Original Article

Evaluating slag–metal deoxidation equilibrium in secondary steelmaking

Viviane Lima Freitas da Silva, Luciano da Silva Leitão Jr., Erik de Aguiar Santos, Antônio Carlos Sant’Anna da Silva, André Luiz Vasconcellos da Costa e Silva

EEIMVR-UFF, Av. dos Trabalhadores, 420, 27255-125, Volta Redonda, RJ, Brazil.

ARTICLE INFO

Article history:
Received 25 April 2019
Accepted 7 June 2019
Available online 28 June 2019

Keywords:
Ladle metallurgy
Non-metallic inclusions
Reoxidation
Computational
Thermodynamics
Steel

ABSTRACT

Steel–slag reactions are important in steelmaking, in special in secondary steelmaking. Currently, desulfurization, deoxidation and inclusion removal are mostly performed during ladle refining. The extent to which these reactions proceed is governed by the initial state of the material reaching the ladle, the additions made to the ladle and by undesired interactions such as reoxidation and steel-refractory reactions. In this work, the extent to which equilibrium is approached for the different deoxidation reactions is Al-killed and Si–Mn deoxidized steel is evaluated using thermodynamics. These results are compared to measurements performed in industrial ladle furnaces. The comparisons make possible evaluating the efficiency of the deoxidation process. The results indicate that reoxidation by air caused by agitation probably play a key role on the ability to approach equilibrium, reaching low oxygen content in steel. It is also concluded that relatively long treatments with controlled agitation are needed to achieve steel–slag equilibrium.

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1. Introduction

Steel–slag reactions are of great importance in steelmaking. Many secondary steelmaking processes focus on these reactions. Currently, desulfurization, deoxidation and inclusion removal are mostly performed during refining in ladle furnace (LF) [1]. The extent to which these reactions proceed, and approach equilibrium depend on the initial state of the material reaching the ladle, the additions made to form slag and adjust the chemical composition of the steel and by undesired interactions such as reoxidation and steel-refractory reactions.

Under some LF processing conditions deoxidation equilibrium is achieved or closely approached. This is not a general rule, however. When equilibrium is attained, it is relatively easy to calculate the expected steel composition, in special if one has access to computational thermodynamics tools. If, however, equilibrium is not reached, the final state depends on many process variables and, in principle, a complex kinetic model would be needed. Process evaluation and improvement can only be achieved after correct understanding. Thus, in this work, a thermodynamic evaluation of the state of deoxidation reactions is performed in two industrial LFs. One producing Al-killed steel and the other Si–Mn deoxidized steel. This is done by evaluating the individual metal-oxide equilibria and comparing the results to the actual oxygen content in the steel. Results are discussed with the aim of improving the deoxidation practice and the LF process.

* Corresponding author.
E-mail: andre@metal.eeimvr.uff.br (A.L. Costa e Silva).
https://doi.org/10.1016/j.jmrt.2019.06.012
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Fig. 1 – When metal-slag equilibrium prevails in the ladle, the soluble oxygen content is such that it satisfies all metal-oxide equilibria [16]. Here μ<sub>steel</sub> is the oxygen chemical potential in the steel, directly related to the oxygen content in solution in the steel.

1.1. Deoxidation thermodynamics and kinetics

The thermodynamics of deoxidation of steel has been well reviewed in many publications (e.g. Refs. [2,3]). Although there are still some doubts concerning thermodynamic data for Al [4], Ca and Mg [5], in special, the present knowledge is sufficiently good to perform predictions in the range of commercial steels. It is generally agreed that the deoxidations reactions involving Al and Si are not limited by nucleation and that the oxygen in solution in steel approaches equilibrium with the dissolved deoxidants very rapidly [6], at least when the pure oxide is formed. If, however, equilibrium must be attained with an oxide that is not pure, but dissolved in the slag, kinetics may play an important role (e.g. Refs. [7–10]).

While ladle stirring is critical for the kinetics of the metal-slag reactions, it is well established that control must be exercised to avoid reoxidation and slag entainment [6,11]. Comparing the different calculated deoxidation equilibria to real values in the ladle is a known practice to evaluate the approach to equilibrium. For steel processed in LF under ideal conditions of agitation and with due care to prevent reoxidation, it has been observed that the final composition is very close to equilibrium (e.g. Refs. [10,12,13]). In this case, the equilibrium of all possible oxidation reactions should prevail and the single value of oxygen in solution should satisfy all the calculated equilibria, as indicated in Fig. 1. If processing time is short, agitation is inadequate (either too weak or too strong [6]) and if reoxidation is not properly controlled, this condition, however, is not fulfilled. In this case, the observed values of the chemical composition of the steel and of the slag will indicate how the process is evolving. This has been demonstrated, for instance, by Ref. [14], who tried to understand the reasons for the observed deviations. Due to the complexity of the problem, efficient kinetic models for the LF are still being developed (e.g. Refs. [7,15]).

2. Experimental

Heats made in an oxygen converter (BOF) and in an electric arc furnace (EAF) were processed in ladle furnaces without vacuum protection. During LF processing slag and metal were sampled at defined points of the process. Temperature and oxygen dissolved in steel were measured using commercial, disposable electrolytic cell probes.

Experiments in BOF steel were performed in heats of a low-sulfur HSLA steel containing around 1% Mn and 0.1% C that was aluminum deoxidized and calcium treated. All sampling was done in the LF before the calcium treatment. Experiments performed in EAF steel were performed in heats of an engineering bar steel containing around 0.15% C. The steel was silicon-manganese deoxidized. Sampling was performed in the LF and in the tundish. Tables 1 and 2 give more details about the steels and slags used in these experiments the steelmaking processing, and sampling timeline.

Computational thermodynamics calculations were performed using Thermo-calc [17] in conjunction with two thermodynamic databases: SLAG3 database [18], originally derived from the IRSID model, using the Kapoor–Frohberg–Gaye cell model [19,20] and TCOX7 [21], using the ionic liquid model developed at KTH [22,23]. The application of these databases to steelmaking is described and discussed elsewhere [12,20].

3. Evaluating the deviation from metal-slag equilibrium

In order to evaluate the deviation from equilibrium, the following strategy was adopted. Using the composition of the slag and temperature measured in the LF the activities of the oxides in the slag were calculated using computational thermodynamics. In the case of aluminum deoxidation, the alumina activity was also calculated using Ohta and Suito’s empirical formulæ [24,25]. The agreement of the activities calculated using the two databases was reasonable, as shown in Fig. 2. The agreement of the results of Ohta and Suito’s formulæ with those calculated using computational thermodynamics was also reasonable (see Fig. 3).

For each applicable oxide-metal reaction (Eqs. 1–4), equilibrium was calculated considering the metal activity determined from the steel chemical analysis (Al, Si, Mn and Fe) and the oxide activities, to determine the oxygen content in equilibrium with these conditions. If equilibrium had been achieved, all calculations should result in the same value for the oxygen content dissolved in the steel, which should agree with the experimental measurements. The difference between these values indicate the extent of deviation from metal-slag equilibrium.

\[
\begin{align*}
2\text{Al} + 3\text{O} &\rightarrow \text{Al}_2\text{O}_3, \\
\text{Si} + 2\text{O} &\rightarrow \text{SiO}_2, \\
\text{Mn} + \text{O} &\rightarrow \text{MnO}, \\
\text{Fe} + \text{O} &\rightarrow \text{FeO}
\end{align*}
\]
Thus, when the calculated values of oxygen in equilibrium with each metal and oxide are compared among each other and with the measured oxygen content, an estimate of the deviation from equilibrium is obtained as well as insights into the effectiveness of the deoxidation process.

### 3.1. Aluminum killed steel

In the case of aluminum killed steels, the oxygen content that would be in equilibrium with the elements and the oxides (according to Reactions 1-4) were calculated for Al, Mn and Fe. As observed in previous work [26] in the same LF, the deviation between the measured oxygen and the Fe/FeO equilibrium was large. For this reason, the comparison between these calculations and the measured values is not presented in the following figures.

Fig. 3 presents the comparison of the measured oxygen content with the oxygen calculated according to the Al/Al2O3 equilibrium. This calculation was performed for three different values of alumina activity:

(a) Pure alumina, \( a_{\text{Al}_{2}\text{O}_3} = 1 \) which is the condition prevailing right after the aluminum addition to the liquid metal,

(b) Alumina activity calculated based on the LF slag composition at the sampling moments, using Ohta and Suito’s formula and,

(c) Alumina activity based on the same slag composition and temperature, calculated using SLAG3 and Thermo-calc.

The results in Fig. 3 show that the oxygen content in the steel is lower than that which would be in equilibrium with pure alumina. This indicates that the dissolution of alumina and lowering of its activity is having some effect on the aluminum deoxidation. However, the calculated oxygen in equilibrium with conditions (b) and (c) above are lower than the measured oxygen content. The apparent equilibrium occurs with \( a_{\text{Al}_{2}\text{O}_3} = 0.60 \pm 0.17 \).

Fig. 4 presents the oxygen content in equilibrium with Mn/MnO. There is no equilibrium between Mn and MnO, the slag content of MnO being substantially higher than that which would be in equilibrium.

Among the oxides considered in the calculations, MnO and FeO are part of the passing slag from the BOF tapping operation. In order to follow the evolution of MnO and FeO, their values during the LF treatment were compared. The values of MnO and FeO along the treatment in the LF are presented in Fig. 5.

#### Table 1 – Steelmaking processing information and sampling timeline.

<table>
<thead>
<tr>
<th>Process</th>
<th>Heat size (t)</th>
<th>T range in ladle (°C)</th>
<th>Argon stirring ( \text{Nm}^3/\text{h}t )</th>
<th>Sampled heats</th>
<th>Sampling times, starting at arrival at LF (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOF-LF</td>
<td>220</td>
<td>1570–1590</td>
<td>0.11–0.48</td>
<td>17</td>
<td>0,15,25, release form LF (45–60 min)</td>
</tr>
<tr>
<td>EAF-LF</td>
<td>98</td>
<td>1550–1600</td>
<td>0.18–0.42</td>
<td>14</td>
<td>0, release from LF (14–16 min) Arrival at caster (Release + 15 min)</td>
</tr>
</tbody>
</table>

#### Table 2 – Slag and steel compositions used in the experiments.

<table>
<thead>
<tr>
<th>Process</th>
<th>Ladle slag composition (oxides)</th>
<th>Steel composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CaO} ) – ( \text{MgO} ) – ( \text{SiO}_2 ) – ( \text{Al}_2\text{O}_3 ) – ( \text{FeO} + \text{MnO} )</td>
<td>( \text{C} ) – ( \text{Mn} ) – ( \text{Si} ) – ( \text{Al} )</td>
</tr>
<tr>
<td>BOF-LF</td>
<td>35–57 – 8–12 – 7–21 – 8–27 – 1.7–27</td>
<td>0.1 – 0.8–1.2 – 0.02–0.09 – 0.0–0.06</td>
</tr>
<tr>
<td>EAF-LF</td>
<td>30–50 – 7–12 – 10–20 – 1–4 – 0.9–15.5</td>
<td>0.15 – 0.4–1.2 – 0.09–0.19 – –</td>
</tr>
</tbody>
</table>

This can also be expressed by recalling, from Fig. 1, that equilibrium must fulfill Eq. 5, since there is only one value for the dissolved oxygen content in the steel.

\[
\text{O}_{\text{Al}} = \text{O}_{\text{Si}} = \text{O}_{\text{Mn}} = \text{O}_{\text{Fe}} = \text{O} \tag{5}
\]
Fig. 4 – Calculated values of oxygen concentration in equilibrium with Mn and MnO. Oxide activity calculated using computational thermodynamics. Dashed line shows measured values for each heat.

Fig. 5 – Evolution of FeO and MnO during the treatment in the LF for various Al-killed heats. Samples from the same heat are on a single line. Arrow indicates evolution with time. Dashed line indicates equilibrium FeO/MnO relation proposed by Turkdogan [3].

Fig. 6 – Calculated values of oxygen concentration in equilibrium with Si and silica. Silica activity calculated using computational thermodynamics. Dashed line shows measured values for each heat.

Fig. 7 – Calculated values of oxygen concentration in equilibrium between Mn and MnO and Fe and FeO. Oxide activities calculated using computational thermodynamics. Dashed line shows measured values for each heat.

3.2. Silicon manganese killed steel

Most heats consistently approach lower values of FeO and MnO and the MnO/FeO equilibrium relationship. At least in one heat, the approach is interrupted during the process. The final contents, however, are still high for the level of deoxidation of the steel, as seen in Fig. 4.

The results in Figs. 3–5 indicate that aluminum is indeed the element controlling the lowering of the soluble oxygen in the process. Nonetheless, equilibrium is not attained. This could be caused either by reoxidation of the liquid metal by the atmosphere (“open eye” due to excessive agitation) or by the difficulty in lowering the FeO and MnO contents in the slag.

In the case of silicon manganese killed steels, the oxygen content that would be in equilibrium with the elements and the oxides (according to Reactions 1–4) were calculated for Si, Mn and Fe (Fig. 6).

Fig. 5 presents the comparison of the measured oxygen content with the oxygen calculated according to the Si/SiO₂ equilibrium. As the silica activity in the slag is very low, silicon becomes an excellent deoxidant.

However, the actual oxygen values achieved in the LF deoxidation process are significantly higher than those calculated from the Si/SiO₂ equilibrium.

The values for the Fe/FeO and Mn/MnO calculated equilibria are presented in Fig. 7.

The expected values for oxygen in equilibrium with Mn/MnO and with Fe/FeO are of the same order of magnitude as the experimental values of oxygen content. Furthermore, evaluating the evolution of the content of MnO and FeO in the
LF slag (Fig. 8) indicates that the heats approach the FeO/MnO equilibrium and reach lower values than those shown in Fig. 5, for Al-killed steel. This may be due to the strong slag deoxidation performed with CaC2 during tapping from EAF, in these Si–Mn steels. Direct slag deoxidation seems to be quite effective in lowering its content of the less stable oxides.

3.3. Summary of the observations

In both cases (Al-killed and Si–Mn deoxidation), the equilibrium oxygen contents would be significantly lower than the values measured at the end of the LF process. In the case of Al-killed steels, much lower soluble oxygen contents were reached than in the case of Si–Mn steels. This is reasonable as the equilibrium with a lower oxide activity (in the slag) is not critical to an effective deoxidation with Al. The measured values are in apparent equilibrium with an alumina activity of a_{Al2O3} = 0.60 ± 0.17, between 1 (no effect of the slag) and the calculated value for the slag composition.

In the case of the Si–Mn deoxidized steel, the measured soluble oxygen content deviates significantly from what would be expected. It is, however, much lower than the value expected if equilibrium was established with pure silica, that would be in the range of 120–140 ppm.

There are two plausible explanations to the observed phenomena. First, it could be postulated that the processing time was not enough to achieve metal–slag equilibrium. However, during the processing of the Al-killed heats, for instance, many heats required further additions of aluminum to keep this concentration within the specified range. Furthermore, times as long as 30–40 min were used in some Al-deoxidized heats, which should approach equilibrium, based on information acquired elsewhere in similar conditions, but under vacuum (e.g. Ref. [5]). This seems to indicate that the reduction of less stable oxides is not effective in the process and/or reoxidation by air is playing a relevant role in the process. While FeO and MnO are reduced during the processing of both steels, it seems that in the processing of the Si–Mn steel, the practice of directly deoxidizing the slag is positive for oxygen control. However, in the processing of both steels, the deviations suggest that reoxidation due to exposure to air may be playing a relevant role. This indicates that the formulation of a kinetic model for the LF process is of paramount importance for the further development of the understanding of the deoxidation–reoxidation process. This understanding will have a significant impact on quality of steel and cost control in the melt shop.

4. Conclusions

Contrary to steels processed for longer times and under vacuum, equilibrium between deoxidants in the steel and oxides in the slag was not achieved during the regular ladle furnace processing of Al-killed BOF steel and Si–Mn EAF steels. In the case of Al-killed steels, aluminum clearly controls the oxygen potential in the steel and levels of oxygen close to those expected by equilibrium are achieved. In the case of Si–Mn steels, with somewhat shorter LF processing times, the deviation is quantitatively larger. The use of direct slag deoxidation with CaC2 in the Si–Mn steels was shown to be effective in reducing the content of less stable oxides in the slag but was not enough to make possible slag–metal equilibrium at the end of the process.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors thank GERDAU and CSN for support during the performance of this work. André Costa e Silva thanks CNPq, CAPES and FAPERJ for support during different stages of this work.

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