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Mechanisms of inclusion evolution and intra-granular acicular ferrite formation in steels containing rare earth elements

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Inclusion characteristic and microstructure of rare earth (RE) elements containing steel were evaluated with scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), element-mapping, optical microscopy (OM), and automated feature analysis (AFA) option equipped with ASPEX PSEM. Factsage was used to calculate the equilibrium inclusion composition. Based on the calculation, an inclusion evolution mechanism was proposed. Furthermore, line scanning analysis was used to elucidate the intra-granular acicular ferrite (IAF) nucleation mechanism. The result showed that two different inclusions exist in sample steel: (Mn-Al-Si-Ti-La-Ce-O) +MnS complex inclusion and isolated MnS inclusion. Almost all nucleation sites for IAF are complex inclusions, while single MnS inclusion cannot induce IAF. A possible formation mechanism of complex inclusion is proposed based on calculated results using Factsage, which agrees well with experimental results. A Mn-depletion zone (MDZ) which exists adjacent to the (Mn-Al-Si-Ti-La-Ce-O) +MnS complex inclusion can account for the IAF formation. However, the low volume fraction (1.49×10^{-7}) of effective inclusion may result in only 10% (volume fraction) IAF.

KEY WORDS Intra-granular acicular ferrite; RE containing complex inclusion; Factsage; Inclusion precipitation; Mn-depletion zone

1 Introduction

Non-metallic inclusions are generally believed to be detrimental to the mechanical properties of steels. However, fine inclusions can act as heterogeneous nucleation sites of IAF, which has aroused worldwide interests in recent twenty years. IAF, first discovered by Smith *et al* ^[1] in weld metals, has a chaotic crystallographic orientation, which can refine the austenite grains and retard the propagation of cleavage crack in steel. So IAF can provide excellent combination of strength and toughness in steel, especially for heat affected zone (HAZ) and weld metals.

Much attention had been paid to investigate the nucleation mechanism of IAF on different inclusions, such as low mismatch strain mechanism ^[2], Mn-depletion mechanism ^[3-6], thermal strain difference mechanism ^[7,8] and so on. Among them, Mn-depletion mechanism is the most promising mechanism which arouses worldwide concern. It is generally

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known that Mn is an austenite-stabilized element. Therefore, a depletion of Mn in steel near precipitated MnS inclusions can lead to a reduction of austenite zone and thus promote the nucleation of ferrite in a MDZ during the austenite to ferrite transformation. Different scholars reported that MDZ exists near MnO-SiO₂ with MnS precipitate on it ^[3], cation-vacancy-type inclusions, such as Ti_2O_3 ^[4], Mn titanatesl ^[5] and (Ti-Mn-O)+(Al-Si-Mn-O)+MnS complex inclusion ^[6]. Until now, as far as the authors know, whether MDZ exists or not in steel matrix near complex inclusion containing rare earth (RE) metals is unknown. So investigation on that topic should be done.

RE elements, with a strong affinity to oxygen and sulfur, were widely applied to spherodizing inclusions (such as MnS) to avoid the anisotropy of mechanical properties in final rolling products. Thewlis *et al* ^[9] found that fine CeS inclusions, with high number density embedded in steel matrix can alter the ferrite nucleation from grain boundary to inclusion sites and thus enhance the IAF transformation. Recently the authors ^[10] reported that Ce_2O_3 with a low misfit value with ferrite can act as the nucleation sites for IAF under fast cooling rate. However, the inclusion characteristic and microstructure of furnace-cooled RE containing sample and the inclusion formation evolution have not been discussed yet.

In the present work, an attempt has been made to exploit the inclusion characteristics such as the type, size distribution and number density in laboratory furnace-cooling specimen. Factsage (version 6.2) was used to calculate the equilibrium inclusion composition. Based on the calculated result, a possible inclusion evolution mechanism was put forward. Then IAF nucleation mechanism focusing on Mn-depletion mechanism has been discussed based on experimental results.

2 Experimental

The sample steel was prepared in vertical electric resistance furnace with MoSi₂ heating bars and Al_2O_3 reaction tube. The reaction tube was evacuated by flowing argon gas flow (1.5 L/min) during the whole process. When the iron melt was heated to 1600 °C, Fe-C alloy was added to make 0.1% carbon, electrolyte Si and Mn were added to make 0.25% Si and 1.0 % Mn. Then RE metal was added to the melt. After that, the furnace power was turned off and crucible with the melt for the sample was slowly cooled down in the furnace. Chemical composition (wt pct) of prepared steel is C 0.074, Si 0.22, Mn 1.00, P 0.0072, S 0.0094, Ti 0.0011, Al 0.0017, La 0.0013, Ce 0.0026, N 0.0059 and T.[O] 0.0041. Acid-soluble Al, P, Mn and Si content in steel were analyzed by ICP-AES method. C, S and O contents were analyzed by infrared absorption method.

In order to clarify the inclusions in steel samples, $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ cubic samples were cut from sample steel. The samples were mechanically mirror polished using diamond powder emersion and then subjected to examination using ASPEX Instruments PSEM microscope equipped with EDS. AFA option in this equipment was used to evaluate the inclusions in steel sample automatically. With this option, predefined area was scanned and every particle larger than 0.5 μ m is evaluated and quantified. The information such as size, chemical composition, area, diameter and its classification were recorded to a file, which could transfer to Excel file later. The detected element in present EDS analysis included: Mg, Al, Si, S, Ti, Mn, La and Ce. However, this method cannot detect the multi-phase particles. So these inclusions were detected manually. The total scanning area



Fig. 1 SEM morphologies and EDS spectra of typical inclusions in sample steel: (a) complex inclusion; (b) isolated MnS

is 14 mm^2 .

In order to illustrate the evolution mechanism of inclusion, Factsage 6.2 was used to calculate the equilibrium inclusion composition as the temperature decreased from 1600 to 1000 °C. FSstel and FToxid database were chosen for the calculation and the result was exported to Excel file for graphing. The phases considered in present calculation are liquid steel, molten oxides, δ -ferrite, austenite, α -ferrite, MnS, MnO, SiO₂, AlCeO₃, AlLaO₃, MnAl₂O₄ and Mn₃Al₃Si₃O₁₂. The molten oxides (slag phase) consist of MnO, SiO₂, MnS and Ti₂O₃.

A real color confocal microscope (Lasertec Optelics C130) was used to evaluate the microstructure of steel sample. And the fraction of IAF was quantified based on point counting method ^[11] using a 25 point grid with 1000 points in total.

3 Results

3.1 Inclusion characteristics

Two types of inclusion exist in sample steel: (1) complex oxides (Mn-Al-Si-Ti-La-Ce-O) with MnS phase and (2) isolated MnS inclusion, which are shown in Figs. 1a and 1b, respectively. The complex inclusion is almost spherical while single MnS inclusion appears to be angular .According to this feature, it can be easily inferred that the MnS phase in the type (1) inclusion precipitates and grows on liquid complex oxides, which consist a small amount of sulfur, and the type (2) inclusion forms in solid phase.

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Number density of inclusions in sample steel for different size group is shown in Fig. 2. It shows a typical bell-shape curve (shown in red dash line in Fig. 2), which is also reported in other literature ^[12,13]. The peak of number density for complex inclusion is in range of 1–1.5 μ m, with the value of 4.8 mm⁻² while for isolated MnS inclusion is in range of 3–3.5 μ m with the value of 0.98 mm⁻².

Inclusion in steel matrix is 3D distribution, so spatial distribution of inclusion, such as volume fraction is also a very important character of inclusion. Oh *et* al ^[14] reported that volume fraction is more



effective in IAF formation than their type and size distribution. Volume fraction can be calculated by Dehoff *et al*^[15] equation:

$$d_{\rm V} = \frac{\pi}{2} d_{\rm H} = \frac{\pi}{2} \frac{n}{\sum_{i=1}^{n} (1/d_i)}$$
(1)

$$N_{\rm V} = N_{\rm A}/d_{\rm V} \tag{2}$$

$$f_{\rm V} = \frac{\pi}{6} (d_{\rm V})^3 N_{\rm V}$$
(3)

where $N_{\rm V}$ is number of inclusions per unit volume; $N_{\rm A}$ number of inclusions per unit area; d_i apparent diameter of *i*th inclusion among *n* inclusions; $d_{\rm H}$ harmonic mean of inclusions; $d_{\rm V}$ average diameter of inclusions; $f_{\rm V}$ volume fraction of inclusions.

Volume fractions of isolated MnS and complex inclusion are calculated by Eqs. (1)–(3), as is presented in Table 1. The value is 1.49×10^{-7} and 7.02×10^{-8} , respectively. Oh *et al* ^[14] reported that the minimum volume fraction of inclusion for stable IAF formation is 1.0×10^{-4} , so the small volume fraction of inclusion in present study is far from enough for IAF nucleation.

 Table 1
 Volume fraction of inclusion detected in steel sample

Inclusion type	$d_{\rm V}/{ m mm}$	$N_{\rm A}/{\rm mm}^{-2}$	$N_{\rm V}/{\rm mm}^{-3}$	$f_{\rm V}$
Isolated MnS	6.16	7.50	1.22	1.49×10^{-7}
Complex inclusion	2.74	17.78	6.47	7.02×10^{-8}

3.2 As-cast microstructure and nucleation sites for IAF

Figure 3 shows the microstructures of sample steel with different magnifications, which consist of large amount of polygonal ferrite (PF), a little Perlite (P) and IAF with volume fraction of only 10%. Obviouly, this small amount of IAF structure restricts the application of the steel when high toughness is needed.

Although only small volume fraction of IAF exists in steel, there still exist many nucleating sites for IAF structure. A typical interlocking ferrite laths nucleated on the inclusion



Fig. 3 As-cast microstructures of sample steel



Fig. 4 Effective (a, b) and non-effective (c, d) nucleating sites for IAF

surface, as shown in Figs. 4a and 4b. These ferrite laths have a chaotic crystallographic orientation, which can retard the propagation path for a cleavage crack. Unfortunately, PF dominate the microstructure, as shown in Fig. 3. Careful investigation on the nucleation sites has shown that nearly all nucleation sites for IAF are complex inclusion. Single MnS inclusion cannot induce IAF in present study (see Figs. 4c and 4d), which can be explained by thermal strain difference mechanism, and depicted in detail elsewhere ^[7]. Obviously, obtaining large amount of complex inclusion is critical to control the microstructure.

To make clear the different phases in complex inclusion mentioned above, further investigation, for example, element mapping is conducted to show the phase distribution



Fig. 5 Element mapping pattern of typical inclusion nucleating IAF

in this complex inclusion. Many complex inclusions are chosen for this element mapping, and phase distribution of these selected inclusions is similar. Figure 5 shows the element mapping pattern of typical inclusion nucleating IAF.

4 Discussion

4.1 Evolution mechanism of complex inclusion

According to the discussion in section 3.2, (Mn-Al-Si-Ti-La-Ce-O) +MnS complex inclusion is beneficial for IAF formation. So a clear elucidation of formation mechanism of this inclusion during solidification will facilitate the control of this beneficial inclusion and thus promote the IAF formation.

Figure 6 shows the calculated evolution of the equilibrium inclusion composition as the temperature drops from liquid steel (1600 °C) to solid steel (1000 °C). Possible formation mechanism of the complex inclusion is as follows:

(1) When electrolyte Si was added, solid SiO_2 formed immediately, as Eq. (4) indicated.

$$[Si] + 2[O] = SiO_{2(inclusion)}$$
(4)

Similarly, Mn was added to the melt subsequently, Eq. (5) occurs.

$$[Mn] + [O] = MnO_{(inclusion)}$$
(5)



Fig. 6 Evolution mechanism of inclusion during solidification process

MnO cannot exist in the solid phase, because reaction (6) occurs easily. So relatively high MnO and SiO₂ contents exist in liquid phase between 1500–1550 °C, as illustrated in Eq. (6).

$$SiO_{2(inclusion)} + 2MnO_{(inclusion)} = (2MnO \cdot SiO_2)$$
(6)

Then RE metals are added to the melt, Eq. (7) occurs. So REAlO₃ exists even in liquid phase, as shown in Fig. 6.

$$[RE] + [Al] + 3[O] = REAlO_{3(inclusion)}$$
(7)

At the same time, the existing Ti also reacts with oxygen in steel, as shown in Eq. (8).

$$[\mathrm{Ti}] + x[\mathrm{O}] = \mathrm{TiO}_x \tag{8}$$

To sum up, SiO_2+ (Ce, La) AlO_3+TiO_x solid phase, which may form with the collision of small solid particles (SiO₂, (Ce, La) AlO_3 , and TiO_x) in the inclusion core was most likely formed during initial Si/Mn/RE deoxidation. A liquid phase (mainly MnO-SiO₂-Ti₂O₃) forms around the solid core inclusion in liquid steel at approximate 1500 °C. Added Mn can also contact with S to form MnS solid phase, which is a reason to explain why so many isolated MnS inclusion in sample steel.

(2) When temperature decreases, MnS phase precipitates on the surface of the spherical liquid inclusion in the embedded form. The precipitation of MnS phase on inclusion during solidification has two forms ^[12]: MnS precipitates in embedded form with oxide inclusion and around oxide core wrapping it. Wakoh *et al* ^[16] reported that when the manganese silicate exists in the multi-phase inclusions, MnS would precipitate on it in embedded form, which agrees well with present result. When MnS phase forms, Mn in steel matrix will diffuse into the inclusion boundary, forming a MDZ which will enhance the driving force of IAF.

(3) As temperature decreased further, the remaining liquid inclusion continued to solidify as TiO_x+SiO_2 and (Mn-Si-Al)O_x phases.

4.2 Formation mechanism of IAF

As discussed in section 4.1, proposed mechanism of inclusion formation suggests that MDZ exist around the complex inclusion. To give a direct evidence of MDZ, line scan analysis were employed to scan Mn content in the inclusion and its adjacent matrix. A typical IAF nucleation inclusion (see Fig. 7a) is chosen for this line scan analysis. It is clearly showed a MDZ exists in steel substrate near the inclusion, as shown in Fig. 7b.



Fig. 7 Line scanning analysis of Mn along the nucleation site of inclusion and surrounding steel matrix: (a) SEM image; (b) line scan pattern

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Mn is an austenite-stabilized element. Therefore, a depletion of Mn in steel near precipitated MnS inclusions can lead to a reduction of austenite zone and thus promote the nucleation of ferrite in a MDZ during austenite to α -ferrite transformation. The slow cooling in this experiment may facilitate the formation of MDZ, which is also reported by Kim *et al* ^[17]. However, because of low cooling rate, the number density and volume fraction of this effective complex inclusion is too small ^[12], which account for low volume fraction of IAF .So proper cooling rate should be pursued to keep the balance between the inclusion effectiveness for IAF and volume fraction of inclusion.

5 Conclusions

(1) Inclusion can be classified into two categories: (Mn-Al-Si-Ti-La-Ce-O) +MnS complex inclusion and isolated MnS inclusion in present furnace-cooled steel sample. Almost all nucleation sites for IAF are complex inclusions, while single MnS inclusion cannot induce IAF.

(2) A possible formation mechanism of complex inclusion is proposed based on calculated results using Factsage. The experiment result agrees with the calculated results satisfactorily.

(3) A MDZ exists adjacent to the (Mn-Al-Si-Ti-La-Ce-O)+MnS complex inclusion. This MDZ can be the driving force for IAF formation. However, the low volume fraction (1.49×10^{-7}) of effective inclusion may result in only 10% (volume fraction) IAF. Proper cooling rate should be pursued to keep the balance between the inclusion effectiveness for IAF and volume fraction of inclusion.

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