Role of Lanthanum Addition on Acicular Ferrite Transformation in C–Mn Steel

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Acicular ferrite formation in C–Mn steel after rare earth La addition and the potency of different La-containing inclusions inducing the formation of acicular ferrite have been investigated. It was found that there would be a large amount of acicular ferrite in quenched steel after 0.020 mass% La additions. The size of effective inclusion for acicular ferrite nucleation is mainly 1–4 μm. The best single La-containing effective inclusion is La2O2S. When MnS attached to the surface of La2O2S forming complex inclusion, the potency of inclusion on nucleating acicular ferrite is enhanced significantly. Low lattice mismatch between α-Fe and La2O2S plays an important role on acicular ferrite nucleation. When patches of MnS precipitated on the surface La2O2S forming the complex inclusion, the main mechanism for that inclusion is the combine of low degree of lattice mismatch and existing of Mn-depleted zone.

KEY WORDS: rare earth inclusion; heterogeneous nucleation; acicular ferrite; EBSD; steel.

1. Introduction

High strength low alloy (HSLA) steel has been wildly used in large structure due to its excellent combination of strength and toughness, however, the impact toughness of heat affected zone (HAZ) tends to deteriorate during welding as the harsh thermal cycle.1,2) Improving the toughness of HAZ becomes more significant for higher strength steel application in the field of large-scale structure.3,4) Refinement of microstructure can meliorate the strength and toughness of HAZ effectively.5) Acicular ferrite (AF) produced by “inclusion metallurgy” can enhance the strength and toughness of weld metal due to its chaotic space interlocking nature, which can act as an obstacle for crack propagation.6) The steel toughness increases visibly with an increasing amount of AF.7) While the aligned ferrite laths, such as coarse bainite and widmanstatten, can provide easy routes for crack propagation, reducing the impact toughness. The formation of AF is the competition result of the austenite-to-ferrite transformation at austenite grain boundary and intragranular nucleation sites during continuous cooling.8) With regard to acicular ferrite heterogeneous nucleation on the surface of inclusion within the austenite grain, researches have suggested several mechanisms such as:9–11) (1) small lattice mismatch between inclusion and ferrite, (2) low interfacial energy between inclusion and ferrite, (3) high thermal strain between the inclusion and steel matrix, and (4) development of a Mn depleted zone (MDZ) around the inclusion. So far there is still strong controversy over the above mechanisms for AF nucleation. In many cases, it is difficult to decide which mechanism is the most important for acicular ferrite nucleation.

As is well known that small amount of rare earth could produce a very big effect on microstructure and performance of steel. Thewlis12) and Wen et al.13) found that the inclusions of rare earth (RE) metal Ce can induce AF formation as effective inclusion, improving the performance of steel. They indicated that the low lattice mismatch between rare earth inclusion and α-Fe phase is the reason to make the ferrite nucleated on rare earth inclusion surface. And many researches revealed that the same transformation mechanisms of acicular ferrite in rare earth added steel. Nevertheless there is little research on making a comparison of the other three effects of rare earth inclusions on inducing the nucleation of acicular ferrite in steel beside the low lattice mismatch mechanism as yet.

At this study, several attempts have been made to analysis of four different effects of rare earth inclusion on inducing AF nucleation in C–Mn steel, comprehensively.

2. Materials and Experimental Procedures

About 300 g electrolytic high purity irons was used for the current study. All materials were melted in a laboratory molybdenum resistance furnace equipping an Al2O3 coated PtRh30-PtRh6 thermocouple and an FP93 automatic temperature controller with a temperature accuracy of ±2°C.
The detailed smelting process was described in previous study. After the smelting process when the temperature dropped to 1100 °C, the experimental steel was taken out quickly and quenched into water.

To promote the formation of particular inclusion phases in given steel while suppressing other unwanted inclusion phases, high purity raw materials were added into the molten to adjust the contents of C, Si, Mn, P, S, Al and La. Table 1 shows the chemical composition in prepared steels. The La content was determined by inductively coupled plasma mass spectrometry; the Si, Mn, P and Al contents were measured by inductively coupled plasma atomic emission spectroscopy; and the C, S and total oxygen contents were obtained by infrared spectroscopy.

The samples were sectioned under the same process in the middle of the cooled ingots. They were mechanically ground and polished to prepare metallographic samples and then were etched for 10 s in 4 vol% nital. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) with energy dispersive spectrometer (EDS) were used to inspect the inclusion in tested steels. Scanning electron microscope and optical microscope (OM) were used to statistical count acicular ferrite nucleuses and inclusions respectively. The microstructures in the steels were observed by optical microscope.

3. Results

3.1. The Microstructures of Experimental Steels

Figure 1 shows the microstructures of quenched C–Mn steels. It can be seen that the microstructure of steel without La is mainly martensite (M) and a little bainite (B). While in the steel added 0.020 mass% La, the main microstructure is acicular ferrite (AF), small size of ferrite side plate (FSP) and a amount of grain boundary ferrite (GB), which is very different from the steel without La. Since rare earth metal La has a strong ability of deoxidizing and desulfurization, when 0.020 mass% metal La added into C–Mn steel melt with the composition of 0.0070 mass% oxygen and 0.03 mass% sulfur, more than 99.9 mass% La will react with oxygen and sulfur, forming inclusions in steel. Based on the theory of minimization of gibbs free energy, equilibrium calculation using FactSage thermodynamic software at 1600 °C found that the final equilibrium dissolved La content is extremely low in steel melt, about 1.1 × 10−7 mass% (~0 mass%). It can be considered that the change of microstructure in C–Mn steel after the addition of La mainly caused by the inclusions of La, and the effect of dissolved La can be neglected. La-containing inclusions acting as heterogeneous nucleation site for acicular ferrite is the main reason for microstructure variation when a small amount of rare earth metal La added into C–Mn steel.

3.2. Inclusions in Experimental Steels

Thermodynamically stable non-metallic inclusion presented in each experimental steel was analysed by the calculation of phase diagram (CALPHAD) method and the actual calculation was fulfilled by computer software FactSage 7.0. Figure 2 shows the calculated results of weight percent of inclusion phases in No. 1–No. 5 steel. It can be found that the main conclusions are MnS + MnSiO3, MnS + La2O2S + MnSiO3, MnS + LaAlO3 + La2Si, La2O3 + MnSiO3 and La2O3 + SiO2 in No. 1–No. 5 steels, respectively.

The inclusion size distribution in No. 2 steel was analysed using image processing software Image J statistically. In order to clear the size range of effective inclusions nucleating the acicular ferrite in No. 2 steel, SEM was utilised to find 100 different effective inclusions randomly in the etched samples by 4 vol% nital. The number of effective inclusions was counted in each size range. All the statistical results are shown in Fig. 3. It can be found that the size of effective inclusions mostly between 1–4 μm, which amounts to about 85.2% of the total number of effective inclusions. Simultaneously, inclusion size of 1–4 μm accounted for 53.0% of the total inclusion.

Figure 4(a) shows the acicular ferrite nucleation around La-containing inclusion in C–Mn steel. It can be seen that there are about five ferrite thin slices around the inclusion. It means that the inclusion has very great effective to induce

| Sample | C  | Si  | Mn  | Ni  | P  | S   | O   | Al  | La | Fe   |
|--------|----|-----|-----|-----|----|-----|-----|-----|----|------|
| No. 1  | 0.18 | 0.22 | 1.31 | –   | 0.018 | 0.025 | 0.0065 | –   | –   | Bal. |
| No. 2  | 0.18 | 0.25 | 1.31 | –   | 0.018 | 0.025 | 0.0065 | –   | 0.020 | Bal. |
| No. 3  | 0.18 | 0.26 | 1.32 | –   | 0.015 | 0.022 | 0.0045 | 0.027 | 0.022 | Bal. |
| No. 4  | 0.18 | 0.26 | 1.31 | –   | 0.017 | –     | 0.0067 | –   | 0.021 | Bal. |
| No. 5  | 0.18 | 0.25 | –    | 1.31 | 0.016 | 0.026 | 0.0075 | –   | 0.022 | Bal. |

Fig. 1. Microstructures of tested steels quenched from 1100 °C, (a) No. 1 steel without rare earth addition; (b) No. 2 steel with addition of 0.020 mass% La.
the heterogeneous nucleation of acicular ferrite. The energy dispersive spectrum indicates that the composition of effective inclusion is complex inclusion of La–O–S–Mn–Si as shown in Fig. 4(b).

To further make clear the morphology and composition of the rare earth inclusion in sample of No. 2 steel. Sample prepared by ion beam thinner was explored by transmission electron microscopy and energy dispersive spectrometer. The results are shown in Fig. 5, it can be seen that the rare earth inclusion in No. 2 steel are the complex La2O2S and MnS. Patches of MnS precipitated covering on part of the surface of La2O2S.

3.3. Microstructures of Steels Having Different Inclusions

For the steel having a specific composition, according to the heterogeneous nucleation theory, the most essential condition of all is the presence of effective inclusion. If there is no effective inclusion, acicular ferrite is not considered to form. Effective inclusion which is more effective for intragranular nucleation has the lower activation energy barrier against acicular ferrite formation. In this study, it is found that the main inclusions in the steel without RE addition are MnS and MnSiO3 inclusion, and the microstructures are mainly martensite and a few bainite, as shown in Fig. 1(a), indicating that MnS or MnSiO3 alone/complex have little ability to induce the nucleation of acicular ferrite. When certain amount of La added into steel, the microstructure changed into mainly acicular ferrite, which means La2O2S + MnS inclusion have strong ability to induce the nucleation formation.
of acicular ferrite, as shown in Fig. 1(b).

In Al-killed steel, rare earth La treatment would make the inclusion change into MnS + LaAlO$_3$ + La$_2$S$_3$, and microstructure is turned into mainly parallel bundle like bainite/widmanstatten as shown Fig. 6(a), which means that nucleation of acicular ferrite is almost impossible on simple/composite inclusions of MnS, LaAlO$_3$ and La$_2$S$_3$. In the steel with extremely low sulfur content when some La added, the inclusion is mainly La$_2$O$_3$, and almost no acicular ferrite, manifesting that the ability of La$_2$O$_3$ nucleating acicular ferrite is also very small as shown Fig. 6(b). When Mn is replaced by same content of Ni, admitting that same amount of Mn and Ni have a similar effect on CCT curve in steel, it makes the inclusion is La$_2$O$_2$S, and the microstructure is primarily grain boundary ferrite, pearlite and amount of acicular ferrite as shown Fig. 6(c). It inferred that simple La$_2$O$_2$S is the nucleus of acicular ferrite. However, the amount of acicular ferrite in No. 5 steel is less than that in No. 2 steel having La$_2$O$_2$S and MnS inclusion. In other words, La$_2$O$_2$S and MnS coexist in steel can significantly improve the power of La$_2$O$_2$S inclusions to nucleating acicular ferrite.

The microstructure morphologies in No. 2 and No. 3 steels were observed using scanning electron microscopy, respectively. Electron back-scatter diffraction (EBSD) attachment was used to determine the grain boundary angle and grain orientation in the above two experimental steel. The results of microstructure morphologies, grain boundary angle and grain orientation distribution of the ferrite grains in No. 2 and No. 3 steels are shown in Figs. 7 and 8, separately. It can be seen that bainite/widmanstatten ferrite lath was parallel bundle-like in No. 3 steel, while acicular ferrite has a chaotic crystallographic in No. 2 steel as shown in Figs. 7(a) and 8(a). Figures 7(b) and 8(b) show the grain boundary angle distribution of ferrite laths in No. 2 and No. 3 steel. It can be found that bainite/widmanstatten ferrite pieces are mostly sub grain boundaries, grain boundary angles are very small (mainly $<4^\circ$). While for acicular ferrite, the number of high-angle boundaries increased significantly. The orientations and the grain misorientation distributions of ferrite in two microstructures are shown in Figs. 7(c), 7(d) and 8(c),
8(d), it indicates that the misorientation of acicular ferrite laths in No. 2 steel are larger than that in No. 3 steel, as the percent of low misorientation ferrite (≤5°) in No. 2 steel is less than that in No. 3 steel, and the percent of high misorientation ferrite (>40°) in No. 2 steel is more than that in No. 3 steel. Different acicular ferrite laths nucleating on different positions on the surface of inclusion would have different orientations. The two acicular ferrites at 180 degree angles from each other would make a pair, and the two ferrite laths have the same orientation.

4. Discussion

Acicular ferrite formation depends on the competition of transformation at austenite grain boundary and intragranular nucleation sites during continuous cooling. A lot of researches have been done to identify effective inclusions for intragranular nucleation. About the acicular ferrite nucleation mechanism on the nonmetal inclusion within austenite grain, different people have different outlooks. Babu et al. concluded that the most probable mechanisms for intragranular nucleation were either due to the generation of
thermal strains in the austenite close to the inclusion or the formation of solute depletion. The Mn depletion has been verified several times in heat-treated steels around some special Ti-containing inclusions. Nako et al.16 verified several times in heat-treated steels around some special Ti-containing inclusions. Nako et al.16 considered that acicular ferrite nucleated on Ti–RE–Zr complex oxide had special orientation relationship. Park et al.19 expect that the nucleation of acicular ferrite has little relation to the inclusion composition, only depends on the size of inclusions. He believed that the mechanism of acicular ferrite nucleation is mainly the reduction of interfacial energy mechanism. Mabuchi et al.18 found that Mn depletion can promote AF nucleation at the interface of MnS newly precipitated on (Mn,Si) oxide, but there is no coherency with ferrite matrix.

The following discussion about heterogeneous nucleation mechanism was carried out from different angles in steel treated by rare earth, such as small lattice mismatch between inclusion and ferrite, small interfacial energy between inclusion and ferrite, high thermal strain between the inclusion and steel matrix, and the existence of Mn depleted zone (MDZ) around the inclusion.

4.1. Reduction in Interfacial Energy

This mechanism considers that non-metallic inclusion only provide an inert, incoherent and non-deformable site for ferrite nucleation. It could make the nucleation of ferrite on inclusion easily as the interfacial energy reduction. Grong et al.19 proposed that the free energy barrier reduction is the primary cause of nucleation. Moreover, Zhang et al.,20 Lee et al.21 and Furuhara et al.22 also reported that inclusion could act as an inert substrate, having the ability to reduce the free energy barrier to heterogeneous nucleation.

According to this mechanism, when the surface of inclusion and matrix is a low energy inert interface, the role of inclusion in the process of inducing the nucleation is similar to the classical heterogeneous nucleation theory. Therefore, the size and number of inclusions are very important for AF heterogeneous nucleation as nucleus.

However, this mechanism cannot explain the fact that present result that inclusions with the same size but different compositions, such as La2O3 + MnS, La2O3S, La2O3, LaAlO3 and manganese silicate, have different abilities to induce the nucleation of acicular ferrite in steel. In addition, the interface energy among inclusion, ferrite and austenite is difficult to obtain, as it is difficult to experimentally or theoretically clear which interface of inclusion and ferrite can form low energy inert interface, so the mechanism of reduction in interfacial energy cannot be used to explain the formation of acicular ferrite induced by rare earth inclusions.

4.2. Thermal Strains at the Inclusions

When a non-metallic inclusion is embedded in a metallic alloy, due to the expansion coefficient of matrix is higher than that of the inclusion, it could cause local stress in matrix near the inclusions. Upon cooling, compressive stress strain field in austenite phase around inclusion would be generated. This compressive stress strain field could promote the austenite/ferrite transformation. The greater the thermal expansion coefficient difference between the inclusions and steel austenite matrix, the greater the compressive stress strain field, the easier of formation of acicular ferrite.

4.3. Lattice Mismatch Strain

Epitaxy between acicular ferrite and the nonmetallic inclusions decreases the activation energy barrier greatly for the nucleation of acicular ferrite. The smaller lattice mismatch, the activation energy barrier is lower under the transformation temperature of γ→α (about 912°C). The mismatch between the ferrite matrix and the inclusions can be calculated using the theory according to Bramfitt, as shown in Eq. (1).23

\[ \delta_{(hkl)}^{(M)} = \sum_{i=1}^{3} \left( \frac{1}{d_{(hkl)_n}} - \frac{1}{d_{(hkl)_s}} \sin \theta \cos \theta \right) \times 100\% \quad (1) \]

where \( s \) is the substrate, \( n \) is the nucleated solid, \( (hkl)_s \) is a low index plane of the substrate, \( (hkl)_n \) is a low index direction in \( (hkl)_s \), \( (hkl)_n \) is a low index plane of the nucleated solid, \( [uvw]_s \) is a low index direction in \( (hkl)_s \), \( [uvw]_n \) is the interatomic spacing along \( [uvw]_s \), \( d_{[uvw]_s} \) is the interatomic spacing along \( [uvw]_n \), \( \theta \) is the angle between the \( [uvw]_s \), and \( [uvw]_n \). Bramfitt23 proposed that the nucleating agent is potent when lattice mismatch is less than 6%, while when lattice mismatch is above 12% the agent is impotent. At present, the mismatch between rare earth oxysulfide inclusions and α-Fe at the temperature of austenite/ferrite transformation (about 912°C) is calculated as shown in Table 3. It is evi-
dent that rare earth oxysulfide inclusions and $\alpha$–Fe exhibits very low mismatch at 912°C regardless of Ce or La.

This mechanism is a good explanation that rare earth oxysulfide inclusion is potent to induce the nucleation of acicular ferrite. It suggests that the lattice mismatch plays a significant role in nucleating $\alpha$–Fe for rare earth oxysulfide inclusion.

If the heterogeneous nucleation of acicular ferrite on the inclusion was due to the low mismatch between ferrite lattice and inclusion lattice, and the inclusions were regular crystals, the ferrite laths that nucleated at different positions on the surface of inclusion could have different orientations. While the orientation of acicular ferrite pairs which are 180° to each other could be the same. At present the EBSD result is in good agreement with the hypothesis mechanism of low lattice mismatch between inclusion and ferrite for acicular ferrite heterogeneous nucleation on inclusion surface.

4.4. Depletion of Mn Content Near Inclusions

It is well known that the increase of Mn content can enlarge the austenite zone in steel. While, the decrease of Mn concentration forming a Mn-depleted zone (MDZ) in the austenite matrix near effective inclusion can reduce the austenite zone and boost the transformation temperature of ferrite formation. This, in turn, facilitates the nucleation of acicular ferrite in the zone. Mabuchi et al.18) found that MDZ can promote AF nucleation at the interface of MnS newly precipitated on (Mn, Si) oxide in the HAZ of welded joints by field-emission transmission electron microscopy (FETEM) coupled with EDS.

In the previous experiments, it was found that La$_2$O$_2$S and MnS coexist in steel can significantly improve the capacity of La$_2$O$_2$S inclusion nucleating acicular ferrite as the content of acicular ferrite in the former steel is more than that in the later steel. From the perspective of the effect of Mn on the formation of acicular ferrite near complex inclusion, it can be inferred that beside the lattice mismatch strain mechanism, the MDZ mechanism also played an important role in La$_2$O$_2$S + MnS complex inclusion inducing the nucleation of acicular ferrite. According to MDZ mechanism, when MnS inclusion precipitated on the surface of rare earth inclusion forming an MDZ in the austenite matrix around rare earth inclusion, which can be an active site for the nucleation of acicular ferrite. Ohkita et al.24) got the same conclusion that a decrease in interfacial energy when they explored complex TiN–MnS precipitates promoted AF formation not only by the existing of a MDZ, but also the low lattice mismatch of TiN and ferrite. Yamamoto et al.25) also obtained similar conclusions.

5. Conclusions

(1) After adding about 0.020 mass% metal La into steel, there could be a large amount of acicular ferrite formation in the 1 100°C quenched microstructure. The size of effective inclusion for acicular ferrite nucleation is mainly 1–4 μm.

(2) Different types of rare earth containing non-metal inclusions have different abilities to induce the nucleation of acicular ferrite. The best effective inclusion containing rare earth induce the nucleation of acicular ferrite is La$_2$O$_2$S. When MnS attached to La$_2$O$_2$S forming complex inclusion, the potency of La$_2$O$_2$S on nucleating acicular ferrite is enhanced significantly.

(3) For simple rare earth oxysulfide (La$_2$O$_2$S) inclusion, the mechanism of acicular ferrite nucleation is mainly due to the low degree of lattice mismatch between $\alpha$–Fe and La$_2$O$_2$S. While for the complex La$_2$O$_2$S and MnS inclusion inducing the nucleation of acicular ferrite, the mechanism is the combine of low degree of lattice mismatch and existing of Mn-depleted zone adjacent to the complex inclusion.

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Table 3. The lattice mismatch between RE inclusion and $\alpha$–Fe under 912°C.

| Inclusion | Lattice structure | Lattice parameter \(\alpha/\mu m\) | \(\Delta a/\alpha$–Fe\) | Lattice mismatch/% |
|-----------|------------------|-------------------------------|-----------------|------------------|
| CeO$_2$S  | Cubic            | 0.4053                        | 1.414           | 1.2              |
| La$_2$O$_2$S | Hcp              | \(a=0.40509, c=0.6943\)      | 1.413           | 0.2              |

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