Slag, Steel, Ladle and Non-metallic Inclusions Equilibria in an ASEA-SKF Ladle Furnace

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Doctoral Thesis

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ABSTRACT

This study explores the possibility of prediction and modification of some of the physicochemical properties of non-metallic inclusions by considering top slag-steel-ladle equilibria in an ASEA-SKF ladle furnace.

To test the reliability of an available computational thermodynamic computer program, the first sub project was done. It was concluded that LiMeS, an interface for Thermo-Calc, is a useful tool for slag-steel equilibrium calculations.

The second sub project was set out to find some model/s that could calculate the most accurate oxygen activity of molten steel compared to the measured one. This study concluded that both Wagner’s and Turkdogan’s equations are useful. It was further seen that increasing the Al contents in the molten steel, increasing the CaO/Al₂O₃ ratio in the top slag, and reducing the temperature, resulted in reduction of the oxygen activity of the molten steel.

In the third sub project a comparison was made between measured CaO and Al₂O₃ (normalised to CaO-Al₂O₃) in top slag, calcium aluminate inclusions, and the results of theoretical calculations. The average contents of CaO and Al₂O₃ in all inclusions were close to the composition of the phase Ca₁₂Al₁₄O₃₃ and the contents of CaO and Al₂O₃ in the slags were close to the composition of the phase Ca₆Al₂O₇ in the binary phase diagram of CaO-Al₂O₃.

The forth sub project set out to study the effect of vacuum degassing time on non-metallic inclusions. It was concluded that during the vacuum degassing process the share of calcium aluminates compared to spinels, Ca content of the oxides, and the average equivalent circle diameters of the oxides were increasing, and oxides tended to form spherical shapes.

Finally, based on the preceding four sub projects, the fifth sub project aimed to optimize the steel treatment in an ASEA-SKF ladle furnace. The final results showed that by adding 200 kg fluorite to the top slag of 1200 kg, it was possible to achieve a sulphur content of less than 10 ppm in the steel and a sulphur ratio between slag and steel of 1570, and at the same time reduce the oxygen activity of the molten steel and the degassing time.

Keywords: Clean steel; Top slag; Non-Metallic Inclusions; Oxides; Vacuum Degassing; Deoxidation; Desulphurization; Equilibrium; Computational Thermodynamics; Scanning electron microscopy.
Non-metallic inclusions in SEM
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4- Project planning, literature survey, SEM analysis of non-metallic inclusions, data analysis, and writing the article.

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# TABLE OF CONTENTS

1. Introduction ........................................................................................................................... 1

2. Theoretical background ......................................................................................................... 7
   2.1. Computational thermodynamics ................................................................................... 8
   2.2. Sulphur removal ............................................................................................................. 9
   2.3. Oxygen removal ............................................................................................................ 9
   2.4. Oxygen activity calculations ....................................................................................... 10
   2.5. Non-metallic inclusions ............................................................................................. 12
   2.6. Removal of non-metallic inclusions ......................................................................... 16

3. Experimental .......................................................................................................................... 19
   3.1. Steel melting plant of Ovako Hofors AB ...................................................................... 19
   3.2. Sample analyzing methods ......................................................................................... 20
      3.2.1. Steel and slag ....................................................................................................... 20
      3.2.2. Oxygen activity ................................................................................................... 20
      3.2.3. Scanning electron microscopy .......................................................................... 20

4. Results ................................................................................................................................... 21
   4.1. Results of supplement 1 ............................................................................................ 21
   4.2. Results of supplement 2 ............................................................................................ 24
   4.3. Results of supplement 3 ............................................................................................ 28
   4.4. Results of supplement 4 ............................................................................................ 32
   4.5. Results of supplement 5 ............................................................................................ 38

5. Discussion ............................................................................................................................... 45

6. Summary of conclusions ......................................................................................................... 49

7. Suggestions for future works ................................................................................................. 51

8. References .............................................................................................................................. 53
1. INTRODUCTION

Non-metallic inclusions are naturally occurring and typically undesired products that are formed into various types depending on their favourable thermodynamic conditions in almost all treatment practices involving molten steels.

Apart from some applications where inclusions are supposed to be demanded, like sulphides for improving machinability (that could be argued with recently available cutting machines and tools), they usually deteriorate mechanical properties and surface quality of steel products and could cause nozzle clogging and disruption of steelmaking and forming processes.

It is widely believed that due to the presence of sulphide and oxide inclusions some of the mechanical properties of steels like ductility, toughness, anisotropy, and formability might be negatively affected [1].

One of the ongoing demands at Ovako Hofors AB is to reduce sulphur and total oxygen (TO) content of bearing steels. Regarding sulphur and TO contents of bearing steels, it is believed that under cyclic loadings, sulphide and oxide inclusions can act as crack initiators resulting in fatigue failure and life reduction of bearing components [1].

The harmful effects of non-metallic inclusions on fatigue properties of steel parts are because they can act as potential sites of stress concentration that can initiate cracks under cyclic loadings.

Fig. 1 presents the relation between fatigue life of ball bearing versus number of oxide inclusions larger than 30 µm [2]. From this figure it is clear that the presence of more oxides, especially larger ones, could have very devastating effect on the fatigue life of ball bearings.
Harmful effects of non-metallic inclusions are highly dependent on their chemical compositions, volume fractions, dispersions and morphologies [3-5]. Generally large and unbreakable inclusions with high melting points are the most unwanted ones; however compared to these inclusions, small and breakable ones or those with lower melting points are more preferred [4,6,7]. The reason for these preferences is that inclusions that have lower melting points or are breakable are likely to be deformed, crushed to smaller inclusions, or disappeared in following hot or cold forming processes (effect of forming process and reduction ratio) or heat treatments that steels might have after teeming and solidification process.

Negative effects of non-metallic inclusions on fatigue properties of steels seem to be especially more pronounced in steels with higher tensile
strength, i.e. steels with lower strength may fail under cyclic loadings due to matrix related reasons.

In most of the secondary metallurgical treatment plants of steelmaking companies, slag, steel and ladle are involved. Thus the composition of slag, steel, and ladle are very crucial factors for reaching the desired final steel properties, and they have crucial effects on chemical compositions, volume fractions, dispersions and morphologies of non-metallic inclusions. Fig. 2 presents some of the most important factors that could affect physicochemical properties of inclusions.

![Diagram of important factors affecting inclusions](image_url)

**Figure 2:** Some of the most important factors that could affect chemical composition, volume fraction, dispersion and morphology of inclusions during steelmaking process.

This PhD work set out to study some of the most important factors that could affect physicochemical and statistical properties of non-metallic inclusions in bearing steels during vacuum degassing. In order to achieve this task several sub projects and activities were set. These sub projects were presented in five supplements that are the bases of this PhD work. The specific goals of these supplements are shown in Fig. 3. The brief outcomes of these supplements are presented in the result part of this report.
Figure 3: General overview of five supplements and their respective objectives.

- **Supplement 1:** Slag-Steel equilibrium calculations
  - Goal: Calculation of percentage error of the calculated results compared to the measured results achieved from a computational thermodynamic software.

- **Supplement 2:** Oxygen activity calculations
  - Goal: Calculation of oxygen in the molten steel with the lowest possible deviation to the measured oxygen amounts.

- **Supplement 3:** Ca & Al in top slag & NMIs
  - Goal: Calculation of possible relation between Ca & Al in top slag and non-metallic inclusions.

- **Supplement 4:** NMIs development during VD
  - Goal: Study of the behaviour of non-metallic inclusions during vacuum degassing.

- **Supplement 5:** Top slag optimization
  - Goal: Optimization of steel making metallurgy (O, S, Time) by considering results achieved from the previous supplements.

---

Figure 4: Logic behind the project and each supplement.

1. **Project initiation**
2. Literature review and gathering available knowledge in the field
   - Thermodynamic aspects affecting inclusions
   - Kinetic aspects affecting inclusions
3. Supplement 1: Slag-Steel equilibrium calculations
4. Does computational thermodynamics fulfil our purposes?
   - Yes for most of components
   - No for oxygen activity
5. Supplement 3: Ca & Al in slag-steel-inclusions
6. Supplement 2: Oxygen activity calculations
7. Supplement 4: Inclusion development during degassing
8. Supplement 5: Top slag optimization
10. Project closure
Fig. 4 shows the logic behind different supplements of this project. This project started with a pre-study regarding steel desulphurization [8-18], steel deoxidation [19-55], and removal of non-metallic inclusions [56-87]. These studies implied that in order to study the important factors that affect compositions, volume fraction, dispersion, and morphologies of non-metallic inclusions both thermodynamic and kinetic aspects of steelmaking should be considered.

In order to check the reliability of an available computational thermodynamic computer program, the first sub project was performed (explained in supplement 1); results of this supplement suggested that by considering tolerances of the process, apart from oxygen level of the molten steel that is a very crucial component for this study and is required to be predicted with very high accuracy, other components in top slag and steel could be calculated with acceptable (for this project) error.

The second sub project set out to find some model/s that could calculate the closest oxygen activity of molten steel to the measured oxygen activity in an ASEA-SKF ladle furnace (explained in the supplement 2).

The third sub project that was explained in supplement 3 set out to study the possible relations between Ca and Al in oxide inclusions, top slag, and the results of theoretical calculations.

The forth sub project that was explained in supplement 4 set out to study the effect of vacuum degassing time on development of non-metallic inclusions.

Finally, based on all these four sub projects, the fifth sub project with the aim of optimization of steel treatment in an ASEA-SKF ladle furnace was performed (explained in the supplement 5).

A brief summary of all these supplements are presented in the result part of this report and all supplements in their pre-published format are attached to the end of this report.

The sixth sub project was a continuation and complement for supplement 4. This supplement is also attached to the end of this report but is not explained in this thesis work.
2. THEORETICAL BACKGROUND

Vacuum degassing process in the ASEA-SKF ladle furnace of Ovako was chosen as the main pillar of this project. Vacuum degassing could be considered as one of the most crucial stages of steelmaking and ladle treatment process; this is because at the end of this stage final chemical composition, deoxidation, desulphurization, and inclusion removal should be achieved.

Degassing process, with help of proper top slag-steel stirring and top slag choice is supposed to contribute positively to removal of unwanted non-metallic inclusions as much as possible and result in a cleaner and more homogeneous steel melt; however at the moment it is difficult to predict the optimized thermodynamic and kinetic conditions of the vacuum degassing process that would result in the most favourable and optimized treatment conditions.

Usually after finishing vacuum degassing due to lack of enough slag-steel stirring and possibility of adding any extra material, it is not easy to make any changes to the system; consequently morphology, volume fraction, composition, and dispersions of non-metallic inclusions at the end of the vacuum degassing process could not easily be changed (any possible effects of casting powder in the moulds and mould linings during teeming and solidification are not considered).

Traditional ways to study the effects of various parameters on non-metallic inclusions are performing experimental tests in both production plant and laboratory scales; however these experiments are usually expensive, time-consuming and sometimes even impossible to perform. But, in order to reduce the necessary experiments in the design of new materials, improvement of existing materials, and controlling as well as developing metallurgical processes, computational thermodynamics may be applied [88].

In this project it was tried to contribute to the knowledge of steelmaking and ladle treatment by applying computational thermodynamics, plant experiments and comparing these results with each other in order to achieve a practical understanding regarding morphology, volume fraction,
dispersion, composition, and development of non-metallic inclusions in the ASEA-SKF ladle furnace.

2.1. COMPUTATIONAL THERMODYNAMICS

By means of thermodynamic properties of individual components in a system it is possible to compute equilibrium states of the whole system. Gibbs introduced the possibility of calculating equilibrium states of different phases by having the thermodynamic properties of these phases or individual elements in respective systems [89]. Kaufman and Bernstein [90] took advantage of thermodynamic properties and developed the CALPHAD [91-93] method that allows the calculation of phase diagrams by means of available thermodynamic properties.

In CALPHAD computational thermodynamic calculations [91-93], or computer coupling of phase diagrams and thermochemistry, by means of Gibbs energy, thermodynamic properties are modelled. The minimization of Gibbs energy is the key to the CALPHAD method, and this is due to the fact that the Gibbs energy is a function of both temperature and pressure, and as soon as it is calculated other thermodynamic quantities such as entropy and enthalpy could be derived [93,94].

In recent years computational thermodynamics has had an enormous progress [94]; several different computer programs have been developed and are constantly improving their precision and reliability. By means of these computer programs it may be possible to simulate, predict and optimize different metallurgical processes; i.e. by considering different affecting factors as constant, try to understand the effect of one or some other desired factors in a thermodynamic system.

In some parts of this study Thermo-Calc (databases TCFE7 and SLAG3 were used) and LiMeS [88,95] computer programs were applied to simulate the slag-steel equilibrium in an ASEA-SKF ladle treatment furnace.
2.2. SULPHUR REMOVAL

Equations (1) and (2) are respectively believed to describe sulphur removal reaction and sulphur distribution ratio between top slag and molten steel during the vacuum degassing process [96]. In these equations parenthesis represent (wt%) of component in top slag, and brackets represent [wt%] of components in molten steel. "a_i" denotes the activity of component "i".

By considering equations (1) and (2), it can be concluded that by increasing activity of CaO, and increasing the Al amount in the molten steel, sulphur distribution ratio between slag and steel or (S)/[S] ratio could increase. Although more CaO seems to be very positive, it is believed that after reaching a certain amount of CaO, any further addition of that could decrease the (S)/[S] ratio [96]; this reduction of the (S)/[S] ratio is believed to be due to increasing amount of unmelted CaO in the top slag that could result in increasing the melting point of the top slag or lowering its CaO activity, or appearance of additional heterogeneous and solid phases in the top slag [96].

\[
[S] + (CaO) + \frac{2}{3}[Al] \leftrightarrow (CaS) + \frac{1}{3}(Al_2O_3) \quad (1)
\]

\[
\frac{(S)}{[S]} = K[Al]^{2/3} \frac{a(CaO)}{a^{1/3}(Al_2O_3)}
\quad (2)
\]

2.3. OXYGEN REMOVAL

Active oxygen that is present in molten steel could react with strong deoxidizers like Ca, Al, and Si that are present in molten steel. These reactions (3) to (5) could result in reduction of oxygen activity of molten steel as well as generation of oxide inclusions.

\[
[Si] + 2[O] \leftrightarrow SiO_2 (s) \quad \Delta G^0 = -581,900 + 221.8T \quad [J/Mol] \quad (3) \ [29]
\]

\[
2[Al] + 3[O] \leftrightarrow Al_2O_3 (s) \quad \Delta G^0 = -1,202,000 + 386.3T \quad [J/Mol] \quad (4) \ [29]
\]

\[
[Ca] + [O] \leftrightarrow CaO (s) \quad \Delta G^0 = -645,200 + 148.7T \quad [J/Mol] \quad (5) \ [29]
\]

Each of these elements reduces the oxygen content of molten steel to a certain level. Reduction of oxygen activity does not necessarily result in
lower TO, however by having proper slag-steel stirring, and proper choice of a synthetic top slag that could absorb and dissolve non-metallic inclusions, lower TO might be achieved.

2.4. OXYGEN ACTIVITY CALCULATIONS

In this study in order to calculate oxygen activity of molten steel two equations, Wagner’s equation (10) [3] and Turkdogan’s equation (14) [97] and one computer program (Thermo-Calc [95] with databases TCFE7 and SLAG3) were applied.

Wagner's equation: By considering equations (6) and (7), it would be possible to apply equations (8) to (10) to calculate theoretical oxygen activities of molten steel that is supposed to be in equilibrium with top slag. Equation (9) is from Henry’s law, and equation (10) is called Wagner’s equation.

\[
\begin{align*}
2[Al] + 3[O] &\leftrightarrow Al_2O_3 \quad \text{(s)} \quad (6) \\
\Delta G^0 &= -1,202,000 + 386.3T \text{ J/mol} \quad (7) \quad [3,98] \\
\Delta G^o &= -RT \ln \left[ \frac{\alpha_{Al_2O_3}}{\alpha_{Al}^2 \alpha_{O}^3} \right] \quad (8) \\
\alpha_{Al} &= f_{Al}[\text{wt\%Al}] \quad (9) \\
\log f_{Al} &= \sum e_{Al}^{ij}[\text{wt\%-j}] \quad (10)
\end{align*}
\]

Al\textsubscript{2}O\textsubscript{3} activities that were required for solving equation (8) were calculated by applying three different models and two different constants that were explained in supplement 2 of this study. In order to solve equation (10), interaction coefficient parameters [98] that are shown in Table 1 were applied.
Table 1: Interaction coefficient parameters that were applied in this study [98].

<table>
<thead>
<tr>
<th>Interaction parameters</th>
<th>j</th>
<th>e_{Al}</th>
<th>e_{O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.091</td>
<td>-0.436</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.056</td>
<td>-0.131</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>-0.021</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
<td>-0.133</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.012</td>
<td>-0.0459</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>63/T + 0.011</td>
<td>-20,600/T + 7.15</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-34,740/T + 11.95</td>
<td>-1,750/T + 0.734</td>
<td></td>
</tr>
</tbody>
</table>

Turkdogan’s equation [97]: Equation (14) is a simplified way to present Wagner’s equation (10) and in this study is called Turkdogan’s equation. By means of equations (12) to (14), it is possible to calculate oxygen activities of molten steel.

Equation (13) is presented by Turkdogan and is supposed to give the most comparable result to the oxygen activities that are measured in molten steel at production plants. This equation (13) is believed to consider a correction factor for partial electronic conductions of the MgO-stabilized sensors; this is more explained in supplement 2 of this study. Equation (14) is valid at low aluminium contents [97]: $f_{Al} \approx 1$

\[
\begin{align*}
Al_2O_3 & \leftrightarrow 2[Al] + 3[O] \quad (11) \\
K &= \frac{[\% Al]^3[ppm O_f]^3}{\alpha Al_2O_3} \quad (12) \\
\log K &= -\frac{62.680}{T} + 32.54 \quad (13) [97] \\
\log f_{O} &= -3.98[\% Al] \quad (14) [97]
\end{align*}
\]

$Al_2O_3$ activities that were required for solving equation (12) were calculated from one model and one constant (0.064) that were explained in the supplement number 2 of this study.
2.5. NON-METALLIC INCLUSIONS

Traditionally non-metallic inclusions have been divided into four types (type A: Sulphides, type B: Aluminates, type C: Silicates, and type D: globular Oxides); however because these classifications were designed to be simple, they were not detailed enough for the purpose of this research work; thus it was decided to apply scanning electron microscope (SEM) with different costume defined classifications for analysing and classification of non-metallic inclusions.

By regarding the heats that were considered in this study it was seen that most of oxide inclusions that were formed in steel grade SAE 52100 in ASEA-SKF ladle treatment furnace, could roughly be classified into two main populations. These two types of inclusions are called spinel \(((\text{MgAl})_x\text{O}_y)\) and calcium aluminate \(((\text{Ca-Al-Mg})_x(\text{O-S})_y)\); Chemical compositions (wt% normalized to \(\text{Al}_2\text{O}_3-\text{CaO-\text{MgO}}\)) and typical equivalent circle diameters (ECD in \(\mu\text{m}\)) of some of these spinels and calcium aluminates are shown in Fig. 5.

![Diagram](image)

**Figure 5:** Chemical compositions (normalized to ACM) and typical ECDs (\(\mu\text{m}\)) of some of the observed spinels and calcium aluminates.
Figs. 6 and 7 show two different examples of SEM-EDS mapping analysis of these two main types of observed oxide inclusions. Fig. 6 shows two calcium aluminates and Fig. 7 shows two spinels (In these figures darker areas are those parts of the inclusions that respective elements exist).

A) Figure 6: SEM-EDS mapping analysis of two calcium aluminates.

B) Figure 6: SEM-EDS mapping analysis of two calcium aluminates.
Figure 7: SEM-EDS mapping analysis of two spinels.
It should be mentioned that at the beginning of the vacuum degassing process and exactly after addition of aluminium containing deoxidizers into the molten steel, some aluminium rich oxides (alumina inclusions) could be observed. But some minutes after addition of aluminium containing deoxidizers, because of the thermodynamic conditions of the slag-steel-ladle system, and very low oxygen and sulphur levels of the molten steel, complex inclusions that were either Al and Mg rich spinels (Mg came from remaining EAF top slag after skimming, synthetic top slag, and ladle lining bricks that were made of MgO-C materials), or Ca and Al rich calcium aluminates (Ca came from synthetic top slag or added Ca as Ca-Si) tended to form; consequently spinel and calcium aluminate inclusions were the most abundant types of inclusions that could be observed.

In addition, because the amount of silica (SiO$_2$) in the synthetic top slags that were used in the production plant were always very low (less than 8 wt%), and due to the presence of deoxidizers that had higher oxygen affinity compared to Si in the system (i.e. Al, Ca and Mg), in non-metallic inclusions that were considered in this work, very low amount of silicon were observed; consequently silicate inclusions were not considered in this work.

Regarding sulphide inclusions due to thermodynamic preferences, and because most of the samples of this study were taken from molten steel and were chilled very quickly in a short period of time, sulphide inclusions did not have much time and favourable thermodynamic conditions to form (at least not as much as normal situation when steel ingots were left inside moulds for several hours in the production plant in order to be solidified and cooled); that was the reason that sulphide inclusions were not considered in this work. It should be mentioned that because Ca-treatment was not the focus of this study none of the heats that were considered in this study were Ca-treated, however Ca-treatment of molten steel is known to be a very effective way to make low melting point calcium aluminate and calcium sulphide complex inclusions; this would result in isotropic spherical non-metallic inclusions and ease the removal of unmelted Al-Mg rich inclusions.
2.6. REMOVAL OF NON-METALLIC INCLUSIONS

Theoretically it is known that removal of non-metallic inclusions from molten steel could be achieved by means of several different mechanisms.

1- According to Stokes law, equation (15), because of differences between densities of non-metallic inclusions and molten steel, flotation is a mechanism that could lead to removal of non-metallic inclusions. It is possible to calculate theoretically the rate of inclusion removal due to flotation by means of equations (15) and (16) [61].

\[
S = \frac{f(r)\nu dt}{L} \quad (15) \ [61]
\]

\[
\nu = \frac{2g}{9\mu} \Delta \rho r^2 \quad (16) \ [61]
\]

- **S**: Rate of inclusion removal due to flotation
- **r**: Radius of non-metallic inclusions
- **L**: Depth of molten steel in ladle
- **v**: Terminal velocity of non-metallic inclusions in molten steel
- **g**: Gravity acceleration
- **\mu**: Viscosity of molten steel
- **\Delta \rho**: Mass density difference between inclusions and molten steel

2- Magnetic stirring and argon gas injection can improve the removal of non-metallic inclusions. Rate of non-metallic inclusions entrapment by means of argon gas injection is presented by equation (17) [61].

\[
S_b = N_b \nu_b \frac{b^2 \pi}{V} \quad (17) \ [61]
\]

- **S_b**: Rate of non-metallic inclusions entrapment
- **N_b**: Number of bubbles
- **\nu_b**: Difference between velocities of molten steel and bubble
- **b**: Critical entrapment distance
- **V**: Volume of molten steel
3- Ca-treatment is another effective way that could facilitate the removal of non-metallic inclusions from molten steel. By adding Ca to the molten steel (mostly in form of Ca-Si), it is possible to modify unmelted Al-Mg rich inclusions (spinels) to large, isotropic, and spherical calcium aluminates and calcium sulphides with low melting points; this would ease the removal of molten non-metallic inclusions. It should be mentioned that it might become a problem if for any reasons some of these large calcium aluminates remain or get trapped in molten steel.

4- Optimized top slag properties can enhance the inclusions removal in a ladle furnace. The three mechanisms mentioned above could be used in order to understand inclusions movement from the middle or bottom parts of the molten steel or ladle to the top; however without a proper top slag, it is highly probably that these inclusions could not be removed efficiently. Consequently, in order to ensure a very effective entrapment and absorption of non-metallic inclusions by means of top slag, having an optimized molten top slag with high capacity for non-metallic inclusions (for example high alumina capacity), proper wetting properties and viscosity is necessary.
3. EXPERIMENTAL

3.1. STEEL MELTING PLANT OF OVAKO HOFORS AB

Fig. 8 presents the general schematic of the steel melting plant of Ovako Hofors AB. Scraps are melted in the 100 t, bottom tapped electric arc furnace, molten metal is tapped into the ASEA-SKF ladle furnace station, then by means of ferro-silicon and ferro-aluminum the molten steel is deoxidized (its oxygen activity is reduced), then the slag that is the result of this deoxidation is skimmed, and the ladle filled with molten steel is sent to the ladle treatment station.

In the ladle furnace, synthetic top slag, mainly composed of CaO and Al₂O₃, is put on the molten steel, then the melt is desulphurized, deoxidized, its alloying composition adjusted, vacuum degassed, Ar-gas and magnetic stirred, possibly reheated, and finally after the temperature of the melt is adjusted to the desired temperature, it is poured into 24 ingot moulds with the capacity of 4.2 t each.

Figure 8: Schematic of the steel melting plant of Ovako Hofors AB.
3.2. SAMPLE ANALYZING METHODS

3.2.1. STEEL AND SLAG

Steel samples were tested by two testing instruments: OES ARL 4460 Metal analyzer from Thermo Fisher Scientific Inc was used for metal analyses; an instrument called Leco™ CS-444 was used in order to analyze sulphur and carbon content of the samples. This instrument works based on the Carbon-Sulphur combustion method (ASTM E1019). An instrument called Leco™ TC600 was used in order to analyze total oxygen of the samples, and all slag samples were analyzed by an X-ray fluorescence (XRF) spectrometer instrument called PANalytical Axios mAX Minerals.

3.2.2. OXYGEN ACTIVITY

The Celox instrument [99] that was equipped with commercial consumable MgO-stabilized ZrO$_2$ electrode was applied in order to measure oxygen activity and temperature of molten steel at the respective sampling occasions. This instrument allows operator to measure oxygen activity and temperature of molten steel in situ at different stages of steelmaking process. According to the Nernst’s law the difference between oxygen activity of the electrodes and molten steel would generate an electro motive force (EMF) and by considering this EMF it is possible to calculate oxygen activity of molten steel.

It should be mentioned that in Al killed steels, and at low oxygen activities, measured oxygen activities are believed to be within a factor of two higher than the true equilibrium oxygen activities of molten steel [97]. These higher measured oxygen activities are probably due to partial electronic conduction of the MgO-stabilized ZrO$_2$ electrodes in molten steel that would result in higher EMF [97]. However some other studies have claimed that Celox instrument applies a correction factor that is supposed to consider this partial electronic conduction [100-103].

3.2.3. SCANNING ELECTRON MICROSCOPY

For microscopic scanning of the steel samples regarding oxide inclusions, analytical scanning electron microscope (SEM) brand Leo Supra 35 was applied and for the analysis and classification of non-metallic inclusions, using energy dispersive X-ray microanalysis, INCA Feature software [104] was used.
4. Results

The results of this PhD work could be divided into five different supplements that are briefly explained in separated categories in the following parts of this report. All five supplements are attached to the end of this report.

4.1. RESULTS OF SUPPLEMENT 1

This study presented a comparison between the measured and the calculated results of some slag-steel equilibria in an ASEA-SKF ladle furnace. The new software LiMeS [88,95] available with the Thermo-Calc software package was applied in order to calculate the slag-steel equilibrium after the vacuum degassing process. The input data used in the calculations were those achieved by instrumental analysis of the slag-steel samples that were taken before starting the vacuum degassing process. Finally the calculated results were compared with the measured values.

Fig. 9 shows the calculated results by LiMeS [88,95] versus the measured results achieved by instrumental analysis. In the legends of this figure parenthesis represent (wt%) component in slag, and brackets represent [wt%] of components in molten steel. By considering the fact that results achieved by instrumental analysis could have some errors, some important results that were achieved from this supplement could be summarized as below:

- Regarding the contents of Al, Mn and Si in molten steels and the amount of the Al$_2$O$_3$ and SiO$_2$ in the top slag the calculated results were in a quiet good agreement with the measured results.

- Considering the calculated oxygen activity, S and Mg contents in the molten steel, and S, MgO, and CaO contents of the slag, they disagree with the measured ones.

- Disagreement between the measured and the calculated results of the Mg and its oxide was believed to be due to the fact that MgO-C ladle lining bricks continuously contributed some amount of Mg to the steel melt.
• One of the reasons for the deviation between the measured and the calculated oxygen content of the molten steel could be that the slag-steel system was unintentionally allowed to react with the surroundings during the vacuum degassing process.

• The deviations of the calculated Al contents in the molten steel compared with the measured results could also be explained by the hypothesis that some oxygen was continuously added to the system and consumed Al of the molten steel, and generated some amount of Al$_2$O$_3$.

• Thermodynamic calculations (here using LiMeS [88,95]) were very useful tools when studying e.g. slag-steel systems in ladle treatment plants. The only inputs needed were temperature, pressure and starting material. It should be mentioned that for non regular Thermo-Calc users, using LiMeS [88,95] is much simpler; this would bring the opportunity of taking advantage of this software in a wide areas of applications also for non regular users.
Figure 9: Values calculated by LiMeS [88,95] versus the measured values. (%wt) and [%wt] respectively denote the amount of the components in top slag and molten steel.
4.2. RESULTS OF SUPPLEMENT 2

This study set out to find some model/s that could calculate the closest oxygen activity of molten steel to the measured oxygen activity in an ASEA-SKF ladle furnace. Ten steel heats grade SAE 52100 were chosen, oxygen activities of the molten steel after vacuum degassing process were measured, then by means of two different equations (Wagner’s equation (10) [3] and Turkdogan’s equation (14) [97]) and one computer program (Thermo-Calc [95] with databases TCFE7 and SLAG3) the theoretical oxygen activities were calculated and compared to the measured results.

Four different models: Ohta-Suito [105], Chipman [106], Tanabe [107], IRSID [108,109] and two different constants: 1 and 0.064 were applied in order to calculate the respective Al$_2$O$_3$ activities that were applied for calculating oxygen activities.

Fig. 10 shows the calculated and measured amounts of oxygen in molten steel of the ten test heats that were considered in this work.

Figure 10: The calculated and measured oxygen activities of the ten different test heats.
Fig. 11 shows three models that resulted in the closest calculated oxygen activities among all different applied models versus the amount of the measured oxygen activities.

Fig. 12 shows the possible changes in oxygen activities of molten steel depending on wt% Al in molten steel, temperature of equilibrium, and respective CaO/Al$_2$O$_3$ ratios in the top slag that were normalised to the binary system of CaO-Al$_2$O$_3$. Oxygen activities on this figure were calculated by means of Turkdogan’s equation (14), and Al$_2$O$_3$ activities were calculated from Chipman’s results [106]. Fig. 12 is supposed to give the closest results that are comparable to the oxygen activities that are measured by the Celox instrument [99].

In legend parts of these figures (10 to 12) and regarding the name of series, terms before comma refer to either Wagner’s equation (10) or Turkdogan’s equation (14), and the expressions after comma refer to the methods that were applied in order to calculate the activities of Al$_2$O$_3$ in each calculation.

Figure 11: The closest calculated oxygen activities versus the measured ones.
Figure 12: $\alpha_O$ versus wt% Al at different temperatures and CaO/Al$_2$O$_3$ ratio. Results should be comparable to the measured results of the Celox instrument [99].

As a result of this supplement it was found that Equations (18) and (19) should give the results that are comparable to the measured results of the Celox instrument [99] respectively without and with considering the CaO/Al$_2$O$_3$ ratio in the top slag.

\[
\alpha_O = -19.8 + 0.014Temp - 12.9[Al] \quad R^2 = 86.7\% \quad (18)
\]

\[
\alpha_O = -19.9 + 0.0158Temp - 4.42[Al] - 0.049(CaO) \quad R^2 = 90.1\% \quad (19)
\]

Equation (19) should give the closest results comparable to the oxygen activities that are measured by the Celox instrument [99] by considering
the CaO/Al₂O₃ ratio in the top slag; however it requires the wt% CaO of the top slag as an input that might not always be available.

Some of the results achieved from this study could be summarized as follow:

- Both Wagner and Turkdogan's equations were useful for calculating oxygen activities of molten steel.
- Most of the oxygen activity results that were calculated theoretically were lower than the measured results.
- If the measured oxygen activities of the molten steel by means of Celox instrument [99] are supposed to be the true oxygen activities in the slag-steel equilibrium, it could be said that by applying Turkdogan's equation (14), and calculating the Al₂O₃ activities by means of Chipman's results, or by applying Turkdogan's equation (14), and using activities of Al₂O₃ constant as 0.064, or by applying Wagner's equation (10), and using activities of Al₂O₃ constant as 1 the closest calculated results compared to the measured oxygen activities of the molten steel could be achieved.
- Positive effect of Al addition to molten steel in order to reduce oxygen activities reduced as the wt% Al in molten steel was more than 0.05.
- Temperature of molten steel was an important factor that affected oxygen activity of molten steel.
- Higher ratio of CaO/Al₂O₃ could result in less oxygen activities of molten steel; this could be achieved by lowering activity of Al₂O₃ in the top slag.
- Two regressions were generated that are supposed to be useful to practically calculate oxygen activities of molten steel at different temperatures, depending on wt% Al in molten steel and CaO/Al₂O₃ ratio in the top slag.
- The SEM observations revealed that the main types of observed non-metallic inclusions in these samples were spinels and calcium aluminates, and by increasing the CaO content of the inclusions their ECDs grew.
4.3. RESULTS OF SUPPLEMENT 3

In this study it was investigated if there was any relation between the wt% CaO and Al$_2$O$_3$ in the binary system of CaO-Al$_2$O$_3$ of calcium aluminates (CaO$^{\text{incl}}$ and Al$_2$O$_3^{\text{incl}}$) and their amount in the top slag before teeming (CaO$^{\text{slag}}$ and Al$_2$O$_3^{\text{slag}}$) and the theoretically calculated wt% CaO and Al$_2$O$_3$ normalized to their binary system (CaO$^{\text{calc}}$ and Al$_2$O$_3^{\text{calc}}$). In case a certain relation could be established it would be possible to predict compositions and physicochemical properties of non-metallic inclusions based on the applied top slag during ladle treatment in the desired ways.

Fig. 13 presents the CaO$^{\text{incl}}$, CaO$^{\text{slag}}$, and CaO$^{\text{calc}}$ in all four samples of this study, in this figure there are also two other lines indicating one standard deviation above and one standard deviation below the average CaO$^{\text{incl}}$. Fig. 14 presents the Al$_2$O$_3^{\text{incl}}$, Al$_2$O$_3^{\text{slag}}$, Al$_2$O$_3^{\text{calc}}$ in all four samples of this study, in this figure there are also two other lines indicating one standard deviation above and one standard deviation below the average Al$_2$O$_3^{\text{incl}}$.

![Graph showing CaO and Al$_2$O$_3$ concentrations](image)

**Figure 13**: Measured and calculated CaO$^{\text{incl}}$, slag, calc in all four samples of this study.
Fig. 14: Measured and calculated $\text{Al}_2\text{O}_3^{\text{incl}}$, $\text{CaO}^{\text{slag}}$, and $\text{CaO}^{\text{calc}}$ in all four samples of this study.

Fig. 15 shows the calculated and the measured positions of the $\text{CaO}^{\text{incl}}$, $\text{CaO}^{\text{slag}}$, and $\text{CaO}^{\text{calc}}$ in all four samples of this study in the binary phase diagram of $\text{CaO}-\text{Al}_2\text{O}_3$ [110]. In this figure there are also two other lines indicating one standard deviation above and one standard deviation below the average $\text{CaO}^{\text{incl}}$ in the four different samples of this study.
Figure 15: The calculated and the measured positions of the CaO$^{\text{incl}}$, slag, calc in all four different samples of this study, in the binary phase diagram of CaO-Al$_2$O$_3$ [110].

The following points briefly mention some of the achieved results of this study.

- In the calcium aluminates, Mg were often seen as spinel and Al that did not form spinel, formed calcium aluminates with different CaO$^{\text{incl}}$ and Al$_2$O$_3$$^{\text{incl}}$ ratios (the available Ca was assumed to be the rest of Ca that had already formed CaS phase with all available S).

- The CaO$^{\text{incl}}$ and Al$_2$O$_3$$^{\text{incl}}$ in all samples did not have the same ratio; but they covered a large range.

- The average CaO$^{\text{incl}}$ and Al$_2$O$_3$$^{\text{incl}}$ in all samples had nearly similar compositions that were close to the border of the phase Ca$_{12}$Al$_{14}$O$_{33}$ in the binary phase diagram of CaO-Al$_2$O$_3$ [110].
• The CaO$^{\text{slag}}$ and Al$_2$O$_3^{\text{slag}}$ in all samples had almost similar compositions that were close to the border of the phase Ca$_3$Al$_2$O$_6$ in the binary phase diagram of CaO-Al$_2$O$_3$ [110].

• The results of theoretical calculations were close to the CaO$^{\text{slag}}$ and Al$_2$O$_3^{\text{slag}}$, but they did not follow the same maximum and minimum tendencies of the CaO$^{\text{slag}}$ and Al$_2$O$_3^{\text{slag}}$. 
4.4. RESULTS OF SUPPLEMENT 4

This article set out to study development of oxide inclusions during the vacuum degassing process in an ASEA-SKF ladle furnace. During the degassing process and with about 15 minutes intervals and by means of vacuum interruption technique, five steel samples (argon protected liquid steel samples) and top slag samples were taken and their chemical compositions were instrumentally analyzed. All steel samples were further analyzed by a scanning electron microscope and the results were shown. In this report these five samples are designated S1 to S5.

Fig. 16 shows sampling occasions of the five samples with the respective internal pressures of the ASEA-SKF ladle furnace during the vacuum degassing process. As could be seen the first sample was taken before starting the degassing process and three others were taken with about 15 minutes interval from the start of the degassing, the last sample was taken after finishing the degassing process. The entire degassing process took about 55 minutes.
Fig. 17 shows the content of components in molten steel and top slag and steel temperature at the five sampling occasions of this study during vacuum degassing.

Figure 17: Changes of the amounts of components in samples and temperature during vacuum degassing.
Fig. 18 shows five graphs that were drawn by INCA Feature software [104]. These graphs show the position of all of the oxides that were found and analyzed by SEM in the five samples of this study in normalized ternary phase diagrams of Al$_2$O$_3$, CaO, and MgO (CAM).

Figure 18: Oxides observed in five samples of this study.
Fig. 19 shows five graphs that present wt% Ca versus wt% Al in all oxides observed by SEM, the bubble sizes present the ECDs (µm) of these oxides. Each figure is for one of the five samples of this study.

Figure 19: Wt% Ca versus wt% Al in oxides of five samples of this study, bubble sizes show ECDs (µm) of these oxides.
Fig. 20A) shows the percentage share of spinels and calcium aluminates of all oxides that were achieved from SEM analysis of the five different samples of this study and Fig. 20B) shows the percentage share of oxides ECDs (µm) in the samples. In Fig 20B) oxides, independent of their chemical compositions, were separated into four classes. Minimum ECDs of considered oxides were 5µm. Fig. 21 shows the average ECDs (µm) of spinels and calcium aluminates of all five samples.

Figure 20: A) Percentage share of oxides in the five samples of this study. B) Percentage share of oxides ECDs (µm) in the five samples of this study.
Figure 21: Average ECDs (µm) of spinel and calcium aluminates in the five samples of this study.

Results achieved from this study could be summarized as follow:

During the vacuum degassing process:

- spinels and calcium aluminates were the dominant types of inclusions.
- several factors such as temperature and top slag-steel compositions were changing.
- percentage share of calcium aluminates, compared to spinels were increasing.
- Ca weight percent content of oxides was increasing.
- average ECDs of spinels were constant (around 5µm).
- average ECDs of calcium aluminates were increasing.
- percentage share of oxides with bigger ECDs were increasing.
- oxides tended to form round shapes.
- TO of the samples were decreasing.
4.5. RESULTS OF SUPPLEMENT 5

The aim of this study was to optimize the steelmaking process that would result in increasing the sulphur distribution ratio between slag and steel of synthetic top slag, reduce the oxygen activity of molten steel and reduce the vacuum degassing time in the ASEA-SKF treatment plant of Ovako Hofors AB.

In this paper the synthetic top slag of ASEA-SKF ladle furnace was studied by means of thermodynamic calculations using the LiMeS software [88,95]. It was thus concluded that if fluorite was added to the synthetic top slag, (\%S)/[\%S] ratio would be increased. By considering this, four plant test heats with addition of fluorite to the top slag were performed and compared with the 24 reference heats that had already been produced in the same plant.

Figs. 22 to 24 were calculated by means of LiMeS [88,95]. In order to calculate these figures the molten steel was supposed to be in equilibrium with the top slag at constant pressure of $10^5$ Pa. These figures present the theoretically calculated amount of CaO (kg) in the synthetic top slag that is supposed to be unmelted or heterogeneously dispersed as solid particles in the top slag; these figures respectively consider the changes in the amount of the unmelted CaO in the synthetic top slag by varying the amount of the added CaO (kg) to the synthetic top slag, equilibrium temperature (°C) of the slag-steel, and the amount of the added fluorite (kg) to the synthetic top slag.

![Figure 22: Amount of the unmelted CaO (kg) versus amount of the CaO (kg) in the synthetic top slag, calculated by LiMeS [88,95] at 1600°C.](image)
Figure 23: Amount of the unmelted CaO (kg) versus equilibrium temperature (°C) of the molten steel, calculated by LiMeS [88,95].

Figure 24: Amount of the unmelted CaO (kg) versus amount of the added fluorite (kg) in the synthetic top slag, calculated by LiMeS [88,95] at 1600°C.
By considering equations (1) and (2) and Figs. 22 to 24 it can be concluded that if the CaO/Al₂O₃ ratio in the top slag could be increased or the mass fraction of the CaO in the top slag could be increased, and at the same time slag could be kept molten, it is possible to achieve higher sulphur distribution ratio between slag and steel or higher (%S)/[%S] ratio. It could also be said that by increasing the mass fraction of the molten or active CaO, or reducing the melting point, or increasing the liquid fraction of the top slag, it is possible to increase (%S)/[%S] ratio of the currently used top slag in the ASEA-SKF ladle furnace.

By considering Fig. 25, it was clear that by addition of fluorite to the currently used top slag in the ladle furnace it was possible to achieve higher (%S)/[%S] ratio, yielding sulphur content as low as 10 ppm. Consequently, compared to the normal steelmaking practices, all four test heats at the end of the degassing process and after reheating showed lower sulphur content in the molten steel.

![Sulphur content (ppm) during different treatment steps of the 24 reference heats and the four fluorite added test heats.](image_url)

Figure 25: Sulphur content (ppm) during different treatment steps of the 24 reference heats and the four fluorite added test heats.
Fig. 26 is a representative of SiO$_2$ reduction by Al in the slag-steel system, the equilibrium lines that were calculated by Thermo-Calc (databases TCFE7 and SLAG3 were used) [95] at three different temperatures could be applied as a tool for predicting the flow of oxygen in slag-steel system that is supposed to be in equilibrium. By considering this graph it could be said that by adding 200 kg fluorite to the top slag, it was possible to have lower oxygen potential in the slag comparing with the steel, consequently it could be concluded that oxygen in the steel had a tendency to flow toward the top slag, and in case of other test heats that had the points after vacuum degassing above the calculated equilibrium lines, it was likely that oxygen flows from the top slag to the steel, and probably leads to formation of more oxide inclusions and a less clean steel.

This graph could be used as a very useful guide for understanding the reoxidation possibilities of molten steel from the top slag and even mould powder during following stages of steelmaking process.

![Graph showing the ratio between SiO$_2$ contents (wt%) in the slag and the Si content (wt%) in the molten steel versus Al content (wt%) in the molten steel before and after degassing.](image)

Figure 26: The ratio between the SiO$_2$ contents (wt%) in the slag and the Si content (wt%) in the molten steel versus Al content (wt%) in the molten steel before and after degassing.
By considering Fig. 27 it could be said that in case of adding 200 kg fluorite to the total amount of 1200 kg synthetic top slag comparing with the 24 reference heats, the magnesium content of the molten steel after reheating or before teeming could increase. By regarding the fact that the ladle lining material in the tested heats was composed of MgO-C bricks, this increase was believed to be due to using high amount of fluorite in the synthetic top slag that could lead to higher ladle erosion (probably by reducing oxygen potential of the molten steel, but this should be studied in more details).

Figure 27: Mg content (ppm) of the 24 reference heats and four fluorite added test heats during different treatment steps in ladle furnace.
By considering the achieved results the following conclusions could be made.

By adding 200 kg fluorite to a top slag weight of 1200 kg it was possible to:

- obtain the minimum sulphur content in bearing steel grade SAE 52100 that was equal to 10 ppm.

- increase the sulphur distribution ratio between slag and steel during the vacuum degassing and achieve (%S)/[%S] ratio of 1570.

- have less oxygen potential in the slag compared with the steel. Consequently it could be concluded that oxygen in the steel had a tendency to flow toward the slag.

- Compared with the 24 reference heats, by adding 200 kg fluorite to the top slag weight of 1200 kg, at the end of the ladle metallurgy treatment higher Mg (wt%) in the molten steel could be expected, this Mg probably came from the erosion of the ladle lining material (possibly because of very low oxygen potential of the molten steel that resulted in more ladle erosion).
5. Discussion

In this study it was seen that synthetic top slag plays a very crucial role in affecting chemical composition, volume fraction, dispersion, and morphologies of non-metallic inclusions; composition of top slag could change the composition of non-metallic inclusions, and its ability to absorb and dissolve inclusions could result in less or more clean steel. Generally among slag-steel-ladle, top slag is the easiest and most powerful parameter that could be manipulated and optimized.

It could be said that during steelmaking process, slag-steel-ladle make one system, so in order to study the nature of non-metallic inclusions during vacuum degassing process these three main factors should always be considered.

Interactions among slag-steel-ladle at different treatment durations, temperatures and pressures generate different thermodynamic systems; thus in order to study non-metallic inclusions both kinetic (time dependency of reaction rate) and thermodynamic factors should be considered.

This should be mentioned that during the vacuum degassing processes in this study, slag-steel-ladle made a dynamic system that was not completely homogenous and because this system was not truly isolated (even at very low pressures), it was always altering; these changes probably resulted in different equilibria at different occasions and at various positions inside the treatment ladle; thus it could be said that there were always trends that the system reaches an equilibrium, but because the system parameters were various and were always changing a homogenously equilibrated system was not achieved.

In this study it was tried to understand the nature of the metastable that were achieved during the vacuum degassing; in case it was deeply understood it would be possible to modify chemical composition, volume fraction, dispersion, and morphology of non-metallic inclusions that appear and change during the vacuum degassing process.

During this work it was found that computational thermodynamics is a very powerful tool that could be very helpful for simulating and optimizing steelmaking process; however there were some problems and
insufficiencies that ought to be solved. It was found that the calculated results of O, S, and Mg of molten steel were different from the measured results; however it was known that amount of these elements could always be changed (because initial input system was not isolated), and there were even uncertainties about measuring instruments.

Regarding oxygen of molten steel, it was attempted to establish the most accurate existing models in order to calculate results that were closest to the measured results. Some regressions and graphs were generated that could practically be applied by both engineers and operators at melting plants.

It was seen that chemical compositions, volume fraction, dispersion, and morphologies of non-metallic inclusions at different positions in the same steel heat were very different from each other; however it was seen that non-metallic inclusions were moving toward an equilibrium point, and the average of their chemical compositions may be possible to be calculated.

It was experienced that some of the challenges regarding SEM analysis of non-metallic inclusions were finding a standard way to classify, sample, and prepare steels with the highest possible reliability. Beside, finding results that could be true representatives of each heat was a challenge too.

Degassing time was found to be a dilemma; long degassing time in optimized thermodynamic conditions may be positive because it eases the removal of larger non-metallic inclusions and reduces the TO of final steels, and it may be negative because it may cause the formation of larger inclusions, appearance of more calcium aluminates, more erosion and corrosion of ladle lining, high consumption of resources and lowering production capacity.

In the ASEA-SKF ladle furnace of this study it was found that depending on steel grade, 25 to 35 minutes degassing time could be considered as optimized degassing time. In case of shorter degassing time, reducing H level of molten steel to the desired levels may become a challenge.

During this study it was shown that regarding O and S contents of molten steel and degassing time it was possible to change and optimize the vacuum degassing process.

It could further be added that by increasing alumina capacity of synthetic top slag or ability of top slag to absorb and dissolve Al rich oxides, it is possible to add more Al to the molten steel, this Al would generate Al oxides and reduce oxygen activity of molten steel; then if synthetic top slag is able
to absorb and dissolve these non-metallic inclusions (by having high amount of molten CaO or high CaO activity), it would probably be possible to reduce the TO of steel products to less than 2ppm.

Although Ca-treatment was not focused in this study, Ca-treatment of molten steel is known to be a very effective way to generate calcium aluminates with low melting point; this would facilitate the removal of unmelted Al and Mg rich non-metallic inclusions, this could also result in formation of low melting point CaS inclusions.

Based on the sub projects of this work, the author of this report suggests that during the ladle treatment process in the ASEA-SKF ladle furnace, non-metallic inclusions might go through several stages (occurrence of some stages can even overlap):

1. Before start of the degassing and when Al is added to the molten steel, alumina inclusions form.

2. Some minutes after Al addition (before and during the entire vacuum degassing), the available Al and alumina react with Mg and MgO, and form new compounds with chemical compositions close to MgAl$_2$O$_4$ (spinel); Mg could come from different sources such as EAF top slag left over, synthetic top slag, ladle glaze, and ladle bricks; however ladle bricks that are made of C bounded MgO are likely to be a very important source of Mg.

3. After putting the synthetic top slag on the molten steel, Ca that may enter the ladle either intentionally as the main mineral of the synthetic top slag (and from Ca-Si wires, in case of calcium treatment), or unintentionally as a residual component in slag and alloying additives, react with the available S and O, and depending on the thermodynamics of the system (pressure of the ladle, S and O content of the molten steel are very important) CaO or CaS can form.

4. During the degassing process, most of the formed alumina, spinel, CaO and CaS inclusions enter the optimized top slag that is CaO rich and cause a reduction followed by an increase of the melting point of the top slag (at the eutectic point of the CaO-Al$_2$O$_3$ binary system). At the same time that Ca seek for alumina and spinel inclusions to form low melting point, thermodynamically stable compounds, available spinels in favourable thermodynamic conditions (very low S and O content and low internal pressure of the ladle) can act as nucleation points for forming complex inclusions composing of calcium aluminates and spinel inclusions (Ca cover around some of the
spinels and form complex Ca-Al-Mg-O inclusions with different ratios of these elements).

5. Some minutes after the start of the degassing process, and in optimized conditions, appearance of complex calcium aluminates and spinels result in the reduction of S and O content of the molten steel to very low levels; this could even lead to higher ladle erosion (by absorbing more O from the MgO available in the ladle bricks) and appearance of more Mg in the slag-steel system.

6. Throughout the entire degassing process, depending on the size of inclusions, and in case of having optimized steel stirring, most of the inclusions float toward the surface of the molten steel (it is also possible that many of them, especially smaller ones cannot reach the top of the ladle), and if the physicochemical properties of the top slag are optimized, they could be absorbed by top slag and kept on the higher parts of the ladle until start of the teeming process.

It is worthy to mention that after the degassing process and during solidification of steel, several other types of inclusions may form. If the S content of the steel is high, then MnS inclusions may appear, and in case the right thermodynamic conditions exist, available active elements such as Mn, Al, Ti, and Cr may form other compounds, for example nitrides, carbides and complex inclusions.

During the solidification a part of available sulphur might also cover the surface areas of some of the oxides (typically forming CaS compounds on the surface of calcium aluminates).

Mould powder that is applied in the ingots during teeming could also affect the solidifying steel to some extent; although it is an important factor affecting some types of inclusions, it was not covered during this PhD work.
6. Summary of conclusions

Regarding the calculated results achieved by computational thermodynamics it was seen that the calculated Al, Mn, and Si contents in the molten steel and the amounts of Al2O3 and SiO2 in the top slag were in good agreement with the measurements. The calculated and the measured O, S and Mg contents in the molten steel, and the S, CaO and MgO contents in the top slag, were not in good agreement. It was concluded that LiMeS that is an interface for Thermo-Calc was a useful tool for slag-steel equilibrium calculations.

Considering theoretical calculations of oxygen in molten steel, both Wagner's and Turkdogan's equations were found to be useful. It was seen that increasing wt% Al in the molten steel from 0 to 0.05, increasing the CaO/Al2O3 ratio in the top slag, and reducing the equilibrium temperature of slag-steel could effectively contribute to the reduction of oxygen activity of molten steel.

Regarding CaO-Al2O3 ratios in non-metallic inclusions, top slag, and steel after ladle treatment process, the CaO^{incl} and Al2O3^{incl} in all of the calcium aluminate inclusions of this study did not have the same ratio; but they covered a large range. The average CaO^{incl} and Al2O3^{incl} in all samples had nearly similar compositions that were close to the border of the phase Ca_{12}Al_{14}O_{33} in the binary phase diagram of CaO-Al2O3. The CaO^{slag} and Al2O3^{slag} in all samples had almost similar compositions that were close to the border of the phase Ca_{3}Al_{2}O_{6} in the binary phase diagram of CaO-Al2O3. The results of theoretical calculations were close to the CaO^{slag} and Al2O3^{slag}, but they did not follow the same maximum and minimum tendencies of the CaO^{slag} and Al2O3^{slag}.

It was concluded that vacuum degassing process was a dynamic process and during that spinel and calcium aluminate inclusions were the dominant types of inclusions. In addition it was seen that during this process percentage share of the calcium aluminates compared with the spinels, Ca weight percent content of the oxides, average ECDs of the oxides, and percentage share of the oxides with bigger ECDs were increasing, and oxides tended to form more round shapes.
It was found that depending on steel grade, 25 to 35 minutes degassing time could be considered as optimized degassing time in an ASEA-SKF ladle furnace.

The final results showed that by adding 200 kg fluorite to a top slag of 1200 kg, it was possible to achieve a steel S content of less than 10 ppm and a $(\%S)/[\%S]$ ratio of 1570, and at the same time reduce the oxygen activity of the molten steel and degassing time.
7. SUGGESTIONS FOR FUTURE WORKS

Assessment techniques (both destructive and non-destructive) that are applied for analyzing and classification of non-metallic inclusions should be more developed and standardized. These techniques should cover micro, meso and macro inclusions more deeply with higher capability, reliability, and repeatability.

Databases that are used by computational thermodynamic computer programs should be further developed and expanded; especially O, S, Ca, Mg, N that are very crucial elements regarding making cleaner steels; furthermore more slag properties could be introduced to these computer programs such as viscosity, foaming index, and sulphur potential.

The possibility of predicting inclusion types depending on the thermodynamic and kinetic conditions of steelmaking and ladle treatment process should be further studied and developed.

Behaviour of non-metallic inclusions during vacuum degassing process should be further observed. By gathering more data from argon protected liquid steel samples of different steel grades at different thermodynamic and kinetic conditions it would be possible to optimize steelmaking processes considering both quality and economical perspectives of the process.

Aluminium oxide capacity of synthetic top slags should be further studied and clarified; this would increase the general understanding regarding possibility of O reduction of molten steel by adding more Al deoxidizer and would improve the possibility of absorbing generated oxides by an active slag that would probably result in lower TO in steel products.

Breakability, deformability, melting point, or generally physicochemical properties of different types of non-metallic inclusions in steel matrix at different degrees of reduction ratio and their effects on the final products should be more investigated.

Depending on chemical composition, morphology, volume fraction, and dispersion of non-metallic inclusions in different steel grades, more data should be generated and related to the mechanical performance of steel
parts. The behaviour of different types of inclusions relative to the application of steel grades under different loading conditions should be understood in details. Some types of non-metallic inclusions that are considered devastating for one application may be very positive for another application.

It would be useful to study different parts of ingots or rolled bars by SEM in order to investigate possibility of appearance of some certain types of non-metallic inclusions in some certain parts of ingots or formed products (segregation of non-metallic inclusions).

Mg deoxidation of molten steel should be more studied; as it was seen in this project, spinel inclusions in the respective treatment furnace tended to have smaller ECDs compared to calcium aluminates, it makes Mg an interesting element that might be able to replace Ca; however technical and practical difficulties of using Mg as a deoxidiser should be regarded and solved.

The possibility of Ca treatment at controlled and optimized different S contents could also be considered as an interesting approach. During this study it was observed that CaS inclusions seemed to be as isotropic as calcium aluminates but with smaller ECDs.

In computational thermodynamic computer programs, although it may be a challenging task, it should be possible to consider and calculate the amount of elements that are unintentionally added to the equilibrium system of slag-steel-ladle after starting the vacuum degassing. Elements such as Mg that enters to molten steel from ladle bricks, O that may come from added argon gas, air, and ladle bricks, and N that is added during flushing of instruments inside the furnace should be possible to be considered, calculated and added to initial inputted calculation conditions and parameters. This would give the possibility of calculating actual slag-steel-ladle system, and not merely slag-steel that are affected by the nature of the ladle lining and their surrounding environment.

More resistance ladle lining materials should be developed. Specially in so called clean steels because of the fact that oxygen activity of molten steel is usually very low, and very active deoxidizers are used, ladle linings should be much more resistance against both erosion and corrosion. Otherwise the ladle lining itself could be a source of generating different types of harmful non-metallic inclusions during steel making process.
8. References


Non-metallic inclusions in SEM