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Study on the Control of Rare Earth Metals and Their Behaviors in the Industrial Practical Production of Q420q Structural Bridge Steel Plate

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Abstract: Rare earth (RE) addition can refine and change the shape/distribution of inclusions in steel to improve its strength and toughness. In this paper, the control of RE, specifically Ce and La, and their behaviors in the practical industrial production of high-strength structural steel with 420 MPa yield strength were studied. In particular, the interactions between RE and Al, Nb, S, O were investigated, with the aim of improving the steel toughness and welding performance. The impact energy of the plate with RE is approximately 50 J higher than the regular plate without RE. The toughness of the plate from ladle furnace (LF) refining with RE addition is better than the one from Ruhrstahl and Hereaeus (RH) refining. The RE inclusions could induce the intragranular ferrite and refine the grain size to the preferred size. After welding at the heat input of 200 kJ/cm, the grain size at the heat affected zone was found to be the finest in the plate from the LF process with RE addition. Notably, the microstructure of ferrite was quasi-polygonal.

Keywords: structural steel plate; nonmetallic inclusions; rare earth control

1. Introduction

Structural steels are applied in various infrastructure, such as bridges, shipbuilding, and construction. Nowadays, the performance requirements of structural steel are getting higher and higher under various loading conditions such as earthquake, fire, wind, etc. [1–3]. Among the various performance properties, the most important requirements are low temperature impact toughness and welding. There are many laboratory studies on the effects of rare earth (RE) metals addition to the toughness of steels [4–8]. RE can refine and change the shape/distribution of inclusions in steel to improve strength and toughness. The addition of lanthanide metals to continuously cast steel is particularly advantageous because of their ability to refine as-cast structures, reduce segregation, and increase hot ductility at temperatures just below solidification [9]. People studied the optimum mass ratio of La and Ce in La + Ce combined treatment, and the best incubation time of Le + Ce (3:1) treatment [10]. There were some works on the efficiency of Ti-bearing inclusions in refining the grain size, and dealing with Al and Mn contents in weld metal inclusions [11,12]. Moreover, some research has focused on the effect of RE in high-heat-input welding, and the induction of acicular ferrite behavior [13–15]. During World War II, it was found that the addition of RE metals to steel could significantly improve its properties. Since then, RE metals have been widely applied in steel manufacturing. The RE nitride and the austenite grain size could be controlled to around 10 nm,

when the amount of RE metals is more than 50 ppm [12,16–19]. RE can spheroidize inclusions that mainly rely on the combination of sulfur, reducing MnS formation, which results in RE sulfides and oxysulfide [13]. This leads to more applications in the special steel field [20]. It is shown that Ce is effective in the range 0.04–0.2 mass pct, but there is a rare report on the interactions between RE and other elements in the inclusions when S is less than 0.003 mass pct and RE is less than 0.005 mass pct, aiming to improve the toughness of steel. Due to the low amount of RE that is added, the production cost remains low. In this paper, we studied the control of RE, specifically Ce and La, and their behaviors in the practical industrial production of high-strength structural steel with 420 MPa yield strength, especially the interactions between RE and Al, Nb, S, O in the steel plate, with the aim of improving the steel toughness. Tests and analysis in the steelmaking process were tracked by some manufacturers in the production of structural steel of 420 MPa.

2. Experimental

The steelmaking process of high-strength structural steel with 420 MPa yield strength is shown in Figure 1. Through the RE treatment combined with heat treatment and controlled rolling, it was possible to control the cooling stability, which could limit the yield ratio to less than 0.85. Moreover, the toughness and welding performance of the final product could be enhanced.

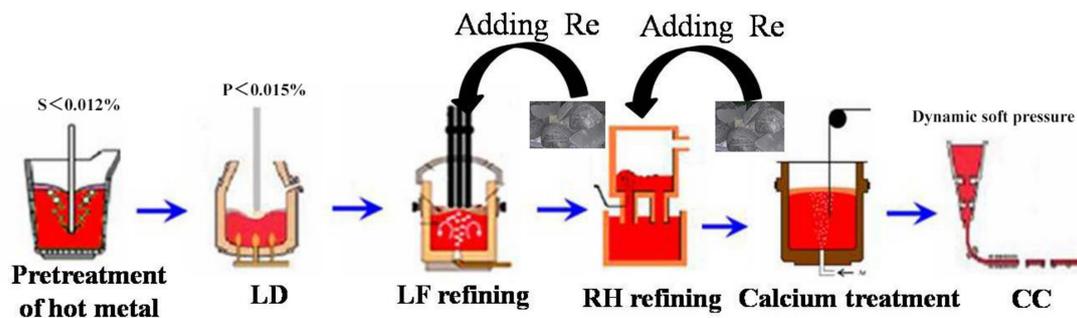


Figure 1. Steelmaking process of structural steel of 420 MPa plate.

The RE content in the alloy used in the present research was >95 mass pct, with a ratio of Ce and La in 2 for structural steel of 420 MPa plate production. The 2:1 ratio of Ce and La is nearly the same as their original ratio in nature. Their use avoids the complicated process of RE purification, which saves the overall cost of the whole process. The RE alloy was purified by refining treatment, and it was added by vacuum packaging. The chemical composition of structural steel of 420 MPa plate was shown in Table 1. The steelmaking process for Q420q steel involved pretreatment of hot metal, top blown oxygen converter (LD), ladle furnace (LF) refining, Ruhrstahl and Hereaeus (RH) refining, calcium treatment, and continuous casting (CC). In this steelmaking process, deoxidation was realized by aluminum after the LD process. The deep desulfurization and adjustment of alloying composition were performed in LF refining. The main function of RH refining was degassing and removal of inclusions. Hence, the protection of the casting was enhanced to prevent the secondary oxidation. Moreover, the process of calcium treatment was also used to control the morphology of inclusions. In addition, the sampling of liquid steel used a special “sampler”, which is a high-temperature-prove alloy steel sampler with a cork binding on it. This sampler could prevent the contamination of liquid steel and slag.

Table 1. The chemical composition of the high-strength structural steel with 420 MPa yield strength, mass pct.

The Position for RE Alloy Added	C	Si	Mn	P	S	(Nb + Ti + etc.)	La	Ce
LF refining	0.144	0.28	1.46	0.014	0.0019	<1	<0.0010	<0.0020
RH refining	0.148	0.27	1.5	0.014	0.0016	<1	<0.0030	<0.0060

The inclusion behaviors of the steel, such as particle size, composition, and species were investigated via an automated scanning electron microscope (ASPEX explorer, Hillsboro, OR, USA). We could find the inclusion by EDS scanning automatically, and calculate the inclusion's center. Then, the equipment would scan towards eight dimensions from the center to obtain the spinning line. The inclusion structure and size would be determined via this information. The samples were cut into 25 mm × 25 mm × 20 mm shapes by line cutting, followed by coarse and fine grinding, and polishing.

The composition and type of inclusions were shown with the use of CaO-MgO-Al₂O₃ and CaO-Al₂O₃-CaS ternary phase diagrams. The chemical composition of inclusions was determined by EDS (S3400N) analysis, from which they were converted into the content of oxide and sulfide. The impact toughness testing was performed with a pendulum impact hammer (SANS, JB-300B, Shenzhen, China), which could generate a standard strike energy of 300 J, using the Charpy V-notched impact test method for metals. The high heat input welding experiments were realized with an electric gas welding tester (255 A, 34 V). The steel plate sample is 20 mm in thickness. Flux cored wire was used in the test, and the welding angle was 17°.

3. Results and Discussion

The chemical composition of the high-strength structural steel with 420 MPa yield strength was shown in Table 1. Nb and Ti are present. However, it was known that they have small effect on the oxide metallurgy, especially with high aluminum. The main inclusion of our present study is calcium aluminate, which contains rare Ti. Moreover, the Nb addition improved the strength, and the addition of RE would also cause some transformation to Nb. This will also be discussed in detail in this paper.

Component distribution of inclusions in structural steel of 420 MPa plate with RE in some practical industrial production was shown in Figure 2. It could be found that the component distribution of inclusions, in most cases, was calcium aluminate. It is known that most of the calcium aluminate inclusions have a high melting point >1873 K (1600 °C) [21]. The inclusions with high melting point exist in the form of spinel or calcium aluminate wrapped with CaS. The size of most of the inclusions was between 1 and 20 μm, and the most significant inclusions in class B are calcium aluminate with a low melting point <1773 K (1500 °C), [22] which could reach maximum 180 μm in size. As to the inclusions from LF refining process with RE addition, they are Al₂O₃-CaS inclusions in Al₂O₃-CaS-CaO system. We could not find calcium aluminate with low melting point. The size of most of the inclusions size is between 1 and 10 μm. The same phenomenon was also observed from the RH refining process with RE addition. However, some calcium aluminate inclusions were found with a low melting point. The size of most of the inclusions is between 1 and 15 μm. The average sizes of inclusions in a plate are 2.75 μm (LF with RE) and 3.11 μm (RH with RE), which are less than 4.42 μm of the regular structural steel without RE. The addition of RE would decrease the size of the inclusions.

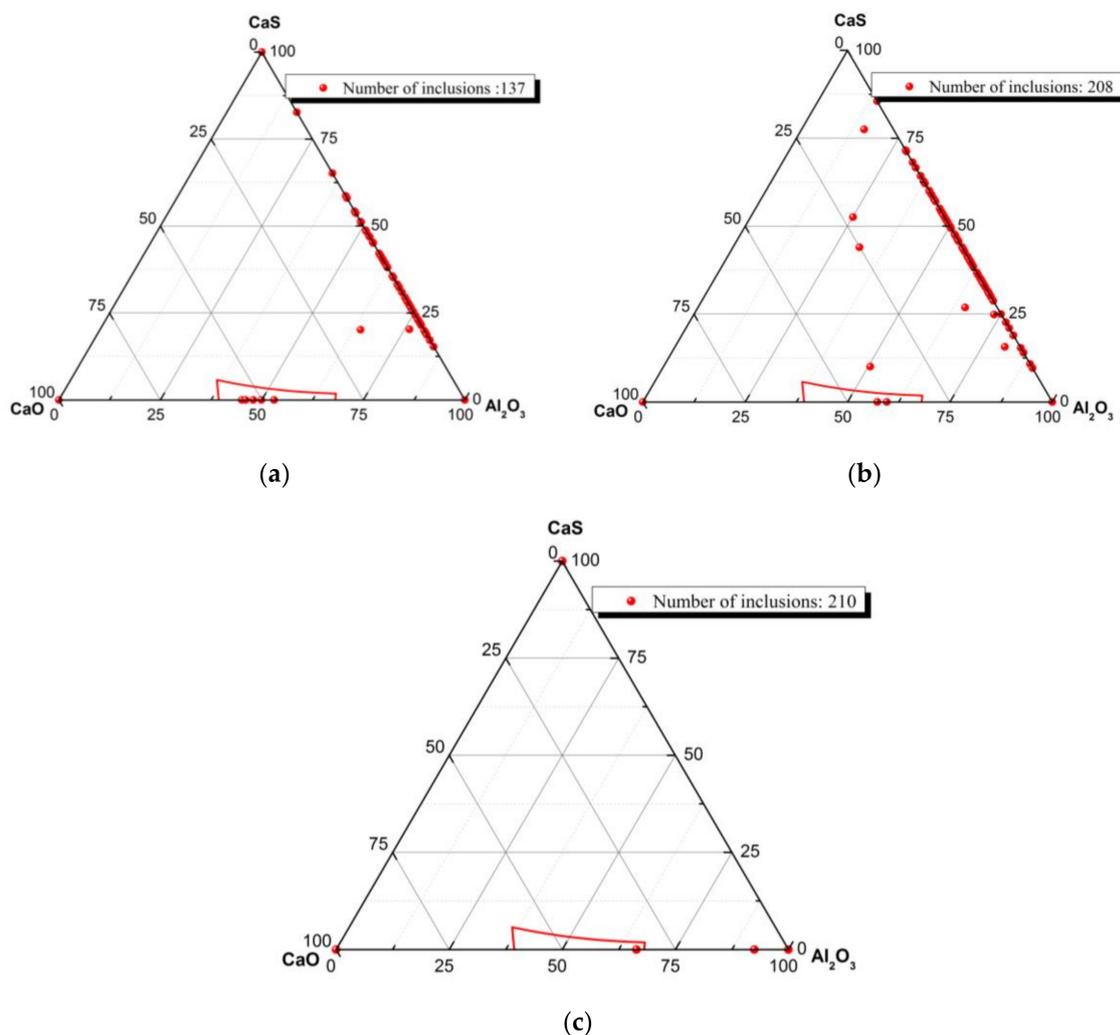


Figure 2. Component distribution of inclusions in structural steel. ((a) Inclusions of regular structural steel without rare earth (RE); (b) inclusions in structural steel from ladle furnace (LF) refining with RE addition; (c) inclusions in structural steel from Ruhrstahl and Hereaeus (RH) refining with RE addition).

3.1. Comparison of Inclusions Resulted from Ladle Furnace (LF) and Ruhrstahl and Hereaeus (RH) Processes

Figure 3 shows the size distribution of inclusions in structural steel of 420 MPa plate from different processes. It was resulted from the scan of the plate cross-section, from center to margin, with ASPEX explorer. It could be found that the inclusions that are $>10\ \mu\text{m}$ are concentrated in the center. They were calcium aluminate with high melting point ($\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$). These inclusions could become B type stringer inclusions (mainly calcium aluminate) after the hot rolling process, especially in bulky plate steels. The calcium aluminate with low melting point ($12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$) was easy to transform during hot rolling, and this would also become a B type stringer inclusion [23,24].

The large-scale B type non-metallic inclusions distributed along the rolling direction in the steel plate would severely damage the serving performance of steel. In the regular plate without RE, the size of most of the inclusions is between 1 and $5\ \mu\text{m}$ and they are distributed evenly. The number of inclusions of size in 5– $10\ \mu\text{m}$ is 45, slightly less than that of 87 in 1– $5\ \mu\text{m}$. The size distribution in 5– $10\ \mu\text{m}$ is more uniform. The number of inclusions $>10\ \mu\text{m}$ is 5, with a bad distribution, especially in the thickness direction. The number of inclusions in plate produced from LF refining with RE addition is 208. The inclusions are evenly distributed through thickness direction. There are only

48 RE inclusions, and the rest are calcium aluminate inclusions. The RE inclusions in a plate produced from RH refining with RE addition are clearly increased. All the inclusions are the mixture of RE and calcium aluminate.

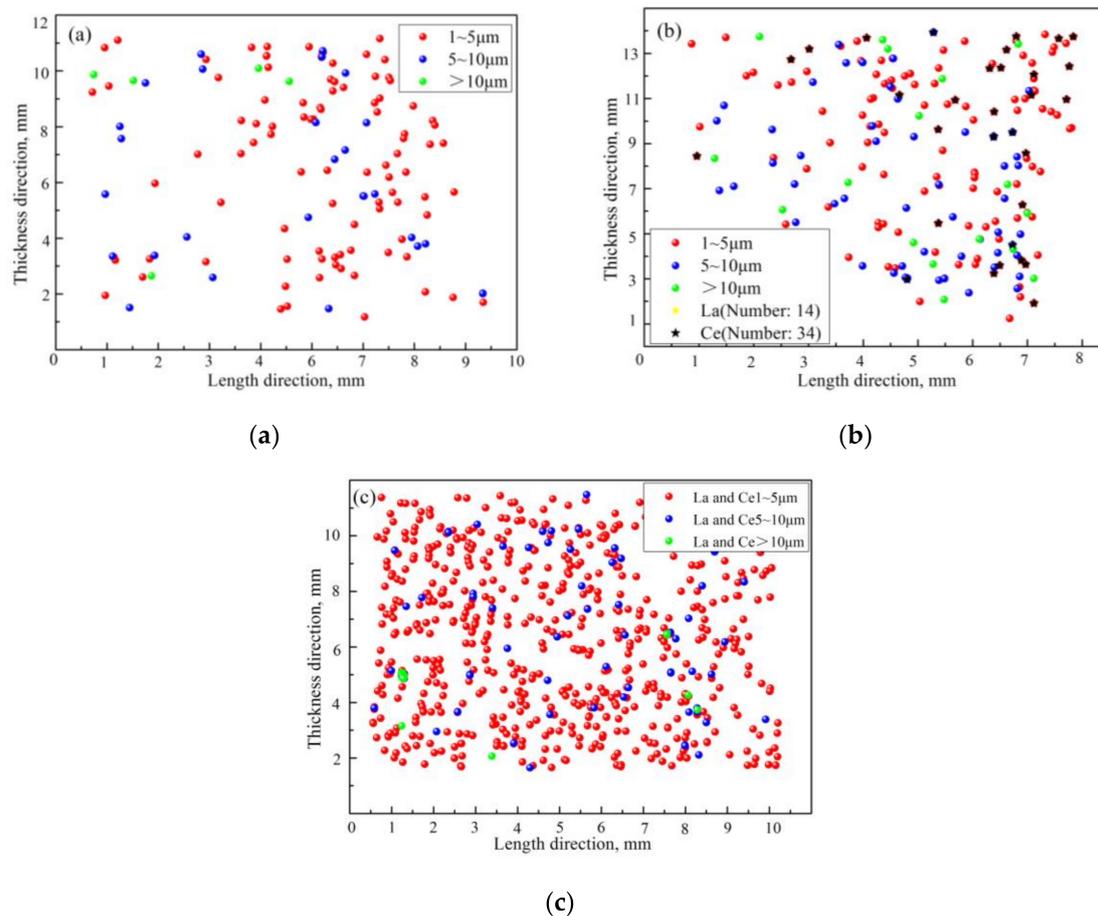


Figure 3. Size distribution of inclusions in structural steel. ((a) inclusions in regular structural steel without RE; (b) inclusions in structural steel from LF refining with RE addition; (c) inclusions in structural steel from RH refining with RE addition).

The quantity of RE inclusions from the LF refining process was less than that from RH refining. The main reason for this was that the RE content of steel is low in the LF refining process due to the removal of RE inclusions from the slag. We also found inclusions such as La and Ce, which occasionally appear alone or coexist together. The composition of the inclusions in structural steel from LF refining process with RE addition was shown in Table 2. It was also found that there are many Nb precipitates in the inclusions. When the inclusions contained Nb, there would be no existence of RE in the inclusions (Figure 4).

Table 2. The composition of the inclusions from LF refining process with RE addition, mass pct.

Element	Mg	Al	S	Ca	Nb	La	Ce
Average content	0.4	3.14	1.33	0.75	17.84	5.54	7.9

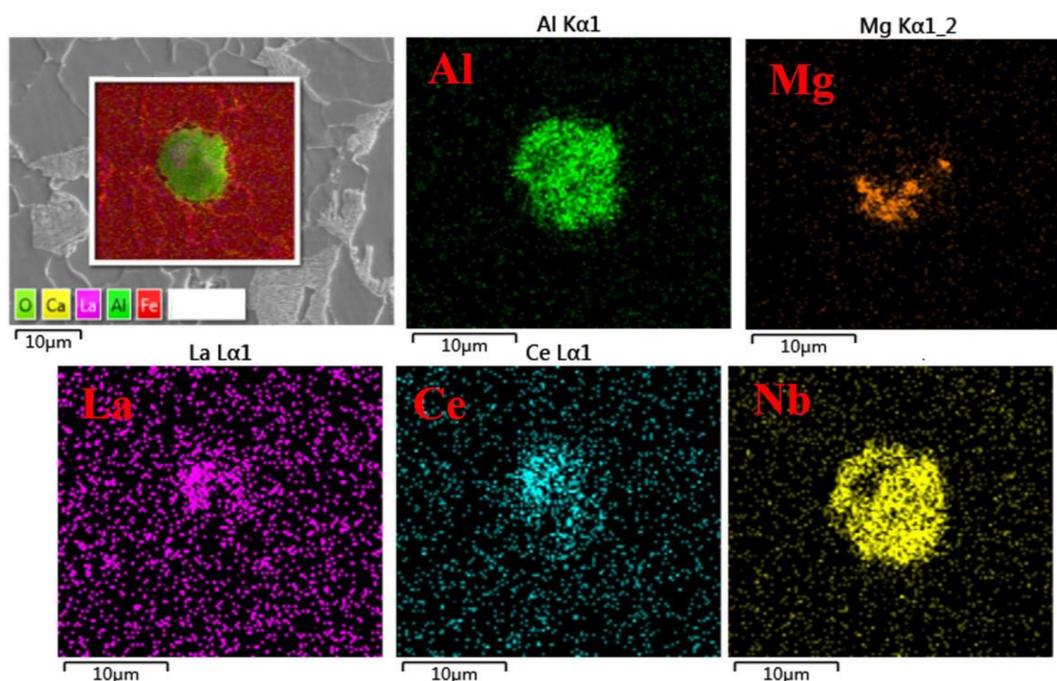


Figure 4. Surface scan of inclusion in structural steel from LF refining process with RE addition.

It could be seen that the quantity of RE inclusions from RH refining process is more than that from LF refining, due to the higher content of RE. The inclusions of RE all coexist together in the inclusions in the whole bulk of sample. The composition of the inclusions from RH process with RE addition is shown in Table 3. It was also found that there is no Nb precipitation in the inclusions, and the content of Al and Mg in the inclusions is also drastically reduced (Figure 5).

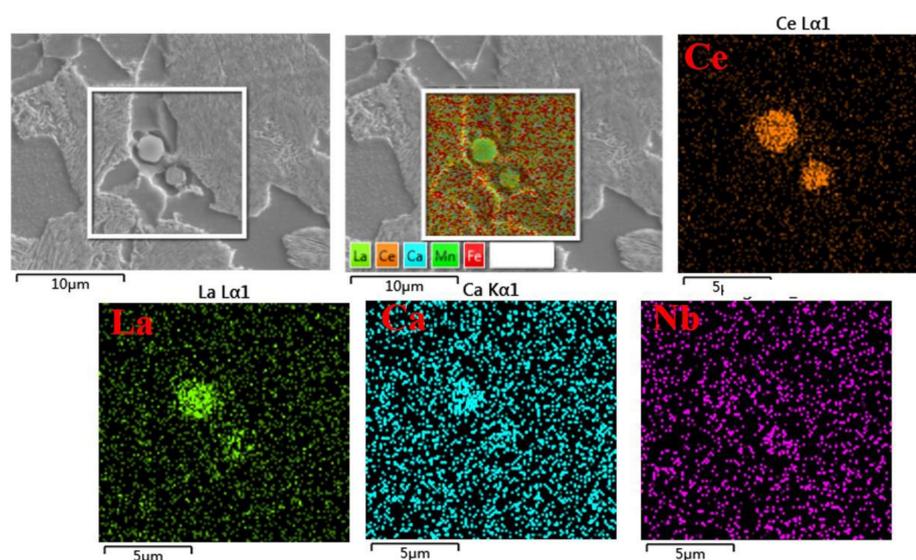


Figure 5. Surface scan of inclusion in structural steel from RH refining process with RE addition.

Table 3. The composition of the inclusions from RH refining process with RE, mass pct.

Element	Mg	Al	S	Ca	Nb	La	Ce
Average content	0.01	0.005	5.19	0.43	0.00	12.42	18.73

There is a mechanism of inclusions formation between strong deoxidation elements, and alloying elements by adding RE in the different refining process. The inclusions from LF refining process contained aluminum, which shows the reverse phenomenon of the RH refining process. As a robust deoxidizing element, calcium could attract aluminum oxide to become calcium aluminate inclusions when RE is not included. This showed that RE also has this ability, like calcium, which could reduce aluminum oxide inclusions or calcium aluminate inclusions.

From the composition analysis, it was found that the Nb precipitation was remarkably reduced. The reason for this might be that RE firstly forms inclusions with other nonmetallic elements such as O and S, which left little chance for Nb to form inclusions during the cooling process. In general, the Nb is precipitated during the cooling, and forms NbCN. However, there is only a small fraction of inclusions which can be neglected. The Nb inclusions are all small in size, and would become the nucleation particles. With the addition of RE, the precipitation of Nb takes place along with the formation of inclusions. Nb usually coexists with O/S/Ca/Al in LF process with RE addition. However, this coexistence disappeared in RH process with RE addition. RE, instead of Nb, is presented in the calcium aluminate inclusions. It could also be observed that the S content was increased in the inclusions. The reason for this is that the binding capacity was robust between RE and S. Meanwhile, CaS could also be formed. The temperature of RH is lower than that in the LF process which is more conducive to the precipitation of sulfide.

There might be another mechanism affecting the formation of RE inclusions. The RE inclusions formation begin with a nucleation from the oxide and sulfide inclusion with high melting point. The RE with high activity would be absorbed into that hard core. Moreover, due to the chemical site, there would be a density difference between the nucleus and the RE atoms, which enhanced the diffusion of RE to the hard core. This phenomenon contributed to the formation of the oxide and sulfide inclusion with RE. In addition, the size of inclusion has a relationship with RE aggregation. The more RE present, the higher the content of the other absorbing element.

3.2. Toughness and Welding Performance

It can be seen from Figure 6 that the impact energy of the plate with RE is approximately 50 J more than the one without RE. The toughness of the plate with RE from LF process is slightly more than that from RH process. RE has a positive effect on the toughness of the plate. The product performance can meet the requirements of high-heat-input welding.

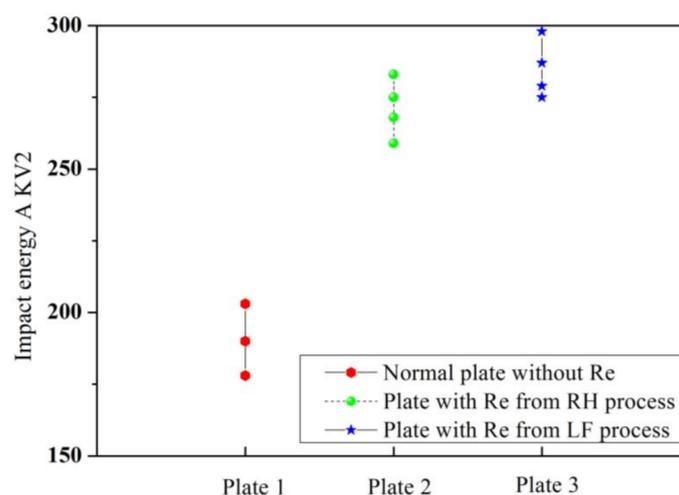


Figure 6. Impact energy of different plate.

The grain sizes of the plate are 8.63 μm (LF with RE), 9.93 μm (RH with RE), and 10.32 μm (regular plate without RE). The refinement of grain size would increase the toughness of the plate. A

conclusion can be drawn from Figure 7 that the plate from the LF process with RE at the coarse-grain area is the finest with a high heat input of 200 kJ/cm. It also can be seen that the grain size of a regular plate without RE is the largest during the high heat input welding. As for the toughness performance, the plate with RE from LF process is not very different to that from the RH process. However, the difference in the grain size is more substantial after the high heat input welding. All these reasons show that the RE inclusions could induce the intragranular ferrite to refine the grains to the preferred size (Figure 8). The number of inclusions in the selected format is more than that in RH process.

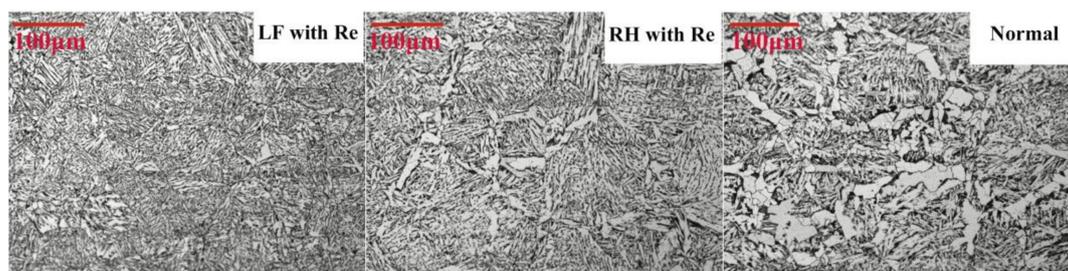


Figure 7. Microstructure of different plate in high heat input welding.

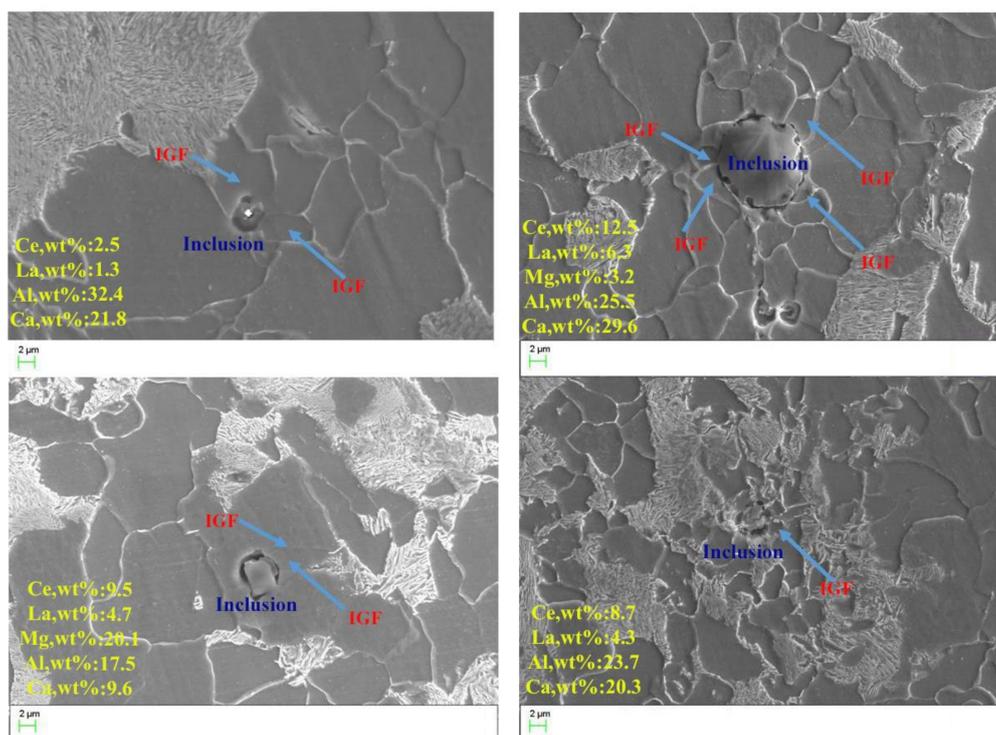


Figure 8. Inclusions induce intragranular ferrite to refine the grains.

The type of ferrite is not acicular but quasi-polygonal, more like a lath bainite structure. The grain is refined by inducing acicular ferrite in the general oxide metallurgy. However, the RE inclusions changed their structure to quasi-polygonal. In the current welding process, the steel plate would generate grain boundary ferrite, and coarsening during the high heat input welding. Therefore, we tried to lessen the effect from grain boundary ferrite to improve the roughness. It was clear that the RE inclusion induced the quasi-polygonal ferrite to refine the grain, and increased the toughness.

From Figure 9, it is possible to see that the inclusions of RE can induce the intragranular ferrite. The inclusions produced a depleted manganese zone, a depleted manganese zone would result

in the formation of the intragranular ferrite. These inclusions of preferable size could induce the intragranular ferrite and refine the grain size. The intragranular ferrite that they influenced is not acicular, but quasi-polygonal. The ability to refine the grains of quasi-polygonal ferrite is weaker than that of acicular ferrite.

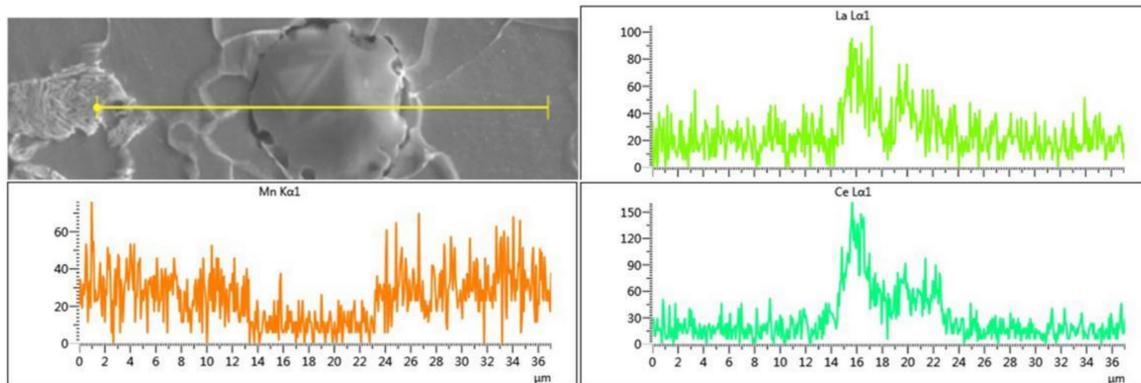


Figure 9. Inclusion particle produces depleted manganese area.

4. Conclusions

- (1) Regarding the structural steel of 420 MPa plate without RE, most of the inclusions were calcium aluminate with a high melting point >1873 K (1600 °C), and other inclusions were calcium aluminate with a low melting point <1773 K (1500 °C). The most significant inclusions in class B could reach a size of 180 μm . The addition of RE in the LF refining process found that no low melting point calcium aluminate inclusions were precipitated. The addition RE in the RH refining process showed the presence of low melting point inclusion.
- (2) The quantity of RE inclusions from the LF process was low. La and Ce inclusions occasionally appeared alone or coexist together. There is no Nb content in the RE inclusions, and only Nb mono-precipitates exist. The La and Ce inclusions from the RH process would always coexist together. Nb precipitation did not appear, and Al was also drastically reduced, while S increased in the inclusions.
- (3) RE has a positive effect on the toughness of the steel plate. The impact energy of the plate with RE is approximately 50 J higher than for a regular plate without RE. The toughness of the plate with RE from LF refining is better than that from RH refining.
- (4) RE inclusions could induce the intragranular ferrite, and refine the grains to the preferred size. After the welding at a heat input of 200 kJ/cm, the finest grain size at the heat affected zone was found in the plate from LF process with RE addition. The microstructure of ferrite was quasi-polygonal.

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