Effect of Addition ZrO₂ Nanoparticles on Inclusion Characteristics and Microstructure in Low Carbon Microalloyed Steel

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The inclusion characteristics and microstructure in the low carbon microalloyed steel with addition ZrO₂ nanoparticles were investigated by high temperature experiment and metallurgical analysis. The results showed that after ZrO₂ nanoparticles were added, a large number of Zr–Al–Si–O+MnS inclusion, ZrO₂+Al–Si–O+MnS inclusion, and ZrO₂+MnS inclusion appeared in the steel, and these Zr-containing inclusions were effective to induce acicular ferrite (AF) formation. With the amount of added ZrO₂ nanoparticles increased from 0.013% to 0.054%, the inclusions types had no significant effect, but the inclusions size distribution, number density and average diameter were affected. When the addition amount of ZrO₂ nanoparticles was 0.027%, the proportion of large inclusions (larger than 5.0 μm), the inclusions number density and average diameter all were reached the extremum values, respectively 10.81%, 111/mm², 2.62 μm. Moreover, as ZrO₂ nanoparticles adding into steel, the majority solidification microstructure changed from bainitic ferrite (BF) to AF. With the adding amount of nanoparticles increase, the proportion of AF first increased and then decreased, also reached the maximum of 67.65% as the addition amount was 0.027%. Finally, Mn-depletion zone (MDZ) in the vicinity of Zr-containing inclusion was observed, and the MDZ was believed to be one of the possible mechanisms of Zr-containing inclusions inducing AF formation.

KEY WORDS: ZrO₂ nanoparticles; inclusion characteristics; microstructure; acicular ferrite; Mn-depletion zone; low carbon microalloyed steel.

1. Introduction

Nowadays, a good combination of strength and toughness was the development trend of low carbon microalloyed steel. In the commonly used strengthening methods, grain refinement could simultaneously increase the strength and toughness.¹⁾ In terms of grain refinement, researchers found the second phase particles could refine grains, in addition to play a role in precipitation strengthening. With the deepening of the research, the role of the second phase particles in refining the grains was mainly two aspects: on the one hand, the second phase particles could effectively pin the grain boundary during the austenitizing process, weakening the migration and growth of the austenite grain boundary.^{2,3)} On the other hand, when the phase transition occurred during the cooling process, the intragranular second phase particles could induce the acicular ferrite (AF) nucleation, thereby dividing the prior austenite grains and further refining the grains.^{4,5)} However, not all the second phase particles could play the above role. The researchers found the fine dispersed oxides with high melting point could play the above role bet-

ter. In view of the above, the concept of “oxide metallurgy”⁶⁾ was proposed, which used the fine oxides to improving the mechanical properties of steel.⁷⁾ In the study of obtaining the fine dispersed oxides in steel, the different types, combinations and addition amounts of deoxidizers were adjusted.⁸⁾ Ti, Mg, Zr, and Re as the most popular deoxidizing alloying elements, which were often selected to deoxidize alone or in combination to obtain the effective deoxidation products to refine grains.^{9–13)} Ti₂O₃,⁹⁾ MgO,¹⁰⁾ ZrO₂,¹¹⁾ Ti–Zr–O,¹²⁾ and Ti–Re–Zr–O,¹³⁾ they were all confirmed as the effective oxides to induce AF formation and refine grains.

The oxides obtained above were precipitated through internal reaction of steel, which was generally called as internal precipitation method. Correspondingly, there was an external addition method that the oxides added from outside into the molten steel. In 1978, Hasegawa *et al.*¹⁴⁾ first injected the nanoparticles of Al₂O₃ or ZrO₂ into the molten steel by spray-dispersion method. They found the fine dispersion of Al₂O₃ or ZrO₂ of less than 120 nm could effectively improve the strength, hardness and impact toughness of steel. Their research results demonstrated the feasibility of the external addition nanoparticles into steel. Since then, there were many researchers trying in this direction.^{15–21)} Gregg *et al.*¹⁵⁾ developed a technique that made steel samples with controlled

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additions of powered mineral phase. The TiO_2 , Ti_2O_3 , TiN, MnS, MnAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ were chosen as the additive particles, and the experimental results found the Ti oxide particles were the most efficient in inducing AF formation. From then on, the Ti oxide particles were chosen as the main external particles to study by Nedjad *et al.*,¹⁶⁾ Kiviö *et al.*,^{17,18)} Mu *et al.*,¹⁹⁾ Xuan *et al.*,²⁰⁾ and Cai *et al.*²¹⁾ And the main study contents were the Ti oxide particles on controlling the inclusions in steel and the influence of Ti oxide particles on refining grains. In the study of the existence behavior of the additive particles, it could find the added particles could react with other elements to form the new inclusions or act as the nucleation core of other phases (MnS, TiN, *et al.*) during the solidification process, which would change the original inclusion morphology and composition, and affect the original solidification microstructure. Of course, except the Ti oxide particles, MgO nanoparticle also was confirmed as one of effective external particles to refine grains by Yang *et al.*^{22–24)}

ZrO_2 , as a thermally stable oxide, had a similar lattice parameter with MnS.^{11,25)} And addition ZrO_2 nanoparticles into steel would have a great influence on MnS precipitation location and morphology during solidification. However, there was little study on these effects of inclusions and solidification microstructure in low carbon steel. The aforementioned literature¹⁴⁾ showed that adding nano ZrO_2 could effectively improve the proof strength and tensile strength due to the dispersion strengthening of fine particles. When the adding amount of nano ZrO_2 increased from 0 to 1.15%, the increments of proof strength and tensile strength were 79 MN/mm² and 94 MN/mm², respectively. But the effects of nano ZrO_2 addition on inclusions and solidification microstructure were not studied. Dabiri *et al.*²⁶⁾ considered addition ZrO_2 nanoparticles in the electrode coating could improve impact toughness of welds because of the increase in the volume fraction of AF and grain refinement, while

equally for the effects of ZrO_2 nanoparticles on the inclusions and solidification microstructure of the molten pool were not studied. Therefore, the purpose of this paper was to choose the ZrO_2 nanoparticle as additive, add it into high-temperature molten steel, analyze the change pattern of inclusions characteristics (morphology, composition, number density, size distribution, *etc.*) and solidification microstructure, and explore the evolution of inclusions and the mechanism of Zr-containing oxides inducing AF formation.

2. Experimental Procedure

2.1. Pre-dispersion of ZrO_2 Nanoparticles

In order to ensure that ZrO_2 nanoparticles could be successfully added into molten steel, the ZrO_2 nanoparticles were pre-dispersed. **Figure 1** showed the flow diagram of the pre-dispersion process. Firstly, the ZrO_2 nanoparticles (average particles size of 100 nm), absolute ethanol, and iron powder (micron scale) were added into the planetary ball mill (QM-4L, Nanjing Chishun Science and Technology Development Co., Ltd., China) with the ratio 7:100:70 (where ZrO_2 and iron powder were mass fraction, while absolute ethanol was volume fraction). Then in argon atmosphere, the total rotation time of ball mill was 15 hours with the rotation speed of 400 rpm. For the sake of avoiding high temperature arising from particle collisions, the planetary ball mill was set to rotate for 2 minutes and stop for 3 minutes. After finishing the pre-dispersion in planetary ball mill, the damp mixed powder was obtained. Finally, the damp mixed powder was dehumidification drying for 8 hours in vacuum drying oven at 50°C to get the dry mixed powder that the average size was 5.0 μm . **Figure 2** showed the morphology and mapping images of the dry mixed powder. It could be found the elements Zr and O mainly existed in the interior of iron particles, which presented the ZrO_2 coated with iron.

Fig. 1. Flow diagram of the pre-dispersion process. (Online version in color.)

Fig. 2. SEM and EDS analyses of the pre-dispersed ZrO_2 nanoparticles. (Online version in color.)

2.2. Experimental Procedure

In order to facilitate the addition of the dry mixed powder in the experimental process, the machine with sap pressure was used to press the dry mixed powder into cylindrical blocks.²²⁾ The materials of low carbon microalloyed steel used for experiment were cut from the ingot that was prepared by melting in a 30 kg vacuum induction furnace. In each experimental group, about 700 g of material was used. And the high temperature experiments were carried out by MoSi₂ resistance furnace. Firstly, the material was heated to 1 600°C, and held for 10 minutes at this temperature. Then, the different weights cylindrical blocks were added into the molten steel according the different addition amount of ZrO₂. Finally, a molybdenum rod was used to stir the molten steel for 10 seconds every 5 minutes. After the stirring was repeated two times, the samples were cooled in the furnace, with the cooling rate about 2.3°C/min on average during cooling from 800 to 500°C.

In these experiments, three different mass fractions of ZrO₂ nanoparticles, 0.013%, 0.027% and 0.054%, were added into the low carbon steel to investigate. The chemical compositions of these samples were shown in **Table 1**.

2.3. Characterization Methods

When the samples were cooled to ambient temperature, the specimens, which size of 10×10×10 mm, were sectioned at 1/2 radius of these samples. Firstly, these specimens were treated by standard grinding and polishing, and the inclusion characteristics of these specimens were analyzed by using an automatic SEM (EVO18) equipped with an EDS (X-Max-80) and electron microprobe analyses (EPMA). Then these specimens were etched by 4% Nital (volume fraction) to observe the microstructure by optical microscope (OM, OLYMPUS DSX500) and SEM. At the same time, the three-dimensional morphology and element

distribution of inclusions were examined by the manual SEM-EDS.

Thermo-Calc-2017b was used for predicting the inclusions precipitation behavior during solidification and calculating the ferrite formation driving force during austenite decomposition in this paper.

3. Results and Discussion

3.1. Effect of Addition ZrO₂ Nanoparticles on Inclusion Characteristics

Figure 3 showed the morphology and energy spectrum analysis of the typical inclusions in the S-0 steel. From the analysis results, it could be found that for the steel without ZrO₂ nanoparticles addition, the inclusions mainly were Al–Si–O–Mn–S inclusion and MnS inclusion. For these two types of inclusions, MnS could be easily identified as a pure inclusion. While for Al–Si–O–Mn–S inclusion, **Fig. 4** presented the EDS mapping images of this composite inclusion, which elements distribution confirmed this inclusion was a composite inclusion of Al–Si–O coated with MnS.

In order to understand the inclusion evolution during solidification and analyze the reliability of EDS test

Fig. 3. SEM morphologies and compositions of typical inclusions in S-0 steel. (Online version in color.)

Table 1. Chemical composition of experimental steels (mass%).

Samples	C	Si	Mn	S	Cr	Ni	Mo	Al	N	O
S-0	0.158	0.23	0.77	0.0060	0.51	0.59	0.2	0.0023	0.0021	0.0030
S-1	0.157	0.23	0.78	0.0057	0.50	0.59	0.19	0.0021	0.0025	0.0053
S-2	0.158	0.23	0.77	0.0045	0.50	0.59	0.19	0.0021	0.0026	0.0067
S-3	0.161	0.22	0.76	0.0039	0.49	0.59	0.19	0.0025	0.0034	0.0058

Note: S-1: 0.013%; S-2: 0.027%; S-3: 0.054%.

Fig. 4. SEM micrograph and EDS mapping images of Al–Si–O–Mn–S composite inclusion. (Online version in color.)

results, the precipitated inclusions were determined by equilibrium calculations using the commercial software Thermo-Calc-2017b based on the composition of S-0 steel.²⁷⁾ **Figure 5** showed the results of equilibrium calculations of precipitated phase in the S-0 steel. It could be found that a small amount of Corundum phase (Al_2O_3) would be generated in the steel at the initial cooling stage of 1 600°C, because of the higher binding capacity of [Al] and [O] than other elements (such as [Si], [Mn], *etc.*). When the steel was cooled to 1 507°C, the amounts of Corundum phase reached the maximum. But as the temperature continued to decrease, the Corundum phase would react with [Si] and [O], and formed the new Mullite phase (Al_2SiO_5). When the temperature dropped to 1 487°C, all of the Corundum phase was consumed to generate the Mullite phase. At the same time, the liquid phase (SiMnO_3) was formed, but its amount gradually decreased with the decrease of temperature, and finally disappeared at 1 122°C. As the temperature continued dropping, the MnS phase precipitated at 1 430°C. Because there existed a few Mullite phase in steel and the energy of heterogeneous nucleation was lower than homo-

Fig. 5. Equilibrium calculations of precipitated inclusions in steel without addition ZrO_2 nanoparticles. (Online version in color.)

geneous nucleation, MnS phase would be preferentially formed on that, as the composite structure shown in Fig. 3(a). As the calculating temperature dropped to 1 000°C, the inclusions precipitation was basically balanced and the equilibrium phases were mainly MnS phase and Mullite phase (Al_2SiO_5), which constituted the main inclusion types in S-0 steel.

Figure 6 showed the morphology and energy spectrum analysis of the typical inclusions in the steels with addition ZrO_2 nanoparticles. It could be found that except for the typical inclusions of Al-Si-O+MnS and MnS, there were a lot of Zr-containing oxides in these steels. From the analysis results, these Zr-containing oxides were double-layer composite structure or three-layer composite structure. For the sake of obtaining the elements distribution, the EDS mapping images of elements were carried out, as shown in **Fig. 7**. As the EDS mapping images results showed, for inclusions in the Figs. 6(c) and 6(e), they were mainly double-layer composite inclusions, with Zr-Al-Si-O or ZrO_2 at the center and MnS wrapped in the outer layer. While for inclusions in Fig. 6(d), there were three layers: ZrO_2 in the core, Al-Si-O in the sub-outer layer and MnS wrapped in the outer layer. Moreover, it could be seen from the morphology of inclusions that the size of these Zr-containing oxides was about 2–3 μm , which was much smaller than that of the oxides in S-0 steel that didn't addition ZrO_2 nanoparticles.

Figure 8 showed the evolution of inclusions in the steels with addition ZrO_2 nanoparticles, which was obtained based on the thermodynamic calculation of Fig. 5 and the EDS mapping images of Zr-containing composite oxides of Fig. 7. As mentioned above, in the initial stage of 1 600°C, the dissolved [Al] in the steel would first react with [O] to generate Al_2O_3 , and the addition of ZrO_2 nanoparticles would not have a significant effect on it. However, as the temperature decreased, more Al_2O_3 would be formed, and some of the subsequent Al_2O_3 would preferentially precipitate on the ZrO_2 particles in the form of heterogeneous nucleation, forming $\text{Al}_2\text{O}_3 + \text{ZrO}_2$ composite inclusion. With the temperature continues to decrease, Al_2O_3 would react

Fig. 6. SEM morphologies and compositions of typical inclusions in steels with addition ZrO_2 nanoparticles. (Online version in color.)

Fig. 7. SEM micrograph and EDS mapping images of Zr-containing composite oxides. (Online version in color.)

Fig. 8. Evolution of inclusions after addition ZrO_2 nanoparticles. (Online version in color.)

with $[\text{Si}]$ and $[\text{O}]$ to form Al_2SiO_5 , as mentioned previously. Some of the new formed Al_2SiO_5 would precipitate heterogeneously with ZrO_2 particles as nucleation core, forming $\text{ZrO}_2 + \text{Al}_2\text{SiO}_5$ composite inclusions, and the others would react with ZrO_2 particles to form Zr-Al-Si-O inclusions. Therefore, before the precipitation of MnS , there were a large number of Zr-containing oxides in the steels, as ZrO_2 , Zr-Al-Si-O and $\text{ZrO}_2 + \text{Al}_2\text{SiO}_5$. When MnS began to precipitate, except to nucleate on Al_2SiO_5 , MnS would preferentially nucleate on these Zr-containing oxides and

generate Zr-containing oxides + MnS composite inclusions, as the Figs. 6 and 7 showed.

From the above analysis results, the addition of different amounts of ZrO_2 nanoparticles had no significant effect on the types of inclusion in the low carbon microalloyed steel. However, it had a certain effect on the size distribution, number density and average size of inclusions. **Figure 9** showed the inclusion characteristics in these experimental steels. From the inclusions size distribution, it could be seen that with the increase of ZrO_2 nanoparticles addition,

Fig. 9. Characteristics of the inclusions in experimental steels (a) Size distribution of inclusions; (b) Number density and average size of inclusions. (Online version in color.)

Fig. 10. Microstructures of the experimental steels with different magnifications (a), (e), (i) S-0 Steel; (b), (f), (j) S-1 Steel; (c), (g), (k) S-2 Steel; (d), (h), (l) S-3 Steel. (Online version in color.)

the proportion of large size inclusions (larger than $5.0 \mu\text{m}$) in steel first decreased and then increased, while that of small size inclusions (less than $1.0 \mu\text{m}$) showed the opposite trend, that was, first increased and then decreased, all reaching the extremum values when the addition amount of ZrO_2 nanoparticles was 0.027%. Moreover, when the addition amount of ZrO_2 nanoparticles was more than 0.027%, the proportion of large size inclusions in steel increased obviously, which might be due to the increase of the collision growth probability of particles by adding more ZrO_2 nanoparticles. Figure 9(b) presented the number density and the average diameter of inclusions in the experimental steels. It could be found that with the addition amount of ZrO_2 nanoparticles increased from 0 to 0.027%, the number of inclusions per unit area increased from $67/\text{mm}^2$ to $111/\text{mm}^2$, while the average diameter of inclusion decreased from $2.94 \mu\text{m}$ to $2.62 \mu\text{m}$. When the addition amount of

ZrO_2 nanoparticles was large 0.027% and increased to 0.054%, we could find the average diameter of inclusions increased to $3.96 \mu\text{m}$, and the number of inclusions per unit area decreased to $70/\text{mm}^2$. The variation laws of number density and the average diameter of inclusions were similar to that of inclusion size distribution, which could be considered addition excessive ZrO_2 nanoparticles (more than 0.027%) resulted in their agglomeration and clusters floating on the air-steel interface.²⁴⁾ Particles collision resulted in an increase in the proportion of large inclusions, and the floating of large inclusions resulted in a decrease in the number of inclusions.

3.2. Effect of Addition ZrO_2 Nanoparticles on Microstructure and AF Formation

Figure 10 showed the solidification microstructure of the experimental steels with different magnifications. It could

be seen from the Figs. 10(a)–10(d) that with the increase of ZrO_2 nanoparticles addition amount, the grain size of the prior austenite decreased gradually, which could be presented by the grain boundary ferrite (GBF). The reduction in the austenite grain size would increase the nucleation position of GBF and Widmanstätten ferrite (WF), which resulted in a decrease in the proportion of intragranular ferrite (IGF).^{28,29} For the WF, it nucleated on grain boundary or GBF, and grew into austenite matrix.³⁰ In order to analyze the main types of IGF, the microstructure magnification was increased to 1 000 times, and the detailed morphology of IGF could be easily distinguished under OM. For the S-0 steel without addition ZrO_2 nanoparticles, the main types of IGF were intragranular bainitic ferrite (BF) and polygonal ferrite (PF). For the BF, it nucleated entirely in the austenite grain and appeared as parallel growth of multi-strip ferrite, which morphology was similar to WF.³⁰ With the addition of ZrO_2 nanoparticles, AF began to appear in the microstructure, and when the addition amount increased to 0.027%, the BF barely observed in the microstructure, the proportion of AF reached the maximum. However, when the addition amount increased to 0.054%, the proportion of AF decreased and a large number of PF appeared in the grain. For the sake of analyzing the proportion change of different types of IGF with the addition amount of ZrO_2 nanoparticles, the method of systematic manual point count basing on the ASTM-E562-02 standard was selected for statistics. To reduce the errors, at least 10 images for each sample were chosen. The statistical results were shown in Fig. 11. It could be found with the amount of ZrO_2 nanopar-

ticles added increasing from 0 to 0.054%, the proportion of BF and PF first decreased and then slightly increased. When the addition amount of ZrO_2 nanoparticles was 0.027%, they were reached the minimum, 6.96% and 6.98% respectively. However, for the proportion of AF, with the increase of ZrO_2 nanoparticles addition amount, it presented the opposite rule, first increased and then decreased, and also reached the maximum of 67.65% when the addition amount was 0.027%.

Figure 12 presented the morphology and EDS mapping images of Zr-containing inclusions inducing AF formation

Fig. 11. Proportion of different intragranular ferrite types in experimental steels. (Online version in color.)

Fig. 12. The SEM micrograph of AF lath and EDS mapping images of the effective inclusion (a) $\text{ZrO}_2 + \text{Al-Si-O} + \text{MnS}$ inclusion; (b) $\text{Al-Si-Zr-O} + \text{MnS}$ inclusion; (c) $\text{ZrO}_2 + \text{MnS}$ inclusion. (Online version in color.)

in the experimental steels with ZrO_2 nanoparticles addition. For these inclusions inducing AF formation, they were all composite inclusions containing MnS, but the existence forms of MnS were different. Some of them were in the form of outer layer interspersed composite (as shown in Fig. 12(a)), some were in the form of parallel composite (as shown in Fig. 12(b)), and some were in the form of outer layer completely wrapped (as shown Fig. 12(c)).

The mechanisms of intragranular effective inclusions inducing AF formation were generally believed as follows: (1) inclusion as effective interface reduced the energy barrier of ferrite formation;³¹⁾ (2) thermal strain at inclusions increased the driving force of ferrite formation;³²⁾ (3) low lattice misfit between inclusion and ferrite reduced the energy barrier of ferrite formation;³³⁾ (4) Depletion of austenite stable elements (such as Mn,¹⁵⁾ C,³⁴⁾ etc.) or enrichment of ferrite stable elements (such as P,³⁵⁾ Si,³⁶⁾ etc.) near inclusions increased the driving force of ferrite formation. Among of them, the mechanism (1), inclusion as effective interface, was independent of the inclusion composition and was only related to the inclusion size. Our previous study¹²⁾ calculated that the critical diameter of inclusion inducing AF formation was 0.21–0.37 μm in low carbon steel. This meant that when the inclusion size was larger than the critical size, the inclusion could act as the effective inclusion that reduced the energy barrier of ferrite formation. However, in fact, not all inclusions larger than the critical size could be used as AF nucleation core, such as the inclusion in the steel without addition ZrO_2 nanoparticles. Thus, it could be seen that the inclusion size larger than the critical size was only a necessary condition but not a sufficient condition. Moreover, for the mechanism (2), the thermal strain energy would produce

in the vicinity of inclusion during cooling process, which could promote the ferrite formation. But, Lin *et al.*¹⁰⁾ found the strain energy was much smaller than the ferrite formation driving force, which was gradually considered as a non-main mechanism. Therefore, with the development of exploratory research, the single theory of above could not fully explain the intragranular inclusion inducing AF formation, often two or more theories worked together.^{10,35–37)}

From above discussion, MnS precipitated at the Zr-containing oxides out layer, and the Mn-depletion zone (MDZ) might be one of reasons for Zr-containing inclusion inducing AF formation. EPMA was used for linear scanning analysis to detect the variety of Mn content in the vicinity of Zr-containing inclusions, and the result was presented in Fig. 13. It was important to note that in order to avoid the gap existing near the inclusions after etched, in this study, non-etching samples were selected for line analysis of Zr-containing inclusions. It could be seen that there were MDZs in the vicinity of Zr-containing inclusions, and the width of MDZ was 0.2–0.5 μm . General speaking, Mn was an austenite stable element, and the variety of its content in the local region had a great influence on the austenite decomposition and ferrite formation.³⁸⁾ In this regard, the effect of variation of Mn content on the driving force of γ/α transformation was calculated with the composition of S-1 steel by the thermodynamic software, Thermo-Calc-2017b. The calculation results were shown in Fig. 14. It could be seen that the formation of MDZ in the vicinity of inclusion could obvious increase the ferrite formation driving force. The similar result was also reported by Mu *et al.*³⁹⁾ Compared with reference,³⁹⁾ for the same Mn content, the ferrite formation driving force in this study was slightly smaller due to

Fig. 13. Elements line analyses of Zr-containing inclusion in the steels with ZrO_2 nano particles addition (a) ZrO_2 +MnS inclusion in S-1 steel; (b) ZrO_2 +Al-Si-O+MnS inclusion in S-2 steel. (Online version in color.)

Fig. 14. Ferrite formation driving force calculated at 700°C according to difference Mn contents in the S-1 steel.

the difference of other matrix compositions. But the effect of the unit Mn content change on the ferrite formation driving force was almost same. In this study, when the Mn content near inclusions decreased 0.1%, the driving force of ferrite formation increased 5.85 J/mol. Of course, for the specific value of Mn content variety near Zr-containing inclusions in this study, we still need to conduct in-depth detection and analysis using transmission electron microscope with high resolution, which is one of our next research contents.

4. Conclusions

The inclusion characteristics and microstructure in the low carbon microalloyed steels with addition the pre-dispersion ZrO₂ nanoparticles were investigated by high temperature experiment and metallurgical analysis. The results obtained were as follows:

(1) After ZrO₂ nanoparticles were added, a large number of Zr–Al–Si–O+MnS inclusion, ZrO₂+Al–Si–O+MnS inclusion, and ZrO₂+MnS inclusion appeared in the steels, and these Zr-containing inclusions were effective to induce AF formation.

(2) The amount of added ZrO₂ nanoparticles had no obvious effect on inclusion types, but had a great influence on the size distribution, the number density and the average diameter of inclusions. When the addition amount of ZrO₂ nanoparticles was 0.027%, the proportion of large inclusions (larger than 5.0 μm), the inclusions number density and average diameter all were reached the extremum values, respectively 10.81%, 111/mm², 2.62 μm.

(3) As ZrO₂ nanoparticles adding into steel, the majority solidification microstructure changed from BF to AF. With the addition amount of nanoparticles increase, the proportion of AF first increased and then decreased, and reached the maximum of 67.65% as the addition amount was 0.027%.

(4) MDZ in the vicinity of Zr-containing inclusion was observed, and the MDZ was believed to be one of the pos-

sible mechanisms of Zr-containing inclusions inducing AF formation.

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