Research Article

Xu Chen, Zhang Mingya, Li Jianli, Ran Songlin, Shan Mengwei, Yue Qiang, and Kong Hui*

The effect of MgTiO_3 Adding on Inclusion Characteristics

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Abstract: MgTiO_3 powder was directly added into molten steel at 1873K, and its effect on inclusion characteristics was studied by a scanning electron microscope and an energy dispersive spectrometer. Thermodynamic calculation indicates that MgTiO_3 is unstable in molten steel and may decompose into [Ti], [O] and MgO. However, only Ti-bearing inclusions were observed in the treated sample, and Mg-bearing inclusions were absent. This can be explained by the features of wettability and stability for MgO. Compared with a Non-treated sample, both oxide and coarse MnS in treated sample were refined. For the oxide, this originates from the formation of Ti-bearing inclusion. For coarse MnS, this may be due to the fact that Ti can aggravate S segregation. Besides, this aggravation makes coarse MnS less globular. After etching, it was found that in the treated sample, Ti-bearing inclusion can induce the nucleation of intragranular acicular ferrites. This appearance was totally different from that of Non-treated sample, and indicates the effectiveness of external adding method in oxide metallurgy.

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

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***Corresponding Author: Kong Hui:** School of Metallurgical Engineering, Anhui University of Technology, Maanshan, Anhui, 243002, P R China; Key Laboratory of Metallurgical Emission Reduction & Resources Recycling (Anhui University of Technology), Ministry of Education, Maanshan, Anhui, 243002, P R China; Email: konghui@mail.ustc.edu.cn

Xu Chen, Zhang Mingya, Shan Mengwei: School of Metallurgical Engineering, Anhui University of Technology, Maanshan, Anhui, 243002, P R China; Key Laboratory of Metallurgical Emission Reduction & Resources Recycling (Anhui University of Technology), Ministry of Education, Maanshan, Anhui, 243002, P R China

Li Jianli: The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei, 430081, P R China; Key Laboratory of Metallurgical Emission Reduction & Resources Recycling (Anhui University of Technology), Ministry of Education, Maanshan, Anhui, 243002, P R China

1 Introduction

In 1990, the concept of Oxides Metallurgy is proposed by Takamura and Mizoguchi [1]. Its key is to utilize fine inclusions to induce nucleation of intragranular acicular ferrite (IAF) during austenite-ferrite transformation. Because of the interlocking nature of IAF, its formation enhances both strength and toughness [2, 3].

Many kinds of inclusions have been suggested as effective sites for IAF nucleation, and their formation can be classified into Internal Precipitation Method (IPM) [4, 5] and External Adding Method (EAM) [6]. The former means that preferred inclusions generate either during de-oxidation or solidification processes. Thus precise control of steel composition and fine adjustment of production process are crucial. The latter means that pre-prepared particles are directly added into steel. So how to evenly distribute them in steel and make them as potential nucleation sites during phase transition is the focus of the research.

Recently, Ti-bearing and Mg-bearing inclusions have attracted much attention. The former is suggested as the most efficient inclusion for IAF nucleating, and the latter's IAF nucleation effect is still under discussion. Thus, both of them are the hot topic of EAM study, and different methods have been developed, which is summarized respectively.

For Ti-bearing inclusion, three methods have been adapted. Firstly, Ti-bearing oxides and steel were bonded together at solid state [7, 8]. Secondly, Ti-bearing oxides were mixed with steel powder [9, 10] or put inside the hollow of steel cylinder [11, 12]. Then oxide and steel were melted almost simultaneously. Thirdly, Ti-bearing oxides were directly added into molten steel. For example, the

Ran Songlin: Key Laboratory of Metallurgical Emission Reduction & Resources Recycling (Anhui University of Technology), Ministry of Education, Maanshan, Anhui, 243002, P R China)

Yue Qiang: School of Metallurgical Engineering, Anhui University of Technology, Maanshan, Anhui, 243002, P R China; The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei, 430081, P R China

Table 1: Chemical composition of steel samples (mass percentage)

Mass Pct.	C	Si	Mn	P	S	Als	Ti	Mg
EAM-Treated Sample	0.16	0.36	1.11	0.033	0.028	0.0021	0.0023	0.0006
Non-Treated Sample	0.18	0.39	1.20	0.022	0.022	0.0008	-	-

cored wire, which contains a high number density of oxides, was feed into molten steel by Grong *et al.* [13]. Moreover, different additives with metallic Ti and TiO_2 were added into the steel melt just before casting or into the mold during casting to create Ti-bearing inclusions [14].

It can be seen that for the first and second methods, both as-sintered steel and co-melting of oxide and steel are totally different from actual steel-making process, which may limit their application. For the third method, the presence of acicular ferrite could not be confirmed definitely, and the holding time is required as short as possible to avoid particle floating.

For Mg-bearing inclusion, two methods have been adapted. Firstly, an approach for pre-dispersing MgO with AlSi alloy nanoparticles was established, and the resulting nanoparticles were added into steel melt both in laboratory scale and real production [15, 16]. Secondly, chemical modification of the surface of MgO nanoparticles for steel-making was developed [17].

In this paper, MgTiO_3 powder was introduced into molten steel for the first time to our knowledge. The aim is to utilize the decomposition reaction of MgTiO_3 to release Mg/Ti into molten steel and play a role in IAF nucleation effect.

2 Experimental Procedure

The preparation of powder mixture consisted of two steps. Firstly, approximate MgTiO_3 (Aladdin, purity > 99.9%, size < $2\mu\text{m}$) and pure iron powder were weighted. Secondly, planetary ball milling was used to mix them for three hours in order to achieve homogeneous composition.

Commercial low-carbon steel (about 1500g) was used as raw material and put in an alumina crucible. The alumina crucible was located inside the graphite crucible in a high-heat tube-type resistance furnace. The experimental temperature was 1873K, and high purity argon gas was used as protecting gas during the melting experiment. The powder mixture was directly added into the molten steel and the mixture dissolved quick. Then after being held for 10 minutes at 1873K, the crucible was taken out. After solidification, steel sample was quenched into water. It should

be mentioned that the surface of EAM-treated sample was smooth and no laminations were observed. Moreover, a comparison sample without EAM treatment was also prepared. The samples were sent to NCS Testing Technology Co., Ltd (China National Analysis Center for Iron and Steel) for composition analysis, and the content of Al_s and Ti were measured by the method of ICP-AES. The composition of both samples is shown in Table 1.

The morphology and composition of inclusions were characterized by scanning electron microscope (SEM: JSM-6510LV) and energy dispersive spectrometer (EDS: INCA Feature X-Max 20). In both samples, inclusions were classified as oxide and sulfide. The latter was pure MnS. In fact, MnS segregation, which heterogeneously nucleates on oxides, was also observed. This kind of inclusion was attributed as oxide.

The data processing for EDS point analysis was carried out following Wang Xinhua *et al.* [18]. Firstly, iron was excluded to eliminate the contribution of signals from steel matrix. Then oxygen was ruled out due to insufficient accuracy. Finally, the content of remaining elements was normalized to 100%, and reported in mass percentage. Beside point analysis, area mapping functions of EDS was also applied to intuitively characterize the distribution of each element in inclusion. This is helpful to reveal the inclusion complexity [19–21].

Software of INCA Feature was applied to automatically find and analyze inclusions in preselected area. It should be mentioned that the inclusion size is its Feret maximum, and the inclusion aspect ratio φ is the ratio of its Feret maximum to Feret minimum.

3 Results and discussion

Thermodynamic calculation of MgTiO_3 in molten steel is carried out based on following equations [22, 23]:

$$\Delta G_1^\theta = -2271200 - 157.5T \text{ J} \cdot \text{mol}^{-1}$$

$$\Delta G_2^\theta = -675600 + 234T \text{ J} \cdot \text{mol}^{-1}$$

It should be mentioned that Ti in molten steel can form many oxides, such as TiO , Ti_2O_3 , Ti_3O_5 , and TiO_2 , and inconsistent results have been present. To simplify, equation (2) is applied. Thus, equation (3) can be derived:

$$\begin{aligned}\text{MgO} \cdot \text{TiO}_2(\text{s}) &= \text{MgO}(\text{s}) + [\text{Ti}] + 2[\text{O}] \\ \Delta G_3^\theta &= -2946800 + 76.5T \text{ J} \cdot \text{mol}^{-1}\end{aligned}\quad (3)$$

If the activities of $\text{MgO} \cdot \text{TiO}_2(\text{s})$ and $\text{MgO}(\text{s})$ are assumed as unity and the activity of $[\text{Ti}]$ is simplified as its mass percentage, the ΔG_3^θ is negative in 1873K even though the mass percentage of $[\text{O}]$ is 1. Thus the deposition of $\text{MgO} \cdot \text{TiO}_2(\text{s})$ in molten steel may occur, which releases $[\text{Ti}]$, $[\text{O}]$ and MgO at the same time. To confirm this effect, systematic inclusion analysis has been conducted.

Based on SEM-EDS mapping analysis, the figures of typical oxide are shown in Figure 1 ((a) for Non-treated sample and (b) for EAM-treated sample). In Non-treated sample, the oxide was Mn-Si-Al-O. For EAM-treated sample, the elements of Ti, Mn, Si, and Al coexisted in oxide, while element of Mg was not found. In fact, the similar results have been also observed in our previous studies in addition of TiO_2 and MgO , respectively. To confirm this characteristic, statistically analysis for inclusion has been carried out by INCA Feature software. The total number of measured inclusions in EAM-Treated Sample was 2080. Among them, only 5 Mg-bearing inclusions were observed. For these Mg-bearing inclusions, the Mg contents were all below 1%, and their sizes were all smaller than $1\mu\text{m}$. As for Ti-bearing oxide, its number was much larger. Considering accuracy, only the inclusion, whose size was larger than $1\mu\text{m}$, was taken into account. The resulting number was 1310. Among them, 35% inclusions (number percentage) can be classified as Ti-bearing oxide, and their average content of Ti was 14%.

Then a question should be answered: why only Ti-bearing inclusions were observed, nevertheless, Mg-bearing inclusions were absent? This can be explained by the wettability between molten steel and MgO .

In 2017, sessile drop method has been employed to study the wettability between liquid iron and sintered MgO substrate at 1823K by Ren *et al.* [24]. In their experiments, two iron samples were used, and their Al concentrations were 18 ppm and 370 ppm, respectively. The former sample's results were used to analyze since the Al concentration in our sample was 21 ppm.

On the one hand, the stable contact angle between the sintered MgO substrate and the liquid iron was approximately 134° at 1823K. This means that in our sample with similar Al content, MgO is nonwetting with molten iron, and can easily float up. On the other side, EDS analysis in-

Figure 1: SEM micrographs and EDS mapping images of various elements for typical oxide (a) For Non-treated sample (b) For EAM-treated sample

dicated that the composition of iron sample surface after sessile drop experiment was relatively uniform Fe. However, the iron sample with 370 ppm Al was covered with an oxide layer. This hints that for the low Al sample, a reaction between MgO and liquid steel is difficult.

Based on upper two sides, the released MgO was absent in our sample. In fact, to introduce MgO into molten steel, special technology should be applied [15–17]. While for $[\text{Ti}]$, it can easily react with other elements in molten steel, and simultaneously released $[\text{O}]$ may accelerate these reactions. These lead to the formation of Ti-bearing oxides, which may refine the oxides.

To confirm this conclusion, the relationship between oxide size and number density in EAM-treated sample and Non-treated sample is present in Figure 2. Considering accuracy, only the oxide with size larger than $1\mu\text{m}$, was taken into account. It can be seen that oxide was fined, and its number density was increased. This was consistent with upper analysis.

Except oxide, pure MnS was also observed in both samples, and their typical figures are shown in Figure 3 ((a) for Non-treated sample and (b) for EAM-treated sample). It's known that due to high concentration of product ($a_{[\text{Mn}]} \times a_{[\text{S}]}$, a means the activity), MnS normally cannot form in molten steel. Based on origination, Zheng *et al.*'s [25] indicates that MnS may be classified as coarse ($>1.5\mu\text{m}$) and fine ($<1\mu\text{m}$). The former originates from the eutectic reaction during solidification, and the latter is attributed to the probable precipitation after complete solidification.

Figure 2: The relationship between oxide size and number density in EAM-treated sample and Non-treated sample

Figure 4: The relationship between coarse MnS size and number density in EAM-treated sample and Non-treated sample

Figure 3: SEM micrographs and EDS mapping images for typical pure MnS (a) For Non-treated sample (b) For EAM-treated sample

Since the external adding method is closely related to solidification, coarse MnS was our focus.

The relationship between coarse MnS size and number density in the EAM-treated sample and non-treated sample is shown in Figure 4. It can be seen that with EAM treatment, coarse MnS was refined, and its number density was increased. Moreover, the number percentage (aspect ratio $1 < \varphi < 2$) has decreased from 87.5 to 79.4, which means that the adding of MgTiO_3 makes coarse MnS less globular.

The contrary trend has been reported and explained by Zheng's *et al.* [25]. They found that surfactants of Te can increase the percentage of coarse MnS (aspect ratio $1 < \varphi < 2$) and decrease its number density. Based on their theory, our results can be well explained, which is shown below in brief and divided into following five parts.

Firstly, Sulfur segregation is the key to MnS precipitation since S (partition coefficient $k_s = 0.05$) [26] segregates much easier than Mn ($k_s = 0.76$) [26] during solidification.

Secondly, since the content of Ti is only about 23 ppm, its effect on activity coefficient of Sulfur can be negligible.

Thirdly, since Ti doping decreases the surface tension of liquid iron [27], it preferentially accumulates at the liquid-solid steel interfaces as surfactant.

Fourthly, Zheng *et al.* [25] pointed out that due to fast solidification, solute concentration in the newly formed solid monolayer is in excess of the equilibrium solubility. Then, the solute will diffuse back to the liquid phase across the interface because of its supersaturated state. Thus it's feasible to assume that surfactant, which accumulates at solid-liquid interface, could affect mass transfer rate across interface [28, 29].

Fifthly, the interaction between S and Ti is stronger than that of between Fe and S. This is confirmed by the negative interaction coefficient e_S^{Ti} (-0.27 , JSPS). Based on Zheng's discussions [25], this may increase vacant sites for adsorption, accelerating solute back-diffusion from the solid phase to the liquid phase across the solid-liquid interface. This would aggravate the segregation of Sulfur into the interdendritic regions, and increase its supersaturation.

Thus, Ti doping made coarse MnS less globular and higher density. This trend is contrary to Te doping effect. This is due to the fact that the interaction between S and

Te is weaker than that of between Fe and S, which is contrary to Ti property. Moreover, since Te is extremely surface active in liquid steel [30], its effect on coarse MnS is more obvious than that of Ti.

Figure 5(b) describes SEM micrograph and EDS mapping images of typical Ti-bearing oxide in EAM-treated sample after etching in 3Vol% Nital solution. It can be seen that IAF plates initiates from a single Ti-bearing inclusion. This phenomenon was similar to the induced nucleation effect of Ti-bearing inclusion originating from IPM method [4], and totally different from that of Non-treated sample (shown in Figure 5(a)).

Figure 5: SEM micrograph and EDS mapping images for typical oxide after etching (a) For Non-treated sample (b) For EAM-treated sample

Figure 1(b) has indicated that with EAM treatment, Ti-bearing oxides were formed. Till now, different mechanisms have been proposed to explain the reasons why Ti-bearing inclusion can promote IAF nucleation [2], such as inert surface, lattice disregistry, thermal coefficient, and Mn-depletion zone (MDZ). Among them, MDZ mechanism has been widely accepted. This mechanism is based on the assumption that inclusions can absorb neighboring Mn atoms from Fe matrix. If a corresponding supplement isn't applied, Mn depleted zone will be formed in Fe matrix around inclusion. This promotes the nucleation of ferrites since Mn element is the stabilizer of austenite.

In 2018, Li *et al.* [20] indicates that in Al-Ti-Mg killed steel with low Al content, MDZ is formed by the combined effect of the precipitation of MnS and diffusion of Mn atoms into TiO_x and $MgTiO_x$. In EAM-treated sample, Al content was as low as 21ppm and Ti-bearing oxide was also found. This hint that a similar absorption may occur,

which promote acicular ferrite nucleation. While in the Non-treated sample, no Ti-bearing oxides were found. The difference of inclusion characteristic leads to the different microstructure in two samples.

4 Conclusion

$MgTiO_3$ powder was directly added into molten steel, and its effect on inclusion characteristic has been explored. At 1873K, $MgTiO_3$ may decompose into [Ti], [O] and MgO, which results in the formation of Ti-bearing complex inclusions and the refinement of oxide. While for MgO, its wettability and stability led to the absence of Mg-bearing inclusion. Compared with a Non-treated sample, coarse MnS in the EAM-treated sample became less globular and higher density. This may be interpreted by the fact that Ti can aggravate S segregation. After etching, IAF plates have been observed in the EAM-treated sample, which is induced by Ti-bearing inclusions. This appearance was consistent with the Ti-bearing inclusion originating from internal precipitation method, and indicates the effectiveness of external adding method in oxide metallurgy.

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