The Effect of Ladle Vacuum Treatment on Inclusion Characteristics for Tool Steels

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Anyone who doesn't make mistakes isn't trying hard enough.

-Wess Roberts
Abstract

The aim of the present work was to get an overview of inclusion characteristics during the ladle vacuum degassing. The results are based on plant trials and thermodynamic calculations. Trials were made on two different tool steel grades.

The top slag composition was altered and steel and slag samples were collected before and after vacuum degassing. The steel samples were analyzed for their composition as well as the number and size distribution of inclusions and the inclusion composition. With the aid of thermodynamic calculations the oxygen activity for the equilibria steel/inclusion and steel/top slag was calculated and compared among themselves and with measured oxygen activities in the steel melt. The results showed an effect of the top slag composition on the inclusion composition. When the CaO-content in the top slag was increased the CaO-content in the inclusion increased as well. The thermodynamic calculations indicated that the oxygen activity for the steel/inclusion was twice as large as that of the steel/top slag before vacuum degassing. However, after vacuum degassing their values were close.

In order to see how the inclusion characteristics evolved during vacuum degassing the vacuum treatment process was interrupted at five pre-determined points of time. Steel and slag samples were taken and analyzed for their composition. The steel samples were also examined for total oxygen, number and size distribution of inclusions and inclusion composition. Before vacuum treatment the inclusion content was high in number and during vacuum the number was decreased in the case of the smaller inclusions. However, for the larger (>11.2μm) the number of inclusions had increased. It was also noticed that the inclusion composition varied before vacuum degassing, but throughout the degassing process the inclusion composition was approaching the top slag composition. Furthermore, at the end of degassing there was only one type of inclusion composition in the steel melt. After around 10 minutes of degassing the inclusion characteristics reached their minimum (or plateau) value.

Keywords: oxygen activity, inclusion characteristics, vacuum degassing, desulphurization, slag, ladle
Acknowledgements

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To my friend Jenny Backman, thank you for your generosity. I hope our friendship will last forever.

Sister, you are my inspiration. Thank you for believing in me.

My parents, thank you for loving me, supporting me and always being there for me.

Stockholm, May 2005

Karin Steneholm
Supplements

The present thesis is based on the following papers:

**Supplement 1**: “Effect of top slag composition on inclusion characteristics during vacuum degassing of tool steel”  
  **K. Steneholm**, M. Andersson and M. Nzotta and P Jönsson  
  *Submitted for publication to Scandinavian Journal of Metallurgy*

**Supplement 2**: “Change of Inclusion Characteristics During Vacuum Degassing of Tool Steel”  

Parts of this work have been presented at the following conferences:

I: “Influence of Process Step on Inclusion Characteristics”  
  **K. Steneholm**  
  *Nordic Symposium for young Scientists, Production Metallurgy for Iron, Steel and Ferroalloys, June 11-13, 2003, Pobto/Oulu, Finland*

II: “Influence of Process Parameters during Vacuum Degassing on the Non-Metallic Inclusion Content in Tool Steel”  
  **K. Steneholm**, M. Andersson  
  *STÅL2004, 5-7 May, 2004, Borlänge, Sweden*
1. Introduction

Today’s steel production is more and more specialized, due to higher demands from the customers as well as increased competition between different steelmakers. It is therefore important to obtain a deeper insight to how the process can be controlled in order to meet demands on material properties from customers. Here, the inclusion characteristics represent very important parameters to control in order to obtain the desired material properties. The present thesis is focused on tool steelmaking, where important material properties such as polishability and hot strength are influenced by the steel cleanness. The inclusion characteristics should be controlled done both during ladle treatment and casting, because these are the process steps, where it is possible to influence the inclusion parameters. After casting, in the hot-working processes the material dimension is reduced, which mainly affects the inclusion size distribution and shape.

To control the process it is necessary to understand it. Much research has been done on ladle and vacuum treatment, but with new technologies and knowledge it is important to improve the understanding of how process changes will affect the steel cleanness. One way of understanding and controlling the process is by using a process model. With a good model it is possible to predict what will happen if certain actions are taken during the process. However, in order to have a functional process model, which is well tuned with the actual values in the steel shop, it is essential to use the correct input data. Uddeholm Tooling AB is presently (2005) working on a steelmaking process model, where one part of the future model will describe the change of inclusion characteristics in the steel melt during ladle treatment. Besides giving a deeper insight and better understanding of inclusions behavior during the vacuum treatment process, the present study has been done to assist the implementation of the process model under development.
2. Experimental

2.1 Plant description
Uddeholm Tooling AB, Hagfors, Sweden is a scrap-based steelmaking company. The scrap is melted in an electric arc furnace and then transferred to the ladle station in a 65- or 35-tonne ladle. At the ladle station, the molten steel is deoxidized and alloyed. Thereafter, the ladle is moved to the vacuum degassing station, where it undergoes vacuum treatment at a pressure of less than 4mbar. Finally, the steel is cast using uphill teeming.

2.2 Plant trials
Two tool steel grades were evaluated, a modified 420 steel grade (0.25%C, 0.35%Si, 0.55%Mn, 13.3 %Cr, 0.35%Mo, 1.35%Ni, 0.017%Al and 0.12%N) and a H13-steel grade (0.39%C, 1.0%Si, 0.4%Mn, 5.3%Cr, 1.3%Mo and 0.9%V). In the first supplement, samples were taken before and after the vacuum degassing treatment and in the second supplement sampling were done before vacuum degassing and at different times during the vacuum degassing process. Note, that the vacuum treatment was interrupted in order to obtain the samples. The samples obtained were steel, slag and temperature. Two kinds of steel samplers were used, namely the LSHR\textsuperscript{1} and the RS\textsuperscript{2} samplers. The temperature measurement was combined with an oxygen activity measurement.

2.3 Microscope evaluations
The steel samples were analyzed in a light optical microscope (LOM) to determine the number and size distribution of inclusions. This was made using the JK’s chart SS 11 11 16\textsuperscript{3}. Thereafter the chemical composition of the inclusions was determined by a scanning electron microscope (SEM).

2.4 Thermodynamic calculations
A prediction of the oxygen activity for the equilibria steel/inclusion and steel/top slag was made with the use of the data of steel composition, temperature, bulk and top slag weight. The activities were calculated both with Wagner’s equation and with thermodynamic models, which in this case was the thermodynamic software ThermoCalc\textsuperscript{4} together with appropriate databases. The obtained results were compared with the measured oxygen activities.
3. Results and discussion
Presented here is a short review from the two supplements referring to effects of changing the top slag, evolution during vacuum treatment time, and a main discussion.

3.1 Change of top slag (supplement 1)
3.1.1 Inclusion content
In supplement 1, the main focus was to study the effect of a changed top slag composition on the inclusion composition. For three heats (A, B, C) of a 420 modified steel grade, samples were taken before and after vacuum degassing. The top slag composition for the two latter heats were altered in the way that heats B and C had higher CaO-content and lower MgO-content than that of heat A. The slag samples were evaluated for composition and the steel samples were analyzed for composition and investigated with respect to the inclusion characteristics. A comparison of steel slag and steel inclusion equilibria was made by using Wagner’s theory and ThermoCalc4 simulations.

Regarding the total number of inclusions per mm², Figure 1, it can be seen that the number of inclusions decreases during vacuum degassing. After vacuum degassing the total amount of inclusions are similar in number for the different compositions of top slag. It can also be seen that before vacuum degassing the samples show a different amount of inclusions. Hence, from these observations, it does not seem like the different top slag composition does affect the total amount of inclusions.

Figure 1. Total amount of inclusions per mm² vs. process step
On the contrary, a correlation between the change of top slag composition and the number of larger inclusion was found. Since the larger inclusions are of greater concern for the manufacturer, it is of importance to be aware of eventual risks of creating large inclusions. In Figure 2 it can be seen that the number of large (>11.2µm) inclusions have different values before vacuum degassing. For heat A there is a large decrease in number, 70% loss. However, in the case of both heat B and C, there is a slight increase in number, a 20-30% gain. This should be related to the change in top slag composition, since heat A had a lower CaO content than heats B and C. However, it should be noted that the change of inclusion composition (as can seen in Table 1 below) due to increased CaO content in slag also could affect the inclusion interfacial properties, thus making it more difficult for the inclusions to be separated to the top slag.

![Figure 2. Number of inclusions (>11.2µm) per mm² vs. process step](image)

3.1.2 Inclusion composition

The inclusions were also examined for their composition, shown in Table 1. Before vacuum degassing the inclusion composition varies and is not similar to the top slag composition. However, after vacuum treatment, the inclusion composition has been altered and resembles more the top slag composition. Also, there are only small variations, since only one type of inclusion was found. This applies to all three heats. The most common type before vacuum treatment is the type a, the single phase spinel, Al₂O₃•MgO. After vacuum treatment, only the phases d, f and k were found in heat A, B and C, respectively. Also, the top slag of heat A has a higher MgO content than the other two heats, which on the other hand have higher CaO content. This is reflected in the observed inclusion composition after vacuum degassing.
Table 1. Phases of micro inclusions – as analyzed.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Al_2O_3</th>
<th>SiO_2</th>
<th>MnO</th>
<th>CaO</th>
<th>MgO</th>
<th>Cr_2O_3</th>
<th>Found in sample*</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>75-78</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>22-25</td>
<td>-</td>
<td>A1, B1, C1</td>
</tr>
<tr>
<td>b</td>
<td>78</td>
<td>-</td>
<td>-</td>
<td>7</td>
<td>15</td>
<td>-</td>
<td>A1</td>
</tr>
<tr>
<td>c</td>
<td>62</td>
<td>2</td>
<td>-</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>A1</td>
</tr>
<tr>
<td>d</td>
<td>45</td>
<td>6</td>
<td>-</td>
<td>46</td>
<td>4</td>
<td>-</td>
<td>A2</td>
</tr>
<tr>
<td>e</td>
<td>40</td>
<td>8</td>
<td>-</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>B1</td>
</tr>
<tr>
<td>f</td>
<td>33</td>
<td>6</td>
<td>-</td>
<td>61</td>
<td>-</td>
<td>-</td>
<td>B2</td>
</tr>
<tr>
<td>g</td>
<td>33</td>
<td>34</td>
<td>-</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>C1</td>
</tr>
<tr>
<td>h</td>
<td>25</td>
<td>39</td>
<td>23</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>C1</td>
</tr>
<tr>
<td>i</td>
<td>63</td>
<td>-</td>
<td>-</td>
<td>31</td>
<td>6</td>
<td>-</td>
<td>C1</td>
</tr>
<tr>
<td>j</td>
<td>49</td>
<td>20</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>17</td>
<td>C1</td>
</tr>
<tr>
<td>k</td>
<td>30</td>
<td>12</td>
<td>-</td>
<td>58</td>
<td>-</td>
<td>-</td>
<td>C2</td>
</tr>
</tbody>
</table>

(*A1, B1 and C1 are samples taken before vacuum treatment, while A2, B2 and C2 are samples taken after vacuum treatment.)

3.1.3. Thermodynamic calculations

The second part of supplement 1 deals with thermodynamic calculations. Three cases of equilibria were considered, I: steel melt/inclusion (before and after vacuum degassing), II: steel melt/top slag (before and after vacuum degassing) and III: steel melt/top slag (after vacuum degassing). In the first two cases (I and II) the oxygen activity was calculated using the equilibrium reaction

\[ 2Al + 3O = Al_2O_3(s) \]  \hspace{1cm} (1)

Wagner’s equation was applied for calculation of the dissolved element activity coefficients together with the aid of Thermo-Calc software in order to calculate the alumina activity in the oxide phase. In case III only the Thermo-Calc software was used to calculate the metal/top slag equilibrium. The values obtained in all three cases were not close to that of the measured values, which could be due to uncertainties during sampling or errors in the thermodynamic models used. It is seen that the values of the steel/inclusion oxygen activity is closer to that of the steel/top slag after vacuum degassing compared to that before vacuum degassing. This can be related to the fact that the inclusion composition is approaching the top slag composition during the vacuum treatment.

In Figure 3 the difference between the two cases II and III is shown. The difference between the two cases is greater for heat A. One reason could be that heats B and C are closer in top slag composition.
3.2 Evolution of inclusion characteristics during vacuum degassing (supplement 2)

Supplement 2 deals with the evolution of inclusion characteristics during vacuum degassing in an H-13 steel grade. Ten interruptions during vacuum treatment have been made during the same amount of heats. Five different interruptions were made, at 3, 6, 9, 15 and at 22 minutes of vacuum degassing. The experiment were made in two series, a and b. The aim was to get a picture of how the inclusion characteristics change during vacuum treatment. For each heat, steel, slag and oxygen activity samples were collected before and during interruption of the vacuum degassing process. The steel and slag samples were examined for their composition and the steel samples were also cut in order to determine the inclusion characteristics.

3.2.1 Total oxygen content

In Figure 4 the relative decrease of the total oxygen content in the steel is shown. During the first 10 – 15 minutes of the vacuum treatment the total oxygen decreased more than 50%. However, after some fifteen minutes, there seems to be an increase again. The analysis of total oxygen is somewhat uncertain, since a high value of total oxygen could be explained by a large inclusion being in the piece of steel that is analyzed, hence creating a large value of total oxygen. Each point in the figure represents one single heat.
3.2.2 Inclusion content
If the total oxygen content is assumed to be an approximate measurement of the amount of inclusions, Figure 4 can be related to Figure 5. In Figure 5 the same trend as in Figure 4 is noted. In the beginning, there is a decrease in number of inclusions, but after some fifteen minutes the decrease has diminished or even turned into a small increase. The results for the smaller inclusion size classes are the same as for those found in Figure 5. However, not enough data is available for the larger inclusions (>11.2µm) due to a low number of counting, so the results for these inclusions are not statistically reliable.
Figure 5. Decrease of total inclusion content in steel (#/mm²) during vacuum treatment

3.2.3 Inclusion composition
The compositions of the inclusions are shown in Table 2. Before and during the first six minutes of vacuum treatment, several types of inclusions, (types m-v), were found in the steel samples. Thereafter, the inclusion composition seem to approach the top slag composition, type x.

Table 2. Phases of micro inclusions – as analyzed

<table>
<thead>
<tr>
<th>Type</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Found in sample*</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>69</td>
<td>&lt;1</td>
<td>2</td>
<td>29</td>
<td></td>
<td></td>
<td>a and b (BV)</td>
</tr>
<tr>
<td>n</td>
<td>68</td>
<td></td>
<td></td>
<td></td>
<td>32</td>
<td></td>
<td>a (BV, V3)</td>
</tr>
<tr>
<td>o</td>
<td>59</td>
<td>&lt;1</td>
<td>32</td>
<td>4</td>
<td>4</td>
<td></td>
<td>a and b (BV)</td>
</tr>
<tr>
<td>p</td>
<td>48-50</td>
<td>1.5-2</td>
<td>38-41</td>
<td>7-7.5</td>
<td>0-4</td>
<td></td>
<td>b (BV), a (BV)</td>
</tr>
<tr>
<td>r</td>
<td>25</td>
<td>42</td>
<td>43</td>
<td>8</td>
<td></td>
<td></td>
<td>a (V3)</td>
</tr>
<tr>
<td>s</td>
<td>63</td>
<td>&lt;1</td>
<td>1.5</td>
<td>32</td>
<td>3</td>
<td>&lt;1</td>
<td>a (V3)</td>
</tr>
<tr>
<td>t</td>
<td>47</td>
<td>1.5</td>
<td>43</td>
<td>9</td>
<td></td>
<td></td>
<td>a (V6)</td>
</tr>
<tr>
<td>u</td>
<td>25</td>
<td>22</td>
<td>41</td>
<td>12</td>
<td></td>
<td></td>
<td>a (V6)</td>
</tr>
<tr>
<td>v</td>
<td>55</td>
<td>22</td>
<td>1.7</td>
<td>&lt;1</td>
<td>3</td>
<td>16</td>
<td>a (V6)</td>
</tr>
<tr>
<td>x</td>
<td>36.5-40</td>
<td>1.5-4</td>
<td>49.5-55</td>
<td>5-7</td>
<td></td>
<td></td>
<td>a and b (V9, V15, V22)</td>
</tr>
<tr>
<td>y</td>
<td>33</td>
<td>18.5</td>
<td>39</td>
<td>10</td>
<td></td>
<td></td>
<td>b (V15)</td>
</tr>
<tr>
<td>z</td>
<td>25</td>
<td>30</td>
<td>31.5</td>
<td>14.5</td>
<td></td>
<td></td>
<td>b (V15)</td>
</tr>
</tbody>
</table>

(*BV: before vacuum degassing, V3: stop after 3min of vacuum degassing, V6: stop after 6min, V9: stop after 9min, V15: stop after 15 min, V22: stop after 22min.)
3.2.4 Desulphurization rate

In Figure 6, the desulphurization rate is shown as a function of the vacuum treatment time. It can be seen that the rate decreases rather fast up to approximately ten minutes of vacuum treatment. After that, the rate remains constant at a low desulphurization rate. However, there is one heat which has a very high desulphurization rate. This heat also has a higher total oxygen content (Figure 4) and total inclusion content (Figure 5). Furthermore, it has a different inclusion composition. The other five heats at nine, fifteen and twenty-two minutes of vacuum degassing contain mainly one singular type of inclusions, but this heat (sampled after fifteen minutes of vacuum degassing) contains several different inclusion types, types x-z. In general, this heat contains inclusions with a higher amount of SiO$_2$. One possible reason for that may be that the higher desulphurization rate causes a local depletion of aluminum in the steel. Since silicon is another element with a high oxygen affinity it will react with the dissolved oxygen that is supplied during the desulphurization under the formation of silica inclusions.

![Graph showing the rate of desulphurization](image)

**Figure 6. Rate of desulphurization**
4. Final discussion and conclusions

This thesis is based on two supplements. Both are focusing on the inclusion characteristics during vacuum degassing. The first supplement concerns the effect of changing the composition of the top slag and the second is dealing with the evolution of the inclusion characteristics during vacuum degassing.

It has been seen that the inclusion composition is changing with the changing of the top slag composition. Experiments with increased CaO-content in the top slag showed that the CaO-content in the inclusions was increased as well. After vacuum treatment the inclusion composition is approaching that of the top slag and it is also seen that the inclusions have a homogenous composition, i.e. only one type of inclusions is found. Thermodynamic calculations showed that before vacuum treatment, the equilibrium oxygen activity for the steel/inclusion was 2-3 times higher than that of the steel/top slag. It was also concluded that the theoretical equilibrium oxygen activity for the steel/inclusion will become more like the oxygen activity for the equilibrium steel/top slag during the course of vacuum degassing.

The study also shows that the number of inclusions is reduced during the course of vacuum degassing, but for the larger inclusion type (DP) there seems to be a trend of an increase at the end of the treatment. After around 10 minutes of degassing the parameters, inclusion characteristics, have reached their minimum values. It was also observed that with a high desulphurization rate the total oxygen in the steel will remain high, which will then lead to a higher number of inclusions.

The results given in this thesis could be valuable for use in a process model made to ensure stability in the process of steel making. The experiment of interrupted vacuum degassing can be used as a way of verifying the model. However, since the argon flow is not a true value it is difficult to know how reliable the exact numbers are. During
the investigations it has been noted that the argon flow is different for each heat, however the stirring seems to be similar when looking at the plume. It is necessary to have a stirring that is vigorous for the top slag to have effect on the inclusion characteristics. With no stirring the top slag has no or little effect.

This study has also shown that the initial conditions before vacuum treatment, such as sulfur content, are very important to know. The initial conditions will have a great influence on the behavior of oxide inclusions in the steel melt during the degassing. A process model for vacuum treatment should properly take into account all initial conditions.
5. Future work

In this thesis work has been done to investigate the behavior of inclusion characteristics during the vacuum degassing treatment. However, there are still many unanswered questions. In order to get more insight to the area and a deeper understanding of the reasons for the change of the inclusion composition during vacuum treatment, more studies should be performed. Based on the results, the following is suggested as further work:

- Make detailed investigations on the mechanism of the change of the inclusion composition during vacuum treatment.
- Investigate the evolution of inclusion characteristics during vacuum degassing, when other process parameters are varied in plant trials (i.e. initial sulfur content, ladle age, temperature, previous steel grade in the ladle, etc.)
- Study if it is possible to relate the inclusion number to oxygen activity and dissolved oxygen during the ladle treatment process in tool steels.
- Investigate how to accurately measure and control the argon flow in the ladle, in order to quantitatively determine the effect of argon stirring on inclusion characteristics during vacuum treatment.
6. References

4. www.thermocalc.se