A Study of Slag-Steel-Inclusion Interaction During Ladle Treatment

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Licentiate Thesis

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ABSTRACT

The thesis is based on two supplements with two major objectives. In the first supplement equilibrium top slag-steel bulk and inclusions-steel bulk were investigated by comparison between calculated and measured oxygen activity values. This was done by applying different oxide activity models for slags combined with thermodynamic calculations. In the second supplement the inclusion composition is studied during the ladle refining process. The inclusion composition is related to top slag composition and other parameters during ladle treatment.

The work was carried out by collecting data during well controlled sampling procedures at two different steel plants. Extensive inclusion analyses in Scanning Electron Microscope, SEM, were done. The data was used together with thermodynamics for a description of the interaction between slag-steel-inclusion interaction during ladle treatment.

Evaluation of inclusion composition during the ladle refining have revealed that the majority of the inclusions belonged to the system Al$_2$O$_3$-CaO-MgO-SiO$_2$ and showed a continuous composition change throughout the ladle refining process, from high Al$_2$O$_3$, via MgO-spinel to finally complex types rich in CaO and Al$_2$O$_3$. The final composition after vacuum treatment was found to be close to the top slag composition. Small process parameter changes and practical variations during ladle refining were proven to give large differences of the inclusion composition.

Finally, it was concluded that equilibrium does not exist between top slag and steel bulk, with respect to oxygen, for the studied conditions. However, the equilibrium does exist between the steel bulk and inclusion.

Keywords: Ladle treatment, steel, slag, inclusions, ladle, refining, vacuum, tool steel, oxide activity, slag models, oxygen, equilibrium
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Johan Björklund
Stockholm, May 2006
SUPPLEMENTS

This thesis is based on the following supplements:

**Supplement 1:** “Equilibrium between Slag, Steel and Inclusions During Ladle Treatment - A Comparison with Production Data”

**J. Björklund, M. Andersson, P. Jönsson**

**Supplement 2:** “The Effect of Ladle Treatment on Inclusion Composition in Tool Steel Production”

**J. Björklund, M. Andersson, M. Nzotta, P. Jönsson**

The contributions by the author to the different supplements of the thesis:

1. Literature survey, plant trials, assisting inclusion evaluation, calculations, major part of the writing.
2. Literature survey, plant trials, inclusion evaluation, parts of analyses, major part of the writing.

Part of this work has been presented at the following conference:

“Models for Predicting Oxide Activities and Oxygen Activity - A Comparison with Production Data”

**J. Björklund**

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1. Introduction

The goal for the steel producer is often to produce clean steel with low amounts of inclusions. Inclusions can be detrimental for the performance of the steel regarding different material properties like fatigue, ductility, polishability e.t.c. The size distribution is important since larger inclusions can be harmful, while a higher amount of smaller inclusion usually can be accepted. The composition of the inclusions present in the steel are also important since the composition of the inclusion decides the properties of the inclusions and hereby the properties of the steel.

The formation of non-metallic inclusions is influenced by several process parameters during steel production. For example, the inclusions are very much depending on the oxide activity in the melt and the type of added deoxidisers. It is also well known that reoxidation phenomenon will affect inclusion characteristics during ladle treatment. A ladle top slag with high amounts of FeO and MnO, which can react with the dissolved deoxidiser in the steel melt, will be detrimental with respect to inclusions.

The aim with the present thesis is a better understanding of the ladle refining process with the respect to the interaction between steel-slag and inclusions. An improved knowledge will make it easier to control and hereby optimise the process in order to save time and lower the energy consumption. Also, a better understanding will facilitate reproducible production of steel with an even and high quality from one heat to another.

The present thesis is based on two supplements with two major objectives. In the first supplement equilibrium top slag-steel bulk and inclusions-steel bulk were investigated by comparison between calculated and measured oxygen activity values. This was done by applying different oxide activity models for slags combined with thermodynamic calculations.
In the second supplement the inclusion composition is studied during the ladle refining process. The inclusion composition related to top slag composition and other parameters during ladle treatment.

The work was carried out by collecting data during well controlled sampling procedures at two different steel plants. Extensive inclusion investigations in Scanning Electron Microscope, SEM, were done to achieve data of inclusion composition and morphology. The data was used together with thermodynamics for a description of the interaction between slag-steel-inclusion interaction during ladle treatment.
2. **Plant Descriptions**

The trials were carried out at two different steel plants, Ovako Steel AB in Hofors and Uddeholm Tooling AB in Hagfors. Ovako Steel is a manufacturer of mainly bearing steel, while Uddeholm Tooling produces tool steels for different applications. They are both scrap based steel plants and the process route of both plants can be illustrated by Figure 1. After the scrap is melted in the Electric Arc Furnace, EAF, the slag is removed prior to ladle treatment. The ladle is then moved to the ladle refining station, where a new synthetic slag is added and aluminium deoxidation is done. The alloying to reach the final composition is done before the vacuum degassing. After vacuum treatment the steel is cast into ingots.

![Figure 1. The process at Ovako Steel AB and Uddeholm Tooling AB](image-url)
3. **PLANT TRIALS**

The purposes with the two sets of plant trials were different, but at the same time there were a lot of similarities. During both trials samples were taken at different stages of the ladle refining. Samples were taken of steel and slag, in addition the temperature was measured together with the oxygen activity. The sampling equipment was in general the same. The steel samples, taken for steel composition and inclusion analysis, were in all cases taken by argon shielded samplers to ensure high quality samples. Slag was collected by a scoop or a stick while the temperature and oxygen activity were measured by Celox equipment.

3.1 **Ovako Steel AB (Supplement 1)**

The steel examined was bearing steel of the Ovako 800 series with 1%C and 1.4%Cr. For sake of comparison, one heat of a low carbon (0.2%) steel alloyed with chromium (0.2%) and manganese (1.6%) was also examined. An overview of the sampling procedure of the 6 studied heats (A-F) is shown in Figure 2. The samples from Ovako Steel AB are in the present thesis named OS-1 to OS-3. A slag sample was taken just after teeming from the EAF, but the corresponding steel sample could not be collected until the ladle had entered the ladle station. After addition and melting of synthetic slag formers the second sample was taken. Finally, after Al-deoxidation, alloying and vacuum treatment the last sample was taken.

![Figure 2. The sampling procedure at Ovako Steel AB](image)

The synthetic slag, in samples 2 and 3, consisted of mainly CaO (50-65%) and in addition to that: Al₂O₃ (25-30%) and lower amounts of SiO₂ (7-11%) and MgO (3-8%). The slag composition varied only slightly between sampling occasions 2 and 3.
3.2 Uddeholm Tooling AB (Supplement 2)

The steel grade chosen for this study was Orvar 2M (5.3%Cr-1.3%Mo-0.9%V); a low alloyed high temperature tool steel. The current sampling procedure is shown in Figure 3. The samples from Uddeholm Tooling AB are in the present thesis named UT-1 to UT-5. The first sample was taken just after arrival to the ladle station, while the second sample was taken just after deslagging. Sample 3 was taken after addition and melting of the synthetic slag formers. And finally, samples were taken before and after vacuum treatment.

![Figure 3. The sampling procedure at Uddeholm Tooling AB](image)

Two main synthetic slag mixtures were added on the 4 studied heats, one with low CaO (38%) in heats A and B, and one high CaO (49%) for heats C and D. In addition to that, the slag consisted of Al$_2$O$_3$ (30-40%), MgO(10-16%) and SiO$_2$(6-16%).

3.3 Analysis and microscopic evaluations

At Ovako Steel the chemical composition of the steel was analysed using an ARL 3560 Optical Emission Spectrometer (OES). The carbon and sulphur content in the steel and slag samples were determined using a Leco CS200 combustion equipment. The slag was remelted and cast into a disk and then analysed for chemical composition by x-ray fluorescence in a Siemens SRS 303 equipment. The chemical composition of the inclusions was determined at Ovako Steel using a Zeiss Supra 35 scanning electron microscope (SEM). It was equipped with a Gemini FEG-column and the Inca-feature software for automatic detection of inclusions.

At Uddeholm Tooling the chemical composition of steel samples was determined by using X-ray fluorescence analysis method (ARL 8680S SIM/SEQ XRF). The composition of the slag samples was determined in the same machine after the samples had been ground and cast into discs. The carbon and sulphur contents of the slag samples were determined separately in a Philips Perl X-2.
4. **Theory**

The results from the study in Supplement 1 (Ovako Steel AB) have been explained and discussed by using a theoretical equilibrium approach. In the first supplement three different models for oxide activity calculation were applied. The three different models were the IRSID model\(^1\), the ThermoSlag model\(^2\), and the Ohta-Suito model\(^3\). The oxide activity calculations were compared with measured values in order to find out if it is possible to make equilibrium calculations.

The IRSID slag model was used together with the Thermo-Calc software\(^4\). In the present work, the database “Slag2” based on the slag model by IRSID was used for the calculations. The ThermoSlag model is also known as the KTH-model. Like the IRSID model, it is semi-empirical and uses experimental information from binary subsystems to calculate multi component slag system. The Ohta-Suito slag model is an empirical model from experimental equilibrium steel-slag measurements. The result from regression analysis of the data was used to develop expressions for calculation of activities of alumina and silica based on the slag composition. The Ohta-Suito model can not take any contents of MnO and FeO into consideration in the calculations.

To be able to compare the three models with any measured values a thermodynamic calculation must be done. The calculation was based on the assumption of equilibrium conditions between the steel and the oxide phase (top slag or inclusion) in the system. Two different equilibriums were used:

\[
\begin{align*}
{Si} + 2{O} & \leftrightarrow {SiO}_2(s) \quad (1) \\
2{Al} + 3{O} & \leftrightarrow {Al}_2{O}_3(s) \quad (2)
\end{align*}
\]

The Si/O/SiO\(_2\) equilibrium were used in the calculations after Si deoxidation (OS-1, OS-2), while the Al/O/Al\(_2\)O\(_3\) equilibrium were used in the later sampling after Al-deoxidation has been done (OS-3). From reaction (1) and (2) it was possible to derive an expression for the oxygen activity. The expressions were based on the
assumption of equilibrium between top slag and steel bulk or inclusion and steel bulk:

\[
a_2 = \sqrt{\frac{a_{\text{SiO}_2}}{a_{\text{Si}} \cdot e^{-\Delta G'}} R T}
\]  
\[
a_2 = \sqrt{\frac{a_{\text{Al}_2\text{O}_3}}{a_{\text{Al}}^2 \cdot e^{-\Delta G''} R T}}
\]  

In these expressions, the \(a_{\text{SiO}_2}\) and \(a_{\text{Al}_2\text{O}_3}\) are the activity of oxide components in the top slag or inclusions, that were estimated by the three different models mentioned above. The variables \(a_{\text{Si}}\) and \(a_{\text{Al}}\) were calculated by Wagner’s equation using Henry’s law the dilute solution model (1wt% standard state). R is the molar gas constant and T is the temperature in Kelvin. The variable \(\Delta G'\) is the free energy of reaction (1) and (2) respectively:

\[
\Delta G' = -580541 + 220.655 \cdot T \quad [\text{J/Mol}]
\]  
\[
\Delta G'' = -1205115 + 386.714 \cdot T \quad [\text{J/Mol}]
\]

Hereby it is possible to calculate the oxygen activity in the steel, which can be compared with the measured oxygen activity. If the calculation is correct and the assumption of equilibrium is right, a correlation would be expected between calculated and measured values.
5. **RESULTS**

The results from present study are divided into two different sections. First the results from supplement 1 are presented, followed by supplement 2.

5.1 **Supplement 1**

5.1.1 **Equilibrium with top slag after Si-deoxidation**

The results from the comparisons from the calculations of the steel melt oxygen activity based on equilibrium (1) and equation (3) in the two of the compared models are shown in Figure 4 below. In Figure 4, the data for slag sample (OS-0) and steel sample (OS-1) were used to calculate the top slag/steel equilibrium oxygen activity.

![Figure 4](image_url)

*Figure 4.* Calculated oxygen activity after Si-deoxidation for 6 heats with samples OS-0 and OS-1
From Figure 4 it is clear that the IRSID and ThermoSlag models give equivalent results in all heats before deslagging was carried out. In heat E the calculated oxygen activity was significantly higher than for the other heats, which can be explained by the higher silica content in the top slag. The Ohta-Suito model could not be used due to the high FeO contents in the top slag.

In Figure 5, the situation for the next taken slag and steel samples (OS-2) is shown. The results in Figure 5 also show that differences exist between the different model predictions. However, the difference is not large in absolute numbers. When using the Ohta-Suito model, the calculated equilibrium oxygen activity was about 3 times larger than when using the ThermoSlag model. Furthermore, it can be observed that the trends were similar for the predictions using the three models to calculate oxygen activity in the steel melt.

![Figure 5. Calculated oxygen activity after Si-deoxidation for 6 heats with sample OS-2](image)

The calculated oxygen activities from the samples collected after Si-deoxidation in Figures 4 and 5, should be compared with the measured values in Table 1 below. It is obvious that the differences between calculated and measured values were much larger than expected. The agreement between predicted and measured oxygen activity data was better when using the EAF slag composition (slag sample OS-0) than when using the added synthetic slag (slag sample OS-2). If the data in Figure 4 are compared with the values from Table 1, it is possible to see that the equilibrium from EAF-slag (slag 0 and sample 1) has a magnitude of 10 lower than the measured oxygen activity data. The corresponding results for Figure 5 the equilibrium with the synthetic slag (slag and steel sample 2) show that the
predictions are a magnitude of 100 times lower than the measurements. The reasons will be discussed later.

**Table 1.** The measured oxygen activity in the different heats of sample OS-1 and OS-2

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>OS-1</td>
<td>87.3</td>
<td>135.9</td>
<td>78.7</td>
<td>69.2</td>
<td>117.3</td>
<td>63.6</td>
</tr>
<tr>
<td>OS-2</td>
<td>84.4</td>
<td>112.5</td>
<td>64.4</td>
<td>62.9</td>
<td>101.6</td>
<td>56.7</td>
</tr>
</tbody>
</table>

5.1.2 Equilibrium with top slag after Al-deoxidation

The same calculations that were done based on the data for sampling after Si-deoxidation were also done based on the available information from sampling occasion 3. At this stage of the process, after both Al-deoxidation and vacuum treatment, aluminium is assumed to control the equilibrium with oxygen in the steel. Therefore, equation (2) was used in the equilibrium calculations. For the sake of comparison, the calculations have also been done using the Si/O/SiO$_2$-equilibrium, reaction (1).

It is believed that the results from sample OS-3, better represents a situation where the top slag is closer to equilibrium with steel. This should be due to slag-metal reactions during the intense mixing for the period of vacuum, which is promoted by strong gas stirring as well as a lowered pressure above the melt.

The oxide activities from the three models together with equations (3) and (4) respectively were again used to calculate the oxygen activity in the steel. The calculated oxygen activity is presented in Figure 6 together with measured values in the same diagram. Figure 6 shows that the calculations of oxygen activity from the different models are in all cases showing lower values compared to the measured oxygen activity data. However, the calculated oxygen activities show again the same trend as the measured data. It can be seen that after vacuum treatment the predicted oxygen activity data, based on an assumed equilibrium between the slag and steel, was approximately 3 to 10 times lower than the measured oxygen activity data.

To estimate the effect of the models on the calculations the activity of Al$_2$O$_3$ was set to one (corresponding to Al$_2$O$_3$ saturation in the slag) and hereby the use of the slag models and slag composition was neglected. By doing so, the calculated values
of oxygen activity show the best agreement with the measured values. However, the deviation from the measured values was not as systematic as for the cases when activity of alumina was calculated using the slag models.

![Graph showing oxygen activity vs heat](image)

**Figure 6.** Calculated and measured oxygen activity s after Al-deoxidation OS-3

### 5.1.3 Equilibrium with inclusions after Si-deoxidation

The detailed study of the chemical composition of a large amount of inclusions in steel samples was done to provide a sufficient amount of data. This made it possible to make a realistic calculation of an assumed equilibrium between the average composition of the inclusions and the steel bulk chemical composition. The inclusions were from sampling occasion 2, after Si-deoxidation, and mainly consisted of SiO$_2$ (about 52-77%) and Al$_2$O$_3$ (about 10-32%). In addition, they were found to be totally homogenous. The CaO-content was very low (0.5–7 %). The inclusions also contained significant amounts of MnO (11-23 %).

During the SEM study, the inclusions were divided into two groups, one group consisting of inclusions larger than 3 μm (magnification 500x), and one group representing inclusions larger than 12 μm (magnification 125x). The average size of studied inclusions was around 25 μm in the 125x run and 5 μm in the 500x run.

The calculated oxygen activities using data of sample 2 were again compared with the measured values in Figure 7. Note, that it was not possible to use Ohta-Suito’s
model in this case when large amounts of MnO were present. The calculations were based on the Si/O/SiO₂ equilibrium (1) and the corresponding equation (3). The results from calculation of the SiO₂-activity with ThermoSlag show that the composition had reached SiO₂-saturation, and the SiO₂-activity has exceeded one. The results from the IRSID-model also show that the activity was high, and it is believed that the composition was generally close to SiO₂-saturation. This would lead to a SiO₂-phase present in the inclusions, but this was not found during SEM mapping of the inclusions. In case of SiO₂-saturation the activity was set to unity in the calculations of oxygen activity.

From Figure 7 it is possible to compare calculated and measured values. It can be seen that the calculated oxygen activity values were higher than the measured ones. This was different compared to the calculations of the top slag equilibriums. The calculated oxygen activity was higher than the measured value as a result of the high silica content in the inclusions. This is explained by the fact that the inclusions were formed during silicon deoxidation in the steel creating inclusions with high silica content.

Also, equilibrium calculations with respect to inclusion-steel bulk were found to be closer to the measured values compared to the corresponding calculations for the top slag-steel bulk equilibrium.

**Figure 7.** Calculated oxygen activity for inclusions after Si-deoxidation based on OS-2
It is also seen from Figure 7 that inclusions larger than 12 \( \mu m \) were closer to the measured oxygen activity compared to the data representing the smaller inclusions. It is clear that the predictions based on the data for the larger inclusions were closer to the measurements. It was a tendency that as the inclusions grew bigger, they were achieving a composition closer to the top slag. From the inclusion study it was found that the larger inclusions contained higher amounts of CaO and Al\(_2\)O\(_3\).

5.1.4 Equilibrium with inclusions after Al-deoxidation

After Al-deoxidation and vacuum treatment (sampling occasion OS-3) it was not possible to do the same comparison between calculated and measured activity based on inclusion equilibrium. The majority of the inclusions found in the samples taken after the vacuum treatment were smaller than 2-3 \( \mu m \). Due to the small size it was not possible to make an accurate determination of the inclusion chemical composition using the SEM. In addition to that, very few inclusions were found after vacuum degassing and those found were surrounded by a sulphide layer consisting of MnS. Therefore, it was not possible to make any reliable oxygen activity equilibrium calculation.

5.1.5 Discussion of top slag-steel bulk equilibrium

Vacuum degassing is known to move the steel-slag system towards equilibrium. In the present work no vacuum degassing had been done when the steel was only Si-deoxidised. This would explain why calculations based on an equilibrium assumption before vacuum showed worse agreement with the experimental data compared to the equilibrium calculations after vacuum.

The main reason for the large difference between calculated and measured values is believed to be the assumption of equilibrium between top slag and steel bulk. The assumption of equilibrium was used in the calculation of the equilibrium constant, \( K \).

Also, the calculated \( a_{\text{MeO}} \) and \( a_{\text{Me}} \) is from the slag and steel bulk and may not be representative for the conditions in the steel-slag interface, where the actual reactions are taking place. It is believed that the conditions in the interface between slag and steel can be different and a local equilibrium may exist. However, it is not possible to measure the conditions in the interface, especially during vacuum treatment. These gradients in the slag-metal interface may largely affect the equilibrium conditions.
The overall conclusion is that for the studied interaction between top slag and steel bulk no overall equilibrium exists between the bulk of the steel and the bulk of the slag. Thus, it is not possible to calculate the oxygen activity in the steel by assuming an equilibrium situation between slag and steel bulk.

5.1.6 Optimisation of calculated values

In the industry it is important to have tools to predict the production parameters both during the standard process and during design and optimisation of the process. As shown earlier, the calculations have proven to give erroneous results compared to the measured data if a slag - steel equilibrium is assumed. However, since the deviation is systematic, it is possible to calculate a relationship between the measured and calculated oxygen activities. This was done for the $\text{Al}_2\text{O}_3$ equilibrium after vacuum (OS-3). The relationship was found to be close to a linear function in the present case and the $R^2$ values are for all three models in the range of 0.57-0.65. This linear function can be used to recalculate the values to achieve optimised values of oxide activities. These have been optimised for each heat and model values are plotted in Figure 8 together with the measured values. As can be seen, the optimised predictions are much closer to the measurements.

![Figure 8. Optimised calculated and measured oxygen activity from top slag and OS-2](image)

The procedure was done for the six heats, with different but small changes in steel and slag composition. The maximum divergence of the oxygen activity by this method will in all these models be maximum of about $+/- 0.5 \times 10^{-4}$ compared to the
measured general deviation of \(2 \times 10^{-4}\). Thus, it is possible to use such a relationship in industry to follow trends regarding changes of oxygen activities.

5.2 Supplement 2

In the study of the samples taken during ladle refining at Uddeholm Tooling AB two major types of inclusion were identified. The largest group consisted of inclusion of varying composition in the \(\text{Al}_2\text{O}_3\)-\(\text{CaO}\)-\(\text{MgO}\)-\(\text{SiO}_2\) system. The other group consisted of the \(\text{Al}_2\text{O}_3\)-\(\text{MnO}\)-\(\text{SiO}_2\) system. In the following text the first type of inclusion will be discussed and thereafter the second type will follow.

5.2.1 Inclusions found in the \(\text{Al}_2\text{O}_3\)-\(\text{CaO}\)-\(\text{MgO}\)-\(\text{SiO}_2\) system

The average composition of every individual inclusion has been plotted in ternary \(\text{Al}_2\text{O}_3\)-\(\text{CaO}\)-\(\text{MgO}\)-diagrams\[^6\], which visualizes the inclusion composition in a pedagogic way. This was done for each sampling occasion and made it possible to follow the change in inclusion composition during the different process steps in the ladle furnace. The author has not been able to find appropriate phase diagrams of \(\text{Al}_2\text{O}_3\)-\(\text{CaO}\)-\(\text{MgO}\)-\(\text{SiO}_2\) to illustrate the effect of \(\text{SiO}_2\) in the slag in a proper way. To be able to visualize \(\text{SiO}_2\), the markers instead have different shapes for different \(\text{SiO}_2\) levels. It has to be mentioned that the present phase diagrams are, strictly speaking, only valid for inclusions with zero percent \(\text{SiO}_2\). In the study, inclusions were studied in samples UT-2 to UT-5, i.e. from deslagging to the end of vacuum treatment.

Figure 9 shows an example of the average compositions in the \(\text{Al}_2\text{O}_3\)-\(\text{CaO}\)-\(\text{MgO}\) phase diagram of each found inclusion in the examined sample after deslagging (UT-2) in heat C. The inclusions consisted of mainly of alumina and those without \(\text{SiO}_2\) were only consisting of \(\text{Al}_2\text{O}_3\)-\(\text{MgO}\) while those containing \(\text{SiO}_2\) also contained \(\text{CaO}\). The inclusion size was in most cases 5-15\(\mu\)m.

It is interesting to discuss the formation of these alumina rich inclusions which were found prior to the Al-deoxidation. The most probable reason for their formation was that the EAF-slag was reduced by adding Al-granules before the tapping.
When deoxidation had been done and new slag formers were added and melted, the typical average composition of the inclusions was as illustrated in Figure 10. Deoxidation was done by adding 80 kg of aluminium bars just after the previous sampling (UT-2). The time from deoxidation to this sample occasion (UT-3) was 30 minutes. In Figure 10 it is possible to see that the inclusion composition has moved from $\text{Al}_2\text{O}_3$-rich part of the phase diagram towards the stoichiometric $\text{Al}_2\text{O}_3$-$\text{MgO}$ composition. Despite the aluminium deoxidation there were no pure alumina inclusions left. It was possible to see that the inclusions were a mixture between the spinel phase and calcium aluminate, CA or CA$_6$. Beskow\textsuperscript{7} showed that MgO-$\text{Al}_2\text{O}_3$ phase should be stable after aluminium deoxidation in tool steels of the same type studied in present work. This can explain the decrease of alumina and the increase of MgO in the inclusions. Also, Tripathi\textsuperscript{8} suggested that the ladle glaze infiltrates and reacts with MgO refractory to form MgO-$\text{Al}_2\text{O}_3$ spinel. This phenomena could be a possible source of the observed MgO-$\text{Al}_2\text{O}_3$ rich inclusions. Tripathi also suggested that the MgO-$\text{Al}_2\text{O}_3$ spinel inclusions had been brought over from EAF. However, no MgO-$\text{Al}_2\text{O}_3$ spinel was found in the first sample evaluated (UT-2).
Figure 10. The average composition of each inclusion found after deslagging (UT-3) in heat C

Out of Figure 11 it is possible to see that the composition of the inclusions had changed to the sample before vacuum (UT-4). The SiO₂ and CaO content had increased for the majority of the inclusions in all heats. The average compositions have changed from the stoichiometric spinel composition towards the composition range with lower liquidus temperature in the phase diagram. It is clear that the movement was linear, and consequently the component concentrations in the inclusions become functions of each other with fixed ratios.
Figure 11. The average composition of each inclusion found after deslagging (UT-4) in heat C

The inclusion structure consisted of an inner cubic stoichiometric spinel phase of MgO-Al$_2$O$_3$, which was surrounded by a darker slag phase. A typical micrograph of an inclusion can be seen in Figure 12. This darker slag phase was evaluated separately for inclusions in heat C and was found consisting of Al$_2$O$_3$ (55%), CaO (31%), MgO (12%) and SiO$_2$ (2%).

Figure 12. A typical Inclusion with inner structure MgO-Al$_2$O$_3$ spinel inside a Al$_2$O$_3$-CaO-MgO phase. Inclusion taken from heat D, sample UT-4, $\phi$ 14$\mu$m
It was also possible to see a trend, where the inclusion compositions were closer to the top slag for the inclusions belonging to the size group DP (>22.4µm). The spread of composition was also lower for larger inclusions. The fact that larger inclusions have found to have a composition closer to the top slag compared to the smaller can be explained by dispersion of top slag into the steel melt.

The average compositions of inclusions after vacuum treatment is exemplified by the plot of the phase diagram Al<sub>2</sub>O<sub>3</sub>-CaO-MgO in Figure 13, (UT-5). The inclusion composition has converged and become closer to the top slag composition compared to the previous sample, except for heat B.

![Figure 13. The average composition of each inclusion found after deslagging (UT-5) in heat C](image)

In all heats, except B, the MgO·Al<sub>2</sub>O<sub>3</sub> spinel phase has disappeared in the inclusions. Regarding heat B, it can clearly be seen in Figure 14 that the inclusion composition was still distributed towards the stochiometric spinel composition. The inclusion magnesia content was highest in this heat (heat B 19%MgO and heat C 7%MgO) after vacuum. According to Thermo-Calc calculations, due to a high MgO content in the top slag, MgO·Al<sub>2</sub>O<sub>3</sub> spinel was precipitated as the primary solid phase in the top slag of heat B at 1620°C. Thus, at the measured steel
temperature of 1568°C, the top slag was spinel saturated, which obviously influenced the inclusion composition in heat B (UT-5).

![Diagram](image)

**Figure 14.** The average composition of each inclusion found after deslagging (UT-5) in heat B

It was also possible to observe that the share of inclusion with a higher SiO₂ content was higher in heat A and D, compared to B and C. In heat A the average SiO₂ content in the inclusions was 10% while in heat D an average of 13%. Furthermore, the steel analysis showed that the aluminium content was lowest in heat A and D after vacuum. It is believed that this is a result from reoxidation during vacuum degassing from the top slag. The high SiO₂ content in the top slag may lead to reaction between the top slag and steel melt.

$$3SiO_2 + 4Al \Rightarrow 2Al_2O_3 + 3Si$$  \hspace{1cm} (7)

According to reaction (7) SiO₂ becomes more stable at lower Al content in the steel melt. This would be the explanation to the higher SiO₂ content in the inclusions from heat A and D. The highest silica level of the slag throughout the whole process in heat D could possibly be a result from poor deslagging, where silica rich EAF-slag failed to be removed before the synthetic slag formers were added.
5.2.2 Inclusion found in the Al$_2$O$_3$-MnO-SiO$_2$ system

In some samples, inclusions with a composition of mainly Al$_2$O$_3$-MnO-SiO$_2$ were found. The greatest amounts of MnO-rich inclusions were found after vacuum treatment (UT-5) and in heat A and D. These heats also had Al$_2$O$_3$-CaO-MgO-SiO$_2$ inclusions with higher SiO$_2$ contents, as earlier mentioned. The appearance of MnO-type inclusions was often slightly different from the Al$_2$O$_3$-CaO-MgO-SiO$_2$ -inclusions. They were not as spherical and did often appear in a group or along a line. However, there were also MnO-rich inclusions that were similar to the Al$_2$O$_3$-CaO-MgO-SiO$_2$ -inclusions when visually observed in the SEM. A typical view of three inclusions can be seen in Figure 15. Further, they occurred in large numbers in some samples, but were not found at all in others. Their presence could also be explained by occasional problems during sampling. To confirm the origin of the MnO-rich inclusions the Ellingham diagram$^8$ can be used to show that the most easily oxidised metallic components present in the steel was also to be found in significant amounts in the inclusions: Al, Ti, Si, Mn and Cr. The MnO-rich inclusions are then probably also a result of reoxidation, either from poor desoxidation conditions in the steel during vacuum degassing or occasional reoxidation during sampling.

![Figure 15. A view of three MnO-rich inclusions. (37% Al$_2$O$_3$, 46% SiO$_2$, 17% MnO). ø 13, 15 and 17µm](image-url)
6. DISCUSSION

It is clear from the present study that there no absolute equilibrium between top slag and steel with respect to oxygen existed at any stage in the ladle refining process. However, the conditions in steel and top slag were closer to equilibrium conditions after vacuum treatment than before vacuum treatment. This was an expected result, since vacuum treatment with intense stirring promotes slag-metal reactions.

The inclusions formed as a result of Si-deoxidation in supplement 1 were found to be much closer to equilibrium with steel than the top slag. The reason would be the relatively large surface area compared to volume promoting exchange reactions between steel and inclusion. The predicted oxygen activity data in the steel, calculated based on silica activity in data from the inclusions predicted with the ThermoSlag and IRSID models, were always higher than the oxygen activity measurements.

There was a slight trend that the larger inclusions generated oxygen equilibrium activities that were closer to corresponding measured values than the smaller inclusions. Since the top slag-steel bulk equilibrium resulted in values lower than measured oxygen activities, it is reasonable to believe that the larger inclusions had been more influenced by the top slag compared to the smaller ones. This was even more obvious from the result of the plant trials at Uddeholm Tooling.

Even though a lack of equilibrium has been found between top slag and steel, the top slag still affects the inclusion composition. From the study at Uddeholm Tooling it was possible to observe several effects on the top slag on the inclusion composition. The most obvious was the effect of MgO in the inclusions from the top slag, which has been confirmed for all heats. A straight relation between MgO level in the top slag and inclusions has been found for all heats after vacuum (UT-5) as seen in Figure 16.
The influence of SiO$_2$ content in the slag on the inclusion composition was also observed. However, the relation was not as clear for MgO described above. When the high SiO$_2$ top slag interacts with the steel, the dissolved Al in the steel melt will decrease according to reaction (7). This could be observed in the present study during degassing, where the Al-content in the steel melt is crucial to ensure low oxygen activity and preventing undesired reactions that may influence the composition of oxide inclusions.

Both supplements 1 and 2 show that the content of SiO$_2$ in the inclusions is higher when Al is very low in the steel melt. In the case of supplement 1 it was not unexpected, since the steel was only Si-deoxidised. In supplement 2 the decrease of Al in the steel occurred during vacuum treatment and a probable reason could be the high SiO$_2$ content in the top slag. The SiO$_2$ content in the top slag is depending on the SiO$_2$ rich slag brought over during EAF tapping. If the deslagging is not complete the SiO$_2$ content in the ladle top slag will consequently be higher.

Another mechanism affecting the Al content and oxygen activity in the steel melt is the sulphur refining reaction. The mechanism of sulphur refining generates oxygen that can in the end consume dissolved Al in the steel melt. However, this was not observed since the sulphur refining was limited in the plant trials at Uddeholm Tooling.
7. **SUMMARY AND CONCLUSIONS**

Two similar studies have been done with data out of plant trials at Ovako Steel AB and Uddeholm Tooling AB. Samples have been taken at different steps during the ladle refining. Steel and slag composition as well as temperature and oxygen activity have been determined. Extensive SEM-investigations of the inclusion compositions have been done to achieve a good picture of the inclusion compositions and their variations during ladle treatment. Calculations of oxygen activities were based on industrial composition data of slag, steel and inclusions. The study was done to determine if equilibrium conditions between top slag and steel and inclusions and steel exist after silicon deoxidation and after aluminium deoxidation. Three different models for oxide activity predictions were tested to study if it was possible to calculate the oxygen activity in the steel.

Evaluation of inclusion composition during the ladle refining have revealed that the inclusions belonging to the system \( \text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{SiO}_2 \) showed a continuous composition change throughout the ladle refining process, from high \( \text{Al}_2\text{O}_3 \), via \( \text{MgO} \)-spinel to finally complex types rich in \( \text{CaO} \) and \( \text{Al}_2\text{O}_3 \). The final composition after vacuum treatment was found to be close to the top slag composition. Small process parameter changes and practical variations during ladle refining were proven to give rather large differences of the inclusion composition. Some of the parameters affecting the inclusion compositions in the later stages of the ladle treatment are set in the beginning of the process. Examples are the steel melt oxygen activity and the deslagging success. Also, the precision in Al-addition for deoxidation and alloying must be accurate.

A correlation between MgO contents in top slag and inclusions were found. Also, a high SiO\(_2\) content was found in inclusions after vacuum from the heats with highest SiO\(_2\) content in the top slag before vacuum treatment.

The predicted oxygen activity data based on an assumed equilibrium between inclusion and the steel bulk were close to the measured data, which lead to the conclusion that the inclusions formed as a result of Si-deoxidation were found to be close to equilibrium. After Al-desoxidation and vacuum treatment the steel and
top slag was found to be much closer to equilibrium than before. However, even though a lack of equilibrium has been concluded it has been found that the top slag is affecting the inclusion composition. Larger inclusions have generally a composition closer to the top slag than smaller inclusions. The most obvious effect of the top slag on the inclusions is the MgO content for which it is possible to find a clear relation between MgO level in the top slag and inclusions has been found for all heats after vacuum

Finally, it was concluded that no equilibrium exist between top slag and steel bulk for the studied conditions. When the top slag and steel equilibrium were considered the calculation of oxygen activity showed always lower values than the oxygen activity measurements. The conclusion is, however, that the models for calculation of oxide activities were found to be useful if equilibrium conditions exist. The deviation from measured values was in all cases systematic with the same trend and the reason for the difference is believed the lack of equilibrium.
8. **Future work**

The ladle refining process is undergoing a continuous development. The research area is not new, but there is still much effort done to further understand and optimise the ladle refining process. A few questions close to the work done in present thesis have emerged. Some suggestions for future work in the area of understanding the interaction between steel, slag and inclusions are:

- Evaluate how the temperature affects the oxygen activity. During this work there have been indications that the temperature has a large effect on the equilibrium oxygen activity.

- Measure oxygen activity gradients in the ladle during ladle treatment for different stirring conditions.

- Do plant trials with the purpose to further understand how the inclusion composition is changing by time under non-varying conditions. A study with different top slag composition would give a clearer picture of the top slag on the inclusions.

- Do laboratory studies of the interface between slag and steel, to see how the steel composition is varying towards the interface. Investigate the interface with possible local equilibriums.

- Further investigate factors of oxygen activity during industrial ladle refining. The goal would be a model based on ease measurable properties like slag and steel composition, and temperature.

- Look into if it is possible to find a general “grade of equilibrium” during different stages of ladle refining. This would be useful to apply instead of assuming equilibrium between top slag and inclusions.
References


4. www.thermocalc.se 2006-05


