Research Article

Yu-hao Zhao, Xiang Cheng, Hui Li, and Hui Kong*

The comparative study of Ti-bearing oxides introduced by different methods

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Abstract: The Ti-bearing oxides are introduced into HRB400 steel melt through external addition method (EAM, TiO2) and internal precipitation method (IPM, Ti alloy) using a vacuum induction furnace, respectively. For each experiment, the instantaneous evolution of oxide properties was investigated through the analysis of intermediate samples. For the EAM method, it was found that the titanium content gradually increased with increase in the treatment time. Similar increasing trend is also observed for Ti-bearing oxide properties, such as the number density and normalized titanium content. These phenomena are totally different from those in the IPM intermediate samples, in which both Ti content and Ti-bearing oxide features show rapid increase, reaching saturation at 1 min after the addition of Ti alloy, and remain relatively stable thereafter. This comparison hints that after TiO2 addition, they first dissolve in molten steel, then decompose, and finally again form Ti-bearing oxides. Furthermore, in the case of similar titanium content, EAM intermediate samples exhibit higher Ti-bearing oxide number density and higher normalized titanium content compared to IPM samples. After heat treatment, the intragranular ferrite nucleation was observed in cast sample of EAM, which was induced by the introduced Ti-bearing oxides.

Keywords: oxide metallurgy, external addition method, Ti-bearing oxides

1 Introduction

In order to meet the high-quality requirements of steel, precise control over the inclusion characteristics, such as number density, size, distribution, and composition, is necessary [1]. Traditionally, non-metallic inclusions have been widely believed to have detrimental effects on the steel properties. However, recent studies have shown that inclusions can also have positive effects on steel through a process known as oxide metallurgy [2–8]. For instance, specific types of non-metallic inclusions in steel, such as Ti oxides, have been identified as heterogeneous nucleation sites for intragranular ferrite (IGF), leading to improved toughness and other properties of steel [9,10]. This positive effect of inclusions on steel has been discussed in several articles [11–13].

There are two ways to introduce Ti oxide into steel, internal precipitation method (IPM) [14] and external addition method (EAM) [8,13,15]. The former involves adding titanium alloy, which produces suitable types of titanium oxides during de-oxidation or solidification. The latter is to directly add the prepared Ti oxide into molten steel.

As is known, titanium element exists primarily in the form of oxides in nature. Therefore, the conventional process involves reducing and purifying titanium oxide minerals to produce titanium alloys, and then adding them to the steel melt to form appropriate titanium oxides, which meets the requirements of oxide metallurgy. It can be seen that this process involves certain complexities. In contrast, the EAM method avoids the reduction steps of titanium oxide, making the process relatively concise. Thus, its study has attracted much attention [16–20].

It should be noted that the density of TiO2 (4.26 g·cm⁻³) is lower than that of molten steel (7.0 g·cm⁻³), which means that they have the tendency to float upward. In fact, some kinds of oxides, such as MgO, ZrO2, and CeO2, are difficult to be directly introduced into molten steel without surface modification [5,6,13,21]. However, the effective introduction of TiO2 has been confirmed by different groups [12,19,22–24]. In 2012, different types of TiO2 containing materials were added to liquid steel before or during casting to get small
titanium-oxide-rich inclusions in steel [19]. In 2014, the effect of sulfur content on the inclusion and microstructure characteristics of steels where Ti$_2$O$_3$ and TiO$_2$ have been added was studied [22]. In 2016, the dynamics of IGF formation in inclusion engineered steels with either Ti$_2$O$_3$ or TiN addition were investigated using in situ high temperature confocal laser scanning microscopy [24]. In 2023, the transient evolution of oxide was studied after directly adding Ti$_3$O$_5$ powder into HRB400 steel in vacuum induction furnace by our group [25]. Moreover, the microstructure and inclusion characteristics in steels with Ti-oxide and TiN additions have been systematically discussed in the PhD dissertation (KTH Royal Institute of Technology, Sweden) [26]. Therefore, despite the density difference and the effect of electromagnetic stirring, titanium oxides can be effectively added into molten steel by the EAM.

Till now, all the studies of EAM for TiO$_2$ were focused on the cast samples after solidification, and discussions on the oxide evolution with treatment time are still lacking, which makes the reaction mechanism still unclear. Moreover, the comparison between IPM and EAM has not yet been undertaken.

Therefore, this study focused on the transient evolution of oxide properties after adding TiO$_2$ into molten steel. In addition, the comparison of characteristics for Ti-bearing oxides was made between IPM and EAM. For each experiment, four intermediate samples were taken, and the oxide characteristics, such as number density and composition were analyzed, which is convenient to observe their evolution process.

2 Experimental approaches

The experiment was carried out in a magnesium oxide crucible (diameter 60 mm, height 145 mm), using a vacuum induction furnace, same as our previous article [25]. Similar device was applied to describe the transient evolution of nonmetallic inclusions after adding calcium in molten steel [27]. This device can achieve a favorable protective atmosphere, easy operation for feeding, easy sampling, and quick melting of steel [27]. Thus, vacuum induction furnace is widely used in the study of inclusions.

The raw material is HRB400 (C: 0.21 wt%, Si: 0.38 wt%, Mn: 1.46 wt%, P: 0.023 wt%, and S: 0.017 wt%). Before the experiment, the additive was wrapped and put into the feeding chamber. There are four quartz tube samplers (inner diameter 8 mm) in the sampling box, and each sampler can be moved vertically for sampling. It should be noted that when sampling, the sampling hole is located at the middle height of the molten steel. The experimental scheme is shown in Figure 1. The experimental procedures are as follows.

First, the furnace chamber was evacuated to a vacuum lower than 15 Pa using a mechanical pump and then back-filled with a high-purity argon gas (purity >99.999%). This process was repeated twice to decrease the oxygen pressure inside the chamber.

Second, about 1,100 g of steel was melted without adding slag. Through the top window, the melt temperature was measured by a dual-wavelength high-temperature pyrometer (CIT-1MD1), whose temperature calibration was performed in advance. After melting at 1,873 K, the molten steel was held for 5 min to ensure homogenization, and then additive was charged on its surface.

Two experiments were carried out. The additives were Ti alloy (70%) and TiO$_2$ powder (50 nm), respectively, and the corresponding experiment was named as IPM-treated experiment (1#) and EAM-treated experiment (2#). The aim is to introduce Ti-bearing oxides into molten steel. The TiO$_2$ nanoparticles were chosen based on the results of our previous studies [16,17], which confirmed its adding validity. For both experiments, the dissolution phenomena of additive into molten steel were observed through the top window.

Third, after feeding, four intermediate samples were separately taken at 1, 5, 10, and 15 min. At the 20th minute, the furnace was powered off. The content of Ti and Al$_3$ (acid-soluble aluminum) in each intermediate sample was measured using the ICP-OES (Agilent 5110) method.

Besides, a blank sample was prepared without EAM or IPM treatments under the same experimental procedure. And the measured contents of Al$_3$ and Ti are 38 and 10 ppm, respectively.

Mu et al. have added the TiO$_2$ powder, with a particle size in the range of 0.139–0.854 μm, into molten steel. Then, the size range of resultant Ti-bearing inclusion increased between 0.215 and 4.802 μm [28]. Similar conclusion has also been drawn by our previous studies [16,17].

![Figure 1: Feeding and sampling schedule.](image-url)
Thus, scanning electron microscope (SEM) (JSM-6510LV) combined with INCA-feature software is applied in this article. They can characterize the typical oxides and analyze the statistical characteristics of oxides. The INCA-feature enables the SEM to automatically scan the steel sample surface. When the system detects a gray scale difference compared to the metal matrix, supposedly an inclusion, it will perform an energy dispersive spectrometer (EDS; INCA Feature X-Max 20) scan of the area and take a SEM image, and then continue the scanning procedure. The minimum size of the detectable oxide was set as 0.5 μm. For each sample, more than 200 oxides were analyzed.

The data processing for EDS point analysis was carried out following Wang et al. [29]. Iron was ruled out to eliminate the contribution of signals from the steel matrix, and oxygen was excluded due to insufficient accuracy. Finally, the content of remaining elements was normalized to 100%, and reported in mole percentage.

3 Results and discussion

The purpose of EAM is to introduce Ti-bearing oxides into steel. This inevitably leads to the increase of Ti content. Therefore, both Ti content and Ti-bearing oxides were analyzed.

The variation of Ti content in intermediate samples after feeding is shown in Figure 2. The final titanium content is approximately same for both methods, but the increasing trend is different. For EAM method (2#), the titanium content gradually increases with treatment time, exhibiting a slow rise from 11 ppm at 1 min to 139 ppm at 15 min. For IPM method (1#), the Ti content shows a rapid increase after adding Ti alloy, reaching 145 ppm at 1 min. Besides, it can be seen that the Al content changed little with time for both experiments (shown in the inset of Figure 2). This hints at the good inert gas protection during the melting process.

Figure 3 shows the typical Ti-bearing oxides in intermediate samples for EAM-treated experiment. For comparison, the typical inclusion in blank sample is also illustrated in Figure 3(a). The EDS surface scan shows that the oxide is in the center and the sulfur is gathered at the margin, which was attributed to the MnS precipitation during solidification. The corresponding results of EDS point analysis (normalization after excluding elements of Fe and O) are shown in Table 1. For the oxide at the center, TiO2 treatment leads to its evolution from Si–Mn–O (blank sample) to Ti–Si–Mn–O, and along with time, the Ti content increases and the Si content decreases accordingly.

The typical oxides are selected randomly. Thus, these results are not enough to prove the successful introduction of titanium oxide. Therefore, the statistical analysis of oxides was carried out.

The relationship between number density of Ti-bearing oxides and treatment time is shown in Figure 4. Different trends can be observed. For EAM method (2#), the number density increased continuously, from less than 10 Number per mm2 at 1 min to nearly 500 Number per mm2 at 15 min. While for IPM method (1#), the number density rapidly rose to about 200 Number per mm2 within 1 min, and then showed a slow downward trend, which may be caused by the oxide floating. In particular, the number density of the EAM method at 15 min is more than three times that of the IPM method. Similar conclusions also can be drawn in cast samples. At the same height in cast samples (middle section), the number density of Ti-bearing oxide for EAM method is 345 Number per mm2, while this value for IPM is only 77 Number per mm2.

It should be noted that TiO2 powder was added on the surface of molten steel, while the sampling location is in the middle of molten steel. The density of titanium oxides (4.26 g·cm−3) is smaller than that of molten steel (7.0 g·cm−3). Thus, the observation of Ti element and Ti-bearing oxide in transient samples indicates that the diffusion of TiO2 into molten steel is achieved, which leads to the introduction of titanium elements.

In previous studies, the stable and effective addition of TiO2 into molten steel has been attributed to its wettability and reactivity with the molten steel [16,17]. The former refers to the fact that the contact angle between them is less than 90°, indicating good wettability [18]. The latter is supported by theoretical calculations, which suggests that TiO2 spontaneously transforms into Ti3O5 in the molten...
steel [19], releasing oxygen atoms that can react with other elements.

If the above assumptions are correct, the reaction between TiO₂ and molten steel would proceed along with time, which results in two facts. The first is the composition difference between central and margin since this reaction occurs from outside. So in the initial stage, Ti is the main element in oxide, and its content in the center may be higher than that at the margin. The second is the decreasing of Ti content in inclusion with the reaction.

To validate the above hypothesis, further discussions about intermediate samples are needed.

On the one hand, for typical Ti-bearing oxide in Figure 3(b), it can be seen that the Ti content is much smaller than

Table 1: EDS point analysis of typical oxides shown in Figure 3 (mole percentage)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Position</th>
<th>Ti</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1</td>
<td>/</td>
<td>37.8</td>
<td>51.5</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>/</td>
<td>31.0</td>
<td>49.8</td>
<td>19.2</td>
</tr>
<tr>
<td>(b)</td>
<td>1</td>
<td>2.6</td>
<td>67.8</td>
<td>26.8</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.7</td>
<td>70.2</td>
<td>23.3</td>
<td>3.8</td>
</tr>
<tr>
<td>(c)</td>
<td>1</td>
<td>68.5</td>
<td>5.7</td>
<td>20.5</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14.3</td>
<td>10.9</td>
<td>39.6</td>
<td>35.2</td>
</tr>
<tr>
<td>(d)</td>
<td>1</td>
<td>84.5</td>
<td>4.6</td>
<td>10.5</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>27.3</td>
<td>21.7</td>
<td>28.0</td>
<td>23.0</td>
</tr>
<tr>
<td>(e)</td>
<td>1</td>
<td>74.4</td>
<td>3.4</td>
<td>18.1</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>84.7</td>
<td>1.6</td>
<td>8.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>
that of Si, which means it is not the main element. Moreover, mapping analysis indicates that the element distribution of Ti, Si, and Mn is uniform, and expected layering phenomenon is not found.

On the other hand, to accurately characterize the evolution of Ti content in oxide, the concept of normalized titanium content is introduced. Its calculation includes three steps. First, the elements of Fe and O were excluded, whose reasons have been explained in experimental approach. Second, the sulfur element was ruled out. Then, the Mn element, which has same mole as sulfur element was removed. This step was eliminating the contribution of MnS since it precipitates around the oxides during solidification. Third, the content of remaining elements was normalized to 100%, and reported in the mole percentage. From Figure 5, it can be seen that the normalized titanium content gradually increases after TiO₂ addition, which is consistent with the results shown in Table 2, and totally different with the above hypothesis.

Since the reducing reaction between TiO₂ and molten steel cannot explain the results given in Figures 3 and 5, another reasonable interpretation is proposed. When TiO₂ powder was added on the surface of molten steel, it first dissolves since it has good wettability, then decomposes to [Ti] and [O] through reaction (1). These decomposition products diffuse into the molten steel, resulting in a gradual increase in titanium content as the titanium oxide is regenerated during this process. In summary, dissolution, decomposition, diffusion, and regeneration occur in turn after adding TiO₂ powder.

To deeply understand the decomposition reaction (1), the FactSage software and classical thermodynamic method are applied. These two computing tools are relatively classic and reliable especially for the HRB400, whose composition is relatively simple.

First, using the modules of FactPS, Ftoxid, and Ftmisc in FactSage 7.2 software and the contents of Al, C, and Si, the calculated [O] in molten steel is about 10 ppm.

Second, thermodynamic calculations were carried out as follows:

$$\text{TiO}_2 = [\text{Ti}] + 2[\text{O}] \quad \Delta G^\theta = 675,720 - 224.6 \times T, \quad (1)$$

$$K = e^{\Delta G^\theta / RT}, \quad (2)$$

$$K = \frac{a_{[\text{Ti}]} a_{[\text{O}]}^2}{a_{\text{TiO}_2}} = (\text{wt}\% \text{Ti}) f_\text{Ti} \times (\text{wt}\% \text{O}) f_\text{O}^2, \quad (3)$$

where \(a\) is the activity and \(\Delta G^\theta\) is the standard Gibbs free energy change. The activities of [Ti] and [O] can be described as follows:

$$a_i = f_i \times [\% i], \quad (4)$$

where \([\% i]\) is the mass percentage of element \(i\) and \(f_i\) is activity coefficient of element \(i\), which can be calculated as follows:

$$\log f_i = \sum e_i / [\% f_i], \quad (5)$$

Table 2: Activity interaction coefficients in molten steel at 1,873 K

<table>
<thead>
<tr>
<th>(e_i / [% f_i])</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>−0.165</td>
<td>0.05</td>
<td>−0.043</td>
<td>/</td>
<td>−0.27</td>
</tr>
<tr>
<td>O</td>
<td>−0.45</td>
<td>−0.066</td>
<td>−0.021</td>
<td>/</td>
<td>−0.133</td>
</tr>
</tbody>
</table>
where \( e_i \) is the activity interaction coefficient, and is shown in Table 2 [31].

The equilibrium content of Ti can be deduced to about 1,874 ppm based on the above formulae. This value is much higher than the Ti content at 15 min for both experiments (about 150 ppm), which suggests that the decomposition reaction is a rate-controlled step.

If the above-mentioned theory is correct, the following experimental results may be well-explained.

From the view of oxide size, due to the decomposition and regeneration, although the added TiO\(_2\) is at the nanoscale, the micron scale Ti-bearing oxides were observed. In fact, similar results have been reported by Mu et al. [28]. They added TiO\(_2\) powder, with a particle size in the range of 0.139–0.854 \( \mu \)m, into molten steel. Then, the size range of resultant Ti-bearing inclusion increased to between 0.215 and 4.802 \( \mu \)m.

From the view of adding validity, the diffusion of [Ti] leads to the successful introduction of Ti element into molten steel despite the smaller density of titanium oxide. Moreover, since the decomposition reaction is a rate-controlled step, titanium and oxygen elements were continuously supplied to the molten steel along with time. Due to this reservoir effect, the Ti content, number density of Ti-bearing oxide, and normalized titanium content are all steadily increased with treatment time.

From the view of number density, it is found that at 15 min, the number density of Ti-bearing oxide for EAM method is about twice of that for IPM method, though the Ti content is similar. This may be due to two facts. One, the measured Ti content is acid-soluble Ti, while our previous experiments have indicated that TiO\(_2\), Ti\(_2\)O\(_3\), and Ti\(_3\)O\(_5\) are all insoluble in dilute nitric acid and hydrochloric acid. The other, the decomposition reaction supplies both [Ti] and [O], while the adding of Ti alloy only introduces [Ti]. Thus the formation of Ti-bearing oxide is more favorable for EAM method. Furthermore, the dynamic equilibrium between decomposition and regeneration keeps the acid-soluble Ti stable.

The discussion on the above three aspects (oxide size, adding validity, and number density) hints that after TiO\(_2\) adding, the supposed process, including dissolution, decomposition, diffusion, and regeneration, may be rational. However, more evidence is needed to further verify this theory.

The objective of EAM is to introduce titanium oxides, which can stimulate the IGF nucleation. Hence, a rod-shaped sample was extracted from the cast sample, and heat treatment was administered using Gleeble3500. The procedure involved heating at a rate of 10 K s\(^{-1}\) to 1,473 K, holding for 5 min, and subsequently cooling at a rate of 10 K s\(^{-1}\) to room temperature. After etching in 3 vol% Nital solution, the sample was analyzed with microscope (MIRA3 TESCAN). Results in Figure 6 revealed the presence of IGFs, which were induced by titanium oxides. This resemblance is akin to Ti-bearing oxides stemming from the IPM, thereby underscoring the efficacy of EAM in facilitating TiO\(_2\)-induced effects.

4 Conclusions

1. The TiO\(_2\) powder was directly added to the HRB400 molten steel, and the transient evolution of oxide was studied. The results showed that with increasing treatment time, the number density of Ti-bearing oxides and the corresponding titanium content after further normalization gradually increased. This trend is in contrast with IPM method, which involves directly adding Ti alloy.

2. After comparison, it is found that with the similar final titanium content, the number density of Ti-bearing oxides introduced by EAM is significantly higher than that of IPM.

3. Based on the discussions, an interpretation is proposed. That is after adding TiO\(_2\), its dissolution, decomposition, diffusion, and regeneration may occur in turn in molten steel.

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**References**


