are the last solidified part and have the highest temperature all the time. A temperature gradient, therefore, exists all the time also. In summary, the flow of molten steel, together with the buoyancy caused by the different densities between inclusions and molten steel, drives the inclusions to move. This leads to the enrichment of LaS and La-S-As inclusions at the surfaces of the ingots, especially near the top surface. It makes the inner part of the ingots almost free of LaS and La-S-As that dramatically decreases the concentrations of arsenic and sulfur.
- (iii) As the temperature went down, a few (La-S-As)-(La-As) and La-As inclusions formed during and after solidification, shown in Figure 9c. It is believed that the formation temperature of CeAs is at the end of solidification [3,29]. Therefore, the fact that La-As starts to form at the end of solidification is reasonable according to the similar chemical properties of La to Ce. However, these arsenic inclusions do not move away from the inner part of the ingots and do not affect the final arsenic concentration.

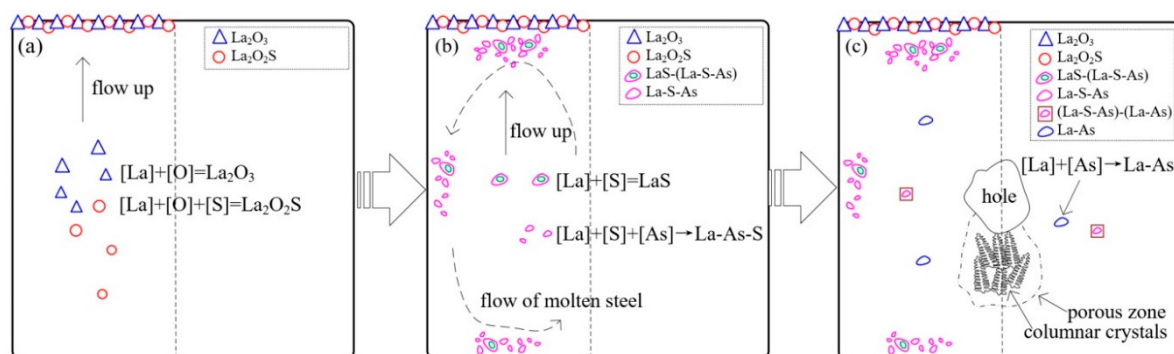


Figure 9. Distribution and formation process of inclusions. (a) Early period after adding lanthanum; (b) second stage after adding lanthanum; (c) during and after solidification.

It is worthy of considerable attention that the La-S-As inclusions form in molten steel and distributes at the top surface within 3 mm and at the side and bottom surfaces within 1.5 mm. We can control the arsenic concentration by peeling off the surface layers of ingots. This control strategy of arsenic can be beneficial in the casting process, especially in the die casting process. Further, we can use electromagnetic stirring to optimize the flow field of molten steel, so that arsenic-rich inclusions can be selectively distributed on the top surface of the billets to reduce the amount needs to be removed. We can also control the chemical compositions to make arsenic-rich RE inclusions form mostly in the molten steel so that they can be mostly removed by floating up.

A key factor that also needs to notice is that the concentration of sulfur needs to be suitable. No such (La-S-As)-enriched zone was mentioned if the initial sulfur concentration was less than 0.0047% [29]. Besides, it would be costly if the initial concentration of sulfur is too high because REs are mainly used to react with sulfur instead.

4. Conclusions

The distribution of arsenic rare earth inclusions in La-containing steel ingots were investigated. It turns out that the addition of lanthanum has a significant effect on the distribution of arsenic by the formation of arsenic inclusions. The arsenic inclusions are mainly La-S-As and La-As, as well as their composite inclusions LaS-(La-S-As) and (La-S-As)-(La-As). La-S-As can be considered as a solid solution of LaS and LaAs. They prefer to distribute mainly at the top surface of the ingot within 3 mm and at the side and bottom surfaces within 1.5 mm. We can use this distribution characteristic of La-S-As to manufacture steel ingots with low arsenic concentration by peeling off these La-S-As-containing layers. Except for reacting with arsenic, lanthanum can also react with phosphorous and antimony, to modify the existing state of these trace elements.

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Conflicts of Interest: The authors declare no conflict of interest.

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