Evolution of Inclusions and Associated Microstructure in Ti–Mg Oxide Metallurgy Steel

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Evolution of inclusions from ladle furnace (LF) to continuous casting in Ti–Mg oxide metallurgy treatment were studied. The results suggested that the composition of inclusions changed from MnS-MnO·SiO2 to (Ti–Ca–Mg–Al–O)·MnS. Furthermore, EDS results indicated that the content of Mg decreased because of reduction reaction, float and gasification. The average size of inclusions was decreased from 0.73 μm to 0.47 μm and the number density decreased from 977/mm² to 595/mm² after continuous casting. The microstructures changed from polygonal ferrite (PF) and ferrite side plate (FSP) to acicular ferrite (AF), PF and bainite (B) gradually after inclusion treatment (Ti–Mg oxide metallurgy) in LF furnace and Ca treatment in RH furnace. Heterogeneous nucleation of AF was observed on the surface of Ti–Mg oxides.

KEY WORDS: Ti–Mg oxide metallurgy; inclusions; steelmaking; microstructure.

1. Introduction

Clean steel is the main objective during steel making process and non-metallic inclusions should be eliminated as completely as possible1) because they can act as nucleation sites of cleavage cracks.2) During thermal cycling of high heat input welding, austenite grain size of heat affected zone (HAZ) coarsens and brittle microstructure such as martensite/austenite (M/A), upper bainite (UB) and ferrite side plate (FSP) are formed, which can deteriorate the impact toughness. To address the problem, the concept of “oxide metallurgy” was proposed.3–5) Fine inclusions (0.2–3 μm) are controlled and dispersed in steel which provide heterogeneous nucleation site for acicular ferrite (AF), or pin the movement of austenite grains, enhancing the toughness.6,7)

In order to realize optimum efficiency of oxide metallurgy, the complete process of steel making needs to be carefully controlled.3) Including deoxidation conditions (deoxidizing elements, temperature, etc.), solidification condition (solidification velocity, cooling velocity, etc.) and condition of heat treatment after solidification. In fact, various inclusions have been reported to have an ability to induce nucleation of AF, such as titanium oxide,1,8,9) TiN,10) MnS,11) and Ti–M–oxide (M = Mg, Ca, Zr, etc.).7,9,12–14) In addition, Lee et al. suggested that when oxygen content changed from 0.005% to 0.013% in Ti-bearing low carbon steel, the percentage of inclusions and areal density was increased, but amount of AF was decreased.15) Oh et al. reported that in order to form AF (50 vol.%), volume fraction of inclusions needs to be greater than 0.01%, with corresponding oxygen content of 0.005%.16) Wen et al. also found that high percentage of AF was obtained in steel, with oxygen content of 0.002%–0.003% after Mg deoxidation.17) Majority of the studies suggest that it is important that the inclusions be dispersed to optimize the microstructure of HAZ when the oxygen content is about 0.005% in steels.

The objective of the present study is to analyze the evolution of inclusions in terms of composition, size distribution and microstructure in Ti–Mg steel.

2. Materials and Methods

Experimental steel with Ti–Mg oxide metallurgy treatment was processed involving converter converting → Si–Mn pre-deoxidation → ladle furnace (LF) refining → Ca treatment in RH furnace for 40 min (Ca alloy was added after vacuum treatment in RH furnace for 15 min and when the vacuum degree was lower than 100 Pa) → continuous casting. When the oxygen content was about 40 ppm, about 250 kg Ti–Fe alloy blocks and 300 m Ni–Mg alloy wires were deliberately added to molten steel in LF furnace to obtain fine inclusion. The sampling positions were LF furnace station, feeding Ni–Mg alloy wires in LF furnace, LF furnace exit station, feeding Ca-containing cored wires in RH furnace, continuous casting ladle, respectively. The sampling timing of each position was shown in Table 1, the chemical composition of experimental steel was measured using a direct-reading spectrograph and a nitrogen oxygen
Continuous cooling transformation diagram was obtained using Formastor-FH full-automatic transformation equipment. Samples from every sampling position were machined to 3 mm diameter and 10 mm length. The specimens were heated to 1250°C and held for 5 min, then cooled at the rate of 5°C/s to ambient temperature. To examine the microstructure, the samples were etched with 4% nital and observed by an optical microscope (OM). The inclusions were analyzed in terms of average size, areal density, size distribution and composition via electron probe microanalyzer (EPMA) and a scanning electron microscopy (SEM) equipped with inclusion automatic analysis system and energy dispersive spectrometry (EDS).

### 3. Results and Discussion

#### 3.1. Evolution Behavior of Inclusions on Phase and Composition

Figure 1 shows the evolution of inclusions in each sampling position, which indicated that the phase changed during the steelmaking process. Figure 2 is the corresponding chemical composition in inclusion of Fig. 1, and the S, Fe were ignored during the analysis. Typical composition of inclusions mainly consisted of oxide and MnS, and the result also indicated that with addition of alloying elements, the core oxide changed from single phase to complex phase. In Fig. 1(a) (LF furnace station), the results of EPMA suggested that the non-metallic inclusions mainly consisted of upper half of MnS and lower half of manganese silicate (Fig. 3), because the effect of pre-deoxidation by manganese and silicon, their content was maximized, as shown in Fig. 2, and the ratio of atomic percent measured by EDS of Mn, Si, O was 1:1:3, respectively. Thus, it can be deduced that manganese silicate was MnO·SiO$_2$. In the sample of feeding Ni–Mg alloy wires in LF furnace, the inclusion was finer and the shape was spherical after addition of Ti–Fe alloy blocks and Ni–Mg alloy wires in LF furnace. The core was a complex phase of Mg containing (Ti–Mg–Al–O), Ti and Mg were major constituents and Al was a residual. The precipitation behavior of MnS was induced by Ti-oxide. In the specimen of LF furnace exit station, the shape of inclusion was polygonal and two kinds of oxides were observed, (Ti–Mg–Al–O) was the core but the content of Mg was decreased because the contact angle between MgO and molten steel was larger ($\theta=125^\circ$) and the density of MgO was lower ($\rho=3.65$ g/cm$^3$). Thus, MgO easily floats and the gasification of Mg and TiO$_x$ reduced by Mg element can also lower the content. After Ti–Mg treatment started and slag was formed, CaO appeared and surrounded part of core

| Table 1. Sampling timing of each sampling position. |
|-----------------|-----------------|
| Sampling positions | Sampling timing |
| LF furnace station | when oxide content about 40 ppm |
| feeding Ni–Mg alloy wires in LF furnace | 10 min after feeding Ni–Mg alloy wires |
| LF furnace exit station | after slag formation period |
| feeding Ca-containing cored wires in RH furnace | 10 min after feeding Ca-containing cored wires |
| continuous casting ladle | 15 min after continuous casting |

| Table 2. Chemical composition of experimental steel in wt.% |
|-----------------|-----------------|
| Steel | C | Si | Mn | S | P | Ti | Ca | Nb | Mg | O | N |
| Ti–Mg | 0.07 | 0.12 | 1.65 | 0.006 | 0.005 | 0.013 | 0.003 | 0.015 | 0.003 | 0.003 | 0.005 |

Fig. 1. Evolution of inclusions in each sampling position. (a) LF furnace station; (b) feeding Ni–Mg alloy wires in LF furnace; (c) LF furnace exit station; (d) feeding Ca-containing cored wires in RH furnace; (e) continuous casting ladle.

Fig. 2. Composition evolution of inclusions in each sampling position (A–E represent LF furnace station, feeding Ni–Mg alloy wires in LF furnace, LF furnace exit station, feeding Ca-containing cored wires in RH furnace, continuous casting ladle, respectively).
oxide. The precipitation behavior of MnS was similar with sample of feeding Ni–Mg alloy wires in LF furnace. In the specimen of feeding Ca-containing cored wires in RH furnace, the core was a complex oxide of (Ti–Ca–Mg–Al–O), and the element Ti and Ca were dominant. MnS was similar as described above. Finally, the composition of inclusion in continuous casting ladle was similar to the particle in feeding Ca-containing cored wires in RH furnace.

Before oxide metallurgy treatment, the content of oxygen needs to be strictly controlled. To verify the validity of technological scheme, the thermodynamic calculations related to the deoxidization process by Si–Mn, Ti and Mg are discussed. The chemical equations and equilibrium constant of single Si and compound Si–Mn deoxidation are:

\[
[\text{Si}] + 2[\text{O}] = \text{SiO}_2 (s) \quad \text{..................................(1)}
\]

\[
\log K_{Si} = \frac{a_{\text{SiO}}}{a_{[\text{Si}]}} \times \frac{a_{[\text{O}]}}{a^2_{[\text{O}]}} = \frac{30110}{T} - 11.4 \quad \text{............(2)}
\]

\[
[\text{Si}] + 2\text{MnO}(l) = 2[\text{Mn}] + \text{SiO}_2 (s) \quad \text{............(3)}
\]

\[
\log K_{Si-Mn} = \frac{a_{[\text{Mn}]}^{2}}{a_{[\text{Si}]}} \times \frac{a_{\text{SiO}}}{a_{\text{MnO}}} = \frac{4590}{T} - 0.16 \quad \text{............(4)}
\]

When deoxidized by Si in molten steel, deoxidized product is SiO$_2$. The Si–O equilibrium at 1 600°C can be calculated and is shown in Fig. 4. However, when deoxidized by Si–Mn, deoxidized products are SiO$_2$, MnO and silicomanganese. Compared to deoxidization by Si, Si–Mn complex deoxidation can lower the oxygen content. Thus, it is necessary to use Si–Mn pre-deoxidation to satisfy the oxygen level before Ti deoxidation in LF furnace.

There are many kinds of Ti oxides in LF furnace, such as TiO, Ti$_2$O$_3$, Ti$_3$O$_5$ and TiO$_2$, the chemical equations are listed in Eqs. (5)–(8), where $\Delta G_m$ is the Gibbs free energy and the equilibrium of different oxides is shown in Fig. 5. It can be seen that compared with Si–Mn deoxidized, Ti has a better deoxidizing capacity and in order to form Ti$_2$O$_3$ inclusions when Ti content was about 0.013%, the oxygen content needs to be controlled above 0.002%. When feeding Ni–Mg alloy wires after Ti addition, the part of Ti oxides should be reduced by Mg to form MgO for Mg is easy to deoxidize compared with Ti and the equation is shown in Eq. (9). Then, MgO was covered on the surface of Ti-oxides to generate (Ti–Mg–O) oxides. The Chai et al. reported that Mg content of 0.002% can refine the inclusions of Ti-based by forming of Ti–Mg–O particles. It was found that deoxidation of Ti followed by Mg is one of the most promising methods to precisely control the deoxidation particles. Hence, appropriate addition of Si–Mn, Ti and Mg will lower the oxygen content progressively to derive the benefit of oxide metallurgy, and finer inclusions are formed.

\[
[Ti] + [O] = \text{TiO}(s) \Delta G_m^{\text{TiO}} = -360 250 + 130.8T \text{ J/mol}^{-1} \quad \text{............(5)}
\]

\[
2[Ti] + 3[O] = \text{Ti}_2\text{O}_3(s) \Delta G_{\text{Ti}_2\text{O}_3}^{\text{Ti}_{2}\text{O}_{3}} = -1 072 872 + 346.0T \text{ J/mol}^{-1} \quad \text{............(6)}
\]

\[
3[Ti] + 5[O] = \text{Ti}_3\text{O}_5(s) \Delta G_{\text{Ti}_3\text{O}_5}^{\text{Ti}_{3}\text{O}_{5}} = -1 392 344 + 407.7T \text{ J/mol}^{-1} \quad \text{............(7)}
\]

\[
[Ti] + 2[O] = \text{TiO}_2(s) \Delta G_{\text{TiO}_2}^{\text{TiO}_{2}} = -675 720 + 224.6T \text{ J/mol}^{-1} \quad \text{............(8)}
\]

\[
3[Mg] + \text{Ti}_2\text{O}_3(s) = 3\text{MgO}(s) + 2[Ti] \quad \text{............(9)}
\]
3.2. The Effect of Evolution of Inclusions on Size Distribution

Figure 6 shows the result of size distribution, average size and number density of inclusions for each sampling position by inclusion automatic analysis system, each sample was observed under ×3 000 magnification, the scanning area was 1.0 × 1.0 mm² and inclusions of diameter smaller than 0.2 μm are ignored. In order to exclude the effect of holes and blots, inclusions which were confirmed by EDS were selected. In Fig. 6(a), size of inclusions was mainly in the range of 0.6–0.8 μm, and some coarse inclusions of 2.0–5.0 μm were also observed. The average size was 0.73 μm and number density was 977/mm². After Ti–Mg treatment, many fine inclusions in the range of 0.2–0.6 μm were formed. The coarse inclusions were decreased by collision and floated into slag, the average size and number density was 0.38 μm and 1 110/mm², respectively. At this moment, if we do not take into account of the situation of collision, the formation of inclusions can be divided into three stages: nucleation, growth and Ostwald ripening. In the beginning, inclusions mainly depend on the degree of supersaturation (S), interfacial energy between inclusions and molten steel (γ) and concentration product of deoxidation equilibrium. The concentration product between Ti/Mg and O increases with time and the inclusions start to nucleate when critical supersaturation (CS) is achieved. Subsequently, S will decrease with the reaction of deoxidation, the process of nucleation will end when CS is achieved again. Prior to the balance of S=1, diffusion of particles will cease and Ostwald ripening occurs. If the value of S is lower and γ is higher, inclusions are difficult to nucleate and areal density decreases. However, after feeding Ni–Mg alloy wires, the content of Mg and O in LF furnace was 0.01% and 0.006%, S[Mg][O] was adequately high at 1 600°C to form fine and dispersed inclusions. Thus, the number density was maximum and this is the most important aspect of oxide metallurgy.

The statistical result in LF furnace exit station is shown in Fig. 6(c), given that it continues to blow argon after feeding Ni–Mg alloy wires, the number density of inclusions is decreased, and the average size of inclusions increased to 0.50 μm. After feeding Ca-containing cored wires in RH furnace, the vacuum treatment decreases the number density to 677/mm². It is proposed that vacuum treatment in RH furnace for a long time (40 min) is not suitable for inclusions to keep a high volume fraction during entire steelmaking process. However, oxides containing Ca are formed at the same time and the average size is refined to 0.44 μm. During continuous casting, because of liquid state of steel, the
number of inclusions will continue to decrease by the effect of collision, diffusion and Ostwald ripening, and its size is increased to 0.47 μm. During the process of steelmaking, without considering the effect of collision and diffusion, inclusions grow up following the theory of Lifshitz, Slyozov and Wagner (LSW). At time of t, the radius of inclusion is related to oxygen concentration and time, because time is enough for inclusions to grow, so oxygen concentration needs to be controlled to prevent the coarsening. As shown in Figs. 6(d) and 6(e), average size of inclusion increased from 0.44 μm to 0.47 μm and number density decreased to 595/mm². It is suggested that ~ 30 ppm oxygen is optimum in restricting coarsening of inclusions.

Based on the results, a schematic diagram of the evolution of Ti–Mg inclusions is presented in Fig. 7. After pre-deoxidation by Si and Mn, large size of MnS, SiO₂ and MnO·SiO₂ were first generated. Then blocks of Ti–Fe alloy were added and formed TiO_x. Later, Ni–Mg alloy wires were added to molten steel, and fine inclusions of MgO and complex phase (Ti–Mg–O) were formed. In addition, a part of TiO_x was reduced by Mg, such that the size is decreased. Finally, during the solidification process, the inclusion with complex phase was precipitated and MnS was also precipitated on the surface of particles.

### 3.3. The Effect of Inclusions on Microstructure

The evolution of microstructure at every sampling position during thermal cycle was shown in Fig. 8. It can be seen in Fig. 8. Evolution of microstructure during steelmaking process. (a) LF furnace station; (b) feeding Ni–Mg alloy wires in LF furnace; (c) LF furnace exit station; (d) feeding Ca-containing cored wires in RH furnace; (e) continuous casting ladle.
that the microstructure in LF furnace station (Fig. 8(a)) composed of FSP and polygonal ferrite (PF), there was no AF observed. Inclusions containing Si and Mn did not induce nucleation of AF. Figure 8(b) shows the microstructure after Ti–Mg treatment in LF furnace. The microstructure consisted of some GBF, PF and prominent AF features. Comparing with the position in LF furnace station, the volume fraction of PF was decreased, and even FSP was not observed. The nucleation of interlocking AF indicated that the (Ti–Mg–Al–O) oxides introduced by oxide metallurgy in LF furnace can provide effective nucleation sites for AF. On the other hand, it is reported that the inclusions induce nucleation of AF during $\gamma \rightarrow \alpha$ phase transformation and can refine the grains and restrain the formation of brittle microstructure such as GBF and FSP.\(^\text{12}\)

The microstructure of LF furnace exit station is shown in Fig. 8(c). Based on statistical results in Fig. 6(c), the number of (Ti–Mg–Al–O) inclusions was reduced, so the area fraction of AF was decreased and FSP was observed. When blocks of Nb–Fe alloy were added to liquid steel after Mg addition, it is reported that Nb can improve the hardenability of steel, but excessive addition of Nb can change the microstructure from intragranular ferrite (IGF) to upper bainite (UB) and deteriorate the toughness of HAZ.\(^\text{10}\) Hence, some bainite (B) was obtained and the thickness of GBF was finer than before. The microstructure of the position in feeding Ca-containing cored wires in RH furnace sample mainly consisted of dominant AF and B, as shown in Fig. 8(d). It is reported that addition of Ca results in higher number density of Ca-containing inclusions and the formation of AF is promoted.\(^\text{24}\) Finally, because of the effect of Ostwald ripening, the nucleation ability of AF was decreased slightly. The microstructural components in continuous casting ladle were mainly AF, B and PF.

It can be seen from Fig. 2(b) that (Ti–Mg–Al–O) inclusions were obtained and MnS precipitated on the surface after Ti–Mg oxide metallurgy treatment. Fig. 9 shows typical morphology and elemental distribution of inclusions at

![Fig. 9. EPMA analysis of inclusion induce AF nucleated in the position of feeding Ni–Mg alloy wires in LF furnace.](image-url)
this position, and nucleation of AF was observed. Inclusions can be divided into inert or active based on their ability to promote AF nucleation.\textsuperscript{25} It is reported that Ti–Mg oxides are effective inclusions for nucleation of AF, and AFs could nucleate at the interface of MnS and oxides or directly on the surface of MnS.\textsuperscript{26,27} From these results, it can be suggested that AF nucleation is related to elemental distribution in oxides. The multilayered inclusions containing Ti–Mg and MnS precipitates on the surface of the oxides promote heterogeneous nucleation of AF.

During the process of oxide metallurgy, besides composition, grain size is also an important factor affecting the nucleation of AF. The oxides need to be randomly distributed and can restrict the movement of grain boundaries after high heat input welding. From the results in Fig. 6, Mg addition was beneficial to form Ti–Mg oxides. Mg-containing oxides have a better thermal stability even at temperatures greater than 1673 K (1400°C). Thus, Ti–Mg treatment can inhibit the coarsening of grains effectively and induce nucleation of AF.

4. Conclusions

(1) The inclusions in the Ti–Mg steel comprised of a core oxide with MnS shell. The composition of inclusions during steelmaking process changed from MnS–MnO·SiO$_2$ (LF furnace station) to (Ti–Mg–Al–O) (feeding Ni–Mg alloy wires in LF furnace), and then to (Ti–Ca–Mg–Al–O) in continuous casting ladle. Moderate addition of Si, Mn, Ti and Mg can lower the oxygen content to avail the benefit of oxide metallurgy. Gasification, reduction reaction and floatation can form fine inclusions and facilitate the heterogeneous nucleation.

(2) During the entire steelmaking process, the average size of inclusions decreased from 0.73 $\mu$m (LF furnace station) to 0.47 $\mu$m (continuous casting ladle) and the number density decreased from 977/mm$^2$ (LF furnace station) to 595/mm$^2$ (continuous casting ladle). The time of vacuum treatment in RH furnace should be accomplished within a short time to avoid inclusions exclude obviously. Roughly 30 ppm oxygen content at final stage is suitable for inclusions.

(3) The microstructure of different sampling position after continuous cooling transformation was changed from FSP and PF (LF furnace station) to AF, B, PF and GBF (feeding Ni–Mg alloy wires in LF furnace), and finally was AF, B and PF (continuous casting ladle). Ti–Mg complex deoxidation can form fine inclusions and facilitate the heterogeneous nucleation of AF.

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