SMETS, S. JANSSENS, J. COLETTI, B. PLESSERS, J. BLANPAIN, B. and WOLLANTS. P. *In situ* measurement of the oxygen activity of low carbon steel ladle slags. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

In situ measurement of the oxygen activity of low carbon steel ladle slags

S. SMETS*, J. JANSSENS*, B. COLETTI*, J. PLESSERS†, B. BLANPAIN*, and P. WOLLANTS*

**K.U. Leuven, Department of Metallurgy and Materials Engineering, Heverlee, Belgium*
†Heraeus Electro-Nite International N.V., Houthalen, Belgium

The oxygen activity of the ladle slag determines the reactivity towards the steel during ladle treatment. Therefore, the *in situ* measurement of the oxygen activity of slags can be an important tool. The applicability of an electrochemical sensor is examined in this work. The sensor measures the electromotive force (EMF) that is established between a sample of the slag phase that is immersed in the liquid steel bath and a reference system (Cr/Cr_2O_3). Industrial and laboratory experiments demonstrated the capability of the sensor to detect the influence of the slag components on the measured oxygen potential. Comparison of the measured values with thermodynamically calculated values shows that the measured oxygen activity is systematically too low. This was attributed to a reaction of the steel with the slag sample. To investigate this, further lab tests were performed where the slag oxygen activity was measured after the slag had been equilibrated with the steel. The measured values were dependent on the oxygen activity (a_O) of the steel. For industrial applications, it is concluded that the a_O of the steel should be known and that this value is necessary for the interpretation of the measured values.

Keywords: low carbon steels slags, slag oxygen activity, on-line sensing, thermodynamic evaluation.

Introduction

Ladle treatment, situated between the converting stage and the continuous casting, has become very important in modern steelmaking practice. The goal is to produce steel with a homogeneous and correct composition and temperature[1]. Oxide inclusions are formed during deoxidation and subsequent reoxidation processes[2]. The impact of these non-metallic particles on the steel quality depends on their amount, size, composition and distribution. An important function of the ladle slag is to absorb the inclusions[3]. This slag, however, contains components that can react with the steel. When, for example, an FeO containing slag contacts an Al killed steel, the reaction

$$3[FeO]_{slag} + 2\underline{Al}_{Fe} = \langle Al_2O_3 \rangle + 3Fe \qquad [1]$$

can occur[4]. If the steel entrains the alumina particles, the cleanliness of the steel worsens. The ability of the slag to reoxidize the steel is thermodynamically expressed by its oxygen activity a_O (= $p_{O_2} / p_{O_2}^0$), with $p_{O_2}^0$ being the oxygen partial pressure in the reference state. If it is higher than that of the steel, oxygen can be transferred to the metal. Therefore, the on-line measurement of the ladle slag oxygen partial pressure could be useful in controlling the slag's reoxidation ability. Other potential applications are optimization of slag foaming in EAF furnaces, improvement of desulphurization and prediction of deoxidant fade[12].

The oxygen potential of a slag can be determined *ex situ* after sampling using several techniques: spectrometric or wet-chemical analysis[12] and electrochemical measurement[13]. In this article an electrochemical sensor, which enables an *in situ* measurement of the oxygen activity of a slag, is studied[5]. The working principle of this device is shown in Figure 1. The sensor is mounted on a lance and brought into the liquid steel.

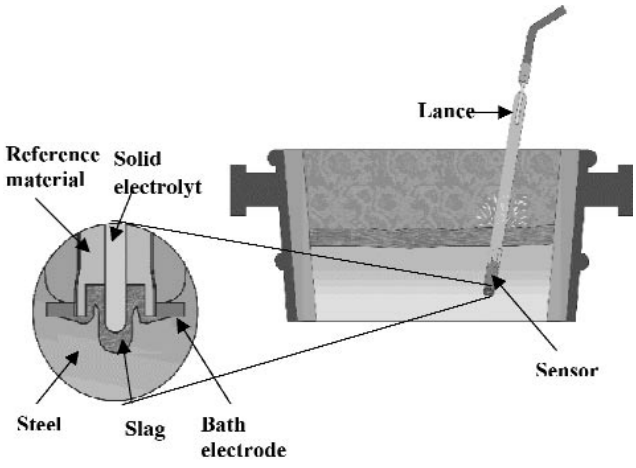

Figure 1 The sensor with an indication of the parts of the electrochemical cell[5].

On its way through the slag the sensor tip drags along a slag layer due to its specific shape. In this manner an electrochemical cell is formed in which a potential is measured between the slag and a $Cr\text{-}Cr_2O_3$ mixture as reference material. MgO stabilized ZrO_2 is used as solid electrolyte that allows transport of oxygen ions between the slag and the reference material. Using Nernst's law[6]

$$E = \frac{10^3 RT}{4F} . \ln \left(\frac{p_{O2}(unknown)}{p_{O2}(reference)} \right) \qquad [2]$$

with the measured potential expressed in mV, the oxygen partial pressure of the unknown material can be calculated. It has to be noticed that in Equation [2] the p_{O2} of the steel does not intervene. Therefore, an influence of the steel composition on the measurement is not expected. The sensor sensitivity is optimal at low p_{O2} (< 10 wt% FeO in the slag) and its use is limited to temperatures between 1580 °C and 1660 °C. To support steelmaking practice the measurement is expressed as a wt% FeO in the slag, as it is believed that FeO determines the oxygen activity of a slag. The relation between the measured potential and the activity of FeO in the slag is[7]

$$\log(a_{FeO}) = 2.15 - \frac{7551 - 10.08E}{T} \qquad [3]$$

The activity coefficient of FeO (γ_{FeO}) in the slag has to be known to express α_{FeO} as a function of wt% FeO. No general formula for γ_{FeO} is available. Empirical expressions such as

$$\log(wt\%FeO) = 0.0042E + 0.582 \qquad [4]$$

are used to estimate the iron oxide content of the slag based on the electrochemical measurement.

Some questions about the measurement remain unresolved. In previous work it was shown that the sensor is capable of detecting the influence of slag components on the measured oxygen potential[11]. However, it was also clear that the steel had an influence on the measured oxygen potential. The goal of the present work is to clarify the influence of the steel from laboratory experiments. Thermodynamic calculations are made to estimate the oxygen potential of the slag. The combination of the previous and present work enables us to elucidate the working principle of the sensor.

Experiments and calculations

Experiments

Sensor measurements were conducted in an induction furnace (Inductotherm, Elphiac) at Electro-Nite (Houthalen, Belgium). The furnace operates at 2000 Hz and has a maximal power of 200 kVA. The inner lining of the crucible consists mainly of Al_2O_3. The influence of individual slag components on the electrochemical measurement was examined. All tests started with a molten steel bath (approximately 250 kg) covered by 5 kg of slag containing 50 wt% lime (85–95 weight per cent CaO) and 50 wt% bauxite (85–95 weight per cent Al_2O_3).

Series of measurements were performed by gradually adding components to the slag. Progressive additions of CaO, Fe_2O_3, SiO_2, MnO and MgO were made. Mixed additions were also possible. Their amount varied from 100 g to 300 g at a time. The temperature of the steel bath was controlled at 1600°C. The steel was aluminium killed and its initial dissolved oxygen content was 2 ppm. This was checked with Celox measurements[8].

In the previous work, the oxygen potential of the steel was kept constant and the influence of the slag components could be recognized[11]. This corresponds to the situation in practice. About 600 measurements were done at the ladle metallurgy station in the Belgian steelplant Sidmar. These lab and industrial results will be summarized. In the present work the steel and slag are allowed to equilibrate, i.e. at regular intervals the oxygen activity of the steel was measured using the Celox sensor (Heraeus Electro-Nite) and the oxygen activity of the slag was measured using an electrochemical sensor (Celox SLAC, Heraeus Electro-Nite) until both measured potentials were the same. Because both sensors contain the same electrochemical cell, at that point the steel and the entrained slag should have the same oxygen potential. This would eliminate the interference of the oxygen potential of the steel as determined previously. At this point of equilibrium a slag sample was taken for XRF analysis (ARL XRF-8680). Steel samples were also taken for spectroscopic spark emission analysis (ARL-3460). After equilibration another slag addition could be made, and again equilibrium between steel and slag was waited for.

Calculations

Thermodynamic calculations were performed to elaborate the experimental results. This was done using the thermodynamic software package FactSage 5.1[9]. The software allows the equilibration of slag and steel in different weight ratios. It is necessary to determine the redox-reactions, e.g. for Fe^{2+}/Fe^{3+}, because they can determine the oxygen potential of the slag[10]. It was chosen to equilibrate 100 g slag with 1 g of steel. This does not change the composition of the slag much and gives a very high Fe^{2+}/Fe^{3+}. It can be interpreted as an underlimit of the oxygen activity of the slag with the given iron content of the slag. If more steel is imported in the calculated system, the oxygen activity decreases and tends towards that of the steel. This method will be used to determine the equilibrium conditions at the sensor tip.

Results

Previous work

Using Equation [2] the measured EMF values for steel and slag can be transformed into values of the oxygen partial pressure p_{O2}. The same values can be calculated theoretically using FactSage if the steel and slag composition are known. This is shown in Figure 2 for 25 random industrial measurements. The measured slag value is located between that of the measured steel and that of calculated slag value. The trend of both measured and calculated slag values is similar, which clearly indicates that there is an influence of the slag on the measurement.

The result of the *in situ* measurement is most often expressed as a weight percentage FeO in the slag (Equation

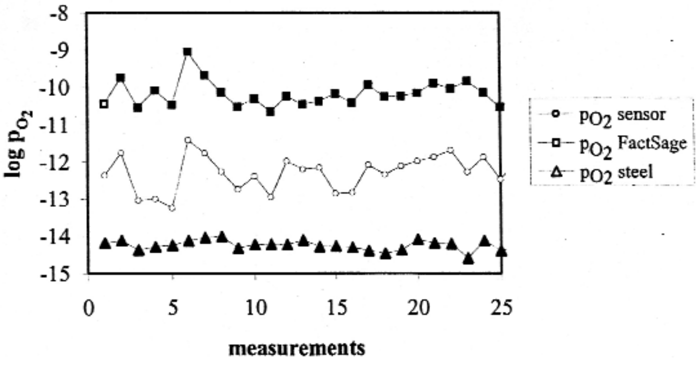

Figure 2 Measured oxygen potential of the steel and the slag and calculated oxygen potential of the slag in 25 industrial measurements

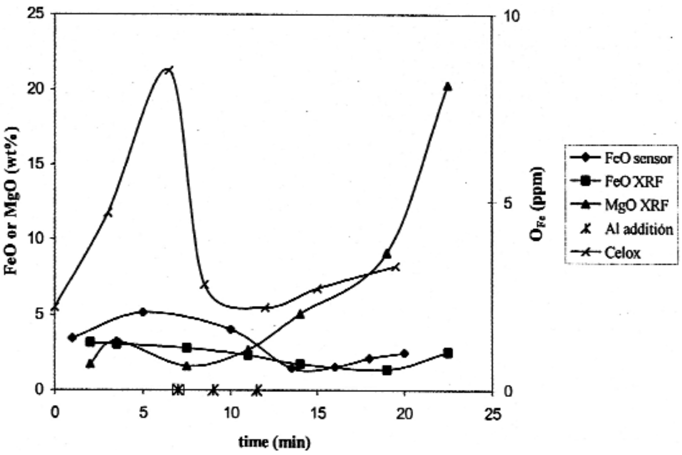

Figure 3. Correspondence between the measured FeO-contents using XRF and the electrochemical sensor of the slag with additions of MgO. The oxygen content of the steel and the moments of Al deoxidation are also indicated

[4]). Figure 3 shows, for example, the results of the lab experiments when MgO was gradually added to the slag. It is clear that the *in situ* determined and XRF FeO-contents correspond very well. The biggest deviations occur when the oxygen potential of the steel increases due to reoxidation by air. After compensation for this with Al additions, both FeO-contents match again.

These results have lead to the hypothesis that steel and slag equilibrate at the sensor tip, rendering an EMF, which is situated in between both oxygen potentials. If the oxygen potential of the steel is constant, this influence is reproduced and can be taken into account.

Present work

Levelling the EMF values for Celox (steel) and electrochemical sensor (slag) measurements was successful, as shown in Figure 4. Thirty-six experiments were conducted. Figure 4 also shows the measured and the corresponding calculated p_{O2} values of the slags. The calculated values vary around a p_{O2} of 10^{-10} atm and the measured values go from $10^{-14.5}$ atm to 10^{-11} atm. The set-up of the experiments has clearly failed: despite the equal values of Celox and electrochemical sensor measurements, the slag has not equilibrated with the steel. The scatter in the experiments even seems enlarged in comparison with the previous tests.

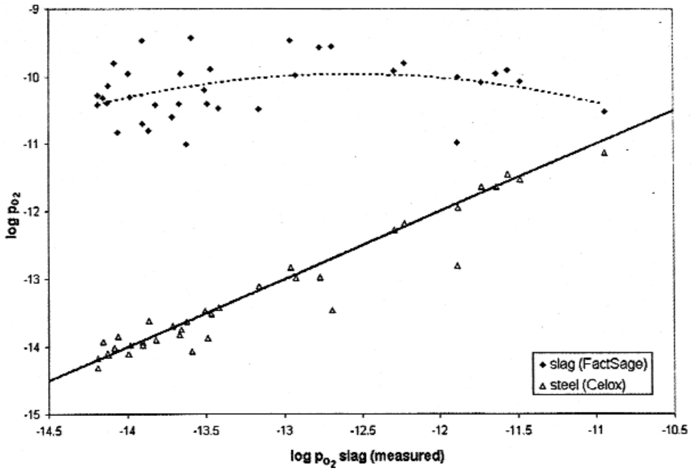

Figure 4. Correspondence between the calculated and measured oxygen potential of the slags and between measured oxygen potential of steel and slag during the equilibrium experiments

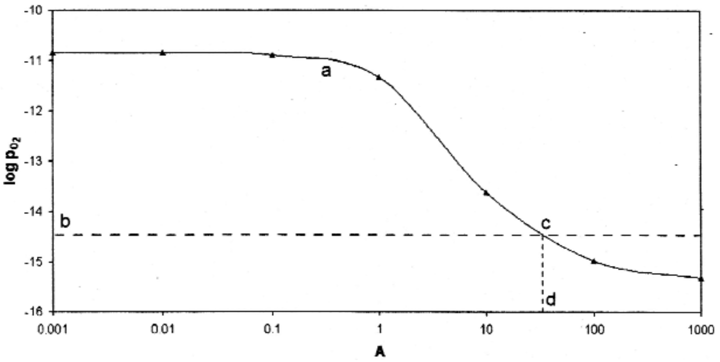

Figure 5. Principle of the determination of the A value. The curve a is calculated using FactSage and b is calculated from the measured potential

Thermodynamic evaluation

In all industrial and lab experiments the measured oxygen potential was lower than the calculated value but never lower than the steel value. It seems that the steel and slag react at the sensor tip and the measured value of the electrochemical sensor is an indication of this equilibrium. Furthermore, the amount of slag and steel that reacts seems to change. This reaction of a changing slag metal system to equilibrium was simulated using FactSage. The measured slags and steels were inserted in the program in different weight ratios. We define A as:

$$A = \frac{weight\ \ steel(g)}{weight\ \ slag(g)} \qquad [5]$$

Figure 5 shows how the calculated oxygen potential of the system varies from that of the slag at low A to that of the steel at very high A. If steel and slag react at the sensor tip to complete equilibrium and a value (point b) is measured, the corresponding A value (point d) can be determined from the intersection of the curve and the measured value (point c). These A values were determined numerically for the experiments.

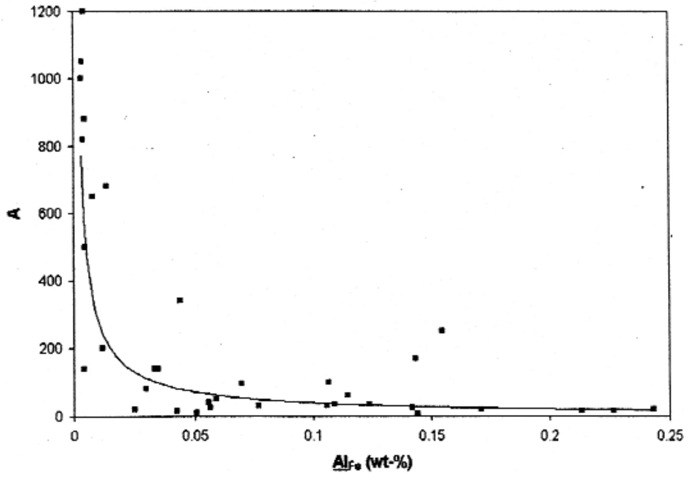

Figure 6. Relation between the aluminium content of the steel and the steel-slag ratio A at the sensor tip

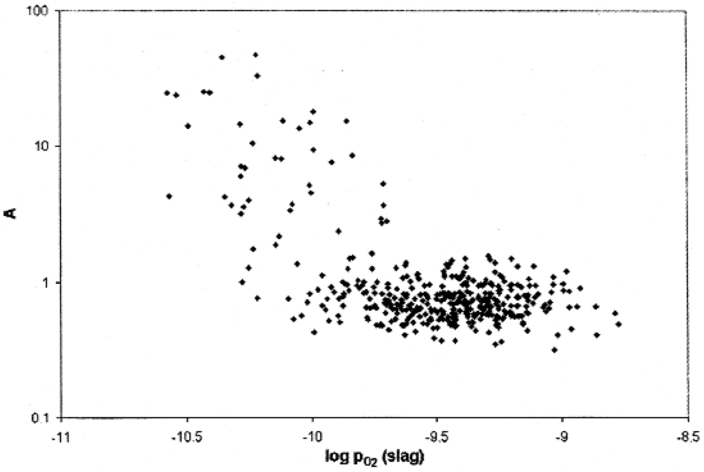

Figure 7. A value at the measurements at Sidmar with Al_{Fe} between 200 and 500 ppm

If the A value would be plotted as a function of time, a constant increase could be noticed except when the steel was deoxidized during the experiment. Then the A value decreases. Figure 6 shows the A value as a function of the aluminium content of the steel. Despite some deviating values we see a good correlation. These deviations are probably caused by the slag. Due to the interaction between steel and slag the FeO-content of the slag did not vary much and, therefore, it is difficult to draw conclusions about the influence of the slag from these experiments.

To elaborate on the influence of the slag, the A value was calculated for the experiments at Sidmar. The aluminium content varied between 200 and 500 ppm to reduce the influence of the steel composition. It seems that A is relatively constant at high oxygen potential of the slags (as calculated with FactSage) but it shows an increase at low p_{O_2} of the slag (Figure 7).

Discussion – working principle of the sensor

The combined results from the lab and the industrial tests seem to indicate that the difference in p_{O_2} between slag and steel is an important factor determining the steel-slag ratio A of the mixture, which is measured by the electrochemical sensor, at the sensor tip. If the p_{O_2} difference between slag and steel is small, the electrochemical sensor measures the p_{O_2} of a mixture with large steel content. The ratio A can become so large that the electrochemical sensor measurement coincides with the Celox measurement for the steel, cancelling any information about the slag. This was observed in the lab tests. Figure 8 shows a schematic representation of the objective (a) and the outcome (b) of the lab tests with the electrochemical sensor. The objective – equilibrating slag with steel—was not met: the tests resulted in equilibration of steel with electrochemical sensor measurements, and not with the slag. Larger p_{O_2} differences, resulting in smaller A ratios, do allow one to generate information about the slag. When the difference is large enough, A stabilizes to an almost constant value. This was observed in the industrial tests (Figure 7).

Physical explanation

A possible explanation for the influence of the p_{O_2} difference is the occurrence of a chemical reaction at the slag/steel interface at the sensor tip (Equation [1]), involving the steel bath ($\underline{Al}_{Fe}$) and the small quantity of slag (FeO$_{slag}$). The Al_2O_3 seals off the measuring volume at the sensor tip from the surrounding steel. To clarify this possible explanation, two extreme cases are presented:

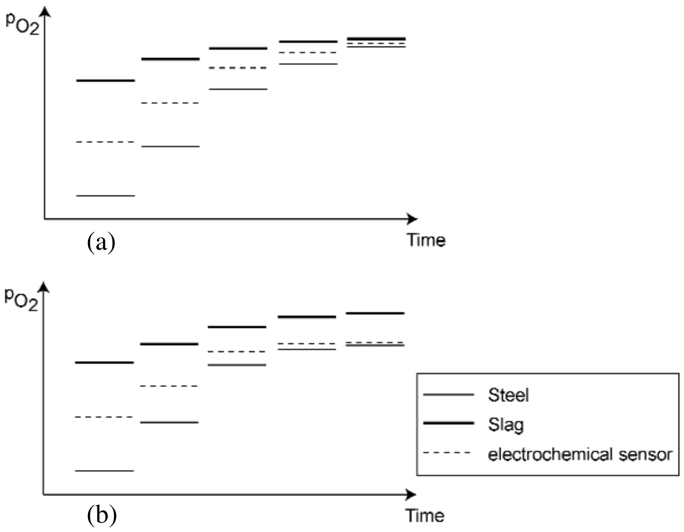

Figure 8 Schematic representation of the objective (a) and (b) outcome for the p_{O_2} as function of test time in the laboratory tests

- Case 1: Δp_{O_2} (slag-steel) high
- Case 2: Δp_{O_2} (slag-steel) small

For ladle treatments we can assume that p_{O_2} steel never exceeds p_{O_2} slag. In case 1, reaction [1] proceeds fast due to high Al-content in the steel (p_{O_2} steel low) and high FeO-content in the slag (p_{O_2} slag high). This, in combination with the high reactivity (high p_{O_2} difference), ensures the rapid formation of an Al_2O_3-layer, which seals off the measuring volume from the steel and establishes a low steel-slag ratio inside the measuring volume.

Case 2 presents an entirely different behaviour. Reaction [6] proceeds slowly due to low Al-content in the steel (p_{O_2} steel high) and low FeO-content in the slag (p_{O_2} slag low). This, in combination with the low reactivity (small p_{O_2} difference), results in slow reaction kinetics. The Al_2O_3-layer formation is too slow and therefore does not succeed in keeping the measuring volume small. The slag flares out in the surrounding steel.

It can be added that for industrial ladle treatment applications, when p_{O_2} of the steel is almost constant and the p_{O_2} difference is large enough, empirical expressions can be formulated, correlating for example EMF to FeO content (Equation [4]). This was also concluded from the previous measurements. More generally, with the use of FactSage it could be possible to obtain a value for A from Celox and test sensor measurements and subsequently for the p_{O_2} of the slag:

$$p_{O_2}^{slag} = f\left(A, p_{O_2}^{sensor}, p_{O_2}^{Celox}\right) \qquad [6]$$

This would require a great number of measurements and FactSage calculations for many different sets of p_{O_2} of the slag and p_{O_2} of the steel.

Conclusions

Slag-metal reactions are of key importance during ladle

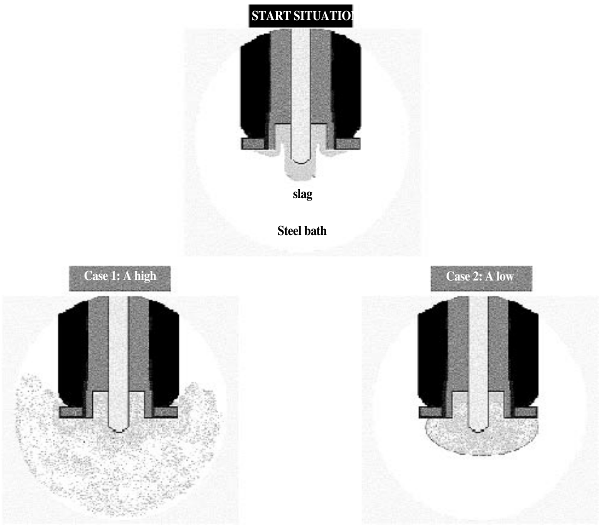

Figure 9. Schematic representation of possible physical interpretation

treatment, influencing chemical composition and steel cleanliness. The oxygen partial pressure of the slag is an important parameter at that point, providing information on the reactivity of the slag towards the steel. The electrochemical test sensor allows the *in situ* measurement of the p_{O_2} of the slag. Previous tests with the sensor have shown that the measured value, although clearly influenced by the slag composition, lies between the actual p_{O_2} of the slag and the p_{O_2} of the steel, indicating a confounding influence from the steel.

In an attempt to cancel the influence from the steel on the measured value, a number of laboratory tests were performed targeting equilibrium between slag and steel. This was attempted by levelling the Celox (p_{O_2} of the steel) measurement and the electrochemical sensor measurement. Slag and steel samples were taken for analysis and additional equilibrium calculations were performed with the thermochemical software package FactSage to compare with the test results. This comparison showed that, despite equal Celox and electrochemical sensor values, the objective of the test was not met: there was no equilibrium between slag and steel and the influence of the steel was not cancelled.

Analysis of the industrial and laboratory test indicated that the amount of steel and slag that reacted at the sensor tip varied from case to case. This behaviour was successfully simulated with FactSage where a parameter A was introduced as the weight ratio of steel to slag, measured at the sensor tip. It was shown that this parameter was dependent on the difference in p_{O_2} between the slag and the steel. A large p_{O_2} difference resulted in a low A ratio and thereby a low steel fraction in the measuring volume. A small difference, however, resulted in a high steel fraction (A high) and a value that approached the p_{O_2} of the steel.

A possible explanation for the influence of the difference in p_{O_2} was offered: the occurrence of a chemical reaction between $\underline{Al}_{Fe}$ and FeO_{slag} at the slag/steel interface at the sensortip. A fast reaction product (Al_2O_3) formation (p_{O_2} difference high) could hinder the spreading of the small slag volume and keep A small. Slow formation, due to low presence of $\underline{Al}_{Fe}$ or FeO_{slag}, would result in a high A value.

Finally, it was mentionned that combined knowledge of Celox and electrochemical sensor values could lead to a value of A and subsequently to a value for the p_{O_2} of the slag. This, however, will require substantially more tests and calculations, but might eventually lead to a more universally applicable sensor.

Acknowledgement

The authors would like to thank Heraeus Electro-Nite for performing the laboratory experiments and providing the sensors. The authors also would like to thank Sidmar NV for sample analysis and industrial data.

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