A Study on the Population and Chemical Development of Non-Metallic Inclusions in the Tool-Steel Making Process

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Doctoral Thesis

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ABSTRACT

The present work was to study the population and chemical characterization of the inclusions at different steps of the tool steel making process based on industrial trial experiments. The inclusion populations were found to increase with ladle age (number of heats ladle being used) before aluminium deoxidation and before casting. A substantial increase in inclusion population was noticed after a certain ladle age. The analyses of the steel samples from the solidified ingot revealed a non-uniform distribution of inclusions. The inclusion populations in the final products were also found to increase with the ladle age.

Totally four types of inclusions, viz. Type-1 (MgO), Type-2 (an oxide solution), Type-3 (spinel), and Type-4 (spinel in the center surrounded by the oxide solution of Type-2) were observed before deoxidation. Thermodynamic calculation revealed that the Type-2 and Type-4 inclusions were generated by the reactions between EAF slag and ladle glaze. Three types of inclusions were found before casting, viz. Type-6 (spinel in the center surrounded by the oxide solution of Type-7), Type-7 (oxide solution with low contents of MgO and SiO₂), and Type-8 (small MgO islands embedded in an oxide solution). Inclusions of both Type-6 and Type-7 were the products of the reaction between inclusions of Type-3 and the liquid metal. On the other hand, the occurrence of pieces of MgO having sharp edges in the oxide solution suggested that the Type-8 inclusions were generated by the ladle glaze. In the steel samples during mould fillings, totally three types of inclusions namely, Type-6, Type-7, and Type-9 (alumina based inclusions) were found. The Type-9 inclusions were originated from the erosion of the nozzles and the closing gates during the mould filling. The steel samples after casting were found to contain inclusions of Type-6, Type-7, Type-9, Type-10 (alumina-silicate oxide solution), and Type-11 (spinel phase with calcium sulphide). The types of inclusions were found to vary with the position in the ingot. In the final products Type-6, Type-7, and Type-11 inclusions were found. While almost all the inclusions in the final products were originated in the ladle before casting, sulphur was detected in all types of inclusions. The increase in the sulphur activity of the steel melt during casting was the cause of the formation of oxide-sulphide and calcium sulphide phases in the inclusions detected after casting and in the final products.

A preliminary examination on the possibility of inclusion separation by bubble flotation using cold models was also carried out. Deionised water and silicon oil were used as the bulk phase. Charcoal particles of different size ranges were employed as the dispersed phase. The examination of the charcoal-water-gas system indicated that the positive flotation coefficient was not a sufficient condition for the inclusion separation. The experimental results were found to be in contradiction with the prediction of a typical model that considers interfacial energies. The omitting of the drag force was believed to be the reason causing the failure of the model prediction in the charcoal-water-gas system. The failure of the model prediction suggested a need of a new model taking into account interfacial energies, drag force, buoyancy force and gravity force.

Key words: non-metallic inclusions, ladle metallurgy, ladle glaze, inclusion population, ladle age, ingot casting, interfacial tension, inclusion separation
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Nagendra Nath Tripathi

Stockholm, July 2004
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**Supplement 1:** “Effect of ladle age on formation of non-metallic inclusions in ladle treatment”

N. N. Tripathi, M. Nzotta, A. Sandberg, and Du Sichen

**Supplement 2:** “Identification of inclusions generated by slag-refractory reactions”

Tripathi Nagendra, Nzotta Mnelly, Sandberg Alf, and Du Sichen

**Supplement 3:** “Non-metallic inclusions in the ingot and final product of a medium-carbon tool steel”

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CONFERENCES

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CHAPTER 1

1. INTRODUCTION

Inclusions not only influence the processing characteristics of steel but also the physical properties of the finished material. A detailed description of various harmful effects of inclusions is given in the references. In general, inclusions are considered undesirable during steel processing. As the standard of steel cleanliness is continuously increasing with time and technological improvements, the control of non-metallic inclusion population has become a serious concern of the steel producers.

In view of the detrimental effects of the inclusions on the properties of the finished materials, it is highly desirable to reach a low level of the inclusion population and controlled size distribution in the steel. In the tool steel making process, the inclusion population is mostly governed by the ladle treatment. The inclusions generated during casting would be very hard to remove. Casting is the step, wherein steel solidifies. The inclusions present in the steel melt in the late stage of the casting process are carried over to the final products, and thereby having a great influence on the quality of the finishing materials. An optimization of the casting process and an efficient control of the same would necessitate a detailed inclusion characterization. In this sense, it is important to study the inclusion characteristics at different steps of the steel making process.

Inclusions may arise from many sources, such as deoxidation, reoxidation, slag entrapment and chemical reactions. A number of studies have been carried out to find the major suppliers of non-metallic inclusions. While many of these studies have focused on the deoxidation process, the possible role of ladle glaze in supplying inclusions has also been proposed.

Ladle glaze is formed during the draining of a ladle. A film of slag is attached on the ladle walls when the top slag moves down following the steel during casting. The molten slag film adheres and penetrates into the pores of the refractory forming ladle glaze. The molten slag will be frozen when the ladle cools down. It has been suspected that the flushing-off of the glaze layer could contribute to the formation of non-metallic inclusions in the next heat.

One of the primary concerns of the ladle treatment process is to achieve high level of cleanliness by separating as many inclusions generated from various sources as possible. During ladle refining, the inclusions from the melt are reported to be removed by collision, agglomeration, floatation and bubble floatation. Since the ladle treatment is very often the final step before casting, the formation of non-metallic inclusions and their separation during this process have a great impact on the quality of steel. In this direction, a deeper insight into the role of ladle glaze in the formation of inclusions would be of essence. The present research work aims at a basic understanding of the effect of ladle glaze on the formation of inclusions during ladle refining. A study on population and chemical characterization of the inclusions at different steps of the steel making process based on industrial trial experiments are carried out at Uddeholm Tooling AB, Sweden. It also involves a preliminary examination on the possibility of inclusion separation by bubble floatation.
CHAPTER 2

2. EXPERIMENTAL

2.1 Industrial

2.1.1 Process description

The present work has been carried out at Uddeholm Tooling AB. Uddeholm Tooling AB has a steel melting shop which deals with recycled steel as a base component. Figure 1 describes the ladle refining and casting process.

![Figure 1: The steel making process at Uddeholm Tooling AB before casting.](image)

(a) tapping; (b) deslagging; (c) ladle furnace treatment; (d) vacuum degassing; (e) up-hill casting

In an electric arc furnace, 35 to 65 tons of recycled steel are melted. After being treated for phosphorous and carbon, the molten steel is tapped into a ladle and transferred to the ladle furnace station. After deslagging, the melt is deoxidized using aluminium bars or wires and various alloys are added aiming at the chemical specification of the steel grade. While the slag formers (alumet, dolomet and lime) are added to form a synthetic slag, the melt is heated up to a temperature between 1853 and 1923 K depending upon steel grade and stirred to ensure homogeneity. Thereafter, the ladle is transferred to a degassing station where a lid is put on the ladle top whereafter the melt is subjected to vacuum pressure below 3 mbar. Argon gas is introduced through the two porous plugs at the bottom of the ladle to ensure the removal of sulphur, nitrogen and hydrogen. This purging exercise is followed by a weak induction stirring to promote the separation of the inclusions from the steel into the slag. After the floatation period, the liquid steel is transferred to the casting station.

During casting steel melt is teemed from the bottom of the ladle. The normal teeming temperature of the steel melt is about 1823 K. The bigger end of the mould is placed upwards.
The steel melt can be cast into 15 different types of ingots weighing from 1.2 to 40 tons. During casting, the steel melt flows through the inner and outer nozzles that are attached to the ladle. Between the inner and outer nozzles, there are two revolving plates (closing gates) with two holes through them. These plates are made of bricks composed mostly of alumina. The inner and outer nozzles are connected and disconnected by rotating the alumina plates (closing gates). At a time, only one hole is opened to fill the mould. In this way, steel melt leaves the outer nozzle and enters into the vertical and horizontal runners. A protection of the steel stream against the atmosphere between the outer nozzle and the vertical runner is achieved by the argon gas flow. Casting powder held in a paper bag is either hung about 10 cm from the bottom of the mould or is placed at the bottom of the mould depending on the steel grades and the mould geometry. The purposes of using the casting powder are to reduce the heat losses at the upper surface of the melt, to protect the steel melt from reoxidation and to form a thin insulating layer between the mould surface and the ingot. At the end of the mould filling, an exothermic plate is placed at the top of the mould to avoid segregation and piping in the ingots during solidification.

After casting, the ingots are directly transferred to the forging press to reduce their dimensions. The top few centimeters of the ingot is called the ingot box. In the forging shop, ingots are pressed under heavy stress to get the bars of the required sizes. During forging, the ingot box is taken away as rejected material. The forged ingot is then cut into a number of bars to meet the requirement. The bars are transferred to the heat treatment shop and then to the machining shop. In the machining shop, the bars are machined into the desired shape and size. A few centimeters of the surface of the heat treated bars are peeled off to get a good surface finish. Thereafter, they are sent for quality control and inspection to check the final properties of the finished material.

2.1.2 Sampling technique

The medium-carbon steel grade ‘ORVAR 2M’ was mainly focused on in the present investigation. The heats of STVAX-ESR, SVERKER 21, DIEVAR and RAMAX-S steel grades were also studied. The samplings were carried out during and after the ladle treatment process at different ladle ages, i.e. the number of times ladle being used. The steel samplings were performed at following steps:

- Before deoxidation
- Before casting
- During mould filling
- After casting
- Final product

A manual LSHR (liquid solidification hot rolling) sampler and an automatic sampler were employed to take steel samples before deoxidation and before casting, respectively. The position of sampling was always near to the ladle wall. In the case of the manual sampling, the samples were taken at 10-15 cm depth from steel-slag interface and while for automatic sampling, the samples were taken at a depth of 35-40 cm from the steel-slag interface. Argon gas was blown through the sampler while immersing through the top slag into the steel melt to prevent the contamination of the sample by dust and the entrainment of the top slag. On the arrival of the sampling position, the sampler was evacuated. Steel sample was then sucked into the sampler by the vacuum. The steel sample along with the sampler was taken out from the ladle and quenched in air. The solidification time of the sample was about a few seconds.
The steel samples from the melt during the mould filling were taken using LSHR samplers. Steel samples were taken at different levels of the mould fillings. The first sampling was carried out at the start of the mould filling (10-20% mould filling); the second sampling was performed when the mould was half filled (40-50% mould filling) and the last sampling was carried out at the end of the mould filling (90-100% mould filling). Due to the high volumetric flow rate and the temperature fall of the steel melt, some times it was not possible to take the steel sample.

Some steel samples were taken from the solidified ingots after casting. The ingot in present study was 1.365 meters in height. While the top dimensions of the ingot were 578x680 millimeters, the bottom dimensions were 540x446 millimeters. After the removal of the ingot box, the remaining ingot was cut by saw along the two central planes as shown in Figure 2. The steel samples were taken at different heights and distances from the centre. The different sampling positions in the ingot are shown in Figure 2.

Figure 2: Sampling positions in the solidified ingot.
It is worthwhile to mention that the trials during the mould filling and after casting were performed for a single heat, wherein the ladle had been used for 7 times (ladle age 7). It would be interesting to study more heats during the mould filling and after casting at different ladle ages. However, due to the heavy economic cost, only one heat was possible.

To study the effect of the ladle age on the inclusion population in the final products, steel samples were taken from the bars of the final products of three heats at different ladle ages (1, 12 and 16). All the samples from the bars of the different final products were taken at an identical position in the ingot, namely at the top and the centre.

2.1.3 Light optical microscopic analyses of inclusions

A light optical microscope was used to count the number and size distribution of the inclusions. On each sample, inclusions were classified according to the Swedish standard SS111116 and assessed at 200 times magnification according to the Jernkontoret’s inclusions chart 2. The number of inclusions per mm² was then calculated for each sample using the PCMIC software.

2.1.4 Inclusion composition analyses

With a view to have an understanding on the formation of various types of non-metallic inclusions found in the steel melt, the chemical compositions of the inclusions were analysed by scanning electron microscope (SEM). A JEOL scanning electron microscope, Model JSM-840 attached with an EDX X-ray analyser (Model: LINK-AN, 10,000) was employed to analyse the compositions of the inclusions in the steel samples. In view of the uncertainties involved in the analyses of the light elements (O and S) using this technique, only the contents of the metallic elements were used to evaluate the compositions of the inclusions.

2.1.5 Chemical compositions of steel samples

The steel composition was determined by using an ARL 8680 S SIM/SEQ XRF system for the concentrations of Mn, S, Cr, Ni, and Mo, while the concentrations of Al, Ti, Ca, Mg and B were determined with the help of Optical Emission Spectrometer. The total sulphur contents of the steel samples were analysed by LECO CS 444.

2.1.6 Chemical compositions of slag samples

In order to study the effect of slag on the inclusions characteristics the slag samples were taken and analysed. The samples were first ground into powder and then pressed into discs of 3 cm in diameter. These discs were analysed by an XRF system (Philips Perl X-2).

2.1.7 Oxygen content measurements

The dissolved oxygen content in the steel melt plays key role in the formation of oxide inclusions. Therefore, both the contents of the dissolved oxygen and the total oxygen in the steel melt were determined. The dissolved oxygen contents in the ladle were measured with the help of Celox sensor designed by Heraeus Electro-Nite. The Celox sensor contains ‘Cr2O3 electrode’ as a reference electrode. The total oxygen contents in the steel samples were determined using a LECO unit, Model TC-436. In general, three measurements of total oxygen content were taken for each steel samples.

2.2 Cold Model

Vacuum degassing is a foremost step for the cleanliness of the steel melt. Therefore, it is helpful to generate a model predicting the behavior of inclusion removal by its attachment to the rising bubbles. To study the influence of various physical parameters on the separation of
inclusion by bubble floatation, a series of simple experiments were carried out using the experimental setup shown in Figure 3. It consisted of a glass container (27 cm in height and 6 cm in diameter) to contain the bulk phase and a mass flow controlling system to measure the amount of air introduced into the system. A BRONKHOST el-flow meter (operating flow rate between 0.3 ml/min to 15 l/min) was adopted for measuring the amount of the gas. The air was introduced into the liquid bath through the nozzle placed at the bottom of the glass container.

Figure 3: Experimental setup.

Deionized water and silicon oil were used as the bulk phase. Charcoal particles of different sizes were employed as dispersed phase. In order to get a uniform two-phase mixture, a magnetic stirrer was used. The two-phase mixture was stirred for 16 hours in a glass container with a speed of magnetic rotation of 600 rpm.

In all runs of experiments, 0.8 litres of the two-phase mixture were poured into the glass container. One initial reading of the concentration of the disperse phase was taken to ensure that the two-phases had been well mixed. Air was then introduced at flow rate of 0.41 l/min from the bottom of the container. The concentration of the charcoal particles in a two-phase mixture was obtained by sampling of the mixture at a fixed depth and analysing the sample. In the case of water-charcoal mixture, each sample having volume of 5 ml were taken and the charcoal powder was filtered out from the liquid. The filtered powder was first dried in an oven about one hour at 383 K and then weighed. The balance employed had a sensitivity of 10 µg. The examination of charcoal-silicon oil mixture showed that it was impossible to separate the charcoal particles from the silicon oil, even after a couple of days. It made the analysis very difficult. Hence, photographs were taken to illustrate the situation that the dispersed phase was not separated from the bulk liquid. These photographs would be helpful for the latter discussion.
CHAPTER 3

3. RESULTS

The present work focuses mainly on the ORVAR 2M steel grade. However, some other steel grades are also studied. In supplement 2, the inclusions types are identified before deoxidation (ladle arrival) and before casting. It is a part of a systematic investigation carried out by the research group, of which the present author is a member. A summary of these studies is presented in a recent publication. All types of inclusions detected at different stages of the process are summarized in a table to unify the notations of the inclusion types. It should be pointed out that these notations are different from that adopted in supplement 2. For the sake of clarity, the present thesis follows the same notations of the inclusions given in the table published recently. Even the new types of inclusions found after the ladle treatment are numbered correspondingly. The inclusion numbers and types are studied at different stages of the steel making process of ORVAR 2M steel grade. Table 1 presents all the types of inclusions found in the production of the ORVAR 2M steel grade.

3.1 Before Deoxidation

3.1.1 Inclusion population

With a view to gain knowledge of the number of inclusions flushed-off from the ladle glaze during ladle filling up, the inclusion populations represented by inclusion number per unit area were analysed in the steel samples taken before deoxidation. The number of inclusions per unit area is plotted as a function of ladle age for one particular steel grade, ORVAR 2M in Figure 4. An increase of the number of inclusions with the increasing ladle age is observed in this figure.

![Figure 4: Inclusion population as a function of ladle age before deoxidation for ORVAR 2M steel grade.](Image)
**Table 1.** The different type of inclusions at different stages of the production of ORVAR 2M steel grade.

<table>
<thead>
<tr>
<th>Type Present notation</th>
<th>Specification</th>
<th>Found in the stages</th>
<th>Earlier notations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ladle Arrival</td>
<td>Initial Stage Al Addition</td>
</tr>
<tr>
<td>1 Pure MgO</td>
<td>X X</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>2 Liquid oxide solution having high SiO₂ content</td>
<td>X X</td>
<td></td>
<td>3 A</td>
</tr>
<tr>
<td>3 MgO₃Al₂O₅</td>
<td>X X X X</td>
<td></td>
<td>2 B</td>
</tr>
<tr>
<td>4 Combination of 2 and 3</td>
<td>X X</td>
<td></td>
<td>4 C</td>
</tr>
<tr>
<td>5 Pure Al₂O₃</td>
<td>X</td>
<td></td>
<td>E</td>
</tr>
<tr>
<td>6 Spinel + oxide solution having low SiO₂ content</td>
<td>X X X X X X X X</td>
<td></td>
<td>7 F</td>
</tr>
<tr>
<td>7 Oxide solution having low SiO₂ content</td>
<td>X X X X X X X X X</td>
<td></td>
<td>5 G</td>
</tr>
<tr>
<td>8 MgO + oxide solution having low SiO₂ content</td>
<td>X X</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>9 Exogeneous, Al₂O₃</td>
<td>X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 Al₂O₃- SiO₂ oxide solution</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 Spinel + (CaS and Al₂O₃)</td>
<td>X X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The inclusion population in the steel samples of some other steel grades was also studied. Figure 5 presents the variation of the number of inclusions with ladle age before deoxidation for all steel grades studied in the current work. Though the process parameters vary considerably with different steel grades, an increase of the number of inclusions with ladle age is well brought out in this figure.

**Figure 5:** Inclusion population as a function of ladle age before deoxidation for all steel grades.

### 3.1.2 Inclusion types

Table 2 presents the all types of inclusions found in the steel samples of ORVAR 2M before deoxidation at ladle age 1, age 16 and age 24, respectively. The number of phases present in each type of inclusions and the compositions of these phases obtained by EDX analyses are also given in the table. Totally four types of inclusions namely; Type-1, Type-2, Type-3 and Type-4 are observed before deoxidation.

**Table 2.** The chemical compositions of different phases found in all types of inclusions in steel samples of ORVAR 2M taken before deoxidation at different ladle ages.

<table>
<thead>
<tr>
<th>Ladle age</th>
<th>Inclusion type</th>
<th>Phase</th>
<th>Compositions (mass %)</th>
<th>In supplement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle age 1</td>
<td>Type-1</td>
<td>Phase I</td>
<td>81-89</td>
<td>7-11</td>
</tr>
<tr>
<td></td>
<td>Type-3</td>
<td>Phase II</td>
<td>20-40</td>
<td>60-75</td>
</tr>
<tr>
<td></td>
<td>Type-2</td>
<td>Phase II</td>
<td>20-23</td>
<td>70-77</td>
</tr>
<tr>
<td></td>
<td>Type-4</td>
<td>Phase II</td>
<td>20-23</td>
<td>70-77</td>
</tr>
<tr>
<td>Ladle age 16</td>
<td>Type-2</td>
<td>Phase III</td>
<td>-</td>
<td>39-48</td>
</tr>
<tr>
<td></td>
<td>Type-4</td>
<td>Phase II</td>
<td>-</td>
<td>39-48</td>
</tr>
<tr>
<td>Ladle age 24</td>
<td>Type-3</td>
<td>Phase II</td>
<td>19-22</td>
<td>72-77</td>
</tr>
<tr>
<td></td>
<td>Type-4</td>
<td>Phase II</td>
<td>22-24</td>
<td>73-75</td>
</tr>
<tr>
<td></td>
<td>Type-4</td>
<td>Phase III</td>
<td>-</td>
<td>32-36</td>
</tr>
</tbody>
</table>
3.1.3 Steel and slag compositions

The compositions of the steel samples taken before deoxidation are listed in Table 3. Even the contents of the dissolved oxygen, which were obtained by Celox oxygen sensor, are given in these tables.

Table 3. Steel compositions, dissolved oxygen contents and temperatures of ORVAR 2M steel melts before deoxidation.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age</th>
<th>Dissolved oxygen (ppm)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 1</td>
<td>12.5</td>
<td>1841</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>-</td>
<td>1835</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 24</td>
<td>-</td>
<td>1852</td>
</tr>
</tbody>
</table>

Compositions of steel samples (mass %)

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 1</td>
<td>0.37</td>
<td>0.58</td>
<td>0.38</td>
<td>0.01</td>
<td>0.001</td>
<td>5.08</td>
<td>0.10</td>
<td>1.16</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>0.38</td>
<td>0.50</td>
<td>0.37</td>
<td>0.01</td>
<td>0.002</td>
<td>5.65</td>
<td>0.15</td>
<td>1.09</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 24</td>
<td>0.39</td>
<td>0.49</td>
<td>0.37</td>
<td>0.02</td>
<td>0.001</td>
<td>5.35</td>
<td>0.11</td>
<td>1.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compositions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag samples</td>
<td>C</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>0.019</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>0.019</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>0.018</td>
</tr>
</tbody>
</table>

In order to study the effect of the electric arc furnace (EAF) slag on the formation of the inclusions before deoxidation, the slag composition is analysed. The composition of the EAF-slag taken before deslagging at the ladle furnace station is presented in Table 4.

Table 4. EAF slag compositions for ORVAR 2M steel melts.

<p>| Slag compositions (mass %) before deoxidation |</p>
<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age</th>
<th>CaO</th>
<th>CaF₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>MnO</th>
<th>Cr₂O₃</th>
<th>V₂O₅</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 1</td>
<td>41.2</td>
<td>2.5</td>
<td>18.8</td>
<td>2.8</td>
<td>32.7</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>39.47</td>
<td>3.24</td>
<td>19.61</td>
<td>7.89</td>
<td>27.42</td>
<td>0.82</td>
<td>0.31</td>
<td>0.50</td>
<td>0.37</td>
<td>0.16</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 24</td>
<td>38.09</td>
<td>4.84</td>
<td>20.59</td>
<td>8.23</td>
<td>25.75</td>
<td>0.85</td>
<td>0.18</td>
<td>0.39</td>
<td>0.12</td>
<td>0.16</td>
</tr>
</tbody>
</table>

3.2 Before Casting

3.2.1 Inclusion population

It is particularly interesting to examine the effect of ladle glaze on the inclusion population in the steel melt before it is sent for casting. Hence, the inclusion populations in all four size ranges (according to Swedish standard SS111116) were plotted against the ladle age for the steel grades of ORVAR 2M and DIEVAR in Figure 6. While the numbers of inclusions in all size-ranges show an increasing trend, the number of inclusions having smallest size increases greatly with the ladle age.
3.2.2 Inclusion types

Table 5 presents all types of inclusions detected in the steel samples of ORVAR 2M and DIEVAR before casting at ladle age 1, age 8 and age 16, respectively. The number of phases present in each type of inclusions is also listed in the table. The table also lists the chemical compositions of these phases obtained by EDX analyses. Totally, three types of inclusions namely; Type-6, Type-7 and Type-8 are found in these steel samples.

**Table 5.** The chemical compositions of different types of inclusions in the steel samples of ORVAR 2M and DIEVAR taken before casting at different ladle ages.

<table>
<thead>
<tr>
<th>Ladle age</th>
<th>Inclusion type</th>
<th>Phase</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>SiO₂</th>
<th>In supplement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle age 1</td>
<td>Type-7</td>
<td>Phase IV</td>
<td>0-3</td>
<td>32-44</td>
<td>53-62</td>
<td>2-4</td>
<td>Type-5</td>
</tr>
<tr>
<td></td>
<td>DIEVAR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ladle age 8</td>
<td>Type-7</td>
<td>Phase IV</td>
<td>0-5</td>
<td>35-45</td>
<td>50-60</td>
<td>0-4</td>
<td>Type-5</td>
</tr>
<tr>
<td></td>
<td>Type-8</td>
<td>Phase IV</td>
<td>2-6</td>
<td>39-45</td>
<td>50-55</td>
<td>1-2</td>
<td>Type-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phase V</td>
<td>&gt;98.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Ladle age 16</td>
<td>Type-7</td>
<td>Phase IV</td>
<td>0-3</td>
<td>41-49</td>
<td>47-52</td>
<td>3-4</td>
<td>Type-5</td>
</tr>
<tr>
<td></td>
<td>Type-8</td>
<td>Phase IV</td>
<td>2-5</td>
<td>40-45</td>
<td>50-55</td>
<td>3-4</td>
<td>Type-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phase V</td>
<td>&gt;98.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type-6</td>
<td>Phase IV</td>
<td>18-40</td>
<td>56-71</td>
<td>3-9</td>
<td>1-3</td>
<td>Type-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phase IV</td>
<td>2-6</td>
<td>47-53</td>
<td>39-50</td>
<td>2-4</td>
<td></td>
</tr>
</tbody>
</table>
3.2.3 Steel and slag compositions

The chemical compositions of the steel samples before casting are analysed. Table 6 presents the chemical compositions of the steel samples before casting.

Table 6. Steel compositions, dissolved oxygen contents and temperatures of ORVAR 2M and DIEVAR steel melts before casting.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age</th>
<th>Dissolved oxygen (ppm)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DIEVAR</td>
<td>Ladle age 8</td>
<td>1.49</td>
<td>1791</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>2.11</td>
<td>1843</td>
</tr>
</tbody>
</table>

Compositions of steel samples (mass %)

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age 1</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 1</td>
<td>0.40</td>
<td>0.99</td>
<td>0.37</td>
<td>0.01</td>
<td>0.003</td>
<td>5.22</td>
<td>0.10</td>
<td>1.26</td>
</tr>
<tr>
<td>DIEVAR</td>
<td>Ladle age 8</td>
<td>0.37</td>
<td>0.20</td>
<td>0.50</td>
<td>0.01</td>
<td>0.001</td>
<td>5.11</td>
<td>0.06</td>
<td>2.38</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>0.39</td>
<td>0.96</td>
<td>0.36</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>5.21</td>
<td>0.15</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Co V Cu W Al Ce B Ca

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Ladle age 1</th>
<th>0.019</th>
<th>0.92</th>
<th>0.077</th>
<th>0.01</th>
<th>0.044</th>
<th>0.003</th>
<th>0.0001</th>
<th>&lt;0.0006</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 8</td>
<td>0.017</td>
<td>0.53</td>
<td>0.046</td>
<td>0.001</td>
<td>0.018</td>
<td>0.001</td>
<td>0.0003</td>
<td>0.0007</td>
</tr>
<tr>
<td>ORVAR 2M</td>
<td>Ladle age 16</td>
<td>0.019</td>
<td>0.91</td>
<td>0.074</td>
<td>0.02</td>
<td>0.041</td>
<td>0.003</td>
<td>0.0001</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

To examine the effect of the synthetic ladle slag on the formation of the inclusions, the slag composition is analysed. The compositions of the ladle slags before casting are presented in Table 7.

Table 7. Chemical compositions of the synthetic ladle slags for ORVAR 2M and DIEVAR steel melts in ladle treatment before casting.

<table>
<thead>
<tr>
<th>Slag compositions (mass %) before casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel grade</td>
</tr>
<tr>
<td>-------------</td>
</tr>
<tr>
<td>ORAVR 2M</td>
</tr>
<tr>
<td>DIEVAR</td>
</tr>
<tr>
<td>ORAVR 2M</td>
</tr>
</tbody>
</table>

3.3 Inclusions During Casting and Final Product

3.3.1 Inclusion population

The steel samples were taken at different levels of mould filling in three moulds. The inclusion populations in these steel samples were examined. Figure 7 shows the inclusion populations in the steel samples taken during mould filling. As mentioned earlier, some times sampling failed due to the high flow rate and the temperature fall of the steel. While there is no clear trend in the number of inclusions with respect to the filling level, the number of inclusions found in the sample obtained at 40-50% filling appears to be bigger than the other samples.
Figure 7: Inclusion populations in the steel melt during the mould filling.

Figure 8 shows the inclusion populations in the steel samples from the solidified ingot. C1, C2 and C3 stand for the positions at the central line, between the central line and the wall and close to the mould wall respectively as shown in Figure 2. Irrespective of the vertical position, the inclusion population shows a maximum at the central line. Close to the mould wall, the concentrations of the inclusions are higher than that at position C2 at all vertical levels.

To study the effect of the ladle age on the inclusion population in the final product, three steel samples from the final products were analysed. Figure 9 presents the inclusion population in the final products refined in the ladles having ladle ages 1, 12 and 16, respectively. The populations of inclusions in the steel melts of the same heats before casting are also included in this figure for comparison. As shown in the figure, the inclusion populations in the final products are higher than the populations in the steel melts before casting. Similar as in the case of the samples before casting, the inclusion population in the final products also reveal an increase with the ladle age. The average value of the inclusion populations in the experimental ingot (ladle age 7) is also included in Figure 9 for comparison.
Figure 1: Inclusion population distribution in the solidified ingot.

Figure 9: Inclusion population as a function of the ladle age in the final product.
3.3.2 Inclusion types

The different types of inclusions are identified on the basis of the chemical compositions after the ladle treatment process. Type-6 and Type-7 are also found during the casting process. Beside these two types, three new types of inclusions, namely; Types 9-11 are detected during casting process.

The chemical compositions of the different phases present in the inclusions of Types 6-7 and 9-11 analysed by SEM-EDX are listed in Table 8. It is noticed that either oxygen or sulphur or both are found in the inclusions during casting. For the convenience of discussion, the compositions of the phases are presented as cation fractions in Table 8.

In phase II, mostly Mg$^{2+}$, Al$^{3+}$ cations with very small fractions of Si$^{4+}$ and Ca$^{2+}$ cations are found. The phase contains primarily O$^{2-}$ anions. No sulphur is detected. The chemical composition suggests that phase II is a spinel phase, MgO·Al$_2$O$_3$. Before casting, phase IV is primarily found to contain Ca$^{2+}$ and Al$^{3+}$ cations and O$^{2-}$ anions. In the samples taken from the ingot and final products, this phase contains also certain amount of sulphur. An examination of the cation fractions in the samples taken before casting and after casting indicate that the phase is an oxide solution of CaO and Al$_2$O$_3$ with little amount of MgO and SiO$_2$. During casting, sulphur is able to dissolve into this phase. The composition of phase V would lead to the conclusion that it is mostly Al$_2$O$_3$ although small amounts of CaO and SiO$_2$ are also noticed. Only Al$^{3+}$ and Si$^{4+}$ cations and O$^{2-}$ anions are found in phase VI. The EDX analysis shows clearly that phase VII is calcium sulphide, as it contains mostly calcium and sulphur. In this phase, traces of Al$_2$O$_3$ are also detected. It is difficult to identify the phase boundary between CaS and Al$_2$O$_3$ due to the size of the inclusion. However, close to the surface of the inclusion only CaS exist.

<table>
<thead>
<tr>
<th>Inclusion type</th>
<th>Cation fractions</th>
<th>In supplement 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Ca$^{2+}$</td>
<td>Al$^{3+}$</td>
</tr>
<tr>
<td>Type-6</td>
<td>Phase II</td>
<td>0.00-0.02</td>
</tr>
<tr>
<td></td>
<td>Phase IV</td>
<td>0.48-0.50</td>
</tr>
<tr>
<td>Type-7</td>
<td>Phase IV</td>
<td>0.45-0.55</td>
</tr>
<tr>
<td>Type-9</td>
<td>Phase V</td>
<td>0.01-0.08</td>
</tr>
<tr>
<td>Type-10</td>
<td>Phase VI</td>
<td>0.00-0.01</td>
</tr>
<tr>
<td>Type-11</td>
<td>Phase VII</td>
<td>0.02-0.04</td>
</tr>
</tbody>
</table>

3.3.3 Steel and slag compositions

The chemical compositions of the steel samples during casting and final product are analysed. Table 9 shows the results of the chemical analyses of the steel samples. Both the chemical analysis of the samples taken from the ingot and the chemical analysis of the final products reveal a significant increase in the total sulphur content in the steel.

To study the effect of the casting powder on the development of the inclusions, the compositions of the casting powder (or mould powder) and the slag after casting are analysed. The results are presented in Table 10.
Table 9. The chemical compositions, total oxygen content, total sulphur content of the steel samples before casting (B.C), mould fillings (M.F), after casting (A.C) and the final product (F.P).

<table>
<thead>
<tr>
<th>Compositions of the steel samples (mass %)</th>
<th>(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Si</td>
</tr>
<tr>
<td>B.C</td>
<td>0.41</td>
</tr>
<tr>
<td>M.F</td>
<td>0.41</td>
</tr>
<tr>
<td>A.C</td>
<td>0.40</td>
</tr>
<tr>
<td>F.P</td>
<td>0.40</td>
</tr>
</tbody>
</table>

| Co  | V  | Cu  | W  | Al  | Ce  | B  | Ca  | Nb  | N  | Total S |
| B.C | 0.016 | 0.93 | 0.069 | 0.820 | 0.019 | 0.003 | 0.0001 | <0.006 | 0.003 | <0.001 | 3 |
| M.F | 0.019 | 0.94 | 0.071 | 0.822 | 0.014 | 0.003 | 0.0001 | <0.006 | 0.003 | 0.012 | 8 |
| A.C | 0.016 | 0.95 | 0.070 | 0.816 | 0.014 | 0.003 | 0.0001 | <0.006 | 0.003 | 0.007 | 31 |
| F.P | 0.016 | 0.92 | 0.068 | 0.816 | 0.014 | 0.003 | 0.0001 | <0.006 | 0.003 | 0.006 | 35 |

Table 10. The chemical compositions of the casting powder and the slag sample after casting.

<table>
<thead>
<tr>
<th>Chemical compositions (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Components</td>
</tr>
<tr>
<td>Casting powder</td>
</tr>
<tr>
<td>Slag after casting</td>
</tr>
</tbody>
</table>
3.4 Possibility of Inclusion Separation by Bubble Floatation

In order to study the effects of various physical parameters on the removal of suspended particles from the bulk phase by their attachment to the rising bubbles, a series of experimental studies were carried out. Deionised water and silicon oil were used as the bulk phase. Charcoal particles of different size ranges were employed as dispersed phase.

3.4.1 Charcoal dispersed in deionised water

The concentrations of charcoal in the deionised water are plotted as functions of time for four experiments in Figure 10. An initial concentration of 1g/dm$^3$ of charcoal was employed for all cases. Two of the experiments, were carried out using the charcoal powder of the same size range, namely 10-30 μm. The reasonable agreement of the results of the two runs shows the reproducibility of the experiments. While the charcoal concentrations decrease with time in the case of the small particles in the ranges 10-30 and 30-50 μm, the concentration of the charcoal particles in the size range 120-150 μm is almost constant.

![Figure 10](image_url)  
**Figure 10:** Concentrations of charcoal in the deionised water as functions of time for different four experiments.
3.4.2 Charcoal dispersed in silicon oil

The initial concentration of charcoal powder in silicon oil was chosen to be 0.0009 g/cm$^3$. Although the density of charcoal is much lower than the density of the silicon oil, it was almost impossible to remove the charcoal powder of any size from the two-phase mixtures. As an example, Figure 11 presents the photographs of the charcoal-oil B mixture at different times, namely 0, 10 and 24 hours. It is seen that even after blowing the air for 24 hours, the mixture looks the same as its initial appearance.

![Figure 11: Photographs of the charcoal-oil B mixture at different times.](image)
4. DISCUSSION

4.1 Impact of Ladle Glaze on the Formation of Inclusions

A comparison of the compositions of the inclusions listed in Tables 2 and 5 with the slag compositions in Tables 4 and 7 shows that the inclusions before deoxidation and before casting are not introduced by slag entrainment.

Ladle glaze has been suspected as a major contributor to the total inclusion population in the steel melt during ladle metallurgy. \(^{4-5}\) A thin coating of slag is formed when the top slag is in contact with the ladle lining during the draining of a ladle. This molten slag layer adheres and penetrates into the pores of the refractory forming a layer called as ladle glaze. When another cast of steel is poured into the glazed ladle, the adhered glaze layer will be removed or partially removed and the frozen slag will be re-melted. Parts of this re-melted slag and the non-metallic particles originally kept in the glaze can be retained in the liquid metal as inclusions. \(^{12-27}\) Figure 12 shows schematically the mechanism of the formation of ladle glaze on ladle wall and its entrainment as inclusions into the steel melt.

![Figure 12: Schematic representation of the mechanism of the formation of the glaze on the ladle walls.](image)

It is thermodynamically expected that the slag-refractory reaction would result in a multi-layer structure, namely,

1. An outer layer
2. A slag infiltrated layer
3. A decarburised refractory layer
4. A normal refractory brick structure

These four layers have been observed by Riaz et al. \(^{9}\) in their pilot plant experiments and Beskow et al. \(^{10}\) in their lining samples taken from industrial ladles.
4.1.1 Before deoxidation

As seen in Figure 4, the number of inclusions in steel grade ORVAR 2M shows a clear increasing trend. The number of inclusions is reasonably low in the new ladle and increases to some extent after a few heats. The increase becomes even more drastic after ladle age 18. The number of inclusions in the melt of a ladle before deoxidation depends on many factors, such as the tapping temperature of the steel, the slag composition, the steel grade, the extent of turbulence in the melt and the ladle age. For a particular steel grade the variation of these processing conditions is limited. Therefore, a plot of the number of inclusions as a function of ladle age would reveal the contribution of ladle glaze to the formation of inclusions. It is reasonable to expect that the intercept of the curve with the y-axis would stand for approximately the number of inclusions brought over from the EAF, while the increase would be due to the contribution of the ladle lining.

Table 2 illustrates the occurrence of four types of inclusions namely; Type-1, Type-2, Type-3 and Type-4 in the steel melt of ORVAR 2M before deoxidation processed in the ladles of age 1, 16 and 24. An examination of Table 2 strongly suggests that at least a part of inclusions of Type-3 are brought over from the EAF and, Type-2 and Type-4 inclusions are introduced by the wearing of the ladle refractory. The present results also suggest that the inclusions of Type-2 and Type-4 are mostly responsible for the increasing number of inclusions when a ladle becomes old as represented in the results shown in Figure 4. The inclusions of Type-1 are introduced into the melt by the breaking of lining of a fresh ladle as indicated by the absence of this type of inclusions in the samples taken from any used ladle.

When the liquid metal is tapped into the ladle from EAF, the EAF-slag is also poured into the ladle at the same time. Hence, both the liquid metal and the EAF-slag have a good contact with the ladle glaze. Phase III in the inclusions of Type-2 could be the product of the reaction between EAF-slag and the ladle glaze. The reaction product(s) would depend on the overall composition of the EAF slag-glaze system locally in contact (It might differ from one location to another). If the activites of MgO and Al\(_2\)O\(_3\) are locally not high enough to form MgO\(\cdot\)Al\(_2\)O\(_3\) (a spinel phase), a liquid oxide solution would be formed. The composition of this solution would be dependent on the amount of EAF-slag and glaze in contact.

The inclusion of Type-4 is found to contain two phases, namely phase II which is spinel phase (MgO\(\cdot\)Al\(_2\)O\(_3\)) and phase III. At some locations, the amount of the 3CaO\(\cdot\)Al\(_2\)O\(_3\) phase (named as phase 2, see Figure 15) in the glaze is large enough in comparison with the EAF-slag. The reaction of 3CaO\(\cdot\)Al\(_2\)O\(_3\) with the EAF-slag would lead to the formation of MgO\(\cdot\)Al\(_2\)O\(_3\) spinel. \(^{[3]}\) The formation of the MgO\(\cdot\)Al\(_2\)O\(_3\) phase would increase the silica content and consequently the activity of SiO\(_2\), \(a_{\text{SiO}_2}\) in the remaining liquid to keep local mass balance. If the temperature is lower than 1863 K and the activity of SiO\(_2\) in the remaining liquid is high enough, even 2CaO\(\cdot\)Al\(_2\)O\(_3\)\(\cdot\)SiO\(_2\) will be formed. Otherwise, the spinel phase would coexist with a liquid oxide solution.

A thermodynamic analysis would throw some lights on the formation of Type-4 inclusions. Since the composition of phase III is very close to that of 2CaO\(\cdot\)Al\(_2\)O\(_3\)\(\cdot\)SiO\(_2\), a reasonable approximation would be to assume phase III having similar thermodynamic properties as the 2CaO\(\cdot\)Al\(_2\)O\(_3\)\(\cdot\)SiO\(_2\) compound. The following two reactions are kinetically favorable, as they involve only slag and glaze contacts:
\[
\begin{align*}
\text{MgO} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{SiO}_2 \text{ (slag)} & + \text{Al}_2\text{O}_3 \text{ (slag)} \rightarrow \\
2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{CaO} \text{ (slag)}
\end{align*}
\]

\[\text{(1)}\]

\[
\begin{align*}
\text{MgO} \text{ (slag)} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{SiO}_2 \text{ (slag)} & + \text{Al}_2\text{O}_3 \text{ (slag)} \rightarrow \\
2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 + \text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{CaO} \text{ (slag)}
\end{align*}
\]

\[\text{(2)}\]

The Gibbs energies for the reactions (1) and (2) were calculated at this temperature. Both Gibbs energies are strongly negative, with \(\Delta G\) being -75055 J and \(\Delta G\) -68973 J, indicating thereby that both reactions (1) and (2) are thermodynamically favorable. At higher temperatures, the liquid corresponding to the composition of 3CaO\cdot Al2O3 would have similar thermodynamic properties as the superheated compound. Therefore, the formation of spinel phase and phase III is still expected. The coexistence of phase II and phase III in the inclusions of Type-4 is a strong evidence of the occurrence of either reaction (1) or reaction (2) or even both.

During the ladle filling, the system is subjected to violent stirring. The two phases formed by the slag-glaze reaction would sometimes be possibly separated by the strong stirring, forming inclusions of both Type-2 and Type-3. Therefore, a part of the inclusions of Type-3 could also be generated due to the reactions between EAF slag and ladle glaze.

As a ladle becomes older, the ladle lining becomes more porous. The high porosity would in turn, enhance the penetration of slag and therefore the slag-refractory reaction. Furthermore, the porous structure of the ladle lining would accelerate the process of the growth of the glaze layer and the increase of the number of solid particles in the glaze in an old ladle. This would increase the probability of the occurrence of reactions (1) and (2). The increased probability of reactions (1) and (2), would lead to the drastic increase in the number of inclusions shown in Figures 4 and 5.

4.1.2 Before casting

The outer layer of the glaze would be removed shortly after the filling of the ladle, resulting in direct contact between the slag infiltrated layer and the liquid steel.

As shown in the Table 5, the inclusions of Type-7 are found in the samples of the steel melts processed in the ladles of all ages. Since ladle glaze does not exist in the ladle of age 1, the common appearance of Type-7 inclusions would imply that the inclusions of this type or at least a part of them are not generated by the refractory. A thermodynamic study by Beskow et al. \cite{3} on chemical development of spinel phase is found to be helpful in explaining the evolution of inclusion of Type-7 during later stage of ladle refining process.

Their analyses reveals that the spinel phase is thermodynamically not stable in the liquid steel after deoxidation. The spinel inclusions either brought over from EAF or generated by slag-glaze reaction would start reacting with the liquid melt. The reaction between the spinel phase and the dissolved oxygen as well as calcium in the melt would result in an oxide solution according to reaction (3).

\[
\text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{Ca(wt%)} + \text{O(wt%)} \rightarrow \text{MgO} + \text{CaO} + \text{Al}_2\text{O}_3
\]

\[\text{(3)}\]
The standard Gibbs energy of reaction (3) at 1873 K is calculated to be $-2.936 \times 10^5$ J. The thermodynamic calculation indicates that reaction (3) would definitely take place after deoxidation and thereafter, resulting in thereby the inclusions of Type-7, which contains only phase IV.

If the spinel inclusions are slightly bigger and the time for the reaction between the spinel inclusions and the steel melt is not long enough, one would expect an un-reacted core of spinel surrounded by the reaction product. The appearance of inclusions of Type-6 in the sample taken from ladle of age 16 is a confirmation of the occurrence of reaction (3). As seen in the mappings shown in Figure 13, the spinel phase is situated in the center surrounded by phase IV, an oxide solution.

![Figure 13: Mappings of inclusion Type-6.](image)

Inclusions of Type-8 were only detected in the old ladles but not in the ladle of age 1, which in turn suggests that the inclusion of Type-8 might be generated by the ladle glaze. The mapped results of the Type-8 inclusions in Figure 14 illustrate clearly that small pure MgO islands are embedded in an oxide solution (phase IV).

![Figure 14: Mappings of inclusion Type-8.](image)
The photomicrographs of this type inclusions share similarity with the photomicrograph of the glaze sample (see Figure 15) obtained by Beskow et al.\(^5\) It is reasonable to expect that the slag infiltrated layer would not be easily removed because of the MgO matrix. A strong stirring by either argon gas or induction would be able to flush-off tiny portions of the MgO matrix along with the remaining slag, mostly the 3CaO·Al\(_2\)O\(_3\) phase (phase 2) with small amount of phase 3. Since the steel temperature is usually higher than the melting point of 3CaO·Al\(_2\)O\(_3\), and this compound would react with the remaining phase 3 (see Figure 15), a liquid oxide solution would be formed, viz. phase IV. To reduce the interfacial energy and the same time to meet the thermodynamic constrain, the inclusions would take a spherical shape embedding the MgO pieces inside the liquid phase. As a result, inclusions of Type-8 would be generated.

![Figure 15: The photomicrograph of the glaze sample. \(^5\)](image)

Even a certain fraction of the Type-7 inclusions could be due to the flushing-off of the pieces of the slag infiltrated layer. In such case, only a tiny amount of the infiltrated slag is peeled off. However, more study is needed to get more evidence to support this reasoning.

The increasing number of the inclusions with the increase of ladle age before casting shown in Figure 6 is a direct indication of this detachment and flushing off of slag infiltrated layer.

4.2 Inclusion During Casting and Final Product

4.2.1 Inclusion population

The steel samples taken during mould filling were found to contain Type-9 inclusions (alumina based inclusions). The morphology and the shape of the inclusions as shown in Figure 16, suggest that these inclusions are exogenous in nature. Since inclusions of this type are not found in the ladle before casting, it is reasonable to believe that these alumina based
inclusions are generated during the casting process. As mentioned in the experimental part, the steel melt passes through the inner nozzle, the closing gates and then the outer nozzle before entering into the mould.

Figure 16: Mappings of alumina based inclusion.

The volumetric flow rate of the steel melt is adjusted by controlling the diameter of the openings of the closing gates. The flow rate is decided by considering the size of the mould and the number of ingots to cast. The volumetric flow rate of the steel melt can be estimated using the information of the density of the steel melt, the mould filling time and the mass of the ingot. The volumetric flow in the case of the present study is calculated to be about 1500 c.m³/sec. It is quite possible that the high volumetric flow of the steel at high temperature can flush off small pieces of the refractory from the walls of inner and outer nozzles as well as the closing gates. These small oxide pieces would follow the stream of the steel into the mould. The chemical compositions of the inner nozzle, outer nozzle and the closing gates are presented in Table 11 along with the composition of the alumina based inclusions.

Table 11. The chemical compositions of the inner nozzles, outer nozzles, closing gates, runners and the alumina based inclusions during the mould fillings.

<table>
<thead>
<tr>
<th>Chemical compositions (mass %)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>ZrO₂</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner nozzle</td>
<td>94.0</td>
<td>1.5</td>
<td>5.0</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer nozzle</td>
<td>7.5</td>
<td>85.0</td>
<td>1.45</td>
<td>0.87</td>
<td>0.05</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Closing gates</td>
<td>9.7</td>
<td>82.4</td>
<td>0.06</td>
<td>0.2</td>
<td>0.4</td>
<td>6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Runners</td>
<td>37</td>
<td>58</td>
<td>0.3</td>
<td>0.5</td>
<td>1.4</td>
<td>1.1</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inclusion</td>
<td>0-10</td>
<td>85-98</td>
<td>0-10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A comparison of the chemical compositions in Table 11 indicates that the inner nozzle, outer nozzle and the closing gates could all be responsible for the existence of the alumina based inclusions. To further examine this aspect, the new inner nozzle, outer nozzle and the closing gate are compared with the used ones. The comparisons indicate the erosion of nozzles and closing gates. As an example, the comparison of the inner nozzles is shown in Figure 17. It is seen in Figure 17 that the new inner nozzle has an inner diameter of 3.8 cm while the used nozzle has an inner diameter of 5.5 cm. The erosion of the inner nozzle is substantial. The refractory is both the horizontal and vertical runners contains high content of silica. The compositions of the runner material are also included in the Table 11. The high SiO₂ concentration of the runner refractory would exclude the runners from being responsible for the presence of the alumina based inclusions.
New inner nozzle          Used inner nozzle

Figure 17: Comparison of the new and used inner nozzles.

The Type-9 inclusions (alumina based inclusions) are also found in the upper part of the ingot, mostly in the ingot box as shown in Figure 18. As mentioned earlier, the inclusions of this type were relatively large. It is also important to note that the alumina based inclusions have high interfacial tension with the steel melt. Large size and high interfacial energy would promote the floatation and separation of the inclusions. Hence, the long casting process (2 hours in present case) would give enough time for alumina based inclusions to float up. The observation of the presence of alumina based inclusions in the ingot box is strong evidence for the above reasoning. The generation and separation of this type of inclusions could probably also explain the higher population of inclusions in the half filled mould in comparison with the almost full filled ones, (see Figure 7) as the full filling would provide longer time for floatation of the big inclusions. However, this aspect needs more detailed study for clarification.

Figure 18: Positions of the samplings and the types of inclusions found in the ingot.
Figure 8 shows the inclusion population distribution in the solidified ingot. The inclusion population is highest in the centre part (C1) of the ingot irrespective of the vertical position. The high inclusion population in the central part of the solidified ingot could be explained by fluid flow mechanisms governed by the natural convection during solidification of the ingot. After the mould filling, the fluid flow in the ingot is primarily governed by the natural convection. The steel melt near the mould surface solidifies rapidly creating a solidification front. After the start of the solidification, a mushy zone is created which extends towards the centre of the ingot. The temperature of the steel melt near the solidification front is lower than the melt away from the front and near to the centre. Because of this temperature difference, the thermal buoyancy forces are generated resulting in strong counter clockwise natural convection current in the melt (If we examine the left half of the mould). The melt near the mushy zone has higher downward velocity than the fluid inside the mushy zone. Due to the low density and consequently low momentum of the non-metallic inclusions, the inclusions would have a tendency to follow the downward stream of the liquid steel, though some inclusions would be trapped in the mushy zone. This leads to the continuous increment of the inclusion population in the steel melt. The centre part of the steel, which solidifies latest would have higher population of inclusions.

As seen in Figure 8, the inclusion populations at C2, namely in the middle position between the central line and the mould wall (see Figure 2) show a minimum at all three vertical positions. The higher inclusion concentration at the wall (C3) in comparison with the position C2 could probably be explained by the rapid cooling close to the wall of the mould. The solidification is so fast, that the inclusions are captured in the solid steel before being flushed away by the downward stream. The entrapment of the mould flux near the surface of the ingot could be another reason for the higher population.

As discussed earlier, the number of inclusions in the melt before casting increases with the ladle age. In order to examine whether the ladle age would have the same effect on the inclusion number even in the final products, the inclusion populations in the final products produced in the ladle of different ages are presented in Figure 9. The inclusion populations before casting are also presented in the figure. Even the average value of the inclusion populations in the experimental ingot (ladle age 7) is included in Figure 9. It is seen that the number of inclusions shows also an increasing trend with the ladle usage in the final products. Even the value taken from the ingot follows the same trend. A comparison of the types of inclusions detected in the fresh ladle (ladle age 1) and in the used ladles along with the thermodynamic analyses have shown that the ladle glaze is responsible for the formation of several types of inclusions. The increasing trend shown in the Figure 9 would suggest that the effect of ladle age on the number of inclusions is even profound in the final product. It further indicates that the inclusions generated by ladle glaze would to great extent affect the quality of the final product and would therefore require special attention.

Figure 9 shows also that the numbers of inclusions in the steel melts before casting are somewhat bigger than in the final products. This difference could be explained by the inclusion segregations in the ingot during solidification as shown in Figure 8. In the steel melt before casting, the inclusion population would lie at the average level. On the other hand, the segregation of the inclusions would lead to higher population of the inclusions at the centre region than the average level. As mentioned earlier, the steel samples from the bars of the final products were always taken from the centre positions. Consequently, the numbers of the inclusions detected in the samples taken from the central part of the final products would be bigger than that of the steel melts before casting. It would also be possible that some new
inclusions are introduced during the casting process. This aspect would need further confirmation. Nevertheless, it is reasonable to conclude on the basis of the present results that the inclusions carried over from the ladle can not be removed or at least substantially removed during the solidification period of casting.

4.2.2 Inclusion types

In the period of mould filling, totally three types of inclusions namely; Type-6, Type-7 and Type-9 are found. While the inclusions of Type-6 and Type-7 are also found to exist in the liquid steel before casting, the Type-9 inclusions are introduced in the mould filling process as discussed earlier.

In the ingot, five types of inclusions are found, namely Type-6, Type-7, Type-9, Type-10 and Type-11. As mentioned earlier, the Type-9 inclusions are only found in the upper part of the ingot as indicated in Figure 18. This observation implies that the Type-9 inclusions float up during the casting process.

The Type-10 inclusions consist mostly of Al2O3 and SiO2. The chemical composition of the casting powder shares similarity with the composition of the Type-10 inclusions. This similarity is a strong indication that the inclusions of this type are generated by the entrainment of the casting powder during the solidification process. Moreover, the Type-10 inclusions in solidified ingot are only found close to the surface of the ingot as shown in Figure 18. In the industrial practice, the surface of the mould is pasted with the casting powder for lubrication. Therefore, there are good chances for the casting powder to get entrained in the melt. Since the surface part of the ingot solidifies rapidly, it gives very little chance for the entrained casting powder to float up. This argument is in line with the fact that Type-10 inclusions are only found at the surface part of the ingot. It is noticed that the runner refractory contains also very high Al2O3 and SiO2 concentrations. The chemical compositions of the runners are presented in Table 11. It is seen that the runner contains 57 mass% Al2O3 and 37 mass% SiO2. On the other hand, the SiO2 concentration in the inclusions of Type-10 is much higher, about 54 mass%. The big difference in silica content between the inclusion and runner material would rule out the possibility that Type-10 inclusions are generated by the runners.

In contrast with the inclusions found before casting and during mould filling, Type-6, and Type-7 inclusions in the ingot and the final products contain sulphur. In inclusions of Type-11, even CaS phase is detected. In order to understand the mechanisms of the formation of the sulphur containing phases (phase IV and phase VII), a thermodynamic study is performed.

As show in Table 10, the mould powder contains quite high concentration of sulphur before casting (0.36 mass%). On the other hand, the sulphur content in the slag formed by the mould powder is very low (0.05 mass%). It is reasonable to suspect that some sulphur would transfer from the mould powder into the liquid metal. The dissolved sulphur might react with the inclusions carried over from the ladle treatment. Hence, the thermodynamic analysis is mostly focused on the phases in the inclusions that have been detected before casting and during the mould filling. As shown in Table 1, these phases are MgO (phase I), spinel phase (phase II), oxide solution (phase IV), and aluminium oxide phase (phase V). To examine the possibility of the formation of the sulphide phase(s) the following reactions are considered:
CaO(s) + [S] = CaS(s) + [O] \quad (4)
MgO(s) + [S] = MgS(s) + [O] \quad (5)
Al₂O₃(s) + 3[S] = Al₂S₃(l) + 3[O] \quad (6)

In the above equations, the square brackets ‘[ ]’ denote Henryan standard states for the oxygen and sulphur (dissolved in liquid iron) on a weight percent basis. The standard states for the oxides and sulphides are the stable phases at the temperature under consideration, as indicated in the round brackets ‘( )’. The standard Gibbs energies of these reactions are calculated using the data from the handbooks \[15\] and the Gibbs energies for the dissolution of oxygen and sulphur \[38\].

Firstly, the possibilities of the formation of the pure sulphides by the corresponding pure oxides are examined. In the calculations, the oxygen activity is kept at 0.0001 (corresponding to 1 ppm). The calculated results are presented in Figure 19, where the required sulphur activities in logarithmic scale is plotted as functions of temperature for the formation of different sulphides.

![Figure 19: The sulphur activities required for the formation of the different sulphides as a function of temperature.](image)

It is seen that irrespective of the oxide studied, the required sulphur activity for forming the corresponding sulphide decreases with the increasing temperature. The formation of CaS from CaO requires reasonably low sulphur activity at the casting temperature, being 0.0034 at 1823 K. In the case of Al₂O₃ and MgO, the sulphur activities must be very high to form their sulphides. The sulphur activity needs to be higher than 1 to form magnesium sulphide at the casting temperature, and higher than 30 to form Al₂S₃. The line for the formation of MgS from the spinel phase is also included in the figure. In this calculation, the activity of MgO is
evaluated to be 0.3 in the spinel (the mole fraction of MgO is 0.5) using Thermo-Calc Software. A sulphur activity of 3.5 is needed for the formation of MgS from spinel.

The Table 1 shows, three types of inclusions are carried over from the ladle to the casting, namely Type-6, Type-7 and Type-8. All these types of inclusions contain phase IV, an oxide solution containing mostly CaO and Al₂O₃ and small amounts of MgO and SiO₂. The calcium oxide content is found to be very high, even 60 mass%. It would be interesting to examine whether phase IV in these types of inclusions would react with the dissolved sulphur forming CaS. Three typical compositions of phase IV are given in Table 12. They are named as oxide solution-A, oxide solution-B and oxide solution-C, respectively. Oxide solution-A contains 60 mass% CaO. According to the phase diagram of the CaO-Al₂O₃ system, pure CaO would precipitate from this solution when the steel is cooled down to the casting temperature (1823 K). The precipitated CaO would have an activity of one, and therefore would follow the CaO-CaS line in Figure 19. It is noticed that oxide solutions have a tendency to be supercooled. However, the super cooled liquid phase would also have very high activity of CaO, being very close to one. To evaluate the affinities of solution-B and solution-C to sulphur, the CaO activities of the two solutions are calculated using Theroslag software. On the basis of the activity data, the equilibrium sulphur activities for the formation of CaS from solution-B and solution-C are evaluated and presented in Figure 19. While it is much easier for solution-B and solution-C to form sulphides in comparison with Al₂O₃, spinel and MgO, they still need quite high sulphur activities, above aₐ = 0.0090 (90 ppm) to form CaS at the casting temperature. On the basis of the thermodynamic calculation and the sulphur contents in the steel samples after casting, it could be concluded that solutions-B and solution-C cannot form pure CaS. Instead, sulphur would be dissolved in solution-B and solution-C.

<table>
<thead>
<tr>
<th>Chemical compositions (mass %)</th>
<th>Solution</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>60</td>
<td>35</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>55</td>
<td>40</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>45</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 9 shows that the sulphur content is more than 30 ppm in the steel samples taken after casting and from the final products. The calculation using the dilute solution model for the steel melt indicates that sulphur exhibits a positive deviation, with the activity coefficient being 1.1. It is known that sulphur analysis by combustion using LECO usually involves uncertainties, probably giving values on the lower side due to incomplete combustion. It is also noticed that the analysed sulphur contents in the steel samples are total contents. Even the employed thermodynamic models would have uncertainties. Nevertheless, the thermodynamic calculation would still indicate that the formation of CaS by phase IV with high CaO content is possible at the casting temperature. The CaS phase detected in the Type-11 inclusions is believed to be formed by this mechanism. In fact, inclusions of Type-11 are evolved from Type-6 due to their high CaO concentration.

Type-7 inclusions are found at all the positions (see Figure 18) in the ingot. As discussed in the results part, unlike the inclusions of the same type found in the ladle, the inclusions of Type-7 in the ingot contain small amount of sulphur. The solidification time of the ingot is approximately 2 hours. It gives sufficient time for sulphur dissolution in the steel melt. The low sulphur content in the slag (which is from the mould powder) after casting and the high sulphur content of the steel provide strong evidence for the sulphur transfer from mould
powder to the liquid steel. As seen in Table 9, the sulphur content in the steel is between 30-35 ppm. The thermodynamic calculation has revealed that inclusions of Type-7 having relative low CaO activities (e.g. solution-B and solution-C) would not form CaS. Instead, sulphur would dissolve in the oxide solutions, forming an oxide-sulphide solutions. In most of the inclusions of Type-7 found in the ingot and even in the final products, small sulphur contents are detected. This observation is in conformity with the thermodynamic consideration.

Similarly, small amount of sulphur is also detected in the phase IV in the inclusions of Type-6 found in the ingot. Despite of the presence of the dissolved sulphur, the spinel phase (phase II) is still found in the central part of the inclusions as shown in Figure 20. This is again in line with the result of the thermodynamic analysis.

![Figure 20: Mappings of Type-6 inclusion.](image)

It is reasonable to expect that the compositions of the inclusions do not change appreciably in the forging and machining process. Hence, the types of inclusions found in the ingot should also be detected in the final products. In the final products, three types of inclusions are found, viz. Type-6, Type-7 and Type-11. It should be mentioned that the removal of the ingot box and the surface layer ensures the absence of the inclusions of Type-9 and Type-10.

The inclusions in the final product are found to be more complex than in the steel samples during the mould filling and after casting. Some inclusions, in fact quite a big fraction of the total inclusion population, are found to be in stringer shape. For example, both round and stringer shape inclusions of Type-7 and Type-11 are found in the final products. As an example Figure 21 presents the photomicrograph of a typical stringer inclusion of Type-11. Although the inclusions of the stringer shape have very different appearances in comparison with the inclusions having the same phase(s) before forging, they are not classified as new types of inclusions. The morphology of the inclusion suggests that the inclusions of stringer shape are resulted from the mechanical deformation of the low-strength globular shape inclusions. The ingots after casting are sent to the forging shop. During forging, a heavy stress is applied on the ingots to reduce their dimensions. Because of the heavy stress, those inclusions which are of low mechanical strength and more exposed to the stress field, would get deformed in the shape.
4.3 Possibility of Inclusion Removal by Bubble Floatation

4.3.1 Prediction using floatation coefficient

Since the introduction of floatation coefficient, this concept has been used by many researchers to determine whether a type of solid particles or liquid drops can be captured by the rising gas bubbles and separated from the liquid in a liquid-particle (or drop)-gas system. The floatation coefficient is defined as

\[ F = \gamma_{lu} - \gamma_{pg} - \gamma_{pl} \]  (7)

where \( \gamma_{lu} \), \( \gamma_{pg} \) and \( \gamma_{pl} \) stand for the surface tension of the liquid, surface tension of the dispersed phase and the interfacial tension between the dispersed phase and liquid, respectively. A necessary condition for the separation of the dispersed phase from the liquid by the gas bubbles would be a positive \( F \). The floatation coefficients for both charcoal-silicon oil-air and charcoal-water-air systems were calculated. The calculated floatation coefficients for charcoal-silicon oil-air and charcoal-water-air systems were found to be \(-11.22 \text{ mN/m}\) and \(+108 \text{ mN/m}\), respectively.

It is seen that the charcoal-silicon oil-air system reveals a negative floatation coefficient. This negative value would explain the difficulty of removing charcoal powder from the oil. As the possibility of the attachment of charcoal particles on the gas bubbles is ruled out by the unfavorable interfacial energy change, gas bubbles can not help in separating the charcoal particles from the silicon oil. In fact, the rising bubbles result in circulation of the liquid, going upward in the centre of the bath and downwards near the sidewalls. This circulation would even slow down the floatation of the particles by buoyancy force. It should be mentioned that no charcoal layer was observed on the surface of the liquid even after 24 hours of gas stirring. This could be explained again by the state of energy of the system. As indicated by the floatation coefficient, the energy change of the system for a particle coming to the surface from the bulk would be positive. This unfavorable energy change would help
the downward stream to drag the particles back to the bulk, although the density of charcoal is much lower than that of silicon oil.

In the case of water-charcoal-gas system, the floatation coefficient is well above zero. The experimental results revealed that the separation of charcoal particles from water depends on the particle size. As shown in Figure 10, while the charcoal particles ranging between 10-30 μm and 30-50 μm were found to be separated from the bulk, the concentration-time curve for the powder having a size range 120-150 μm showed no substantial separation even after about two hours. A flow rate of 6.41 l/min would pass 36.9 litres of gas in 1.5 hours through the water bath, which was only 3.8 litres. It is reasonable to believe that the charcoal particles had very high probability to meet the gas bubbles during such time period. If a positive floatation coefficient would ensure the attachment of the particles on the bubbles, most of the particles would have been removed from the bath. The controversy between the experimental observation and the floatation coefficient suggests that floatation coefficient is only a necessary but not a sufficient condition for separation of particles from the bulk liquid by gas bubbles.

### 4.3.2 Prediction using model by Zhang and Taniguchi

Inspired by the modelling studies \cite{42-53} on mineral floatation, a mathematical model for the removal of silica inclusions from liquid steel by argon bubbles has been proposed by Zhang and Taniguchi \cite{54}. To the knowledge of the present author, the model by Zhang and Taniguchi \cite{54} is so far the most systematic effort trying to introduce the energy aspect into the prediction of inclusion removal by gas bubbles. In their models, the following assumptions have been made:

1. The bubbles are uniformly distributed in the liquid steel. They all have the identical size and, floating with constant terminal velocity.
2. Turbulence of the system is ignored.
3. Particles have a uniform size. The size is very small compared to bubble size to affect the bubble motion.
4. Particles are only removed by attachment to the rising bubbles. Other modes of removal are ignored, such as collision, floatation and coagulation with other particles.
5. The bubble size is independent on the gas flow rate.
6. If stable attachment occurs between bubble and inclusion, the inclusion is considered to be removed from liquid steel because of high bubble rising velocity.

According to the model, the probability of attachment is defined as:

\[
P = P_c P_A (1 - P_d)
\]

(8)

In equation (8), \(P_c\) is the probability of collision, \(P_A\) is the probability of adhesion and \(P_d\) is the probability of detachment. Zhang and Taniguchi \cite{54} assume that the possibility of detaching an inclusion from the bubble after the formation of three phase contact is negligible, i.e. \(P_d = 0\). Zhang and Taniguchi \cite{54} employ the model by H. J. Schulze \cite{43} to evaluate the collision probability. The present calculation uses the same approach. The model by Yoon and Luttrell \cite{42} is employed to calculate the adhesion probability. According to Yoon and Luttrell \cite{42}, the adhesion probability is expressed as

\[
P_A = (\sin \theta_A)^2
\]

(9)
where $\theta_0$ is the maximum adhesion angle, beyond which no adhesion between particle and bubble takes place. The value of $\theta_0$ is evaluated by assuming the induction time being the sliding time. The sliding time equation proposed by Nguyen\cite{53,55,57} is used.

The model was applied to the charcoal-oil-gas system and charcoal-water-gas system. The critical film thickness $H_c$,\cite{57} film drainage time $t_d$,\cite{43}, collision probability, adhesion probability and overall probability have been calculated. The calculated values are listed in Tables 13 and 14 for low Reynolds number, 1.5 and high Reynolds number, 400 respectively. In the calculation, the diameter of the gas bubbles was taken to be 1.32 cm, which was estimated by image analysis in the experiment. It is seen that higher Reynolds number leads to higher collision probability.

### Table 13. Calculated model parameters for creeping flow with Reynolds number being 1.5.

<table>
<thead>
<tr>
<th>$H_c$ $\mu$m</th>
<th>$T_d$ $\mu$s</th>
<th>$P_c \times 10^3$</th>
<th>$P_a$</th>
<th>$P \times 10^3$</th>
<th>Particle size $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>60.2</td>
<td>4.18</td>
<td>$=1$</td>
<td>$4.18 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>1.50 x $10^3$</td>
<td>26.1</td>
<td>$=1$</td>
<td>$26.1 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>2.84 x $10^3$</td>
<td>37.6</td>
<td>$=1$</td>
<td>$37.6 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>3.70 x $10^3$</td>
<td>602</td>
<td>0.78</td>
<td>468</td>
</tr>
<tr>
<td>Charcoal-oil-air</td>
<td>1</td>
<td>1</td>
<td>37.6</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 14. Calculated model parameters for creeping flow with Reynolds number being 400.

<table>
<thead>
<tr>
<th>$H_c$ $\mu$m</th>
<th>$T_d$ $\mu$s</th>
<th>$P_c \times 10^3$</th>
<th>$P_a$</th>
<th>$P \times 10^3$</th>
<th>Particle size $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>60.2</td>
<td>35.19</td>
<td>$=1$</td>
<td>$35.19 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>1.50 x $10^3$</td>
<td>220.0</td>
<td>$=1$</td>
<td>$220.0 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>2.84 x $10^3$</td>
<td>316.7</td>
<td>$=1$</td>
<td>$316.7 \times 10^3$</td>
</tr>
<tr>
<td>Charcoal-water-air</td>
<td>0.05</td>
<td>3.70 x $10^3$</td>
<td>5068</td>
<td>0.04</td>
<td>198.7</td>
</tr>
<tr>
<td>Charcoal-oil-air</td>
<td>1</td>
<td>1</td>
<td>316.7</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

A high $P_a$ implies that a large fraction of the collisions result in attachment of the particles on the bubble. In the case of charcoal-oil-gas system, the calculated value of critical film thickness $H_c$ is imaginary thereby indicating that charcoal particles cannot be removed from silicon oil. This result is in accordance with the experimental observation and the prediction of floatation coefficient.

In the case of the charcoal-water system, the predicted probability of removal for 120-150 $\mu$m size charcoal particles is much higher than low size particles at low Reynolds number. This is in controversy with the experimental evidence, which shows that 120-150 $\mu$m size particles are difficult to remove. In case of high Reynolds number, the over all probability of removal of 120-150 $\mu$m predicted is very high and even higher than the value predicted for 10 $\mu$m size particle, which is again in controversy with experimental observation presented in Figure 10. The disagreement between the model prediction and the experimental results suggests that the model predicts too high probability of attachment for the charcoal-water-gas system.
4.3.3 The need of a new model

The above discussion has shown that while a positive flotation coefficient is a necessary condition for the separation of a dispersed phase from the bulk phase by gas bubbles, it is not a sufficient condition. The insufficiency of this condition has been demonstrated by the results of the charcoal-water-gas system. Similarly, the model by Zhang and Taniguchi[54] is able to predict the failure of separation in the case of charcoal-oil-gas system, but is unable to describe the curves for the charcoal-water-gas system shown in Figure 10. The discrepancy between the experimental results and the prediction of flotation coefficient as well as the model by Zhang and Taniguchi[54] could be well explained by the absence of the drag force in the model development.

In the case of most non-metallic inclusions in steel, the flotation coefficients are positive due to the relatively high surface tension value of liquid steel. On the other hand, difficulties have been encountered in removing small inclusions in the secondary steel making processes. Since most of the available models do not consider the drag force, there would be difficulties in predicting the inclusion removal using these models. The probability model would not be able to predict precisely the removal of small inclusions, even though they try to incorporate the flotation coefficient as a criterion. Very often, the models would over estimate the attachment of the particles on the gas bubbles. In order to predict the removal of inclusions having particle sizes at μm level from steel, new models taking into account interfacial energies, drag force, buoyancy force and gravity force are needed.
5. SUMMARY

In the present study, chemical developments of different types of inclusions during the tool steel making process were studied. The inclusion populations at different stages of the process were analysed. The effect of the ladle glaze on the formation of inclusions during the ladle treatment process was highlighted.

Steel samples were taken at different stages of the steel making process from ladles of different ages. The inclusion population analyses of the steel samples revealed that the number of inclusions increased with ladle age before deoxidation and before casting. The analyses of the steel samples from the solidified ingot revealed a non-uniform distribution of inclusions. The inclusion population was found to be highest in the centre part of the ingot and lowest between the central line and the mould wall. The inclusion populations in the final products were also found to increase with the ladle age.

To identify the types of inclusions generated by ladle glaze, the steel samples from the ladles of different ages were analysed by SEM/EDX before deoxidation and before casting. During the analyses, the types of inclusions were found to vary with ladle age. The results indicated that ladle glaze reacted with EAF slag during ladle filling leading to the formation of inclusions of Type-2 (an oxide solution), Type-4 (spinel in the center surrounded by the oxide solution of Type-2) and even a part of inclusions of Type-3 (spinel). The inclusions of both Type-6 (spinel in the center surrounded by the oxide solution of Type-7) and Type-7 (oxide solution with low contents of MgO and SiO$_2$) were found to be the products of the reaction between inclusions of Type-3 and the liquid metal. The occurrence of Type-8 (small MgO islands embedded in an oxide solution) inclusions only in the used ladle suggested that this type of inclusions were generated by the ladle glaze.

Totally three types of inclusions namely; Type-6, Type-7, and Type-9 (alumina based inclusions) were found in the steel samples during the mould filling. The Type-9 inclusions were originated from the erosion of the nozzles and the closing gates during the mould filling. The steel samples after casting were found to contain inclusions of Type-6, Type-7, Type-9, Type-10 (alumina-silicate oxide solution), and Type-11 (spinel phase with calcium sulphide). The types of inclusions were found to vary with the position in the ingot. In the final products, three types of inclusions were found, viz. Type-6, Type-7 and Type-11. While almost all the inclusions in the final products were originated in the ladle before casting, sulphur was detected in all types of inclusions. Because of the appreciable amount of sulphur in the commercial casting powder, steel would take up sulphur during casting. The dissolved sulphur would to a great extent affect the inclusion chemistry.

In a preliminary examination on the possibility of inclusion separation, a series of simple cold model experiments were carried out. Deionised water and silicon oil were used as the bulk liquid, while charcoal particles of different size ranges were employed as dispersed phase. The applicability of floatation coefficient was examined using the experimental results from cold models. Despite of high positive value of the floatation coefficient in the case of the charcoal-water-gas system, the separation of charcoal particles was found to be dependent on the particle size. The charcoal particles ranging between 10-30 μm and 30-50 μm were found to be separated from the bulk, while particles in a size range 120-150 μm showed no
substantial separation even after about two hours. The experimental results indicated that the floatation coefficient was a necessary but not a sufficient condition for the particles removal by gas bubbles. The experimental results were also compared with the prediction of a model taking interfacial energies into consideration. The comparison showed that the model over predicts the probability of the particle attachment in the case of charcoal-water-gas system, plausibly due to the omission of the drag force in the model consideration. This finding was in accordance with the difficulties encountered in removing small inclusions in the secondary steel making processes, even though the floatation coefficients were almost always positive due to the relatively high surface tension value of liquid steel. The present examination suggested the need of a floatation model taking interfacial energy aspect, buoyancy force, gravity force and drag force into consideration.
6. FUTURE WORK

- A thermodynamic analysis has shown that the spinel phase is not a stable phase during the later stage of ladle treatment process. The analysis has also revealed that the spinel phase reacts with the dissolved Ca in the steel melt. In order to gain a deeper understanding, a laboratory experiment revealing the reaction between spinel phase with dissolved Ca in the steel would be helpful.

- The erosion of the closing gates as well as the nozzles introduce inclusions of Type-9. Although the inclusions of this type are eliminated by the removal of the ingot box, the distance of the appearance of the Type-9 inclusions from the top surface of the ingot would have great impact on the economy of the production. Further study is needed to examine the effect of the materials and qualities of these casting components on the formation of inclusions. Even the effect of casting speed on the erosion of the nozzles and closing gates should be investigated.

- Inclusions of Type-2 and Type-7 are both oxide solutions. To clarify whether phase III in Type-2 inclusions reacts with the liquid metal resulting in the phase IV in the inclusions of Type-7, a further study is needed.

- The real mechanism of inclusion separation from steel melt during ladle treatment process is quite complicated. Inclusions in the steel melt are reported to be removed by collision, agglomeration, floatation and bubble floatation. However, the exact mechanism(s) of inclusion removal is (are) still not clear. A further study should be devoted to finding out the main mechanism of inclusion separation and develop a model predicting the behaviour of inclusion removal from the steel melt.
REFERENCES


32. PCMC, Quantmet AB, SE-81181 Sandviken.


