Effect of carbon and manganese contents on intra-granular acicular ferrite nucleation in steel containing nanoparticles

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Abstract: In the present study, the experimental steels containing nanoparticles were manufactured under different mass fractions of C and Mn. A systematic analysis of inclusion characteristics, Intra-granular acicular ferrites (IAF) inducing potency of active inclusions, and microstructure morphologies revealed that Al₂O₃-MgO had the largest number fraction with higher inducement ratios than other inclusions. Steel samples containing 0.21wt% C contained the largest share of fine acicular ferrite (AF) than other samples due to relatively stronger inducing potency of active inclusions on IAF. On the other hand, the underlying microstructures in steel samples with Mn content less than 0.6wt% were due to weaker inducing potencies of active inclusions on IAF.

1. Introduction

The characteristics of inclusions and microstructures in the cast steel are always two significant factors to influence and determine the mechanical properties of steel materials [1,2]. The removal of inclusions in steel is not easy due to the complexity of metallurgical reactions, and the diversity of inclusion sources. Since the late 1970s, it has been recognized that the mechanical properties of the welded joints in low alloy steel can be greatly improved if the microstructures are largely acicular ferrites (AF) [3-5]. AF is good for its ability to improve strength and toughness at the same time, which is also available for the low carbon steel. Also from then on, many prolonged and detailed studies on improving the toughness of weldments in the fusion zone have been carried out, and considerable knowledge has been acquired. These researches basically focused on the role of inclusions in controlling the microstructure grain size of steels [6-10]. In 1990, the Japanese metallurgists summarized and referenced the past research achievements from welding technologies, then proposed the “oxide metallurgy” theory [11]. This involves incorporating micro second phase particles in the steel to retard the growth of austenite grain and induce AF as the nucleation cores of ferrites. For the inclusions, to become the active ones to induce AF, they have to have some special characteristics at composition and size [12-15].

Except for the characteristics of inclusions, the element content of steel matrix is another significant factor in influencing the AF nucleation potency on inclusions. This is because the adjustment of steel extents would lead to some changes on mismatch between the inclusion and its surrounding structure. The smaller the mismatch between inclusions and AF, the easier the AF nucleation on active inclusions.
However, reports related to the influence of element contents on acicular ferrites nucleation on inclusions are still limited.

In the present study, the contents of alloying elements C and Mn, were taken as the variables to investigate the differences on nucleation potency of AF induced by inclusions in steel containing nanoparticles. The differences on inclusion characteristics, and microstructure morphologies under different mass fractions of the two elements were also compared. Based on the principles of thermodynamics and dynamics, the mechanism of experimental results was analyzed.

2. Experimental procedure
Magnesium oxide (MgO) nanoparticles were chosen to act as the precipitation cores to refine the inclusion size. To ensure that the MgO nanoparticles (15-25 nm) were well dispersed before adding to the liquid steel bath, another nano material, AlSi alloy (50-70 nm, Al-70wt%, Si-30wt%), was used as the pre-dispersion medium. The pre-dispersion process of MgO nanoparticles was performed using a planetary ball mill with a weight ratio of MgO and AlSi alloy of 1: 11 [16].

For the element C, the value ranges of the investigated mass fractions changed from 0.13wt% to 0.25wt%, and for Mn, from 0.26wt% to 0.60wt%. Before adding nanoparticles, these experimental steel ingots were remelted in high-temperature electric pipe furnace. After the ingots in furnace were in liquid state, the mixed nanoparticles were added into the liquid steel with the help of molybdenum rod. The addition amount of MgO nanoparticles in each experimental steel was 0.05wt%. The chemical constituents of each experimental steel ingot was detected, and then the detected values under the same conditions were averaged as shown in Table 1. Basically, the detected results met the initially designed contents for the element variables C and Mn, which was shown in the first column in Table 1.

| Sample [%C] | C     | Si     | Mn     | P      | S      | TiO    | Mg     | Al     | Fe     |
|-------------|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| [%C]=0.13   | 0.134 | 0.211  | 0.384  | 0.0020 | 0.024  | 0.0089 | 0.022  | 0.244  | Bal.   |
| [%C]=0.17   | 0.172 | 0.204  | 0.405  | 0.0018 | 0.021  | 0.0076 | 0.025  | 0.236  | Bal.   |
| [%C]=0.21   | 0.211 | 0.197  | 0.393  | 0.0019 | 0.021  | 0.0071 | 0.023  | 0.271  | Bal.   |
| [%C]=0.25   | 0.253 | 0.207  | 0.389  | 0.0021 | 0.019  | 0.0070 | 0.028  | 0.249  | Bal.   |
| [%Mn]=0.26  | 0.169 | 0.189  | 0.265  | 0.0022 | 0.022  | 0.0076 | 0.025  | 0.260  | Bal.   |
| [%Mn]=0.40  | 0.172 | 0.204  | 0.405  | 0.0018 | 0.021  | 0.0076 | 0.025  | 0.236  | Bal.   |
| [%Mn]=0.50  | 0.172 | 0.201  | 0.517  | 0.0022 | 0.024  | 0.0081 | 0.027  | 0.258  | Bal.   |
| [%Mn]=0.60  | 0.170 | 0.210  | 0.601  | 0.0018 | 0.021  | 0.0077 | 0.024  | 0.273  | Bal.   |

3. Results and Discussion

3.1. Inclusion characteristics
The detected results showed that there was no obvious differences on the inclusion type among the ingots with different C and Mn contents. According to the phase number of inclusion structure, the inclusions in these ingots could be divided into two types: single phase and complex phase. The single-phase inclusions mainly consisted of Al2O3, MnS and Al2O3-MgO. Here, Al2O3-MgO belonged to the single-phase inclusions because of the single structure although it was a hybrid inclusion. The complex-phase inclusions only consisted of Al2O3-MgO-MnS, which had an obvious duplex phenomenon consistently, outer-sphere MnS, and inner-sphere Al2O3-MgO. Such duplex phenomenon also had three types of structures, according to the precipitation characteristics of MnS on the surface of Al2O3-MgO. figure 1 shows the three inclusion structures, including scattered distribution (SD, figure 1A), semi-wrapped structure (SW, figure 1B), and whole-wrapped structure (WW, figure 1C). In this study, the abbreviation symbols, SD, SW and WW, could also represent the inclusions corresponding to their respective wrapping structures. Figure 2 shows the percentage of inclusion types and the average
inclusion size in dependence of type in steel under different contents of C and Mn, which were estimated with the aid of SEM.

Figure 1. Three typical structures for precipitation characteristics of MnS on the surface of Al₂O₃-MgO, A: SD; B: SW; C: WW.

Figure 2. Statistical results on the percentage of inclusion types and the average inclusion size in dependence of type in steel under different contents of C and Mn.
As shown in figure 2A, the total proportion of Al$_2$O$_3$-MgO and SD accounted for the majority, more than 60%, and the percentage of the former inclusion was always higher than that of the latter one. The experimental steels with relatively higher C contents, 0.21 and 0.25wt%, also had a higher proportion on Al$_2$O$_3$-MgO and SD. Correspondingly, the proportions of other inclusions, SW, WW, MnS and Al$_2$O$_3$, were relatively less in these two steels. In terms of the inclusion size, there was no obvious difference for one certain type of inclusion in steels under four C contents as shown in figure 2B. The statistics showed that the size distribution of inclusions ranged from 0.9 μm to 1.2 μm for Al$_2$O$_3$, Al$_2$O$_3$-MgO and SD, from 1.1 to 1.5 μm for MnS and SW, and from 1.6 μm to 1.7 μm for WW. It could be found that the inclusions with a relatively larger proportion of sulfides like MnS, SW and WW, often had a larger inclusion size, compared with the other inclusions. On the whole, there existed a decreased tendency on the inclusions size with the increase of C content in steel.

Figure 2C and D show the statistical results of inclusions in steels corresponding to the different Mn contents. Similar to the situations of steels under different C contents, Al$_2$O$_3$-MgO and SD still counted for the majority of the total amounts of inclusions in steels. Overall, there was a slight decrease tendency on the proportions of these two types of inclusions with the increase of Mn contents in steel. This may had a good relationship with the percentage of MnS in the complex-phase inclusions.

With the increase of Mn content in steel, the percentage of the Mn-bearing inclusions would also increase, which led to a raise in the proportion of inclusions containing the composition MnS. Therefore, the percentage of those inclusions without containing MnS like Al$_2$O$_3$-MgO and Al$_2$O$_3$, decreased accordingly. Meanwhile, some fluctuations also occurred on the inclusion size due to the change of the ratio of MnS in inclusions with the increase of Mn content in steel as shown in figure 2D. There was an obvious increase on the size of MnS-bearing inclusions, especially for the MnS, SW and WW, with the increase of Mn content. Those inclusions without or only containing few proportions of MnS like Al$_2$O$_3$-MgO and Al$_2$O$_3$ had few changes on the size under different Mn contents in steel.

The average inclusion amount per area in these samples was estimated through SEM. The statistic results revealed that the number distribution of inclusions per 1 mm$^2$ on the observed surfaces of the samples with different C or Mn contents, ranged from 490 to 510. Considering the randomness of selected observation surfaces, such differences on the inclusion amount per area among these samples could be ignored.

3.2. Intra-granular acicular ferrites (IAF) nucleation

After etching the polished surface, the inclusions and their surrounding microstructures in the samples could be observed with the aid of SEM. The composition of relevant inclusions was determined through EDS. Figure 3 shows some typical morphologies of IAF induced by inclusions. Some secondary intra-granular acicular ferrites (SIAF) were often found on the branches of IAF as shown in figure 3C and D. The generation of SIAF might help promote the mechanical properties of steel materials via increasing the density and interlocking degree of IAF structures.

**Figure 3.** Morphologies of the IAF induced by inclusions and the main chemical composition of relevant inclusions

The results showed that the majority of IAF induced by inclusions were contributed by the two types of inclusions, Al$_2$O$_3$-MgO and SD, which could act as the effective nucleation cores to induce IAF well. Some of the rest inclusions such as Al$_2$O$_3$, MnS, SW and WW, could also induce IAF, but the percentage
of IAF induced by them only counted for less than one fifth. Considering that those inclusions with a larger percentage on amount, had more possibilities to induce more IAF structures, it could not be ensured that Al$_2$O$_3$-MgO and SD had stronger inducing potencies on IAF compared with the other inclusions. Therefore, another new variable, inducement ratio $f_i$, was defined in this study to develop a kind of quantitative insight on the IAF nucleation potency for one type of inclusion.

$$f_i = \frac{n_i}{N_i} \quad (1)$$

where, $f_i$ represents the inducement ratio which can describe the inducing potency of one type of inclusions $i$. The higher the inducement ratio of one inclusion, the larger the inducing potency of this type of inclusions on IAF. $n_i$ and $N_i$ mean the amount of inclusions $i$ which can induce IAF, and the total amount of inclusions $i$, respectively.

**Figure 4.** Inducement ratio of inclusions on IAF under different mass fractions of C and Mn

According to the Equation (1), the inducement ratios of inclusions in steels with different C or Mn contents are shown in figure 4. As the main nucleation cores to induce IAF, the inducement ratio of Al$_2$O$_3$-MgO was always the highest compared with other inclusions. The inclusions SD had a relatively lower inducement ratio, which indicated that SD had a weaker inducing potency on IAF compared with Al$_2$O$_3$-MgO. Compared with the two inclusions mentioned above, other inclusions such as Al$_2$O$_3$, MnS, SW and WW, had apparently weaker potencies on inducing IAF, and the amount of these inclusions was also relatively less. Thus, the statistics of inducement ratios of these inclusions could be integrated together, which could be found in the item other inclusions in figure 4.

Figure 4A shows the IAF inducement ratios of different inclusions in steels under different C contents. When the mass fraction of C was 0.21wt%, the main nucleation inclusions, Al$_2$O$_3$-MgO and SD, had the highest inducement ratio, 83.6% and 69.2% respectively. Additionally, the amount of these two inclusions among the total inclusions also counted for the largest percentage, 52.0% and 24.9%, which could be found in figure 2A. The lowest inducement ratios of inclusions occurred when the mass fraction of C was 0.13%. Under this C content, the inducement ratios of Al$_2$O$_3$-MgO and SD were 48.2% and 38.9% respectively, and the percentages of the two inclusions were 41.2% and 23.3%. Considering that larger amount of active inclusions (namely Al$_2$O$_3$-MgO and SD) could induce more IAF, the microstructure in the former experimental steel should include a larger percentage of IAF compared with that in the latter steel.

Figure 4B shows the IAF inducement ratios of different inclusions in steels under different Mn contents. The highest inducement ratio of Al$_2$O$_3$-MgO was 62.5% under the mass fraction of 0.26wt%, and under this Mn content, the inducement ratio of SD was 38.2%. The highest inducement ratio of SD was 43.2% under the mass fraction of 0.50wt%, and the inducement ratio of Al$_2$O$_3$-MgO was 51.6% under this Mn content. When the mass fraction of Mn was 0.60wt%, both of Al$_2$O$_3$-MgO and SD had the lowest inducement ratio, and under such Mn content, the two active inclusions also counted for the lowest percentages on amount as shown in figure 2C. It could be indicated that under 0.60wt% in Mn content, the IAF induced by inclusions counted for the minimum percentage.
3.3. Microstructure

Figure 5 shows some typical microstructure morphologies in steels under different mass fractions of C and Mn. The microstructure type was determined according to Chinese Standards GB/T 13320 (2007). These microstructures mainly consisted of three structures: AF, polygonal ferrites (PF) and cementite.

![Microstructure morphologies](image)

Figure 5. Microstructure morphologies in steels under different mass fractions of C and Mn

One type of microstructure often has the particular morphologies, mainly including shape and color. Based on this, the area of each microstructure could be measured with image analysis software, Image Pro. About fifty typical figures of microstructure were selected randomly from the samples in each ingot, and then the area and size of each type of microstructure could be measured with Image Pro. Finally, the percentage and average size of AF could be obtained through averaging the measured data as shown in figure 6.

![Percentage and average size of AF structures](image)

Figure 6. Percentage and average size of AF structures in steels under different C and Mn contents

Figure 6A shows the statistic results of AF structures in steels under different C contents. When the mass fraction of C was ≤ 0.21wt%, the percentage of AF had a smooth increase with the raise of C content, and when the mass fraction of C came to 0.21wt%, the percentage of AF reached the maximum value, 96.0%. The percentage of AF had a decrease tendency with the continuous increase of mass fraction of C. In terms of the AF grain size, with the increase of C content, the average size of AF structures decreased gradually. When the mass fraction of C was ≥ 0.21wt%, the value of AF average size kept steady basically. It was already known that the finer the microstructure, the stronger the mechanical properties of steel materials. Therefore, the microstructure characteristics in steel under 0.21wt% of C content had obvious advantages compared with that under other C contents, due to the largest percentage and relatively finer grain size of AF structures.
Figure 6B shows the characteristics of AF structures in steels under different Mn contents. When the mass fraction of Mn was \( \leq 0.50\text{wt}\% \), the percentage and average size of AF structures only had a slight fluctuation with the increase of Mn content. However, the AF percentage had a sharp decrease, and the average size also became bigger quickly when the mass fraction of Mn increased to be \( \geq 0.50\text{wt}\% \). Namely, the microstructure changed to be worse when the mass fraction of Mn increased excessively.

4. Conclusions

The inclusion in the present experimental steels consisted of single-phase inclusions, Al\(_2\)O\(_3\), MnS and Al\(_2\)O\(_3\)-MgO, and complex-phase inclusions Al\(_2\)O\(_3\)-MgO-MnS. According to the precipitation characteristics of MnS on the surface of Al\(_2\)O\(_3\)-MgO, Al\(_2\)O\(_3\)-MgO-MnS could be divided into three types of inclusions, SD, SW and WW. Under different mass fractions of C or Mn, Al\(_2\)O\(_3\)-MgO and SD counted for the main percentage on amount, more than 60\%. With the increase of C content, the percentages of Al\(_2\)O\(_3\)-MgO and SD had a raise tendency, but the inclusion size of them had few changes. This was mainly related to the decrease on oxide content, which was resulted from the carbon-oxygen reaction. With the increase of Mn content, there was an obvious increase on the size of MnS-bearing inclusions, and the percentage of these inclusions also had a raise tendency.

In the experimental steels, Al\(_2\)O\(_3\)-MgO and SD contributed to the majority of IAF induced by inclusions. They had higher inducement ratios compared with other inclusions, and the values reached the maximum when the mass fractions of C and Mn in steel were 0.21\text{wt}\% and 0.26\text{wt}\% respectively. Due to the relatively stronger inducing potency of active inclusions on IAF, the microstructures in steels under 0.21\text{wt}\% and 0.25\text{wt}\% of C content had finer grain size of AF structures compared with that under other C contents. Compared with the former steel, the latter one had a less percentage in ferrite. There was no obvious distinctions on the microstructure characteristics when the mass fraction of Mn was \( \leq 0.5\text{wt}\% \), but the microstructure became worse with the Mn content increased from 0.5\text{wt}\% to 0.6\text{wt}\%.

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