

Article

Inclusion and Microstructure Characteristics in a Steel Sample with TiO₂ Nanoparticle Addition and Mg Treatment

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Abstract: TiO₂ nanoparticles and Mg alloy were added to molten steel in sequence to investigate the inclusion and microstructure characteristics. Compared with a non-treated sample, these additives resulted in the formation of Ti–Mg-bearing inclusions, which proves that the additives were valid. The size evolution from nanometer-scale TiO₂ to micrometer-scale oxides hints at the agglomeration and growth of the TiO₂ nanoparticles, which is due to the possible formation of a liquid-capillary force, the decomposition reaction of TiO₂, and the higher Gibbs free energy of the nanoparticle. Furthermore, the statistical analysis of the oxides indicated that with the addition of the TiO₂ nanoparticles and Mg alloy, the oxides were refined and their density was higher. Few pure MnS were observed in the treated sample. This is due to the fact that most oxides separated out in the liquid region at 1873 K based on the oxide composition and the calculated Al₂O₃–Ti₃O₅–MgO phase diagram. Thus, MnS preferred to segregate on them during solidification. After etching, it was found that the Ti–Mg-bearing oxide can induce the nucleation of intragranular acicular ferrites. The appearance of these acicular ferrites was not observed in the non-treated sample. This comparison indicates the effectiveness of the external adding method in oxide metallurgy.

Keywords: oxide metallurgy; intragranular acicular ferrite; external adding method

1. Introduction

In 1990, the concept of oxides metallurgy was proposed by Takamura and Mizoguchi [1]. This technology utilizes fine inclusions to induce the nucleation of intragranular acicular ferrites (IAF) during austenite–ferrite transformation. This microstructure is desired in low-alloyed carbon steel and weld metals because IAF can enhance both strength and toughness [2].

Specific kinds of inclusions have been suggested as effective sites for IAF nucleation [3]. To introduce them into steel, the internal precipitation method (IPM) [4] and the external adding method (EAM) [5] have been adopted. The former means that preferred inclusions form during either de-oxidation or solidification processes. The latter means that pre-prepared particles are directly added into steel. At present, the Ti-bearing and Mg-bearing inclusions are the focus of this EAM study [6–12].

Recently, Ti–Mg complex inclusions have attracted much attention. Chai et al. [13] pointed out that the complex treatment of Ti–Mg can refine inclusions, and make inclusion size range more favorable to induce IAF nucleation. Zheng [14] indicates that due to the dual effects of Ti and Mg deoxidation, a large amount of finely dispersed Al₂O₃–TiO_x–MgO inclusions were formed, which can induce the nucleation of interlocking IAFs. Recently, grain refinement in the coarse-grained heat-affected zone of

the Al–Ti–Mg complex in deoxidized steel was studied by Li et al. [15]. Additionally, an Mn-depletion zone (MDZ) mechanism has been proposed by several groups to explain the IAF nucleation effect induced by Ti–Mg inclusions [15–18].

Until now, the Ti–Mg inclusions in steel were all generated through IPM. Our group [19] has tried to introduce MgTiO_3 powder into molten steel, with the aim of utilizing its decomposition reaction to form Ti–Mg complex inclusions. However, only Ti-bearing inclusions were observed, while Mg-bearing inclusions were absent. So in this paper, TiO_2 nanoparticles and Mg alloy were added into molten steel in sequence to form Ti–Mg inclusions by a combination of EAM and IPM. The resulting inclusion and microstructure characteristics were explored. Among many kinds of Ti-bearing oxides, TiO_2 was chosen because Mu et al. [6] have indicated that the TiO_2 powder is a good candidate to add into liquid steel as an additive to induce intragranular ferrite formation.

2. Materials and Methods

Electrical iron (about 1500 g) was used as raw material and put in an alumina crucible. This alumina crucible was located inside a graphite crucible in a high-heat tube-type resistance furnace (XD-1700VCB, T-Long Equipment Co. Ltd, Zhengzhou, China). The experimental temperature was 1873 K, and Ar gas (purity > 99.999%) was used to maintain the inert atmosphere of the chamber.

Firstly, when melting was done, an appropriate amount of Fe_2O_3 was added to reduce the acid-soluble aluminum (Al_s) content since a previous study [15] has indicated that compared with high Al steel, Al–Ti–Mg oxides formed preferentially in low Al steel and promoted IAF nucleation.

Secondly, Si alloy (Si: 72%, mass percentage), Mn alloy (Mn: 97%, mass percentage), preprepared powder mixture, and Mg alloy (Mg: 34%, mass percentage) were added into molten steel in sequence. The time interval between the two additions was 10 minutes. It can be seen that the powder mixture dissolved into the molten steel quickly. It should be mentioned that the preparation of the powder mixture consisted of two steps. At first, approximate TiO_2 nanoparticles (Aladdin, purity > 99.95%, size < 50 nm) and pure iron powder were weighed, and their mass ratio was 1:1. Then planetary ball milling was used to mix them for 3 hours in order to achieve a homogeneous composition.

Thirdly, after stabilizing the molten steel for about 10 min at 1873 K, the crucible was taken out. After solidification, the sample was quenched in water and named the EAM-treated sample. It should be mentioned that the sample surface was smooth and no laminations were observed.

The Al_s , Mg, and Ti contents were measured by the method of ICP-AES in NCS Testing Technology Co., Ltd (China National Analysis Center for Iron and Steel, Beijing, China). Its composition in mass percentage was C: 0.05%, Si: 0.19%, Mn: 1.1%, P: 0.01%, S: 0.005%, Al_s : 0.0036%, Ti: 0.0081%, and Mg: 0.0049%. Moreover, to clarify the influence of the additives on inclusion and microstructure, a non-treated sample without the addition of TiO_2 and Mg was also prepared during the same experimental procedure. Its composition in mass percentage was measured as C: 0.03%, Si: 0.11%, Mn: 1.1%, P: 0.01%, S: 0.004%, and Al_s : 0.059%.

The morphology and composition of the inclusions were characterized using a scanning electron microscope (SEM: JSM-6510LV, JEOL, Tokyo, Japan) and an energy dispersive spectrometer (EDS: INCA Feature X-Max 20, OXFORD Instruments, Oxford, UK). The data processing for EDS point analysis was carried out according to Wang et al. [20]. Firstly, iron was excluded to eliminate the contribution of signals from the steel matrix. Then oxygen was ruled out due to insufficient accuracy. Finally, the content of the remaining elements was normalized to 100%, and reported in mass percentage.

The INCA Feature software (OXFORD Instruments, Oxford, UK) was applied to automatically find and analyze inclusions in the preselected area. Considering accuracy, only the inclusions, whose size was larger than 0.5 μm , were taken into account. It should be mentioned that the inclusion size is its equivalent circle diameter.

3. Results and Discussion

The typical micrometer-scale oxides for the EAM-treated sample are shown in Figure 1, and the corresponding results of the EDS point analysis (mass percentage, and elements of Fe and O are excluded) are presented in Table 1. It should be mentioned that submicron inclusions were also found in this sample and nanometer-scale inclusions could not be observed due to the accuracy limits of SEM. However, many micrometer-scale inclusions still indicate the agglomeration and growth of the TiO_2 nanoparticles. In fact, similar results have been reported by Mu et al. [21]. They found that for the original TiO_2 powders, the particle size range was 0.139–0.854 μm , and after adding into molten steel, the inclusion size range became 0.215–4.802 μm . Furthermore, the typical oxides for the non-treated sample are also shown in Figure 2, and the corresponding results of the EDS point analysis are presented in Table 2. It can be seen that the main type of oxide changed from Al–O for the non-treated sample to Ti–Mg–Mn–Al–O for the EAM-treated sample. This can be explained by the following three reasons.

Firstly, the wettability measurement for the TiO_2 /pure Fe system at 1813 K showed that a TiO_x –FeO melting region was formed (liquid at 1813 K) [22]. Xuan [22] further indicates that for the liquid steel with high oxygen content and a TiO_2 particle addition, the liquid TiO_x –FeO might provide a liquid-capillary force. Previous calculation [23] has pointed out that the strong agglomeration behavior of Al_2O_3 originates from the liquid-capillary force due to the FeO liquid bridge. In our experiment, TiO_2 nanoparticles were mixed well with pure iron powder. Thus, a similar inclusion agglomeration may be expected.

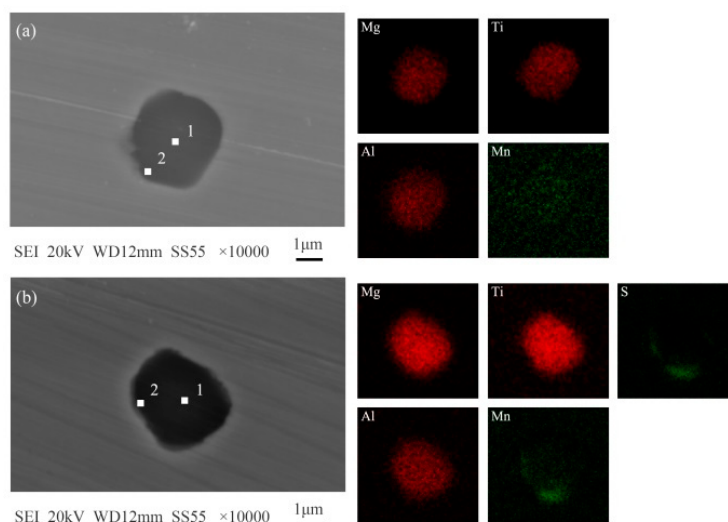


Figure 1. SEM micrographs and energy dispersive spectrometer (EDS) mapping images of various elements for typical oxides in the external adding method (EAM)-treated sample. (a) typical oxide 1 (b) typical oxide 2.

Table 1. EDS point analysis of oxides for the EAM-treated sample shown in Figure 1 (mass percentage).

Figure	Position	Ti	Mg	Al	Mn	S
1a	Point 1	41.98	33.50	17.89	6.63	-
	Point 2	35.04	37.39	21.31	6.26	-
1b	Point 1	39.94	34.78	18.02	7.26	-
	Point 2	22.00	28.45	13.68	23.23	12.64

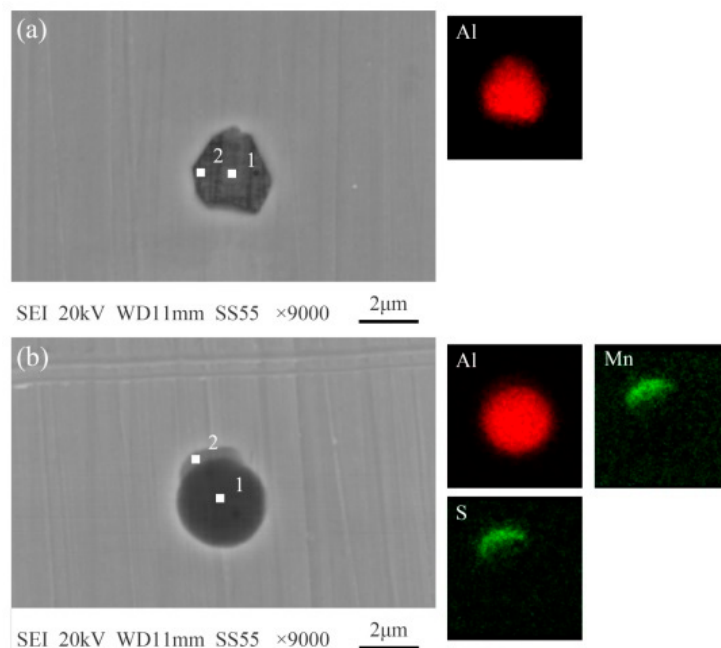


Figure 2. SEM micrographs and EDS mapping images of various elements for typical oxides in the non-treated sample. (a) typical oxide 1 (b) typical oxide 2.

Table 2. EDS point analysis of oxides for the non-treated sample shown in Figure 2 (mass percentage).

Figure	Position	Al	Mn	S
2a	Point 1	100	-	-
	Point 2	100	-	-
2b	Point 1	94.69	3.45	1.86
	Point 2	24.12	47.23	28.65

Secondly, Miia et al. [24] found that TiO_2 was first reduced to Ti_3O_5 in liquid steel at high temperature and then to Ti_2O_3 during cooling at around 1573 K. These reactions liberate oxygen, which may react with other elements to form complex Ti-bearing inclusions. On the one hand, the reaction with Al remarkably decreased the Al_s content. On the other hand, this leads to inclusion growth.

Thirdly, TiO_2 nanoparticles were used in our experiment. Compared with bulk TiO_2 , they have a higher Gibbs free energy per mole due to the Gibbs–Thomson effect, that is, increased surface free energy per unit volume [8]. The increased Gibbs free energy per mole of spherical particle is shown in Equation (1) [8].

$$\Delta G = 2\gamma V_m / r \quad (1)$$

where γ is the specific surface energy of the particle, V_m is the molar volume, and r is the particle radius. Assuming $\gamma = 0.375 \text{ N}\cdot\text{m}^{-1}$ (2073 K) [25], $V_m = 19.6 \times 10^{-6} \text{ m}^3\cdot\text{mol}^{-1}$ [8], and $r = 50 \text{ nm}$ for the TiO_2 nanoparticles, ΔG is determined to be about $294 \text{ J}\cdot\text{mol}^{-1}$. Accordingly, it means that the chemical driving forces increase for both TiO_2 decomposition and reaction with Fe.

This indicated that due to the possible formation of the liquid-capillary force, decomposition reaction of TiO_2 , and higher Gibbs free energy of the nanoparticle, inclusion agglomeration and growth occurred, causing TiO_2 nanoparticles to become micrometer-scale Ti-bearing inclusions. Moreover, Zhang et al. [26] have indicated that if there is a trace of dissolved magnesium in the liquid steel, the Al_2O_3 – Ti_3O_5 system inclusions will be unstable and change into Al_2O_3 – Ti_3O_5 – MgO system inclusions. This was consistent with the results of the elements mapping in Figure 1.

To further explore the inclusion characteristics, INCA Feature was applied to statistically analyze 1335 oxides. Results indicated that Ti exists in 97% of the oxides (number percentage), and its average content is about 16.8% (mass percentage, and elements of Fe and O are excluded). This further confirms the validity of TiO_2 adding.

Previous studies have shown that Mg addition can refine oxide. To confirm this effect, the relationship between the oxide size and number density of the EAM-treated sample was compared with that of the non-treated sample and Ti IPM-treated sample (mass percentage, C: 0.04%, Si: 0.20%, Mn: 1.15%, P: 0.01%, S: 0.005%, Al_s : 0.0031%, and Ti: 0.0064%), which is shown in Figure 3. It is clearly found that with complex treatment of EAM and IPM, the oxides were refined and their density was higher.

It should be mentioned that besides element type and content, other factors, such as oxygen content, cooling rate, etc., also affect the oxide formation [27]. Thus, the focus on a single sample may be more suitable since it can keep different variables as constant as possible. In our sample, the average size of the Mg-bearing oxides was 2.5 μm , and that of the non-Mg-bearing oxides was 4.7 μm . Obviously, the Mg-bearing oxide is refined, which is consistent with previous studies.

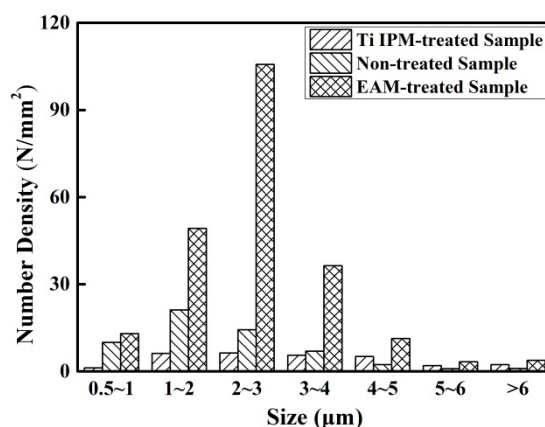


Figure 3. The relationship between oxide size and number density in an EAM-treated sample, a non-treated sample, and a Ti internal precipitation method (IPM)-treated steel sample.

In fact, the oxide characteristics also influenced the features of the MnS. It is known that due to the high concentration product ($a_{[\text{Mn}]} \times a_{[\text{S}]}$, where a is activity), MnS cannot form in molten steel. However, during the solidification process, the concentration product decreases and element segregation occurs. This leads to the MnS segregation. In fact, two types of MnS can be formed. The first is heterogeneous nucleation of MnS on solid substrate in molten steel, which results in sulfur accumulation around the inclusions. The second is pure MnS, which means no other elements coexist with Mn and S. A typical sample of the former is shown in Figure 1b. The INCA Feature software has analyzed the inclusions (size > 0.5 μm) in the area of 5.99 mm^2 . There were 1335 oxides observed, and sulfur was found in 80% of the oxides (number percentage). While only one pure MnS inclusion was observed. This may be due to the essential prerequisite of MnS segregation.

From the view of the oxide features, MnS prefers to heterogeneously nucleate on solid inclusions in molten steel. To assess whether the oxides were in or out of the low melting point region, analysis was carried out, which consisted of two steps. Firstly, the phase diagram and liquid area of the Al_2O_3 – Ti_3O_5 – MgO system were calculated using thermochemical software FactSage 7.2, (Thermfact/CRCT, Montreal, Canada and GTT-Technologies, Aachen, Germany), as shown in Figure 4. The choice of Ti_3O_5 was based on previous research [26], which indicated that the deoxidized product is usually Ti_3O_5 at the common concentrations of titanium and oxygen in the steel production process. Additionally, Miia et al. [24] also pointed out that TiO_2 was first reduced to Ti_3O_5 in liquid steel. Secondly, the INCA Feature analysis results of the oxides were converted into mass percentages

of Ti_3O_5 , MgO , and Al_2O_3 , which were then projected into the calculated Al_2O_3 – Ti_3O_5 – MgO phase diagram, as given in Figure 4. It can be seen that most oxides separated out in the liquid region at 1873 K, which means that they were solid in molten steel. Furthermore, the high density of the oxides provided enough nucleation sites. Thus, MnS preferred to segregate on the oxides and pure MnS was absent.

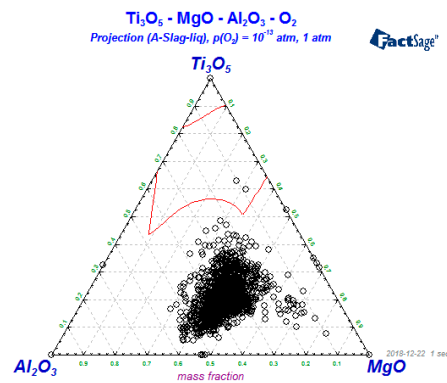


Figure 4. Composition distributions of inclusions in the Al_2O_3 – MgO – Ti_3O_5 phase diagram under $P_{\text{O}_2} = 10^{-13}$ atm. Dotted lines represent the liquidus line (1873 K).

Figure 5a,b shows the EAM-treated sample's optical microstructure after etching in 3Vol% Nital solution. The interlocking appearance was observed among the prior austenite grain boundaries, and some IAFs were formed independently at large-angle boundaries to each other. This appearance was similar to the typical microstructure in Ti-contained steel with IPM treatment [3], and totally different from that in the non-treated sample (shown in Figure 5c,d). To explore the nature of the IAF nucleation, the measurements of SEM and EDS were taken. The results seen in Figure 6 confirmed that inclusions in the EAM-treated sample induced the IAF nucleation. It can be seen that several laths emanated from a single Ti–Mg bearing inclusion, while no nucleation phenomena were observed around Al–O oxide in the non-treated sample (shown in Figure 7). The corresponding results of the EDS point analysis for Figures 6 and 7 are presented in Tables 3 and 4, respectively. The non-treated sample was prepared without the addition of TiO_2 and Mg during the same experimental procedure. Thus, these comparisons confirmed the positive effect of the external adding method in oxide metallurgy.

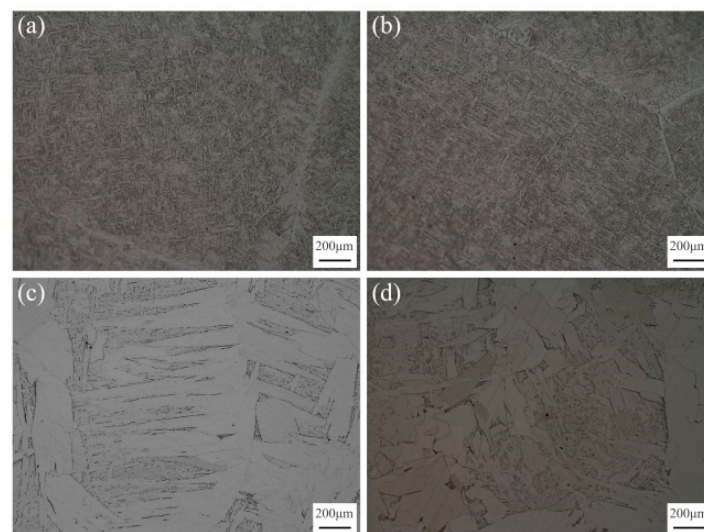


Figure 5. (a,b) The EAM-treated sample's optical microstructure. (c,d) The non-treated sample's optical microstructure.

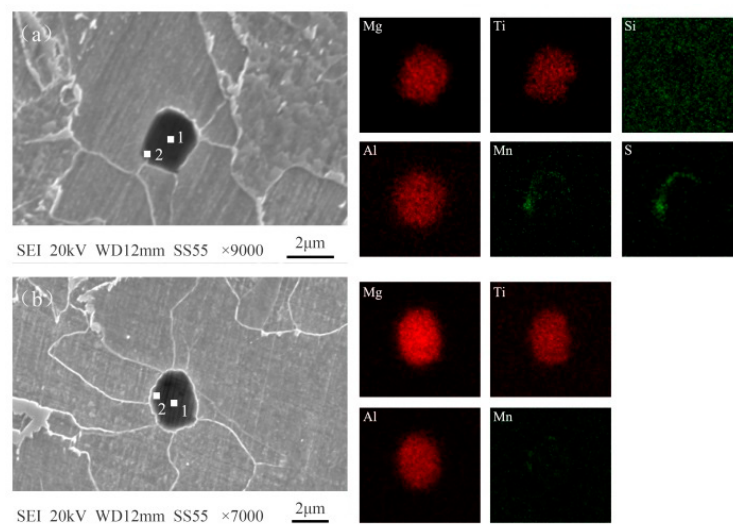


Figure 6. The SEM micrographs and EDS mapping images for typical oxides in the EAM-treated sample after etching. (a) typical oxide 1. (b) typical oxide 2.

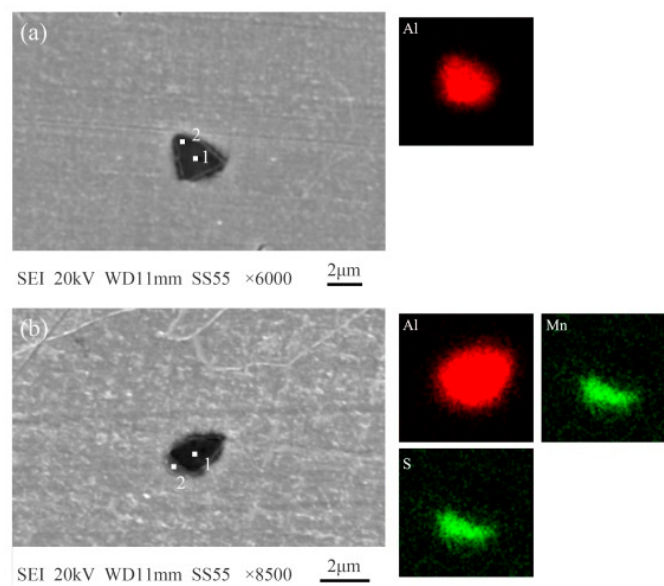


Figure 7. The SEM micrographs and EDS mapping images for the typical oxide in the non-treated sample after etching. (a) typical oxide 1. (b) typical oxide 2.

Table 3. EDS point analysis of oxides for the EAM-treated sample after etching shown in Figure 6 (mass percentage).

Figure	Position	Ti	Mg	Al	Mn	S	Si
6a	Point 1	26.93	41.44	25.91	5.72	-	-
	Point 2	19.29	31.87	18.45	18.75	9.44	2.20
6b	Point 1	23.36	43.02	28.65	4.97	-	-
	Point 2	19.13	46.40	29.29	5.18	-	-

Table 4. EDS point analysis of oxides for the non-treated sample after etching shown in Figure 7 (mass percentage).

Figure	Position	Al	Mn	S
7a	Point 1	100	-	-
	Point 2	100	-	-
7b	Point 1	91.15	5.31	3.54
	Point 2	24.56	45.89	29.55

Until now, different mechanisms have been proposed to explain why oxides can promote IAF nucleation [2], such as inert surface, lattice disregistry, thermal coefficient, and Mn-depletion zone. Among them, the MDZ mechanism has been widely accepted. This mechanism is based on the assumption that inclusions can absorb neighboring Mn atoms from the Fe matrix. If a corresponding supplement is not applied, an Mn-depletion zone will be formed in the Fe matrix around the inclusion. This promotes the nucleation of ferrites since Mn is the stabilizer of austenite.

Table 3 indicates that Ti, Mg, and Al were the major elements in the oxide. Although the exact composition was unknown, Ti_2O_3 , $MgAl_2O_4$, and $MgTi_2O_4$ may coexist in the inclusion. To discuss this clearly and concisely, they were analyzed separately. The detailed discussions are shown below.

For Ti_2O_3 , Auger electron spectroscopy observation suggests that Ti_2O_3 in steel can be denoted as $Ti_{(2-0.052)}O_3$ with cation vacancies [28]. In addition, the effective ionic radius of Mn (six-coordinated Mn^{3+} : 0.0645 nm for high-spin state) is similar to that of Ti (six-coordinated Ti^{3+} : 0.067 nm) [29]. Thus, Ti_2O_3 can absorb neighboring Mn atoms from the Fe matrix. Moreover, the thermodynamic analysis of the MDZ near Ti oxides for intragranular nucleation of ferrite in steel has been carried out by Kang et al. [30].

For $MgTi_2O_4$, first-principle calculations have indicated that it can absorb Mn atoms, which occupy Mg sites in the crystal structure [16].

For $MgAl_2O_4$, its ability to absorb neighboring Mn is still under discussion. On the one hand, the first-principle calculations have indicated that $MgAl_2O_4$ only has very weak ability to absorb Mn atoms [16]. On the other hand, magnesium vacancy is one of its intrinsic defects [31], and the effective ionic radius of Mg (four-coordinated Mg^{2+} : 0.057 nm) is similar to that of Mn (four-coordinated Mn^{2+} : 0.066 nm for high-spin state) [29]. It should be mentioned that the coordination number of Ti^{3+} in Ti_2O_3 is 6, while that of Mg^{2+} in $MgAl_2O_4$ is 4. As for Mn, its values of effective ionic radius are listed according to the corresponding coordination number and valence state. In fact, Mn doping on the Mg site in $MgAl_2O_4$ has been well studied, and the doping concentration is 50% or higher, such as $Mg_{0.5}Mn_{0.5}Al_2O_4$ [32]. Thus, the absorption of Mn by $MgAl_2O_4$ may be feasible. In fact, the existence of an MDZ around Mg–Al–O has been qualitatively verified by previous studies [33,34].

Due to these factors, the Ti–Mg-bearing inclusion may absorb Mn atoms from the surrounding steel matrix, which leads to the MDZ formation. In 2018, Li et al. [15] indicated that in Al–Ti–Mg killed steel with low Al content, the MDZ is formed by the combined effect of the precipitation of MnS and diffusion of Mn atoms into TiO_x and $MgTiO_x$. In our sample, the Al content was as low as 36 ppm and $MgTiO_x$ was also found. These hint that a similar absorption may occur, which promotes acicular ferrite nucleation.

4. Conclusions

TiO_2 nanoparticles and Mg alloy were added into molten steel in sequence to investigate the inclusion and microstructure characteristics. Compared with bulk powder, nanoparticles have a higher Gibbs free energy, which promotes TiO_2 decomposition and reactivity with Fe. The former liberated oxygen, which may generate complex Ti-bearing inclusions. The latter resulted in a TiO_x –FeO melting region, which may enhance the inclusion agglomeration. These led to the formation of micrometer-scale Ti-bearing inclusions. The statistical composition analysis indicated that most inclusions were solid

in molten steel based on the calculated Al_2O_3 – Ti_3O_5 – MgO phase diagram. Thus, MnS prefers to segregate on them. Furthermore, the high density of the oxide provided enough nucleation sites, which resulted in the absence of pure MnS. After etching, it was found that Ti–Mg-bearing oxides can induce the nucleation of intragranular acicular ferrites. Discussions suggested that the Mn-depletion zone may be the possible mechanism.

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Conflicts of Interest: The authors declare no conflict of interest.

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