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Fundamentals of Titanium Deoxidation

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Fundamentals of titanium as an effective actor in deoxidation and inclusion forming additive in steel are discussed. Ti-O equilibria in pure iron and in different example steels are compared and the premises for the influence of titanium are shown. Formation and transformations of titanium containing inclusions during solidification are examined. Examples of final inclusions in Ti deoxidised steels are presented. Titanium in steelmaking slags, occurrence as four- and three-valent titanium and activity of TiOₓ in slags are further discussed.

Key words: Titanium deoxidation, steels, inclusions, slag.

Introduction

Although titanium has fairly strong affinity to oxygen, titanium deoxidation is not such a common practice like deoxidation with aluminium or silicon-manganese. In most cases titanium is added into the steel to bind nitrogen, to form titanium nitrides or carbonitrides. Titanium containing inclusions can promote grain refinement by constitutional supercooling [1] and inhibit grain growth by the Zener pinning effect [2]. Another application of titanium is in boron steels in which it forms nitrides and thus leaves boron free to raise hardenability of steel [3]. A further application of Ti is in stainless steels in which it is used as “stabilizer” to bind carbon and thus to avoid “sensitization”, i.e. precipitation of Cr-carbides and susceptibility to intergranular corrosion [4]. Also in this case Ti-nitrides or carbonitrides are formed.

A relatively new application of titanium concerns the ability of titanium oxides to act as nucleation sites for acicular ferrite [5-10]. Several mechanisms have been proposed to be responsible for titanium oxide inclusions to act as nucleation sites for acicular ferrite. The most prevailing one seems to be the absorption of Mn by Ti₂O₃ resulting in a manganese depleted zone (MDZ) around the inclusions which promotes ferrite formation [5-6, 8-10, 11-14]. Shim et al [10] even concluded that Ti₂O₃ in Mn-free steel is inert in terms of acicular ferrite nucleation but instead formation of (Mn,Ti)₂O₃ inclusions is the key phenomenon. The presence of TiOₓ rich inclusions containing Mn and associated with Mn depletion in the surrounding steel have resulted in steel microstructures rich in acicular ferrite in several studies. [5, 6, 10, 15-18] The inclusions formed in Ti containing steels can be very complex depending on the steel composition (especially Ti, Mn, Al, O, N, S). As shown above, numerous studies have been performed to find out the influence and acting mechanisms of titanium oxides in steels on grain refinement and formation of acicular ferrite. Less attention has been focused on basic phenomena controlling the occurrence of titanium and formation of different Ti-bearing phases in liquid as well as solidified steel. In this study we have emphasized in steel compositions and conditions in which Ti-oxides have a major role instead of other Ti-bearing compounds, nitrides, carbides etc. First Ti-O deoxidation equilibrium is discussed concerning prevalence of different oxidation states of Ti as well as influence of other components in steel on the phase equilibria. Secondly, alteration of equilibria in liquid steel at lowering temperatures, during solidification and cooling are examined. Calculated results are compared with experimental results by the authors and from the literature. Oxidation state of Ti in slags is shortly reviewed too. Finally, eventual
methods to control the performance of Ti-oxides in steels are discussed.

1. Titanium oxides

Titanium has several oxidation states or valencies. In minerals it is appearing mostly in Ti$^{4+}$ form like for instance in TiO$_2$ (anatase or rutile). Other valencies are Ti$^{3+}$ and Ti$^{2+}$, when the most common oxides are Ti$_3$O$_5$, Ti$_2$O$_3$ and TiO, respectively. At high temperatures three- and four-valent oxides have been observed to form several more complex oxides so-called Magneli oxides, Ti$_n$O$_{2n-1}$ like Ti$_4$O$_7$, Ti$_6$O$_{11}$, Ti$_8$O$_{17}$, etc. depending on the temperature and oxygen partial pressure [Lynch 1997][19]. In Fig. 1 the Ti-TiO$_2$ system is presented as a function of temperature. The diagram was calculated with FactSage 6.2 Program Equilibrium Mode using FToxid database [20]. The same program was used in all calculations presented here. At liquid steel conditions the oxygen activity in the steel corresponds to p$_{O2}$ range $10^{-12}$ – $10^{-13}$. This was drawn in the picture, however, the phase relations are quite different when the Ti oxides are as components in slags. This topic will be discussed later.

![Fig. 1. Predominance diagram for different oxides in Ti – TiO$_2$ system as a function of temperature and p$_{O2}$. Magneli phases Ti$_n$O$_{2n-1}$ are left from TiO$_2$.](image)

<table>
<thead>
<tr>
<th>1000/TK</th>
<th>log p$_{O2}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-14</td>
</tr>
<tr>
<td>0.6</td>
<td>-12</td>
</tr>
<tr>
<td>0.7</td>
<td>-10</td>
</tr>
<tr>
<td>0.8</td>
<td>-8</td>
</tr>
<tr>
<td>0.9</td>
<td>-6</td>
</tr>
<tr>
<td>1.0</td>
<td>-4</td>
</tr>
<tr>
<td>1.1</td>
<td>-2</td>
</tr>
<tr>
<td>1.2</td>
<td>0</td>
</tr>
</tbody>
</table>

2. Deoxidation equilibrium with Ti

2.1 Deoxidation with titanium

The deoxidation equilibrium was calculated with FactSage 6.2 Program Equilibrium Mode using FToxid and FSstel databases [20]. The main deoxidation reaction is written:

$$3[\text{Ti}] + 5[\text{O}] = \text{Ti}_3\text{O}_5 \quad (1)$$

However, at high Ti content in steel the stable oxide is Ti$_2$O$_3$. The deoxidation diagram of Ti in pure iron was calculated in Fig. 2. It is equivalent to the evaluation of In-Ho Jung et al [21] based on application of associate model for oxygen in liquid iron. Ti$_3$O$_5$ is the oxide product in wide range of Ti content. Above 0.5% Ti the equilibrium oxide turns to Ti$_2$O$_3$. At very low titanium contents Ti oxide is associated with iron oxide to form FeO·2TiO$_2$. The calculated equilibrium curve is in fairly good accordance with the evaluated curve by Hino et al [22] and the assessment by Kulikov [23]. On the other hand the early evaluation by JIPS shows remarkably higher oxygen level [24]. Related to the current examination, also a corresponding deoxidation equilibrium was calculated for a steel composition of 1.35mass% Mn, 0.2mass% Si, 0.15mass% C, 40ppm N and 20ppm S. The slight rise of oxygen content is due to the influence of nitrogen on activity of Ti. The change of curvature at low Ti content is due to
formation of liquid slag containing oxides of Ti, Mn and Fe.

Fig. 2. Deoxidation equilibrium with Ti in pure Fe-Ti-O melt (lower) and in Steel 1 melt (upper).

2.2 Deoxidation equilibria in steel

When more components are added in iron they influence the deoxidation equilibrium by forming own oxides and by interaction effects. Aluminium is a stronger deoxidizing agent in steels than titanium. Therefore its influence on titanium deoxidation is of great importance. In Fig. 3 the predominance area diagram for Fe-Ti-Al-C-Mn-Si-O-N-S system at 1873K (1600°C) is presented.

The dashed lines in Fig. 3 represent the position of the 2-phase region between Al$_2$O$_3$ and SLAG calculated at constant 30ppm Otot. At the other oxygen contents the 2-phase region is not shown because it is very narrow and close to the Al$_2$O$_3$ line. Addition of Ti and TiO$_2$ to liquid steel and inclusions resulting from these additions have been discussed in previous articles by the authors [25, 26]. The marked points in Fig. 3 represent compositions of the steel used in experiments with Ti and TiO$_2$ additions. They fall mainly in the SLAG and SLAG/Al$_2$O$_3$ regions. The composition of the Slag was mainly Al$_2$O$_3$ (25-29mass%), TiO$_2$ (26-28mass%), Ti$_2$O$_3$ (39-42mass%) and MnO (4-5mass%) [26]. Over 60mass% of the SLAG phase is thus titanium oxides. The Ti/Al ratios in the experiments were between 5 and 14. In order to get pure Ti$_3$O$_5$ inclusions the ratio should be even higher, about 20. However the presence of TiO$_x$ dominant inclusions has been explained and the structure of typical inclusions is discussed in previous articles by the authors [25,26]. Compared to the calculations of Jung et al [21] in Fe-Ti-Al-O the main differences are in the SLAG phase due to the presence of Mn in the calculations of this article.
3. Solidification and cooling of Ti deoxidized steel

The changes of equilibria and transformations of inclusions during solidification and cooling of Ti containing steels are essential for inclusions’ performance and influences on their properties in final steel products. Thermodynamic calculations with Factsage 6.2, using the FSstel and FToxid databases have been performed. The composition used in the calculations was 1.35 mass% Mn, 0.2 mass% Si, 0.15 mass% C, 0.07 mass% Ti, 50 ppm Al, 30 ppm O, 40 ppm N, 20 ppm S and rest Fe. The inclusions formed in Fe-Mn-Si-C-Ti-Al-O-N-S system between 1473 -1873K(1200-1600°C) are presented in Figs. 4 and 5 respectively. In Fig. 4 at 1873K(1600°C) the deoxidation product is not pure Ti3O5 but liquid slag due to the low Ti content. The main components of slag solution are Al2O3, MnO, TiO2 and Ti2O3. The ratio of TiO2 and Ti2O3 in slag corresponds to Ti3O5. At lower temperatures Al2O3 (corundum) phase is formed with <3% Ti2O3 as a minor component. The liquid slag disappears at around 1793K(1520°C) and the stable phase changes to Ti5O8 (pseudobrookite) which is further transformed to Ti2O3 (ilmenite) at around 1723K(1450°C). According to the calculations ilmenite should disappear at lower temperatures and corundum form again but this is hardly realistic to happen due to kinetic reasons. In Ti3O5 (pseudobrookite) solid solution the main component, is TiO2 (nearly 98%), and the rest is mainly MnTi2O5. In Ti2O3 (ilmenite) the main component is Ti2O3 (>93%) and the rest is mainly MnTiO3.

In Fig. 5 the main components in slag are Al2O3, Ti2O3 and TiO2. The slag disappears at 1808K (1535°C) and is mainly replaced by Ti2O3 which is transformed to Ti3O5 at around 1573K(1300°C). The formation of TiN and TiC is quite strong in the calculations. Such a strong formation was not observed by the authors in real experiments with relatively high cooling rate [25, 26]. The effect of manganese can be observed by comparing Figs. 4 and 5. The most significant difference is the change of the transformation of Ti3O5 to Ti2O3 at lower temperatures in the system without manganese. Similar calculations with a lower Ti content were presented in a previous article by the authors [26]. In the previous calculation the transformation temperature was also around 1573K(1300°C) and the formation of the Al2O3 phase was clearly stronger. This depicts the importance of the Ti/Al ratio on the final inclusion types. In Fig. 4 the Ti/Al ratio is 14 and in the previous calculation [26] it was 10. The higher Ti/Al ratio seems to favor the formation of Ti2O3.

The distribution of titanium between different phases in the example of Fig. 4 is presented in Fig. 6. It can be seen that most of the titanium is present in the liquid iron phase at higher
temperatures and at lower temperatures in the austenite (FCC) phase. The FCC phase includes the titanium as dissolved $[\text{Ti}]_{\text{FCC}}$, and TiN and TiC precipitates. According to the calculations a significant amount of Ti in FCC is present as nitrides and carbides. The total oxygen content determines the amounts of oxides formed.

Fig. 4. Calculation of equilibrium phases in Fe-Mn-Si-C-Ti-Al-O-N-S system at 1873-1473°K(1600-1200°C)

Fig. 5. Calculation of equilibrium phases in Fe-Si-C-Ti-Al-O-N-S system at 1873-1473°K(1600-1200°C)
In order to compare the effect of different Ti/Al ratios and to study the effect of time on the inclusions formed industrial samples from a steel plant were studied with SEM-EDS (LEO-SEM 1450, EDS and INCA from Oxford Instruments). The samples were taken from the melt in the ladle after FeTi addition. The first sample was taken 2-3 minutes after addition and the last two in 2-3 minutes intervals. The basic composition was around 0.04mass% C, 0.1mass% Si and 1.75mass% Mn. The Ti and Al contents together with the Ti/Al ratios are presented in Table 1. At least 12 inclusions were analysed in each sample. The average analyses of the inclusions are presented in Table 2. Only inclusions which contained both Ti and Al oxides were included. In addition some inclusions which contained only or mainly titanium oxide were found. Also a lot of titanium nitride dominant inclusions were found. Nitrides are not discussed in this study.

Table 1 Analyses of Industrial samples in mass%

<table>
<thead>
<tr>
<th>sample</th>
<th>Al</th>
<th>Ti</th>
<th>Ti/Al</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>0.153</td>
<td>7.65</td>
</tr>
<tr>
<td>2</td>
<td>0.02</td>
<td>0.153</td>
<td>7.65</td>
</tr>
<tr>
<td>3</td>
<td>0.019</td>
<td>0.15</td>
<td>7.89</td>
</tr>
</tbody>
</table>

Table 2 Average inclusion analyses in Industrial samples in mass%

<table>
<thead>
<tr>
<th>sample</th>
<th>Ti</th>
<th>Al</th>
<th>O</th>
<th>N</th>
<th>C</th>
<th>Mn</th>
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<td>2</td>
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<td>1-2</td>
<td>1-2</td>
<td>1</td>
<td>3-5</td>
</tr>
</tbody>
</table>

A typical oxide inclusion is presented in Fig. 7. Most of the inclusions found in the industrial samples contained aluminium oxide as the main component. Owing to the steelmaking practice the steel was first deoxidized with aluminium. This resulted in alumina inclusions which are hard to transform to Ti-rich inclusions. Anyway, as the example in Fig. 7 shows Ti is the second major metal cation in inclusions, only somewhat lower than Al. These results can be compared to the experimental samples studied in the previous articles by the author [25, 26]. In those samples the inclusions contained titanium oxide as the main component. A representative analysis of the titanium oxide dominant inclusions was 46mass% Ti, 2.5mass% Al, 24mass% O, 2.6mass% C, 17.6mass Mn and 7.5mass% S.
The difference in inclusions type is evidently due to both the different Ti/Al ratio and the absolute Al content in steels. In experimental samples the Ti/Al ratio was typically over 10 (11 in the example sample) whereas in the industrial samples it was below 8. On the other hand in the industrial steel both Al and Ti contents were much higher than in the experimental heats. As discussed earlier the high Al content in the steel at the moment of Ti addition obviously retards the formation of Ti oxide rich inclusions. Finally, the composition of oxide inclusions seems to affect the Mn content of the inclusions too. The higher is the Ti oxide content the higher is also the Mn content in the inclusions. The role of Mn in Ti deoxidized steels has been discussed in more detail, previously [26, 27].

4. Titanium in steelmaking slags

Titanium occurs in steelmaking slags in four- and three-valent forms as Ti$^{4+}$ and Ti$^{3+}$. Therefore in slags titanium oxide is often written TiO$\_x$. The oxidation state of Ti in slags has been examined by several researchers e.g. Turkdogan, Fruehan et al, Tranell et al, Schwerdtfeger et al and Ariyo [28-32]. A general observation has been that the relation can be derived from the reaction equation:

$$\text{TiO}_{1.5} + \frac{1}{4}\text{O}_2 = \text{TiO}_2 \quad (2)$$

Accordingly, the ratio of TiO$_2$/TiO$_{1.5}$ should be somehow related to $p_{O_2}^{1/4}$ provided that the activity coefficients of titanium oxides are not too different. In Fig. 8 values from the literature were collected and organized in groups according to the slag basicity and the experimental temperature. The experimental points fairly well follow the trendline of power $\frac{1}{4}$.

$$K = \frac{a_{\text{TiO}_2}}{a_{\text{TiO}_{1.5}} \cdot \text{p}_{\text{O}_2}^{1/2}} \quad (3)$$
The following further relations have been found:
- Ti$^{4+}$/Ti$^{3+}$ ratio is increasing with increasing basicity
- Ti$^{4+}$/Ti$^{3+}$ is increasing with decreasing temperature
- Ti$^{4+}$/Ti$^{3+}$ has a maximum at certain total TiO$_x$ content in slag (appr. 14 to 20-25% TiO$_x$). The position of maximum depends on the other components of the slag i.e. basicity [30,32]

Fig. 1 showed us that in steelmaking conditions with p$_{O_2}$ in the range 10$^{-12}$...10$^{-13}$ the stable Ti-oxides are Ti$_2$O$_3$ and maybe TiO. This is valid for pure TiO$_x$ and not contradictory to the observations of TiO$_x$ in slags and Fig. 8. By adding slag components the activity of titanium oxides is decreased and higher valence states become more stable. In the case of titanium deoxidation and, more general, in different applications of Ti as alloying element, the knowledge of the thermodynamics of Ti in slags is essential. It influences Ti losses into slag and the reversal pick-up reaction. Also inclusion formation in multi-component deoxidation situation has connections to slags.

**Conclusions**

This short review of titanium in steels can be briefly summarised.

1. Ti is becoming more and more useful with different applications in steelmaking.
2. Ti oxide inclusions in steel to adjust steel properties is a promising new concept.
3. Ti appears in different oxidation states in oxides, Ti$^{4+}$ and Ti$^{3+}$ being most dominant in steelmaking conditions. In deoxidized steel the composition is usually marked as Ti$_2$O$_3$.
4. Ti is a weaker deoxidizer than Al. Therefore Al-content is limited and the Ti/Al ratio should be typically 10...20 in order to get Ti oxide dominating inclusions in steel.
5. By thermodynamic calculations it is possible to reveal equilibrium phases in liquid steel as well as during solidification and cooling.
6. In Ti deoxidized steel most of the added Ti is in liquid steel and in austenite after solidification.
7. Ti$_2$O$_3$ tends to transform to Ti$_3$O$_5$ during cooling.
8. Titanium occurs as Ti$^{4+}$ and Ti$^{3+}$ valent oxides also in slags in steelmaking conditions. The ratio depends on p$_{O_2}$ (oxygen activity), slag composition and temperature.

**References**

20. Factsage 6.2 http://www.factsage.com/
22. Hino M. and Ito K., Thermodynamic Data for Steelmaking; Tohoku Univ. Press, 2010
23. Kulikov I. S.: Deoxidation of Alloys, Moscow, Metallurgija, 1975, pp.504
24. Steelmaking data sourcebook by the Japan Society for the Promotion of Science, the 19th Committee on Steelmaking, Gordon & Breach Science Publishers, 1988 New York