Three Dimensional Determinations of Inclusions in Ferroalloys and Steel Samples

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Doctoral Thesis
Stockholm 2014

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ISBN 978-91-7595-156-0
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ISBN 978-91-7595-156-0

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Abstract

As the requirements on material properties increase, there has been a demand on an additional knowledge on the effect of impurities in the ferroalloys on the steel cleanness. Thus, the number, morphology, size and composition of inclusions in six different ferroalloys (FeTi, FeNb, FeSi, SiMn, LC and HC FeCr) were investigated in this study. This was done in three dimensions (3D) by using a SEM in combination with EDS after electrolytic extraction of the ferroalloy samples. The results show that the non-metallic and metallic inclusions can be successfully analyzed on the surface of a film filter after a separation of the inclusions from the matrix. Overall, the inclusions can be divided into two categories depending on the melting point. Furthermore, the possible transformation of different kinds of inclusions after their addition to the liquid steel can also be determined.

The inclusions and clusters in steel samples of two similar steel grades of high-silicon non-calcium treated (HSiNC) stainless steels were also investigated and compared during ladle treatment and continuous casting. Samples of liquid steel and slag were taken at different stages of the ladle treatment and casting during two plant trials: a low Al steel (LAl) and a high Al steel (HAl). Spherical (SP), irregular and regular (IR) inclusions and clusters (CL) were observed in the samples from both heats. It was found that the morphology and composition of inclusions and clusters in both heats were significantly changed during the ladle treatment and casting. Most of inclusions (44-98%) in a low Al steel are MgO-CaO-SiO$_2$-Al$_2$O$_3$ spherical inclusions. The compositions of irregular and regular inclusions and clusters in steel samples of a high Al steel were mostly MgO-Al$_2$O$_3$ spinel, but also complex spherical inclusions containing Al$_2$O$_3$-MgO-CaO-SiO$_2$. In addition, the phase stability diagram based on Darken’s quadratic formalism and Redlich-Kister type polynomial was estimated for both heats at a non-infinite solution.

It is known that clusters in liquid steel have a harmful effect on the casting process and the quality of the final steel product. Therefore, clusters of rare earth metals (REM) were investigated in steel samples of a S30185 stainless steel grade from a pilot trial (PT, 250 kg) and from an industrial heat (IH, 100 t). Samples were taken from the liquid steel at different holding times after the addition of a mischmetal. The morphology, composition, number and size of clusters in PT and IH steel samples were analyzed and compared as a function of the holding time. It was found that typical clusters with regular and irregular inclusions were the main type of clusters (69%-98%) in all PT and IH steel samples. The composition of
inclusions in clusters corresponded mostly to REM-oxides. The size of clusters that were observed in different samples varied mainly from 2 to 23 μm. In addition, the size and number of most clusters in PT are larger than those in IH samples.

Large size inclusions are recognized to be crucially harmful for the mechanical properties of steel products. Therefore, predictions of the maximum size of Al₂O₃-CaO spherical inclusions in an Fe-10 mass% Ni alloy have been examined based on two dimensional (2D) and three dimensional (3D) investigations. The effects of the number of measurements and unit volume on the estimated 3D results were also investigated.

**Key words:** Three dimensional, Ferroalloy, Inclusion, Spinel inclusion, Thermodynamic calculation, REM clusters, Formation mechanism, Statistical analysis, Maximum size
Acknowledgements

First of all, I direct a deep acknowledgement to two great supervisors Dr. Andrey Karasev and Professor Pär Jönsson. Your critical thinking, endless support and positive spirit are very helpful for me during my study and growth at KTH. You have truly taught me a lot about how to conduct research and you always give me hope, which is the most precious thing in the world.

Millions of thanks should be sent to Prof. Dengfu Chen and Prof. Ying Li in China. Thank you for helping me go into an interesting and promising research world.

Prof. Sichen Du is acknowledged for the useful advice all the time. Erik Roos is appreciated for all the valuable input throughout this work. I would like to thank Dr. Ola Ericsson and Dr. Yuichi Kanbe for their support starting from the beginning. Thanks also to Changji Xuan for the help on manipulating the software for high alloy steel. David Dilner is acknowledged for the discussion on the thermo-calc software.

I would like to thank Ms. Wenli Long, who helps me a lot on the technical problem at the KTH lab. The same thanks go to Dr. Miroslava Sedlakova from Swerea KIMAB for the help with laser ablation ICP mass spectrometry (LA-ICP-MS) technique.

Many thanks for the help from the friends and colleagues at the Department of Material Science and Engineering, KTH. You are always helpful and friendly to me in any situation. Without the kind help from Dr. Zhi Zhang and Dr. Zhili Song, it would be not so easy to stay in the beginning when I arrived. Special thanks to Alicia Gauffin for being a great roommate. Drs. Mei Fang, Xiaolei Zhang, Jun Li and Qiang Liu, I miss you guys so much! Forgive me that I could not list all the names. There are lots of happy memories with you all!

I am grateful to the Chinese Scholarship Council for the financial support. Olle Eriksson Foundation is acknowledged for the financial support of the conference.

Last but not least, without the constant support from my family, this thesis would be impossible to accomplish.

Supplements

The present thesis is based on the following supplements:


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

I. Literature survey, experimental work, major part of the writing.

II. Literature survey, experimental work, major part of the writing.

III. Literature survey, experimental work, thermodynamic calculations, major part of the writing.

IV. Literature survey, experimental work, thermodynamic calculations, major part of the writing.

V. Literature survey, experimental work, mathematic calculations, major part of the writing.
Parts of this work have been presented at the following conferences:


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1. Introduction

1.1 Background

Increasing requirements on the material properties of the steel will result in demands on a more controlled steelmaking process. For producers of clean steels this means that, for instance, alloying additions will have to be controlled with respect to the inclusion characteristics. This is especially true in those cases where alloy additions need to be added late in a process and where there is not enough time to remove the additional inclusions that are added to the steel. Jönsson et al. [1] concluded the future demands on ferroalloys from the viewpoint of customers. The first kind of ferroalloys is the high purity ferroalloys that are used for late additions during ladle refining. The second is the less refined grades of lower cost, which should be added earlier in the steelmaking production line. Thus, in order to meet the forthcoming demands, ferroalloys should be characterized with respect the number, morphology, size and composition of inclusions.

Nozzle clogging is also a serious problem during continuous casting in the steel industry due to its harmful effect on the steelmaking process and the final product. Clogging problems caused by spinel inclusions and rear earth metal (REM) clusters have been reported by some researchers. The clogs in the nozzle change the nozzle flow pattern, disrupt the flow in the mold, and result in top slag entrainment and surface defects. [2] Therefore, the study of the formation mechanisms and evolution of spinel inclusions and REM clusters is very important to inhibit their formation and nozzle clogging during casting.

The maximum size of inclusion in steel controls the fatigue behavior and other mechanical properties. [3] The information of the large size inclusions is very useful for the steelmakers to predict the quality of steel. Prediction of the largest size of inclusion in a large volume of steel from observations of small volume of steel is always a key problem for the steelmakers. Thus, it is extremely useful to investigate the maximum size of inclusions that have been distributed in the steel.

1.2 Inclusions in ferroalloys

Ferroalloys are commonly used in the steel industry to alloy or deoxidize the steel during the secondary steelmaking process before casting. However, the addition of ferroalloys may cause a supply of deleterious impurities to the liquid steel. In some cases, these impurities are
clearly related to the raw material and the way of producing an ferroalloy and are more or less unavoidable. [4]

**Table 1-1. Inclusions found in different ferroalloys**

<table>
<thead>
<tr>
<th>Ferro alloy</th>
<th>Method**</th>
<th>Inclusion</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTi (35,70)</td>
<td>AD SEM EDS AIA</td>
<td>Si/SiO₂, Al-TiO, Al₂O₃, iron oxides, Fe-TiAl₂O₃, TiN, MgO</td>
<td>Inclusions in the matrix are in good agreement with the extracted inclusions. Inclusions in FeTi35 increased the product rejection. FeTi70 is cleaner than FeTi35. [4-8]</td>
</tr>
<tr>
<td>FeNb (65)</td>
<td>AD SEM EDS</td>
<td>SiO₂, Al₂O₃, Si₃N₄, (Al₂O₃)₃, Fe₃C, Ti₃O₂, (Al₂O₃)₂, Fe₃C₃O₄, Si₃N₄, Al₂O₃, SiO₂, Al₂O₃</td>
<td>The microstructure of FeNb reveals two phases with no apparent inclusion types. [4]</td>
</tr>
<tr>
<td>FeSi (65,75)</td>
<td>FGA QTM SEM EMP AIA EDS</td>
<td>SiO₂, Al₂O₃, FeSiO₃, Si₃N₄, (Al₂O₃)₃, Fe₃C, Ti₃O₂, (Al₂O₃)₂, Fe₃C₃O₄, Si₃N₄, Al₂O₃, SiO₂, Al₂O₃, SiO₂, MnO</td>
<td>Impurities are mostly intermetallic phases and oxide inclusions are very rare. The grade of ferrosilicon has a direct impact on the inclusions in the liquid steel. FeSi with a lower Al content results in a low oxygen content and a small quantity of Al₂O₃ inclusions. Al in FeSi enhances the formation of spinel inclusion, but Ca prevents it. [5, 9-11]</td>
</tr>
<tr>
<td>FeMn (75,80)</td>
<td>AD SEM AIA PC MIC</td>
<td>C, Si/SiO₂, MnS, SiMn oxide, MnO, MnO-SiO₂-MnS</td>
<td>The FeMn alloy contains distinguishable carbide and nitride phases. The amount of inclusions is inversely proportional to the carbon content in FeMn. Low oxygen FeMn has lower inclusion mean diameters. [4, 5, 12-16]</td>
</tr>
<tr>
<td>FeCr (65)</td>
<td>SEM AIA</td>
<td>CaS, Cr₂O₃, MnO, Cr₂O₃-Mn₂O₃-Silicate</td>
<td>The type of oxide inclusions in ferrochromium depends on its silicon content and there is a connection between the silicon content and the steel cleanliness. [5, 17]</td>
</tr>
<tr>
<td>FeCr (65,70)</td>
<td>SEM EDS WD EDS</td>
<td>(Cr₃MnFeTi), Cr₃S₆, MnS, (Cr, Ti) (C,N), FeO(Cr, Al₂O₃, CrS, CrO-SiO₂, Al₂O₃)</td>
<td>The amount of inclusions with and without carbon depends on the silicon contents. The FeCr features Cr-rich and Fe-rich regions in the matrix. In addition, the inclusions are exclusively located in the Fe-rich regions. [6, 12, 18, 19]</td>
</tr>
<tr>
<td>FeMo (70)</td>
<td>AD SEM EDS</td>
<td>Si/SiO₂, Al₂O₃, SiO₂-Al₂O₃, CaO-SiO₂-Al₂O₃</td>
<td>Inclusions in the matrix are in good agreement with the extracted inclusions. [4, 6]</td>
</tr>
<tr>
<td>FeP (30,35)</td>
<td>AD SEM EDS AIA</td>
<td>(Fe₃P₃,Mn,Ti)O</td>
<td>The distribution of Ca, Mn and Ti is inhomogeneous. High P phase with Si and low P phase with Mn, Ti and Cu. [4, 5, 16]</td>
</tr>
</tbody>
</table>

*: () - the content of alloying element; HC - high carbon; LC - low carbon.
**: AD - Acid dissolution (3D); AIA - automated inclusions analysis; PC MIC - Computer software; FGA - fractional gas analysis; QTM - Image Analyzer Qantimet; EMP - electron microprobe, WD - wavelength dispersive.
Some publications about the inclusions in different kinds of ferroalloys as well as characterization method are listed in Table 1-1. [4-19] SiO₂, Al₂O₃ and some intermetallic phases were observed in FeTi alloys. [4-8] Inclusions in FeSi have a direct link to the Al and Ca contents in the ferroalloys. [5, 9-11] Similarly, the types of inclusions in FeMn alloys depend on the silicon [12, 13] and C [4, 16] contents in the ferroalloys. Also, the inclusions in different grades of FeSi alloys have a connection to the steel cleanliness. However, inclusions in FeMn only have a temporary influence on the inclusions in liquid steel according to previous laboratory and plant trials. [14, 15] The inclusions present in the LCFeCr alloy are mainly Cr-Silicates and Cr-Mn-Silicates. [5, 17] However, sulphides and carbonitrides and some oxides are mostly observed in HCFeCr alloys. [6, 12, 18, 19] This is because the inclusions that are present in the ferrochromium are related to the ferroalloy production route. Finally, inclusions in FeMo, FeNb, FeP alloys has also been studied by some researchers. [4-6, 8]

The above mentioned studies have been concentrated on two dimensional (2D) investigations, except for the study by Pande. [4] They used acids to dissolve ferroalloys and to study the impurities in three dimensions (3D). However, some impurities might dissolve during the acid extraction. Moreover, very few researchers tried to provide information about the particle size distribution of inclusions in ferroalloys. [1] Therefore, some new analytical technique is needed for the investigation of inclusions in ferroalloys.

1.3 Inclusions in metal samples

Clogging problems caused by spinel inclusions and rare earth metal (REM) clusters have been reported by some researchers. The formation mechanism of spinel inclusions in stainless steel has been discussed based on the thermodynamic consideration of molten steel [20-25] and on the slag composition. [26-31] The formation of spinel inclusions was considered as a result of a formation of singular spinel (only consisting of MgO·Al₂O₃) and/or of a spinel crystallization from liquid droplets of CaO-SiO₂-MgO-Al₂O₃ during solidification. [32] Park [24] reported that the inclusions containing the MgO·Al₂O₃ crystals were not observed in an Fe-16Cr-14Ni steel if the concentration of Al₂O₃ in the inclusions was smaller than 20 mass%. However, the number of these inclusions increased drastically at Al₂O₃ concentrations larger than 20 mass%. Todoroki and Mizuno [29] found that an increased content of silica in the slag can enhance the formation of spinel inclusions in Fe-18Cr-8Ni steels deoxidized with aluminum. Furthermore, the effect of ferrosilicon additions on the composition of inclusions
has also been studied previously. [33-35] For instance, Park and Kang [34] reported that the addition of FeSi with a higher Al content promoted an increase in the amount of Al$_2$O$_3$ in the inclusions and results in a formation of spinel inclusions.

In recent years, there has been a considerable interest in rare earth elements due to the beneficial effects of their use in steels. It is reported that the rare earth metals (REM) can modify the shape of sulfide inclusions and to improve the hot workability of steel. [36] Further studies [37, 38] reported that rare earth metals reduce the degree of undercooling for nucleation, refine the as-cast structure, and limit solidification segregation in steels. However, the addition of a mischmetal to liquid steel often leads to formation of REM clusters and nozzle clogging, [39-41] which is a serious problem during continuous casting in the steel industry. Kojola et al. [39] found that the main part of the nozzle accretion was caused by an agglomeration of Ce inclusions and clusters. Katsumata and Todoroki [41] suggested that the ratio of Ce to Al should be carefully controlled in order to avoid the formation of Ce$_2$O$_3$ that easily adheres to the nozzle wall.

The previous studies of inclusions were carried out by using 2D investigations, in which the surface layer composition cannot be determined precisely. In addition, a 3D observation is more preferable and accurate than a cross sectional observation in 2D, especially for clusters whose shapes are irregular. Furthermore, the above mentioned thermodynamic calculations for spinel inclusions are based on the Henrian standard state, which is not recommended for high alloy steels.

### 1.4 Statistical Analysis

Large size inclusions are recognized to be crucially harmful for the mechanical properties of steel products. Therefore, it is extremely useful to investigate the maximum size of inclusions that have been distributed in the steel. Prediction of the largest size of inclusion in a large volume of steel from observations of small volume of steel is always a key problem for the steelmakers. Here, statistics of extreme values (SEV) is widely applied [42-47] for the evaluation of the largest size of inclusions in steel samples. This analytical method can determine the probable maximum size of an inclusion in a certain volume, based on the extreme value distribution (EVD). [42] The slope of the EVD lines would be different for the different inclusions types. [44] A numerical simulation model is used to study the relationship between the EVD obtained from two dimensional (2D) and three dimensional (3D) measurements. [46, 48, 49] As a result, a proper translation term is required to estimate the
unit volume precisely from the unit area. [46] It has also been reported that the EVD data for single inclusions obtained from 2D measurements agrees fairly well with 3D determinations, if the pores are excluded in the measurements. [45]

However, the relationship between 2D and 3D measurements has not been studied comprehensively. It is also important to obtain a standard number of measurements and unit volume in order to get an accurate result.

1.5 Objectives of the work

The present study is concentrated on three dimensional investigations of inclusion characteristics (such as composition, size, number and morphology) in ferroalloy and steel samples. The electrolytic extraction method was used in this study. This dissolution technique leads to less dissolution of inclusions in comparison to the acid method. [50] More specifically, the electrolytic extraction method is recommended for the analyses of REM oxides, Al$_2$O$_3$ and SiO$_2$ inclusions, which also are observed in this study. The scope and focus of the different supplements in this thesis work is schematically illustrated in Fig. 1-1.

In supplement I and II, three dimensional investigations of inclusion characteristics are studied for the following six ferroalloys: FeTi, FeNb, FeSi, SiMn, LC and HCFeCr. The particle size distribution was determined for most of the major non-metallic inclusion types found in the samples. In addition, the possible transformation of different inclusions after their addition to the liquid steel has also been discussed.

In supplement III, two grades of high-silicon non-calcium treated (HSiNC) stainless steels were investigated by a 3D analysis. The characteristics of inclusions and clusters in steel
samples taken during ladle treatment and casting in the low Al steel were compared to those in the high Al steel. The formation mechanisms and evolution of different inclusions were investigated and discussed for both heats. Furthermore, the phase stability diagrams based on Darken’s quadratic formalism and Redlich-Kister type polynomial were estimated for given steel grades at a non-infinite solution.

In supplement IV, the characteristics of REM clusters in stainless steel were investigated in 3D after electrolytic extraction of steel samples taken during: a pilot trial (PT) and an industrial heat (IH). The characteristics of clusters in PT samples at different holding times after mischmetal addition were compared to those in the IH samples. Furthermore, the formation mechanisms and evolution of different type of REM clusters were discussed for both PT and IH heats.

In supplement V, the prediction of the maximum size of Al$_2$O$_3$-CaO spherical inclusions in an Fe-10 mass% Ni alloy have been examined based on two dimensional (2D) and three dimensional (3D) investigations by using SEV method. The effects of the number of measurements and unit volume on the estimated 3D results were also investigated.
2. Methodology

2.1 Sample Preparation

The investigations of inclusions in ferroalloys were carried out by using the following commercially obtained ferroalloys: FeTi, FeNb, FeSi, SiMn, LC and HCFeCr. The typical chemical compositions of these ferroalloys are listed in Table 2-1. The specimens were cut from a ferroalloy lump to small pieces (15x10x3 mm) before electrolytic extraction.

Table 2-1. Composition of different ferroalloys (mass%)

<table>
<thead>
<tr>
<th>Ferroalloys</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Ti</th>
<th>Si</th>
<th>Nb</th>
<th>Al</th>
<th>C</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTi</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>71.56</td>
<td>0.21</td>
<td>-</td>
<td>3.14</td>
<td>0.18</td>
<td>0.008</td>
<td>0.012</td>
</tr>
<tr>
<td>FeNb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.82</td>
<td>2.48</td>
<td>66.23</td>
<td>1</td>
<td>0.15</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>FeSi</td>
<td>0.0058</td>
<td>0.0039</td>
<td>0.032</td>
<td>0.083</td>
<td>75.975</td>
<td>-</td>
<td>1.166</td>
<td>0.089</td>
<td>0.006</td>
<td>0.023</td>
</tr>
<tr>
<td>SiMn</td>
<td>0.03</td>
<td>0.03</td>
<td>61.471</td>
<td>0.2</td>
<td>29.219</td>
<td>-</td>
<td>-</td>
<td>0.053</td>
<td>0.0059</td>
<td>0.046</td>
</tr>
<tr>
<td>LCFeCr</td>
<td>70.6</td>
<td>0.135</td>
<td>-</td>
<td>-</td>
<td>0.826</td>
<td>-</td>
<td>-</td>
<td>0.057</td>
<td>0.007</td>
<td>0.027</td>
</tr>
<tr>
<td>HCFeCr</td>
<td>69.4</td>
<td>0.25</td>
<td>0.07</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>8.2</td>
<td>0.032</td>
<td>0.023</td>
</tr>
</tbody>
</table>

In addition, two high-silicon non-calcium treated (HSiNC) stainless steel grade were investigated during ladle treatment and continuous casting. An Fe-23Cr-19Ni-3Si steel grade with 0.009% Al (denoted below as a “High Al steel”) has a much higher possibility for nozzle clogging in comparison to an Fe-19Cr-12Ni-2Si-0.003Al steel grade with 0.003% Al (denoted below as a “Low Al steel”). The content of the main elements in these two steel grades is given in Table 2-2. Plant heats (70-75 ton) of both steels were done in a scrap-based steel plant. The main Si alloying of liquid steel was carried out by FeSi addition at the final stage in an AOD converter. Thereafter, the chemical composition of liquid steel was corrected by additions of some amounts of FeSi and other alloys during ladle treatment. Samples of liquid steel were taken from the ladle and tundish during the ladle treatment and casting by using lollipop samplers (12 mm thickness, 35 mm diameter) equipped with an Ar protection, as shown schematically in Fig. 2-1. Furthermore, slag samples were taken by scoop-type samplers at the same times.

Table 2-2. Typical composition of different steel grades (mass%).

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mn</th>
<th>Mg</th>
<th>Al</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAl</td>
<td>0.05</td>
<td>19.00</td>
<td>11.70</td>
<td>1.90</td>
<td>1.15</td>
<td>0.0016</td>
<td>0.003</td>
<td>0.0033</td>
<td>0.022</td>
<td>0.0011</td>
<td>-</td>
</tr>
<tr>
<td>HAl</td>
<td>0.02</td>
<td>23.36</td>
<td>19.16</td>
<td>2.68</td>
<td>1.72</td>
<td>0.0011</td>
<td>0.009</td>
<td>0.0031</td>
<td>0.024</td>
<td>0.0006</td>
<td>-</td>
</tr>
<tr>
<td>PT</td>
<td>0.04</td>
<td>20.00</td>
<td>11.80</td>
<td>1.64</td>
<td>0.92</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>0.023</td>
<td>0.001</td>
<td>0.08</td>
</tr>
<tr>
<td>IH</td>
<td>0.085</td>
<td>21.00</td>
<td>10.90</td>
<td>1.84</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Investigations of clusters were carried out by using REM alloyed (Ce, La, Pr and Nd) stainless steel samples (S30185) taking from a pilot trial (PT, 250 kg) and an industrial heat (IH, 100 t). The typical chemical composition of this steel grade is listed in Table 2-2. It should be pointed out that only the Ce content in REM was given in this table. For PT, a stainless steel charge was melted at 1470 °C in an Al₂O₃ crucible in an induction furnace. Argon was added continuously to the melt surface to prevent reoxidation. A 12/4 mm dual thickness lollipop sample was taken at different holding times (3, 6, 9 and 12 minutes) after a mischmetal addition, as shown schematically in Fig. 2-2 (a). After 10 minutes of holding, the melt was started to be cast. A complete nozzle clogging (a nozzle with a diameter of 5 mm) occurred at about 15 minutes after the mischmetal addition. IH samples were taken from the ladle at 3, 5 and 15 minutes after the mischmetal addition and from the tundish after 12 minutes of casting by using 12 mm lollipop samplers, as shown in Fig. 2-2 (b).

The sample used for statistics analysis was a Fe-10%Ni alloy which was prepared in the laboratory using an induction furnace. More specifically, high purity electrolytic Fe and Ni were melted in an aluminum oxide crucible under an Ar atmosphere. The melt was held for 10 minutes at 1873 K after stirring by a Al₂O₃ rod. The liquid alloy was initially deoxidized with 0.12 mass% Al. After two minutes, it was further deoxidized with 0.02 mass% Ca. During the experiment, samples were taken at one (S1), three (S2) and five (S3) minutes using quartz
tube sampler after a calcium addition. Thereafter, the melt was cooled to 1673 K and water quenched to take ingot sample (S4). The metal specimens (15x10x3 mm) for 2D and 3D investigation were cut out from the central part of a vertical slice of each solidified sample.

2.2 Investigation of inclusions

Electrolytic extraction was applied for 3D investigations of the inclusion characteristics in the ferroalloys and metal samples. The EE of samples was carried out using 10% AA (10 v/v% acetylacetone - 1 w/v% tetramethylammonium chloride - methanol) and 2% TEA (2 v/v% triethanol amine - 1 w/v% tetramethylammonium chloride - methanol) electrolytes. The current density was set to 30-50 mA/cm$^2$ during the EE. The weight of the dissolved samples during EE was 0.08-0.19 g. After extraction, the solution containing inclusions was filtrated through a polycarbonate membrane film filter with an open pore size of 1 or 3 μm. The extracted inclusions were investigated in 3D on a surface of film filters by using scanning electron microscopy (SEM). The size of the spherical inclusions is expressed as the diameter $d_\nu$. In addition, the equivalent size of non-spherical inclusions and clusters $d_{equ}$, was calculated from Eq. (2-1):

$$d_{equ} = \frac{L_{max} + W_{max}}{2}$$

(2-1)

where $L_{max}$ and $W_{max}$ is the maximum length and width of the inclusion, respectively.

The number of inclusions per unit volume ($N_\nu$) was calculated as follows:

$$N_\nu = \frac{n \cdot A_f}{A_{obs}} \cdot \frac{\rho_m}{W_{dis}}$$

(2-2)

where $n$ is the number of inclusions in the appropriate size interval, $A_f$ is the area of the film filter (1396 mm$^2$), $A_{obs}$ is the total observed area, $\rho_m$ is the density of the sample matrix and $W_{dis}$ is the dissolved weight of the samples during extraction.

The composition of inclusions was determined by energy dispersive spectroscopy (EDS). The total observed area of film filter for different samples was varied from 0.22 to 3.38 mm$^2$. Furthermore, conventional 2D observations of inclusions on polished cross sections of samples were also conducted for the comparison with the results obtained from 3D investigations.

2.3 Statistics of extreme values (SEV)

The statistical of extreme values in the present work was performed according to Murakami’s method [42] and using the ASTM E2283-03 standard. [43] The size of each
spherical inclusions, $\sqrt{\text{area}_{\text{max}}}$, was calculated by Eq. (2-3). Then, the size of the inclusions was ranked in an increasing order as follows, $\sqrt{\text{area}_{\text{max}1}} \leq \sqrt{\text{area}_{\text{max}2}} \leq \sqrt{\text{area}_{\text{max}k}} \leq \cdots \leq \sqrt{\text{area}_{\text{max}n}}$ $(1 \leq k \leq n)$. The reduced variate, $y_k$, of each size data was calculated using Eq. (2-4).

$$\sqrt{\text{area}_{\text{max}}} = \sqrt{\pi \times \frac{d_{\text{max}}}{2}}$$

(2-3)

$$y_k = -\ln(-\ln\left(\frac{k}{n+1}\right))$$

(2-4)

where $d_{\text{max}}$ is the maximum diameter of the spherical inclusion in 2D and 3D observations, $n$ is the number of measurements.

The largest inclusion size, $L_{\text{max}}$, in a reference weight of a steel specimen, $W_{\text{ref}}$, could be predicted by using the reduced variate, $y$, determined by the return period, $T$, as follows:

$$y = -\ln(-\ln\left(\frac{T-1}{T}\right))$$

(2-5)

$$T = \frac{W_{\text{ref}}}{W_0}$$

(2-6)

where $W_0$ are the unit weight of SEV. In the 2D determinations, it was calculated by the following equation: [51]

$$W_{2D} = h_0 \cdot A_{2D} \cdot \rho_m$$

(2-7)

$$h_0 = \frac{1}{n} \sum \sqrt{\text{area}_{\text{max}}}$$

(2-8)

In the 3D determinations, it was given in Eq. (2-9).

$$W_{3D} = \frac{A_{3D}}{\lambda_f} \cdot W_{\text{dis}}$$

(2-9)

$$L_{\text{max}} = -\delta_{ML} \cdot y + \lambda_{ML}$$

(2-10)

where $h_0$ is the thickness of a metal layer analyzed in the 2D observations, $A_{2D}$ and $A_{3D}$ are the unit area for 2D and 3D and $\rho_m$ is the density of the Fe-10%Ni alloy. Furthermore, $\delta_{ML}$ and $\lambda_{ML}$ are the scale and location parameters of the extreme value distribution (EVD) function. The maximum likelihood method was used to estimate the values of these parameters.

The result of the extreme value determination is presented with a 95% confidence interval (CI), and the standard error (SE) for it is based on a 99.9% probability. This may be expressed as follows:

$$95\% \ CI = \pm 2 \ SE$$

(2-11)

$$SE = \delta_{ML} \cdot \sqrt{(1.109 + 0.514 \cdot y + 0.608 \cdot y^2)/n}$$

(2-12)
3. Results and Discussion

3.1 Inclusions in Ferroalloys

3.1.1 Inclusions in FeTi alloy

The typical photos, size ranges, composition and percentage of the inclusions observed after EE of FeTi alloy are shown in Table 3-1. There are two types of intermetallic phases in ferrotitanium, a faceted Type FeTi A and a flower-like Type FeTi B. The size range of the Type FeTi A inclusions is much larger than that for Type FeTi B inclusions. However, the percentage of Type FeTi B inclusions is about eight times larger than the Type FeTi A inclusions. The Ti, Fe contents and the ratios are different in these two types of intermetallic phases. The element N is present in both types of intermetallic phases, as can be seen from the elemental mapping in Fig. 3-1. However, the light element, such as C and N cannot be analyzed in an accurate manner by EDS. The average value of N in these two types of inclusions is 0.008 and 0.1 mass% respectively. Therefore, it is not possible to say that the titanium carbides and nitrides, which have high melting points, exist or not in this case.

The Type FeTi C inclusions are almost pure Ti, with small amounts of O, Al and Fe. They also contain some N as can be seen from Fig. 3-1. However, the distribution of N is not homogenous. Also, the Type FeTi D inclusions mostly consist of REM (Ce, La, Pr, Nd) oxides. These oxides easily form clusters, which may cause nozzle clogging [39-41]. According to the literature review, no REM oxides have been observed in FeTi. The existence of the REM oxides might due to the raw material. The particle size distribution of this type of inclusion is shown in Fig. 3-2.

Table 3-1. Classification of inclusions in FeTi alloys

<table>
<thead>
<tr>
<th>Type</th>
<th>Type FeTi A</th>
<th>Type FeTi B</th>
<th>Type FeTi C</th>
<th>Type FeTi D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="image" alt="Type FeTi A" /></td>
<td><img src="image" alt="Type FeTi B" /></td>
<td><img src="image" alt="Type FeTi C" /></td>
<td><img src="image" alt="Type FeTi D" /></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>6-25</td>
<td>1-8</td>
<td>3-15</td>
<td>1-21</td>
</tr>
<tr>
<td>Composition</td>
<td>Ti-Fe</td>
<td>Ti-Fe</td>
<td>Ti-Fe-Al-O</td>
<td>REM-Si-Cr-Al-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>9</td>
<td>75</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

According to the results reported by Pande [4, 8], the quantity of inclusions in a FeTi35 alloy is much higher than that in a FeTi70 alloy. Moreover, the size range of inclusions in a FeTi35 alloy is wider because of the different manufacturing routes for these alloys. This is in
good agreement with the result reported by Kaushik [7], who showed that the sliver index in an FeTi33 alloy is higher than in an FeTi70 alloy. In addition, Al2O3 and SiO2 were observed in a FeTi70 alloy [4, 7]. However, REM oxides were detected instead of Al2O3 and SiO2 in the FeTi70 alloy in this study. The reason for this might be that the REM metal has a higher affinity to oxygen compared to aluminum and silicon.

![Type FeTi A](image)
![Type FeTi B](image)
![Type FeTi C](image)

**Fig. 3-1.** Elemental mappings of different inclusion types in FeTi alloys

![Particle size distribution](image)

**Fig. 3-2.** Particle size distribution of Type FeTi D inclusions

According to the Fe-Ti-Al phase diagram [52], the melting points of Type FeTi A, Type FeTi B and Type FeTi C inclusions are about 1200 °C, 1300 °C, 1600 °C, respectively. The
melting points are lower or approximately equal to a steel temperature of 1600 °C. Therefore, it is assumed that these intermetallic phases will dissolve after an addition to the liquid steel.

3.1.2 Inclusions in FeNb alloy

The typical inclusions in a FeNb alloy are shown in Table 3-2. As can be seen, Type FeNb A inclusions are mostly made up of pure aluminum oxides. Also, inclusions are present as single inclusions (Type FeNb A (I)) as well as clusters (Type FeNb A (II)). The presence of Al₂O₃ is linked to the aluminothermic reduction of FeNb. It is well known that Al₂O₃ inclusions can significantly affect the mechanical and fatigue properties and also cause nozzle clogging problems during casting [2].

Type FeNb B inclusions are Ti-Nb-S-O inclusions. The sulfur content in a FeNb alloy is 0.05 mass%. This is the highest value among the ferroalloys that have been analyzed in this study. According to the elemental mapping of this type of inclusion in Fig. 3-3, the distribution of Ti, Nb, S and O is homogenous, which means that only one phase exists in this type of inclusions. However, up to now, only the Ti-Nb system [53] and the Ti-S system [54] were studied. Therefore, the physical and chemical characteristic of the Ti-Nb-S-O system is not known. However, no matter if they will dissolve or not after the addition to the liquid steel, they will definitely be deleterious to the cleanliness of the steel due to the presence of S and O. The particle size distribution of these two type inclusions is shown in Fig. 3-4.

Table 3-2. Classification of inclusions in FeNb alloys

<table>
<thead>
<tr>
<th>Type</th>
<th>Type FeNb A (I)</th>
<th>Type FeNb A (II)</th>
<th>Type FeNb B</th>
<th>Type FeNb C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="image1" alt="Typical photo" /></td>
<td><img src="image2" alt="Typical photo" /></td>
<td><img src="image3" alt="Typical photo" /></td>
<td><img src="image4" alt="Typical photo" /></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>2-12</td>
<td>5-27</td>
<td>1-14</td>
<td>2-21</td>
</tr>
<tr>
<td>Composition</td>
<td>Al-O</td>
<td>Al-O</td>
<td>Ti-Nb-S-O</td>
<td>Nb-Ti-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>20</td>
<td>4</td>
<td>17</td>
<td>59</td>
</tr>
</tbody>
</table>

The Type FeNb C inclusion is almost a pure Nb phase. The melting point of the Type FeNb C phase is 2400 °C [55] if only the Nb and Ti are considered. In addition, the Type FeNb C inclusions represent the majority (59%) of the inclusions in a FeNb alloy. This is followed by the Type FeNb A (I) and Type FeNb B inclusion. Finally, a Type FeNb A (II) inclusion is present, which is an Al₂O₃ cluster. The size range of the Type FeNb A (II) and Type FeNb C inclusions is wider than that for Type FeNb A (I) and Type FeNb B inclusions.
Fig. 3-3. Elemental mapping of Type FeNb B inclusions in FeNb alloys

Fig. 3-4. Particle size distribution of Type FeNb A and Type FeNb B inclusions

No inclusions could be observed in a FeNb alloy in Pande’s study after the dissolution when using strong acids [4]. However, the characteristics of inclusions in FeNb, such as the number, morphology, size and composition can accurately be investigated on the surface of a film filter after electrolytic extraction. This implies that the electrolytic extraction method is more suitable than the acids dissolution method for extraction of inclusions present in FeNb alloys.

3.1.3 Inclusions in FeSi alloy

Typical inclusions and the information about them in FeSi alloy are shown in Table 3-3. Type FeSi A inclusions are made up by REM oxides with some amounts of Si, Fe and Ti. Ce oxides have also been observed by other researchers in FeSi alloys. [5] The particle size distribution of this type inclusion is shown in Fig. 3-5. Type FeSi B inclusions are CaSi intermetallic inclusions that contain small amounts of Al and Ni. The melting point of the CaSi intermetallic phase is about 1300 °C [56] if only the Ca and Si contents are considered. Type FeSi C inclusions represent as a Fe-Si-Ti-Al intermetallic phase. The phase diagram of Fe-Si-Ti-Al system calculated by the Therm-Calc software is shown in Fig. 3-6. As can be seen, the melting point of Type FeSi C inclusions is about 1460 °C. The Type FeSi B and
Type FeSi C intermetallic compounds were also detected by Wijk. [9] Also, the Type FeSi D inclusions contain almost only pure Si, but with small amounts of O and Al. The melting point of the pure Si phase is about 1400 °C [57]. Overall, the Type FeSi D and Type FeSi A inclusions are the main inclusion present in an FeSi alloy. Moreover, the size range of them is wider than that for Type FeSi B and Type FeSi C inclusions.

Table 3-3. Classification of inclusions in FeSi alloys

<table>
<thead>
<tr>
<th>Type</th>
<th>Type FeSi A</th>
<th>Type FeSi B</th>
<th>Type FeSi C</th>
<th>Type FeSi D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="type_fe_si_a.png" alt="Image" /></td>
<td><img src="type_fe_si_b.png" alt="Image" /></td>
<td><img src="type_fe_si_c.png" alt="Image" /></td>
<td><img src="type_fe_si_d.png" alt="Image" /></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>2-20</td>
<td>5-9</td>
<td>2-10</td>
<td>1-26</td>
</tr>
<tr>
<td>Composition</td>
<td>REM-Si-Fe-Ti-O</td>
<td>Ca-Si-Al-Ni-O</td>
<td>Fe-Si-Ti-Al-O</td>
<td>Si-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>36</td>
<td>4</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

Fig. 3-5. Particle size distribution of Type FeSi A inclusions

It is reported that Al in FeSi alloy enhances the formation of MgO-Al₂O₃ spinel inclusion, and that Ca in FeSi alloy has an effect to prevent it [11]. However, Ca may react with aluminum and form calcium aluminates that lead to nozzle clogging [58]. Therefore, the Al and Ca contents in FeSi alloys should be accurately determined before being added to the steel. It should be mentioned that the acid extraction is not suitable to use for an FeSi alloy due to that Si is not directly soluble in acids [4]. Therefore, the electrolytic extraction method is more appropriate to use for FeSi alloys.
Fig. 3-6. Phase diagram of Fe-Si-Ti-Al system

3.1.4 Inclusions in SiMn alloy

The characteristics of inclusions in SiMn alloy are shown in Table 3-4. As can be seen, Type SiMn A inclusions contain REM oxides with some amounts of Si, Mn, and Mg, Al. Moreover, Type SiMn B inclusions are almost pure Al₂O₃ inclusions. Type SiMn C inclusions are mostly silicon oxide with some amounts of Ca and Mg. Type SiMn D inclusions are also silicon oxide, but with small Mn contents. Type SiMn E inclusions are Mn-Si intermetallic phases with small Fe contents. The melting point of a Type SiMn E inclusion is 1250 °C, if only Mn and Si are considered [59]. Overall, REM oxides are the main type of inclusions found in SiMn alloys. This is followed by Type SiMn E intermetallic phases. The particle size distribution of Type SiMn A inclusions is shown in Fig. 3-7.

Table 3-4. Classification of inclusions in SiMn alloys

<table>
<thead>
<tr>
<th>Type</th>
<th>Type SiMn A</th>
<th>Type SiMn B</th>
<th>Type SiMn C</th>
<th>Type SiMn D</th>
<th>Type SiMn E</th>
</tr>
</thead>
<tbody>
<tr>
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<td><img src="image1" alt="Typical photo" /></td>
<td><img src="image2" alt="Typical photo" /></td>
<td><img src="image3" alt="Typical photo" /></td>
<td><img src="image4" alt="Typical photo" /></td>
<td><img src="image5" alt="Typical photo" /></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>1-26</td>
<td>2-5</td>
<td>6-12</td>
<td>1-8</td>
<td>3-16</td>
</tr>
<tr>
<td>Composition</td>
<td>REM-Si-Mn-O</td>
<td>Al-O</td>
<td>Si-Ca-Mg-O</td>
<td>Si-Mn-O</td>
<td>Mn-Si-Fe-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>56</td>
<td>2</td>
<td>6</td>
<td>8</td>
<td>28</td>
</tr>
</tbody>
</table>
3.1.5 Inclusions in LCFeCr alloy

LCFeCr alloys are primarily used for late additions during the secondary steel making process. Therefore, the inclusion types in LCFeCr alloys should specifically be known to enable possible counteractions to improve the steel cleanliness. Typical photos, size ranges and percentage of the inclusions observed after EE of LCFeCr alloy are shown in Table 3-5. Overall, two types of oxide inclusions exist in LCFeCr alloys, named Type LC A and Type LC B. According to the morphology, the Type LC A inclusions could further be divided into two groups: spherical - Type LC A (I), and rod-like with or without round tips - Type LC A (II). The main composition of Type LC A inclusions is silicon-chromium oxides. The presence of SiO₂ might due to the ferroalloy manufacturing route, which is a silicothermic reduction of a LCFeCr alloy. The composition of Type LC B inclusions is mostly chromium oxides. It is assumed that chromium oxides have no large effect on the cleanliness of steel when added in an EAF or an AOD, due to the reduction of chromium from the slag afterwards. However, if it is used for late additions in a ladle just before casting, an addition will be deleterious to the steel quality.

The Type LC C inclusions are ferrochromium intermetallic particles. There are two types of ferrochromium intermetallic phases according to the morphology. The average N content analyzed by EDS in Type LC C (II) inclusions is a little bit higher (about 3%) than that in Type LC C (I) inclusions. A Type LC D inclusion represents a complex inclusion, which inner part consists of a Type LC A inclusion and the outer part consists of a Type LC C intermetallic phase. The size range of the Type LC C inclusions (3-77 μm) is quite wider than
the others. This is followed by the Type LC D inclusions and finally the Type LC A and Type LC B inclusions. It can be noted that the inclusions in FeCr alloy are highly dependent on the C content, due to the different production processes of LC and HCFeCr alloys. The sulphur content in a LCFeCr alloy is quite lower than that in a HCFeCr alloy. Therefore, no sulfides inclusions were observed in the LCFeCr grade selected for the present study.

Table 3-5. Classification of inclusions in LCFeCr alloy

<table>
<thead>
<tr>
<th>Type</th>
<th>Type LC A (I)</th>
<th>Type LC A (II)</th>
<th>Type LC B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Size range (µm)</td>
<td>2-16</td>
<td>4-36</td>
<td>6-30</td>
</tr>
<tr>
<td>Composition</td>
<td>Si-Cr-Mn-O-N</td>
<td>Si-Cr-Mn-O-N</td>
<td>Cr-Fe-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>26</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Type LC C (I)</th>
<th>Type LC C (II)</th>
<th>Type LC D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Size range (µm)</td>
<td>3-77</td>
<td>20-50</td>
<td>8-45</td>
</tr>
<tr>
<td>Composition</td>
<td>Cr-Fe-Mn-O-N</td>
<td>Cr-Fe-Mn-O-N</td>
<td>Cr-Si-Fe-Mn-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>51</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Fig. 3-8. Elemental mapping of Type LC A inclusions

It is clear from the results that two phases exist in the Type LC A inclusions. The elemental mapping of the surface layer of this type of inclusions after EE is shown in Fig. 3-8. As can be seen, the Si content in the grey part is higher than that in the bright part. However, the Cr and Mn contents in the bright part are higher than that in the grey part. Also, some amounts of N, Al and Fe are present in both phases. It is interesting to note that two different
morphologies of Type LC A inclusions exist. To clarify the reason for this phenomenon, the composition of the two typical Type LC A inclusions and the mole fraction of SiO$_2$ in the different zones (analyzed in 3D) is shown in **Fig. 3-9**. The mole fraction value represents the average data for 20 points in each zone. As can be seen, the average mole fraction value of zone A is similar to that in zone C. In addition, the value of zone B is similar to that for zone D. According to the CrO-SiO$_2$ phase diagram for a Cr equilibrium, [60] the melting points of zone A, zone B, zone C and zone D are around 1770 °C, 1540 °C, 1840 °C and 1670 °C, respectively. The different morphologies of Type LC A (I) and Type LC A (II) inclusions might due to that they are formed at different degrees of supersaturation. [61]

<table>
<thead>
<tr>
<th>Position</th>
<th>Zone A</th>
<th>Zone B</th>
<th>Zone C</th>
<th>Zone D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction (SiO$_2$/CrO)</td>
<td>0.65</td>
<td>0.48</td>
<td>0.76</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Fig. 3-9.** Typical Type LC A inclusions found in LCFeCr alloys, including the mole fraction of SiO$_2$ in the different zones

According to the different phases found in Type LC D inclusions, the solidification path is expected to be the following: an initial solidification of Type LC A inclusions which is followed be a solidification of a Type LC C intermetallic phase. The melting point of the Type LC C intermetallic phase is about 1800 °C, if only the Cr and Fe compositions are taken into account. [62] It has been reported that the Cr and Mn contents can increase the solubility of N in liquid and solid FeCr alloys. [52] Furthermore, that the presence of N could lower the melting point of an Fe-Cr intermetallic phase. The phase diagram of an Fe-Cr-Mn-N system calculated by Thermo-Calc software is shown in **Fig. 3-10**. As can be seen, the melting points of the Type LC C inclusions ranges from 1560 °C to 1800 °C as the N content varies between 0 to 6 mass%. It should be mentioned that the O content in the metallic is not considered when calculating the melting point.
Fig. 3-10. Phase diagram of a Fe-Cr-Mn-N system as a function of the N content

The majority (52%) of the inclusions in the LCFeCr alloy used in this study is Type LC C inclusions. This is followed by Type LC A inclusions and finally Type LC D and Type LC B inclusions. The particle size distributions of Type LC A and Type LC C inclusions are shown in Fig. 3-11. The number of Type LC A (I) inclusions per cubic millimeters is much larger than that for Type LC A (II) inclusions in the size range of 0-10 µm. However, the sizes of mostly Type LC A (II) inclusions is larger than those of Type LC A (I) inclusions. In addition, the number and size of Type LC C intermetallic inclusions is dramatically larger than that of Type LC A inclusions.

Fig. 3-11. Particle size distributions of (a) Type LC A and (b) Type LC C inclusions

3.1.6 Inclusions in HCFeCr alloy

The demand for a lower cost HCFeCr alloys has increased rapidly owing to the introduction of modern stainless steelmaking practices. For example, it is now possible to
remove large amounts of carbon from liquid steel without serious losses of chromium in processes such as the AOD converter. The characteristics of inclusions found in HCFeCr are shown in Table 3-6. One type of inclusions found in the alloys is Type HC A inclusions, which consist of Cr-Mn-S inclusions that contain some amounts of O and Fe. The Type HC A inclusions can further be divided into three subgroups based on the morphology: globular Type HC A (I), rodlike Type HC A (II) and irregular Type HC A (III). In addition, the Type HC A inclusion have a composition close to the stoichiometric phase CrS·2MnS. Based on the CrS-MnS phase diagram, [63] the melting point of a Type HC A inclusion is around 1450 °C.

Table 3-6. Classification of inclusions in a HCFeCr alloy

<table>
<thead>
<tr>
<th>Type</th>
<th>Type HC A (I)</th>
<th>Type HC A (II)</th>
<th>Type HC A (III)</th>
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</tr>
<tr>
<td>Size range (μm)</td>
<td>2-5</td>
<td>4-10</td>
<td>6-14</td>
</tr>
<tr>
<td>Composition</td>
<td>Cr-Mn-S-O</td>
<td>Cr-Mn-S-O</td>
<td>Cr-Mn-S-O</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>38</td>
<td>12</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>Type HC B</th>
<th>Type HC C</th>
<th>Type HC D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical photo</td>
<td><img src="image4" alt="Typical photo" /></td>
<td><img src="image5" alt="Typical photo" /></td>
<td><img src="image6" alt="Typical photo" /></td>
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<tr>
<td>Size range (μm)</td>
<td>2-14</td>
<td>3-28</td>
<td>2-26</td>
</tr>
<tr>
<td>Composition</td>
<td>Cr-C-N</td>
<td>Si-Al-Ca-Mg-O</td>
<td>Ca-O-P</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>10</td>
<td>6</td>
<td>27</td>
</tr>
</tbody>
</table>

The HCFeCr alloys also contain Type HC B inclusions, which is a chromium carbonitride inclusion. The phase diagram of a Cr-C-N system is limited at high temperatures and in the narrow compositions range of chromium, carbon and nitrogen. [64] However, the chromium carbonitrides are known as being high-temperature compounds. Therefore, it is assumed that the melting point of the Type HC B inclusion is higher than that for the steel temperature, 1600 °C. Another inclusion type is the Type HC C inclusions, which consist of Si-Al-Ca-Mg-O. These inclusions most likely originate from the slag which is created during the HCFeCr alloy production. The melting point of them is around 1300 °C. [65] Finally, some other types of inclusions might be found in HCFeCr alloys. The Type HC D inclusions consist of Ca-O-P.
The melting point of them is also around 1300 °C. [65] The size range of Type HC C and Type HC D inclusions is wider than those of Type HC A and Type HC B inclusions.

**Fig. 3-12.** Elemental mapping of Type E inclusions in HCFeCr alloy

The elemental mapping of the different morphologies of Type HC A inclusions is shown in **Fig. 3-12.** As can be seen, the distribution of Cr, Mn and S is almost homogeneous in all three types of Type HC A inclusions. In addition, no measureable composition differences between these three types of Type HC A inclusions can be found from the EDS composition analyses. These three types Cr-Mn-S inclusions morphologies were also observed by K. Oikawa et al. [63] It is concluded that the globular Type HC A (I) inclusions are formed through the metastable monotectic reaction. Furthermore, that the rodlike Type HC A (II) inclusion is the product of a stable eutectic reaction and irregular Type HC A (III) is the result of a stable monotectic reaction.

**Fig. 3-13.** Particle size distribution of Type HC A and Type HC D inclusions in HCFeCr alloy

Type HC A Cr-Mn-S inclusions are the main inclusion type that can be found. In addition, a globular Type HC A (I) inclusion type is the most common Type HC A inclusion. This is followed by the Type HC D inclusion type and the Type HC B and Type HC C inclusion types. The particle size distribution of the Type HC A and Type HC D inclusions are presented in **Fig. 3-13.** The number of Type HC A inclusion per cubic millimeter is larger than for the Type HC D inclusions in the small size range (< 6 µm). However, the number of
Type HC D inclusions is larger than that of the Type HC A inclusions in the larger size range (6-22 µm). It is probable that the whole volume of Type HC D inclusion is larger than that of the Type HC A inclusion.

3.1.7 Soluble impurities

According to the future demands on the ferroalloys from the stand point of the customers in the steel industry, it is imperative that more comprehensive investigations of the dissolved element contents in the ferroalloys will be needed. [1] The ferroalloy quality depends on the specific use. However, in general the oxygen, carbon, sulphur, phosphorous and nitrogen contents are important to know. The total oxygen content does not only reflect the total amount of oxides inclusions, but it also represents the mean diameter of the inclusions in ferroalloys. [12] It is reported [12] that a similar trend was observed between the C content and the amount and mean diameter of inclusions, just in an inversely proportionality. Also, sulphur and phosphor are known to have a deleterious effect on the mechanical properties of steels.

Strong deoxidizers like Al, Ca, Mg, Ti, and Ce have a large effect on the inclusion formation in the steel. These elements may react with the oxides that exist in the liquid steel after the addition of a ferroalloy to form complex inclusions. For example, the TiO$_2$ inclusions change to Al-Ti-O complex inclusions after the addition of Al to the steel. [66] Another problem is that large size inclusions may be formed through the growth of a new layer on the surface of the existing inclusions. For example, large size REM oxides with hollow holes were observed after the addition of REM alloys to the liquid steel. [67] A very small amount of Al in FeSi enables the formation of MgO·Al$_2$O$_3$ spinel inclusions in molten steel. Also, calcium in the FeSi alloy may form Ca-aluminates that lead to severe clogging problems during casting. Furthermore, Ti in FeSi will prevent an effective grain growth due to the precipitation of TiO$_2$ at the grain boundaries. Ti will also react with C and N and form hard carbon-nitrides, which will negatively affect the material properties of the final steel product.

Trace elements such as Pb, Sn, Sb, Zn and Bi should also be investigated more in-depth. The use of ferroalloys with lower contents of these tracing elements reduce the bad quality steel from 30.8 to 4%. [6] Therefore, the exact quantity of these non-metal impurities, strong deoxidizers and trace elements in the ferroalloy should be known before its introduction to the liquid steel. This is especially important if additions are needed during the final stage of the
secondary refining, since there is only a short time to promote inclusion separation by optimized stirring.

3.1.8 Insoluble impurities

The dissolution kinetics of ferroalloys in the steelmaking process was studied. [68] The dissolution time for 10-30 mm size ferroalloys is in a range from 2s to 160s for FeSi, SiMn and FeMn at 1873K. However, the dissolution of the insoluble impurities in the ferroalloys is not mentioned.

3.1.8.1 Non-metallic inclusions

The inclusions in ferroalloys may undergo some physical or chemical change after the addition to the liquid steel. Depending on the melting point and the thermodynamic stability of the specific inclusions at the steelmaking temperature and composition, the inclusions will dissolve or stay solid. If the inclusions dissolve, a local high oxygen or sulfur content may lead to a formation of new inclusions. If the inclusions stay solid, the first possibility is that strong deoxidants that dissolved in the liquid steel may react with them under the formation of complex inclusion. The second possibility is that these solid inclusions may act as nucleation sites if the sizes are small. The third possibility is that these solid inclusions collide with each other and form clusters, which have a bad effect on the casting process as well as on the final product.

The non-metallic inclusions observed in this study are the REM oxides in FeTi, FeSi and SiMn, Al₂O₃ and Ti-Nb-S-O in FeNb, silicon oxides in SiMn, Cr-O and Si-Cr-O inclusions in LCFeCr and all the inclusion types in HCFeCr. The REM oxides and Al₂O₃ inclusions probably remain solid and form clusters. These two types of clusters are known to be responsible for the nozzle clogging and to cause decreased mechanical properties in the final product. The Cr-O inclusion has no harmful effect on the cleaness of steel, except for at a late addition just before casting. However, the Si-Cr-O inclusions should be paid special attention since they have a phase that has a melting point higher than 1600 °C. Also, silicon oxides might dissolve in steel and thereafter form new inclusions. Furthermore, they might react with strong deoxidizers to form complex or large size inclusions. Overall, it is seems that further studies of the Ti-Nb-S-O inclusions are needed in the future.

In HCFeCr alloys, the Cr-Mn-S-O, Si-Al-Ca-Mg-O and Ca-O-P inclusions will dissolve after an addition to the liquid steel. The sulfur and phosphor are known to be deleterious
elements with respect to the mechanical properties of the steel. Therefore, HCFeCr alloys should be added earlier in the steel making process, such as before the desulfurization and dephosphorization steps. The known sulfide and phosphide compound are also beneficial for the chosen of the desulfurization and dephosphorization reagents and method in the ferrochromium industry. The Si-Al-Ca-Mg-O inclusions which originate from slag and the high melting point Cr-C-N inclusions might go through some physical and/or chemical changes depending on the specific steelmaking conditions.

3.1.8.2 Metallic inclusions

The intermetallic phases observed in this study are a Ti-Fe phase in FeTi alloys, Ca-Si and Fe-Si-Ti phases in FeSi alloys, a Mn-Si phase in SiMn alloys and a Cr-Fe phase in LCFeCr alloys. Furthermore, the mostly pure single metallic phase is pure Ti in FeTi, Nb in FeNb, and Si in FeSi. According to the phase diagram of these metallic phases, the majority of the melting points of them are lower than the steelmaking temperature 1600 °C, with the exception of the Cr-Fe phase in LCFeCr alloys and the almost pure Nb phase in FeNb alloys. Therefore, the majority of the metallic phases are assumed to dissolve after the addition to steel. The effect of an insoluble metallic phase that the melting points lower than 1600 °C on the cleanliness of the steel is that they can be treated as soluble elements. Although the size range of the metallic inclusions in ferroalloys in this study is large and the proportion of the number percentage is tremendous, no further investigation was conducted in this study. However, the metallic inclusions which have a melting point that is higher than the steelmaking temperature should be studied more in depth in the future. In addition, the solubility of them in steel for steelmaking conditions should also be considered.

By using the ferroalloys with known inclusion information, it will help the steelmakers to optimize the inclusion characteristics during the steelmaking process so that the desired material properties can be reached.

3.2 Inclusions in high-silicon non-calcium treated (HSiNC) stainless steels

3.2.1 Morphology of inclusions

The non-metallic inclusions in all steel samples from the Low Al (LAl) and High Al steel (HAl) were classified into three different groups based on the morphology: Spherical (SP), irregular and regular (IR) and clusters (CL). The typical SEM images, size range and composition of different types of inclusions are shown in Table 3-7. It can be seen that the
size ranges of SP and IR inclusions in the Low Al steel is significantly wider (1.0-10.5 μm) than those in the High Al steel (1.0-5.5 μm). However, the size range for clusters in the High Al steel is slightly wider than that in the Low Al steel. It should be mentioned that the composition of inclusions are listed in a descending order based on the oxides content.

**Table 3-7. Morphology of inclusions in steel samples from Low Al (LAl) and High Al steel (HAl).**

<table>
<thead>
<tr>
<th>Steel</th>
<th>Inclusion shape</th>
<th>Spherical (SP)</th>
<th>Irregular and Regular (IR)</th>
<th>Cluster (CL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAl</td>
<td>Typical photo</td>
<td><img src="image1.png" alt="Image" /> 1μm</td>
<td><img src="image2.png" alt="Image" /> 1μm</td>
<td><img src="image3.png" alt="Image" /> 1μm</td>
</tr>
<tr>
<td></td>
<td>Size range (μm)</td>
<td>1.0 - 10.0</td>
<td>2.5 - 10.5</td>
<td>4.5 - 10.0</td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>SiO$_2$-MgO-Al$_2$O$_3$-CaO</td>
<td>MgO-Al$_2$O$_3$-SiO$_2$-CaO</td>
<td>MgO-Al$_2$O$_3$-SiO$_2$-CaO</td>
</tr>
<tr>
<td>HAl</td>
<td>Typical photo</td>
<td><img src="image4.png" alt="Image" /> 1μm</td>
<td><img src="image5.png" alt="Image" /> 1μm</td>
<td><img src="image6.png" alt="Image" /> 1μm</td>
</tr>
<tr>
<td></td>
<td>Size range (μm)</td>
<td>1.0 - 4.5</td>
<td>1.5 - 5.5</td>
<td>3.0 - 11.5</td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>Al$_2$O$_3$-SiO$_2$-MgO-CaO</td>
<td>Al$_2$O$_3$-MgO-SiO$_2$-CaO</td>
<td>Al$_2$O$_3$-MgO-SiO$_2$-CaO</td>
</tr>
</tbody>
</table>

It was found that the morphology of inclusions in Low Al and High Al steel were significantly changed during ladle treatment and casting. **Fig. 3-14** shows the frequency of different type inclusions in different steel samples. As can be seen in Fig. 3-14 (a), the frequency of clusters and IR inclusions in the Low Al steel decreases drastically during ladle treatment and casting. Specifically, from 16% CL and 40% IR in the L1 sample to 1-2% CL and 1-2% IR in the T1 and T2 samples. The frequency of spherical inclusions in this steel grade increased and reached values of 96-98% in the cast steel (samples T1 and T2). This fact can be explained by the removal of some clusters and by a gradual transformation of IR inclusions and some clusters to spherical inclusions. The spheroidizing of IR inclusions and clusters indicates a change in the inclusion composition (wholly or partially on the surface), which corresponds to the composition of a liquid phase at the given temperature range. A formation of a new liquid oxide layer on the surface of the existing cluster and IR solid inclusions can completely change the morphology and behavior of these inclusions regarding
clogging problems during casting. The composition of inclusions with different morphologies will be discussed below.

![Graph](image1.png)

**Fig. 3-14.** Relationship between morphology of inclusions and sampling moment during ladle treatment and casting from (a) a Low Al and (b) a High Al steel.

As can be seen in Fig. 3-14 (b), the frequency of clusters in the steel samples of the High Al steel tends to increase from 3% (sample L1) to 15% (sample T2) during ladle treatment and casting. The frequency of IR inclusions decreases from 24% to 12%. However, the frequency of spherical inclusions in steel samples is almost the same during all the times of ladle treatment and casting (73-76%). Based on the obtained results, it can be assumed that the clusters in the High Al steel are formed from IR inclusions, which reached a maximum frequency in sample T2. Therefore, it was concluded that the clusters and IR inclusions are responsible for nozzle clogging during casting of the High Al steel.

![Graph](image2.png)

**Fig. 3-15.** Relationship between morphology and size of inclusions and clusters in steel samples from (a) a Low Al and (b) a High Al steel.
The frequency of different type of inclusions in Low Al and High Al steel as a function of size is shown in Fig. 3-15. It can be seen that most inclusions in the range of $d_V \geq 4 \, \mu m$ are spherical (50%) and irregular (31%) inclusions in Low Al steel. Only 19% of the observed inclusions in this size range correspond to clusters. Furthermore, the frequency of IR inclusions and clusters decreases drastically during ladle treatment and casting of the Low Al steel, as was shown in Fig. 3-14. However, the large size clusters (with $d_V \geq 4 \, \mu m$) are dominant (80%) in the High Al steel samples. The frequency of IR and SP inclusions in this size range reaches only 15 and 5%, respectively. Moreover, the inclusions in the range of $d_V$ from 2 to 4 $\mu m$ in this steel are mostly IR inclusions (45%) and clusters (35%). Therefore, the large size clusters and IR inclusions in the High Al steel can be considered as the most possible causes for nozzle clogging during casting of this steel grade.

3.2.2 Composition of inclusions

The compositions of different inclusions and clusters in steel samples were determined from 2D (analysis of central zone of inclusion on the SEM photos and mapping of distribution of the main elements in inclusions founded on a polished surface of steel sample) and 3D (analysis of surface layer of inclusions on a film filter after electrolytic extraction) methods.

A distribution of the main elements in different inclusions on the surface of steel sample obtained by EDS mapping is shown in Table 3-8. It was found that the spherical inclusions in the samples of a Low Al steel consist of homogeneous (SP1) and heterogeneous (SP2) inclusions. All elements (such as Ca, Si, Mg, Al and O) in SP1 inclusions are distributed almost homogeneously. The SP2 inclusions consist of a solid MgO phase and a CaO-SiO$_2$-Al$_2$O$_3$-MgO shell. The irregular and regular (IR) inclusions and clusters (CL) in LAl steel consist of pure MgO or inclusions partially covered by a CaO-SiO$_2$-Al$_2$O$_3$ layer. The spherical inclusions in the samples from the High Al steel are presented mostly by heterogeneous SP2 and SP3 inclusions. The SP2 inclusions have a similar construction as those in LAl steel. The SP3 inclusions contain solid phases of pure MgO and Al$_2$O$_3$, which are covered by a CaO-SiO$_2$-MgO-Al$_2$O$_3$ shell. The IR inclusions and clusters in HAl steel consist of almost homogeneous MgO-Al$_2$O$_3$ inclusions.

The compositions of typical inclusions in Low Al and High Al steel obtained from the 3D investigations after electrolytic extraction are shown schematically using MgO-Al$_2$O$_3$-(SiO$_2$+CaO) diagrams in Fig. 3-16. Data are given for different stages of ladle treatment and casting. The compositions of slags from ladle and tundish for appropriate sampling moments
are also shown in these diagrams by circle-marks with corresponding colors. It can be seen that the compositions of most SP inclusions (blue zones) during all stages are located in the left-side part of these diagrams for both heats. According to the MgO-Al₂O₃-SiO₂-CaO diagrams, [65] most of these spherical inclusions in the LA1 steel correspond to the liquid phase zone at the given steel temperatures (1750-1840 K).

Table 3-8. Distribution of main elements in different inclusions and clusters in steel samples from Low Al (LA1) and High Al steel (HA1).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Shape</th>
<th>Typical photo</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mg</td>
</tr>
<tr>
<td>LAl</td>
<td>SP1</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>SP2</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>CL</td>
<td><img src="image19" alt="Image" /></td>
<td><img src="image20" alt="Image" /></td>
</tr>
<tr>
<td>HA1</td>
<td>SP2</td>
<td><img src="image25" alt="Image" /></td>
<td><img src="image26" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>SP3</td>
<td><img src="image31" alt="Image" /></td>
<td><img src="image32" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td><img src="image37" alt="Image" /></td>
<td><img src="image38" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>CL</td>
<td><img src="image43" alt="Image" /></td>
<td><img src="image44" alt="Image" /></td>
</tr>
</tbody>
</table>

The IR inclusions and clusters in L1 and L2 samples (black and grey zones) of Low Al steel and in all samples of High Al steel located in the zones of solid phases. However, the composition of the surface layer that cover the IR inclusions from L1 to T2 samples in LA1
steel are close to the liquid phase zone of SP inclusions. It should be mentioned that the surface layer compositions of the spherical inclusions (without these located left side of the phase diagram) in the LAI steel and mostly the spherical inclusions in HAI steel located in the solid phase zone. [65] This fact may be explained by the presence of a thin outer layer (< 1 µm) of a liquid phase on the surface of the solid IR inclusions. In this case, the analyzed volume during the 3D investigations of inclusion composition captured some part of the solid phase in the center of the inclusion. The total content of SiO₂+CaO in these inclusions increases significantly during ladle treatment and casting, while the MgO content decreases. However, as shown in Fig. 3-16 (b), the compositions of IR inclusions and clusters in HAI steel samples tend to move to a higher concentration of Al₂O₃ and a lower content of SiO₂+CaO, which correspond to the zone of a solid phase at the given temperature range.

![Fig. 3-16. Compositions of different inclusions obtained from the 3D investigations in (a) a Low Al and (b) a High Al steel.](image)

### 3.2.3 Formation and modification of inclusions

Change of inclusion morphology and compositions during ladle treatment and casting of LAI and HAI steel are schematically illustrated in Table 3-9. The content of each oxide in typical inclusions is represented in this table by the average value as well as the standard deviation (±σ) obtained by the 3D investigations.

As was described above, the samples of LAI steel contain homogeneous (SP1) and heterogeneous (SP2) SP inclusions. The CaO content in SP1 inclusions in the LAI steel significantly decreases from 49±3 mass% in L1 sample to 10±9 mass% in T2 sample, while the SiO₂ content increases from 21±1 mass% in L1 to 49±15 mass% in T2 samples. The
composition of most SP1 inclusions could be found in the liquid phase zone at the given steel temperatures (1750-1840 K). [65] Thus, it can be assumed that these inclusions are involved from liquid slag and then the composition of these slag inclusions was changed due to the reaction with liquid steel.

**Table 3-9.** Morphology and content of main oxides (mass%*) in typical inclusions from Low Al (LAl) and High Al steel (HAl).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Shape, Components</th>
<th>Sample</th>
<th>L1</th>
<th>L2</th>
<th>T1</th>
<th>T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAl</td>
<td>SP1</td>
<td></td>
<td><img src="10%C2%B11" alt="MgO" /></td>
<td><img src="20%C2%B12" alt="Al₂O₃" /></td>
<td><img src="21%C2%B11" alt="SiO₂" /></td>
<td><img src="49%C2%B13" alt="CaO" /></td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td><img src="10%C2%B11" alt="MgO" /></td>
<td><img src="15%C2%B13" alt="MgO" /></td>
<td><img src="17%C2%B17" alt="MgO" /></td>
<td><img src="20%C2%B111" alt="MgO" /></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td><img src="20%C2%B12" alt="Al₂O₃" /></td>
<td><img src="22%C2%B19" alt="Al₂O₃" /></td>
<td><img src="20%C2%B16" alt="Al₂O₃" /></td>
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<tr>
<td></td>
<td>SiO₂</td>
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<td><img src="43%C2%B18" alt="SiO₂" /></td>
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<td></td>
<td>CaO</td>
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<td><img src="30%C2%B13" alt="CaO" /></td>
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</tr>
<tr>
<td></td>
<td>IR-&gt;SP2</td>
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<td><img src="70%C2%B13" alt="MgO" /></td>
<td><img src="40%C2%B17" alt="MgO" /></td>
<td><img src="25%C2%B113" alt="MgO" /></td>
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<td>MgO</td>
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<td><img src="70%C2%B13" alt="MgO" /></td>
<td><img src="40%C2%B17" alt="MgO" /></td>
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<tr>
<td></td>
<td>Al₂O₃</td>
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<td><img src="20%C2%B15" alt="Al₂O₃" /></td>
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<tr>
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<td>SiO₂</td>
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<td><img src="35%C2%B12" alt="SiO₂" /></td>
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<td></td>
<td>CaO</td>
<td><img src="4%C2%B14" alt="CaO" /></td>
<td><img src="6%C2%B11" alt="CaO" /></td>
<td><img src="10%C2%B15" alt="CaO" /></td>
<td><img src="15%C2%B14" alt="CaO" /></td>
<td></td>
</tr>
<tr>
<td>HAl</td>
<td>SP2, SP3</td>
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<td><img src="12%C2%B17" alt="MgO" /></td>
<td><img src="8%C2%B16" alt="MgO" /></td>
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<td><img src="26%C2%B116" alt="SiO₂" /></td>
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*Content of each oxide represented by average and standard deviation values.

Moreover, the L2, T1 and T2 samples of a LAl steel contain the heterogeneous SP2 inclusions. The formation of these spherical inclusions is more interesting for modification of
IR inclusions and clusters to the spherical inclusions. It was found that the composition of most IR inclusions and clusters in the L1 sample of the Low Al steel are almost pure MgO (>80 mass% MgO). However, the content of MgO in these inclusions and clusters decreases drastically during ladle treatment and casting from 87±7 mass% in the L1 sample to 25±13 mass% in the T2 sample. During the same period, the SiO₂ content in the surface layer increases from 5±3 mass% to 40±2 mass%. The contents of Al₂O₃ and CaO in these inclusions also increase on average from 4±3 mass% to 20±5 mass% and from 4±4 mass% to 15±4 mass%, respectively. It may be explained by precipitation of a SiO₂-Al₂O₃-MgO-CaO liquid oxide layer on the surface of a solid MgO phase. If the precipitated liquid phase covered all surface of the solid phase, the IR inclusions and clusters was modified to the heterogeneous spherical inclusions (SP2). As a result, the sum of IR inclusions and clusters in LAl steel drastically decreases from 56 mass% in L1 sample to 2-4 mass% in T1 and T2 samples.

It was also found that a few IR inclusions in the L1 sample of the LAl steel are pure Al₂O₃ (>97 mass% Al₂O₃) inclusions. Their presence in the melt may be explained by some content of Al oxides in added ferroalloys (such as FeSi) and deoxidizers. However, these Al₂O₃ inclusions are only present in the L1 sample. This might be explained by the reaction of the Al₂O₃ inclusions with the liquid steel and by the heterogeneous precipitation in the other inclusions during ladle treatment and casting.

The HAl steel samples contain mostly heterogeneous spherical inclusions (SP2 and SP3). However, the Al₂O₃ content (30-80 mass%) and a scattering of the Al₂O₃ concentrations in these spherical inclusions in the High Al steel are significantly larger compared with those in the Low Al steel. Furthermore, the content of Al₂O₃ in the surface layer of spherical inclusions tends to increase, whereas the content of SiO₂ decreases significantly during ladle treatment and casting. It may be explained by the higher activity of Al in the melt in comparison to the Si activity during formation and modification of inclusions in the HAl steel. The solid cores of SP3 inclusions are not homogenous spinel inclusions as the typical IR inclusions and clusters. The SP3 inclusions often contain separate phases of Al₂O₃ and MgO. Although the composition of most spherical inclusions corresponds to the solid phase, the surface layer that covered the solid core correlates with the liquid zone at a given melt temperature of HAl steel (1711-1761K). As a result, about 75% of the inclusions in the High Al steel have a spherical shape.
The Al₂O₃ content in IR inclusions and clusters in the HAl steel is slightly increased from 66 to 73 mass% on average whereas the contents of SiO₂ and CaO are decreased to 2 mass% during ladle treatment and casting. These inclusions and clusters are mostly MgO-Al₂O₃ spinels. According to the MgO-Al₂O₃-SiO₂-CaO diagram, [65] all IR inclusions and clusters in HAl steel inclusions are solid. 

![Fig. 3-17. Ratio of MgO and Al₂O₃ contents in different type of inclusions and clusters in (a) a Low Al and (b) a High Al steel.](image)

Based on the consideration of contact angle (θ) between Fe-Cr melt and pure MgO or pure Al₂O₃ at 1923 K under an Ar atmosphere, Park and Kim [28] concluded that the Al₂O₃-rich inclusions in the Fe-Cr melt have a larger tendency for cluster formation than the MgO-rich inclusions. Moreover, the Al₂O₃ inclusions are often responsible for nozzle clogging. In this study, an effect of an increased Al₂O₃ concentration in the surface layer of inclusions is considered and discussed regarding the possibilities for cluster formation and nozzle clogging during casting of the given steel grades. The ratio of the MgO to Al₂O₃ contents in the surface layer of inclusion as a function of size is shown in Fig. 3-17. Data are given for typical inclusions and clusters in Low Al and High Al steels. It can be seen that the (mass% MgO)/(mass% Al₂O₃) ratio for most IR inclusions and clusters in the LAl steel is drastically higher than that for spinel inclusions. Therefore, the spinel inclusions were not observed in this steel grade. The IR inclusion that are located below the line for MgO·Al₂O₃ in Fig. 3-17 (a), correspond to the almost pure Al₂O₃ inclusion that is present only in the L1 sample. Almost all IR inclusions and clusters in the High Al steel are spinel inclusions. However, the (mass% MgO)/(mass% Al₂O₃) values for most IR inclusions and clusters in the HAl steel samples are smaller than the value for spinel inclusions. It means that the concentration of Al₂O₃ in the inclusion surface layer exceeds the value that is stoichiometrically required for a
spinel formation to take place. Based on the obtained results, it can be concluded that the surface layer of IR inclusions and clusters in HAl steel was enriched by an Al$_2$O$_3$ oxide. As a result, these IR inclusions can easily be clustered and precipitated on the inner nozzle walls during casting.

Fig. 3-18. Number of IR inclusions and clusters in different size ranges in steel samples of the High Al steel.

A relationship between the number of IR inclusions and clusters, size and sampling time during High Al steel is shown in Fig. 3-18. It can be seen that the number of smaller size spinel inclusions and clusters (< 2 µm) decreases significantly during ladle treatment due to the clustering. As a result, the numbers of larger size spinel IR inclusions and clusters (2-4 and > 4 µm) increases during all times of ladle treatment and casting. However, it should be noted that the number of clusters (> 4 µm) increases significantly during casting when the Al$_2$O$_3$ contents in the surface layer of inclusions reached their maximum values (73 ± 4 mass% in T2 sample). This is in good agreement with that the Al$_2$O$_3$ rich inclusion can easily be clustered, as mentioned before. The material of the nozzles is alumina-graphite in both heats in this study. The alumina rich layer of the nozzle will be exposed to the liquid steel after dissolution of the graphite rich layer has taken place. [69] Therefore, the Al$_2$O$_3$ rich spinel inclusions can easily be clustered and precipitated on the alumina network of the nozzle wall.

3.2.4. Thermodynamic consideration of inclusion formation

A phase stability diagram was calculated in order to confirm the conditions for the formation of different oxide phase in Low Al and High Al steels. The thermodynamic model in this study is based on Darken’s quadratic formalism and Redlich-Kister type polynomial,
which is more suitable for high alloy steels. The thermodynamic interaction parameters employed in the present study are shown in **Table 3-10**.

**Table 3-10.** The thermodynamic interaction parameters used in the present study.

<table>
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<tr>
<th>Interaction parameters</th>
<th>Values (J)</th>
<th>Region of validity</th>
<th>Ref.</th>
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As was discussed above, the SiO$_2$-CaO-MgO-Al$_2$O$_3$ phases precipitated on a surface of MgO or Al$_2$O$_3$ inclusions after an alloying by FeSi had taken place. Unfortunately, reliable data of $\Omega$ (the interaction parameter) values for Ca in high alloy steels have not been presented in the literature up to now. Moreover, the content of CaO in all IR and most spherical (SP2 and SP3) inclusions is significantly smaller in comparison to the SiO$_2$ and
Al₂O₃ values. Therefore, the following reactions were considered for calculations of the phase stability diagram of a Mg-Al-Si-O system in the Low Al and High Al steels:

\[
\begin{align*}
\text{Si}(l) + 2\text{O}(l) & = \text{SiO}_2(s), & \Delta G^{o}_{(3-1)} = -946350 + 197.64 \cdot T \text{ [69]} \\
2\text{Al}(l) + 3\text{O}(l) & = \text{Al}_2\text{O}_3(s), & \Delta G^{o}_{(3-2)} = -1682927 + 323.24 \cdot T \text{ [69]} \\
\text{Mg}(l) + \text{O}(l) & = \text{MgO}(s), & \Delta G^{o}_{(3-3)} = -607600 + 115.0T \text{ [73]} \\
3\text{Al}_2\text{O}_3(s) + 2\text{SiO}_2(s) & = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s), & \Delta G^{o}_{(3-4)} = -8600 - 17.41 \cdot T \text{ [69]} \\
2\text{MgO}(s) + \text{SiO}_2(s) & = 2\text{MgO} \cdot \text{SiO}_2(s) & \Delta G^{o}_{(3-5)} = -67200 + 4.31 \cdot T \text{ [69]} \\
\text{Al}_2\text{O}_3(s) + \text{MgO}(s) & = \text{MgO} \cdot \text{Al}_2\text{O}_3(s) & \Delta G^{o}_{(3-6)} = -20790 - 15.7T \text{ [21]} \\
2\text{MgO}(s) + 2\text{Al}_2\text{O}_3(s) + 5\text{SiO}_2(s) & = 2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2(s) & \Delta G^{o}_{(3-7)} = -20790 - 15.7T \text{ [69]}
\end{align*}
\]

where, \( \Delta G^{o} \) represents the Gibbs free energy change (J/mol), \( T \) represents the temperature (K).

By combining Eqs. (3-1) - (3-7), the \( \Delta G^{o} \) value can be determined for the following reaction:

\[
\begin{align*}
6\text{Al}(l) + 2\text{Si}(l) + 13\text{O}(l) & = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s), & \Delta G^{o}_{(3-8)} = -6950081 + 1347.59 \cdot T \\
2\text{Mg}(l) + \text{Si}(l) + 4\text{O}(l) & = 2\text{MgO} \cdot \text{SiO}_2(s), & \Delta G^{o}_{(3-9)} = -2228750 + 431.95 \cdot T \\
2\text{Al}(l) + \text{Mg}(l) + 4\text{O}(l) & = \text{MgO} \cdot \text{Al}_2\text{O}_3(s), & \Delta G^{o}_{(3-10)} = -2311317 + 423.45 \cdot T \\
4\text{Al}(l) + 2\text{Mg}(l) + 5\text{Si}(l) + 18\text{O}(l) & = 2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2(s), & \Delta G^{o}_{(3-11)} = -9015414 + 1637.3 \cdot T
\end{align*}
\]

Equations for determination of the partial molar excess for free energy change of Mg, Si, Al and O based on Redlich-Kister type polynomial are given in the Appendix. The activity of MgO, SiO₂, Al₂O₃, 3Al₂O₃·2SiO₂, 2MgO·SiO₂, MgO·Al₂O₃ and 2MgO·2Al₂O₃·5SiO₂ phases are taken as unity. The equilibrium phase stability diagrams for Mg-Al-Si-O system in Low Al and High Al steel are shown in Fig. 3-19. As can be seen, the compositions of both LAl and HAl steels are located in the MgO stable zone during the initial period of the ladle treatment. Therefore, the pure MgO inclusions can precipitate in both heats during the initial stage of ladle treatment. Then, in Low Al steel the 2MgO·SiO₂, MgO·Al₂O₃ and 2MgO·2Al₂O₃·5SiO₂ phases can precipitate in the melt. However, the amount of MgO·Al₂O₃ phase is small due to the small Mg concentration range for this phase (around from 2 to 0.08 ppm). Thereafter, the 3Al₂O₃·2SiO₂ and SiO₂ phases will heterogeneously precipitate on a surface of formed solid inclusions. It should be noted that the amount of 3Al₂O₃·2SiO₂ and SiO₂ phases can be significantly larger (particularly in the inclusion surface layer) than that of the MgO·Al₂O₃ phase. This fact is in good agreement with the obtained composition results for the SP2 inclusions. For these inclusions, the concentrations of SiO₂ and Al₂O₃ increased during ladle treatment and castings of LAl steel while the MgO content decreased.
Fig. 3-19. Phase stability diagram for a Mg-Al-Si-O system in (a) a Low Al and (b) a High Al steel.

M: MgO, A: Al₂O₃, S: SiO₂

In the High Al steel, after formation of some amount of MgO phase, the MgO-Al₂O₃ spinel phase may precipitate heterogeneously and homogeneously in this melt. However, the amount of MgO-Al₂O₃ phase is significantly larger in comparison to the MgO phase. Finally, according to the obtained phase stability diagram for a HAl steel, the Al₂O₃ and/or 3Al₂O₃·2SiO₂ phases can precipitate as a surface layer on the inclusions. The 3D composition analysis of inclusions in the HAl steel shows some increase of the Al₂O₃ content in the IR inclusions. Some increase of Al₂O₃ and decrease of SiO₂ contents in the SP2 and SP3 inclusions may be explained by a precipitation of 3Al₂O₃·2SiO₂ and 2CaO·Al₂O₃·SiO₂ phases. For these, the (mass% SiO₂)/(mass% Al₂O₃) ratio is close to the value obtained in the T2 sample (=0.49 on average). As a result, the CaO contents in SP2 and SP3 inclusions increased in both heats.

Fig. 3-20. Phase stability diagram for SiO₂, 3Al₂O₃·2SiO₂ and Al₂O₃ phases in (a) a Low Al and (b) a High Al steel.
It is difficult to estimate the content of soluble Mg in steel samples with enough accuracy at steelmaking companies. Furthermore, the SiO$_2$ and Al$_2$O$_3$ are the main components of inclusions in the T2 samples in LAI and HAI steels, according to the experimental results. Therefore, the phase stability diagram of Al-Si-O system is also considered in the high-Si steel case in this study. The phase stability diagram of the Al-Si-O system for the LAI and HAI steel is shown in Fig. 3-20 for different temperatures corresponding to each heat. It can be seen that the contents of Al and Si in the Low Al steel corresponds to the 3Al$_2$O$_3$·2SiO$_2$ phase stable zone. In this case, the possibility for a pure Al$_2$O$_3$ precipitation and a MgO-Al$_2$O$_3$ formation is very low. As a 3Al$_2$O$_3$·2SiO$_2$ phase is deposited, the Al content in the melt decreases and the SiO$_2$ starts to precipitate. Depending on Al and Si contents, the 3Al$_2$O$_3$·2SiO$_2$ and/or SiO$_2$ phases can precipitate during ladle treatment and casting. This fact is verified by the inclusion compositions obtained from the experimental results. However, the composition of steel in the High Al steel correlates to the Al$_2$O$_3$ stable zone. It means that the Al$_2$O$_3$ and/or MgO·Al$_2$O$_3$ phases are precipitated in this steel, as was verified by the inclusion compositions in the HAI steel. Moreover, the zone of Al$_2$O$_3$ precipitation increases with an increased content of Al and with a decreased temperature of the liquid steel. Therefore, a higher Al content (till 0.009 mass%) and a lower temperature (till 1711 K) in the High Al steel might be the main reasons for obtaining a higher Al$_2$O$_3$ content in the surface layer of spinel inclusions.

To avoid a spinel formation in liquid HSiNC stainless steels and nozzle clogging problem during casting, the critical concentration of Al content in the melt can be determined for different Si contents and melt temperatures based on the obtained phase stability diagram. For instance, the Al content in the melt for the given High Al steel should be lower than 0.006 mass%.

### 3.3 Inclusions in REM treated stainless steels

The variations of the Ce and O contents in the given PT and IH samples are shown in Fig. 3-21. As can be seen, the Ce contents in the PT samples decrease gradually with time. However, the Ce contents in the IH samples first increase from IHL3 to IHL15 samples and then decrease for the IHT12 sample. This is due to that the size of the mischmetal pieces added to the IH (~20 kg) is times larger than that added to the PT (1-1.2 kg). Therefore, a longer time is needed for a full dissolution of the mischmetal pieces and to homogenize the steel composition in the IH. The O content decreases rapidly and then it reached almost
constant values in the PT samples. However, it increases slightly in the PT12 sample, which most likely is due to reoxidation. The O content in the IH samples is almost constant from sample IHL3 to IHL15 and then it decreases slightly in sample IHT12. The much lower initial O content in the IHL3 sample compared to the PT3 sample can be explained by the addition of ferrosilicon alloys before the mischmetal addition in the industrial heat. The initial levels of Ce and O content in the PT samples are significantly larger compared to those in the IH samples. However, the difference tends to decrease with the time for both Ce and O.

![Graph](image)

**Fig. 3.21.** Variations of (a) Ce and (b) O contents with time in different PT and IH samples.

### 3.3.1. Morphology of clusters

In this study, clusters in PT and IH samples were classified into different groups based on the morphology. The typical photos and size ranges of different types of clusters are shown in Table 3-11. All PT samples contain Type A and Type B clusters. Type A clusters consist of big size (1-3.6 µm) irregular and regular (IR) inclusions and small size (≤ 0.5 µm) spherical (SP) inclusions. Moreover, the spherical inclusions are located mainly at the edge of the IR inclusions. According to the obtained results, it can be assumed that the small size SP inclusions precipitated later than the IR inclusions. It can be explained by oxidation of the liquid steel surface in the furnace during holding or by additional reoxidation of the melt during sampling. [74] The Type B clusters are composed of irregular inclusions, which most likely are made up of oxidized REM pieces on the surface of the mischmetal. This is due to that the big size REM pieces are crushed into small sizes before an addition to the liquid steel. The oxidation process might occur both at a room temperature and at a high temperature right before the addition. It should be pointed out that the size range of Type A clusters is much wider (1.5 to 20.0 µm) than that for Type B clusters (2.0-8.0 µm).
Table 3-11. Classification of clusters in steel samples from the PT and IH trials.

<table>
<thead>
<tr>
<th>Heat</th>
<th>Type</th>
<th>Type A</th>
<th>Type B</th>
<th>Type C</th>
<th>Type D</th>
<th>Type E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT</td>
<td>Typical photo</td>
<td><img src="https://example.com/image1.png" alt="Image" /></td>
<td><img src="https://example.com/image2.png" alt="Image" /></td>
<td><img src="https://example.com/image3.png" alt="Image" /></td>
<td><img src="https://example.com/image4.png" alt="Image" /></td>
<td><img src="https://example.com/image5.png" alt="Image" /></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>1.5-20.0</td>
<td>2.0-8.0</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IH</td>
<td>Typical photo</td>
<td><img src="https://example.com/image6.png" alt="Image" /></td>
<td><img src="https://example.com/image7.png" alt="Image" /></td>
<td><img src="https://example.com/image8.png" alt="Image" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size range (μm)</td>
<td>1.7-14.0</td>
<td>4.0-23.0</td>
<td>3.0-16.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Clusters in IH samples were classified into three groups: Types C, D and E. Type C cluster is the typical cluster, which is similar to the Type A clusters found in PT samples. However, there are no small size spherical inclusions at the edge of the IR inclusions. The size of IR inclusions in Type C clusters in IH samples is similar to that in PT samples. Type D clusters have a spherical shape with hollow holes inside. The size of these clusters varies in a wide range (from 4 to 23 μm). It is believed that these clusters were formed due to a reduction of the surface layer of spherical inclusions (such as SiO$_2$ or some big size slag type inclusion) by REM elements. A central part of these clusters is missing in most cases. It can be explained by a dissolution of SiO$_2$ phases from the central zones due to the rapid decrease of the dissolved O content in the melt around inclusions after a REM addition. The Type E clusters are composed of faced inclusions. The morphology of the inclusions depends both on its phase and the degree of supersaturation. [61] Spherical inclusions formed at higher supersaturations than the faced inclusions. [61] Usually, the supersaturation in the liquid steel goes through a maximum value after the addition of a deoxidizer. Then it decreases with time due to the consumption of oxygen and deoxidizer. Therefore, spherical inclusions were formed first, which later agglomerated to generate Type C clusters. Afterwards, the morphology of the spherical inclusions in the Type C clusters changed to IR inclusions due to sintering. At the end, the Type E cluster which consisting of faced inclusions formed as the supersaturation in the liquid steel decreased.
The frequency of different type of clusters in PT and IH steel samples depends on the holding time after the mischmetal addition, as shown in Fig. 3-22. The typical clusters with regular + irregular inclusions are the main type of clusters in both the PT and IH heats. The frequency of Type A clusters in PT samples increases with time. On the other hand, the frequency of Type B clusters decreases with time. This phenomenon may be explained by the agglomeration of small size Type B clusters into big size Type A clusters during holding and stirring of liquid steel. In IH samples, the frequency of Type C clusters tends to decrease with time, while the frequency of Type E clusters tends to increase with time. This might be due to a decreased degree of supersaturation in the liquid steel. Thereby, it is easy to form the faced Type E clusters. The clusters of Type D were mostly observed in sample IHL3 and then the frequency decreased with time. The possible reason is that no spherical SiO$_2$ or slag type inclusions exist anymore in the liquid steel due to the addition of a mischmetal. Therefore, there is no chance for a formation of new Type D clusters.

3.3.2. Composition of clusters

Rare earth elements (such as Ce, La, Pr, Nd) are strong oxide and sulfide formers owing to the high affinity to oxygen and sulphur. In addition, the equilibrium of Ce-Al-O system was also studied. [75] The compounds that will form in the liquid steel depend on the concentrations of Ce, La, Al, O and S dissolved in the steel. It was reported that CeO$_2$ is unstable under steelmaking conditions. [76] Furthermore, the precipitation order of the REM oxi-sulphides is expected to be REM$_2$O$_5$S, REM$_3$S$_{4+x}$ and REMS. [76] Thus, REM$_2$O$_3$, REM$_2$O$_2$S and CeAlO$_3$ can be expected to be the most probable compounds in this steel grade.
**Fig. 3-23.** Composition of inclusions in different types of clusters in different (a) PT and (b) IH samples.

The composition of REM clusters on a surface of film filter after electrolytic extraction was analyzed without any influence of the steel matrix. The composition of inclusions in clusters corresponded mostly to REM-oxides. The amount of Al and S content in the clusters in all PT and IH samples is smaller than 2 mass%. As can be seen in **Fig. 3-23**, the Ce and La content of the different kinds of REM clusters is almost stable in both the PT and IH heats, except for the Type D cluster in the IH samples. For this sample the La content tends to decrease while the Ce content tends to increase with time. The La content is larger than the Ce content in all the PT samples. There is no obvious difference of the composition between Type A and Type B cluster. However, in IH samples, the La content is larger than the Ce content only in the Type D clusters. The Ce content is larger than the La content in both the Type C and Type E clusters. Furthermore, in Type E clusters the Ce content is higher and the La content is lower than that in Type C clusters.

**Fig. 3-24.** Phase stability diagrams of Ce-La-Al-O-S system in (a) PT and (b) IH trials.
The phase stability diagram of the Ce-La-Al-O-S system at 1743K in PT and IH samples are plotted in Fig. 3-24. It should be pointed out that the calculation for IH was done with 0.006% Al and 0.001% S in the melt. The reactions and the equilibrium constants that are considered for calculating the phase stability diagram are summarized in Table 3-12. A general reaction in the Ce-La-Al-O-S system can be expressed as follows:

\[
\begin{align*}
M_2O_3 (s) &= 2M + 3O \\
M_2O_2S (s) &= 2M + 2O + S \\
MAI_3 (s) &= M + Al + 3O
\end{align*}
\]

The standard Gibbs free energy \(\Delta G^0\) for chemical reaction (3-14) is

\[
\Delta G^0 = -RT \ln K
\]

with

\[
K_{(3-12)} = a_M^2a_O^3; K_{(3-13)} = a_M^2a_O^2a_S; K_{(3-14)} = a_Ma_Al^2a_O^3
\]

where, \(K\) is the equilibrium constant, and \(a_M\), \(a_O\), \(a_S\) and \(a_Al\) are the activity of the reactants M, O, S and Al respectively. The activity of the elements in liquid iron can be calculated by adopting the infinitely dilute solution with a 1% (mass content) as standard state and can be expressed as

\[
a_i = f_i[\% i]
\]

with

\[
\log f_i = e_i^I[\% i]
\]

where, \(f_i\) is the activity coefficient, \(e_i^I\) is the interaction coefficients. The interaction coefficients employed in this study is shown in Table 3-13. The data without a notation are from Ref. [77]. Also, the activity of the pure solid phase for oxides or oxy-sulfides is taken as unity.

It can be seen in Fig. 3-24, that the composition of all the PT samples are located in the \(La_2O_3\) stable zone or at the boundary between the \(La_2O_3\) stable zone and the \(Ce_2O_3\) stable zone. This is in agreement with the experimental results that the clusters in the PT samples are La rich REM oxides. However, there is about 30-35 mass% Ce content in the clusters. The reason for that might be that there is a mixed \(Ce_xLa_yO_z\) zone between the \(Ce_2O_3\) and \(La_2O_3\) stable zone. For IH samples, only the IHL3 sample is located in the \(La_2O_3\) stable zone. The other samples are located at the boundary of the \(La_2O_3\) stable zone and the \(Ce_2O_3\) stable zone or in the \(Ce_2O_3\) stable zone, which is also in agreement with the experimental results except for sample IHL3. The composition of the main cluster (Type C, 85%) is Ce rich in sample IHL3. However, the composition of the liquid steel is located in the La rich zone. Although
the reason for this discrepancy is not fully understood yet, it is suggested that the thermodynamic databases for REM elements need to be improved. Furthermore, with all the plots are located almost on the boundary of the Ce$_2$O$_3$ and La$_2$O$_3$ stable zone, the existence of the Ce$_x$La$_y$O$_z$ phase is also a possible reason. The details for this sample will explain more in the following paragraph. The composition of both the PT and IH samples are located far away from the La$_2$O$_3$S stable zone. Even more, the Ce$_2$O$_3$S and CeAlO$_3$ stable zones do not exist in the composition range of Ce and La given in the Fig. 3-24. This is a good indication that the Al and S content in the clusters in all PT and IH samples are quite small.

Table 3-12. Equilibrium constants of reactions used in this study

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta G^\circ$ (J/mole)</th>
<th>log K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$O$_3$ (S) = 2Ce + 3O</td>
<td>1827424 - 643.8T</td>
<td>-95487/T + 33.64</td>
<td>[76]</td>
</tr>
<tr>
<td>La$_2$O$_3$ (S) = 2La + 3O</td>
<td>1443880 - 337T</td>
<td>-75373/T + 17.59</td>
<td>[78]</td>
</tr>
<tr>
<td>CeO$_2$S (S) = 2Ce + 2O +S</td>
<td>135359 - 332T</td>
<td>-70657/T+17.33</td>
<td>[78]</td>
</tr>
<tr>
<td>La$_2$O$_2$S (S) = 2La + 2O +S</td>
<td>1341200 - 301T</td>
<td>-70081/T+15.71</td>
<td>[78]</td>
</tr>
<tr>
<td>CeAlO$_3$ (S) = Ce + Al + 3O</td>
<td>725506 - 111.7T</td>
<td>-37900/T + 5.84</td>
<td>[75]</td>
</tr>
</tbody>
</table>

Table 3-13. Interaction coefficients employed in this study

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Ce</th>
<th>La</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>S</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>80.5/T</td>
<td>-</td>
<td>-</td>
<td>0.0096</td>
<td>-</td>
<td>0.029</td>
<td>0.035</td>
<td>-1.98</td>
<td>0.056</td>
</tr>
<tr>
<td>Ce</td>
<td>20500/T-13.53</td>
<td>0.0039</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
<td>-</td>
<td>-40</td>
<td>-106</td>
<td>-</td>
</tr>
<tr>
<td>La</td>
<td>-</td>
<td>-</td>
<td>-0.0078</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>-79</td>
<td>-1.77</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>-1.17</td>
<td>-11.2</td>
<td>-0.2</td>
<td>-0.052</td>
<td>-0.021</td>
<td>0.006</td>
<td>-0.133</td>
<td>-0.17</td>
<td>-0.066</td>
</tr>
<tr>
<td>S</td>
<td>0.041</td>
<td>-9.1</td>
<td>-18.3</td>
<td>-0.01</td>
<td>-0.026</td>
<td>0</td>
<td>-0.05</td>
<td>-0.27</td>
<td>0.075</td>
</tr>
</tbody>
</table>

To confirm the existence of the Ce$_x$La$_y$O$_z$ phase, an example of the elemental mapping of the typical cluster in PT is shown in Fig. 3-25. The distribution of the Ce and La is almost homogeneous, which is also the case for the typical clusters in IH. According to the element analyses, the most clusters in PT have a composition close to the stoichiometric phase Ce$_4$La$_6$O$_{15}$ (2Ce$_2$O$_3$·3La$_2$O$_3$). In addition, the most Type C clusters in IH are probably Ce$_6$La$_4$O$_{15}$ (3Ce$_2$O$_3$·2La$_2$O$_3$). It is also concluded that additional investigations are necessary to determine the constituent phases in the different types of clusters in this study.

Fig. 3-25. Elemental mapping of the typical cluster in PT
Both the Type C cluster and Type D cluster are observed in sample IHL3. However, the composition of them is different, since the Type C contains Ce rich oxides while Type D contains La rich oxides. In order to explain this phenomenon, the following mechanism can be proposed as shown schematically in Fig. 3-26. During period I, which is just after a mischmetal addition, the activity of La is higher than the activity of Ce. Therefore, the clusters that formed are La rich cluster. However, at this moment, the oxygen potential on the surface of the exiting SiO$_2$ or slag type inclusions is higher than that in the liquid steel. Furthermore, a heterogeneous nucleation occurs more easily than a homogeneous nucleation. Thus, Type D cluster forms primarily during this time as the La content decreases to a larger extent in the liquid steel. Then, during period II the activity of La is equal to the activity of Ce and the oxygen content in the steel that surrounds the Type D cluster is still higher than at other places in the liquid steel. Thus, a layer with equal content of La and Ce is still formed dominantly at the surface of Type D clusters than in the liquid steel.

![Fig. 3-26. Schematic illustration of evolution of clusters in different period of stages in IH samples.](image)

La+: La rich, La=Ce: La and Ce are equal, Ce+: Ce rich

Afterwards, during period III the activity of La is lower than the activity of Ce. Then, Ce rich inclusion will form at the surface of Type D clusters and also in the liquid steel. The oxygen potential around the Type D clusters is equal to or lower than the oxygen potential in
the liquid steel. This is due to the consumption of oxygen to form Type D clusters during the whole period. Therefore, the Type C clusters will mainly form during period III and the average composition of the Type C cluster is Ce rich cluster. The reason that the average composition of Type D cluster is La rich in all samples is due to the analyzed volume during the 3D investigations captured some part of the La rich zone. [80]

### 3.3.3 Average size and size distribution of clusters

The average size of clusters in PT and IH samples as a function of holding time is shown in Fig. 3-27. The error bar represents the arithmetic standard deviation for analyzed $d_V$ values. As can be seen, the average size of Type A clusters in PT samples tend to increase during the holding time after the mischmetal addition. However, after the start of casting the $d_V$ value drastically decreases. The average size of Type B clusters is almost constant. The $d_V$ value of Type C cluster in IH samples increases slightly during 15 minutes of holding in the ladle after a mischmetal addition. Then, it decreases during transportation and casting of steel (IHT12 sample). The transformation tendency of the average size of the Type A clusters in the PT samples and Type C clusters in the IH samples is similar. The average size of Type D clusters in the IHL3 sample is significantly larger than the other types of clusters in all IH samples. This is due to the presence of large size liquid SiO$_2$ or slag type inclusions in the steel before the mischmetal addition. Then, the average size of Type D cluster decreases dramatically. This indicates that the small size of Type D clusters is more stable than the large size clusters during holding and stirring of liquid steel. The average size of the Type E clusters in industrial steel samples increases with an increased time. This can be explained by the collision of small size Type E clusters under the formation of the big size clusters.

![Fig. 3-27. Average size of different clusters in (a) PT and (b) IH samples.](image-url)
Fig. 3-28 gives the particle size distribution of Type A clusters in different PT samples and Type C clusters in IH samples, as these clusters are the main type of cluster in PT and IH respectively. In PT samples, the number of large size clusters per cubic millimeter from PT3 to PT9 tends to increase due to an agglomeration of REM oxide inclusions and clusters. On the other hand, the number of small size clusters decreases during the same period. However, an opposite trend was observed for the PT12 sample, where the number of small size clusters increases while the big size clusters decreases. The reason for the increase of the small size cluster might due to the reoxidation as the oxygen content increases in the PT12 sample. A removal of Ce clusters by floatation will be difficult owing to their relatively high density \( p_{Ce_2O_3} \approx 0.007 \) g/mm\(^3\). It is reported [81] that Ce oxides easily accumulate on the crucible walls and crucible bottoms instead of flotation, which might be a reason for clogging. The number of big size clusters has decreased extremely much in PT12 sample, which implies that the big size clusters more easily adhere to the nozzle wall or the refractory than the small size clusters.

Fig. 3-28. Particle size distribution of Type A clusters in different samples of (a) PT and Type C clusters of (b) IH heats.

It is interesting to note that the size distribution of the PT9 samples contain more peaks rather than a single peak. According to the cluster growth mechanism, [82] Brownian collisions \( \beta_{ij}^B \), Stokes collision \( \beta_{ij}^S \) and Turbulent collision \( \beta_{ij}^T \) are the main collision-aggregation mechanisms among the inclusion particles in the molten steel. In addition, all the values of the collision-aggregation rates, \( \beta_{ij}^B, \beta_{ij}^S \) and \( \beta_{ij}^T \) are large when the value of radius of the two inclusion are large. This means that big size clusters easily aggregate with the other big size clusters. This is also confirmed by the Appelberg et al [83] results based on the
confocal laser scanning microscope technique. Thus, there are more peaks in the size distribution of the PT9 sample, which also indicate that the cluster size distribution of Type A cluster in PT9 sample do not follow the log-normal distribution, exponential, pseudo-normal or some other distributions which only have a single peak.

In the IH samples, the size distribution of Type C clusters shows a similar tendency as for most PT samples. Namely, the number of big size clusters tends to increase and then decrease, while the small size clusters tend to first decrease and thereafter increase a little bit. The number of the clusters per cubic millimeter in PT samples is larger than that in IH samples for both the small and large size ranges. This is because the frequency of Type A clusters in PT samples (87%-90%-96%-98%) is larger than that of the Type C clusters in the IH samples (85%-85%-80%-69%) for all studied cases. The other possible reason is that the Ce content in most PT samples is larger than that in the IH samples. Furthermore, the O content in PT samples is larger than that in IH samples in all cases. Therefore, the driving force for the inclusion formation is stronger in PT samples than in IH samples for most cases.

### 3.3.4 Evolution of clusters in PT and IH

The evolution of different type of clusters in PT and IH samples are shown schematically in Table 3-14. Typical Type A and irregular Type B clusters are observed after the addition of a mischmetal in the PT samples. The composition of the both cluster types corresponds to the La rich REM oxides. The average size of the Type A clusters tend to increase and then decrease, while the average size of Type B cluster remains almost constant. Moreover, the frequency of the Type B clusters decreases continuously due to an agglomeration to the Type A clusters.

For the IH heat, it is believed that big size La rich Type D clusters first formed on the surface of the existing spherical inclusions. Thereafter, a typical Ce rich Type C cluster was formed. The average size of Type B cluster decreases rapidly with time. In addition, the Ce content increases and La content decreases with time. The average size of the Type C clusters tends to first increase and then decreases in sample IHT12. This is a similar trend as for the Type A cluster in the PT samples. The faced Type E cluster was first observed in a IHL5 sample, and the average size of them tend to increase with an increased time. The composition of Type C and Type E clusters is almost constant and both of them are Ce rich clusters. The frequency of Type E clusters increases, while the frequency of Type C clusters decreases with time.
Based on the results of the 3D investigation of clusters after electrolytic extraction of steel samples, it is possible to clarify the mechanisms for formation and evolution of different types of REM clusters in the pilot experimental trials and in the industrial heats of stainless steels.

**Table 3-14. Evolution of different kinds of clusters in PT and IH samples.**

<table>
<thead>
<tr>
<th>Heat</th>
<th>Type</th>
<th>Characteristics</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PT3</td>
</tr>
<tr>
<td>PT</td>
<td>Type A</td>
<td>Morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>Ce36La49</td>
<td>Ce33La52</td>
</tr>
<tr>
<td></td>
<td>Average size</td>
<td>3.1</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Type B</td>
<td>Morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>Ce37La50</td>
<td>Ce34La53</td>
</tr>
<tr>
<td></td>
<td>Average size</td>
<td>3</td>
<td>2.9</td>
</tr>
<tr>
<td>IH</td>
<td>Type C</td>
<td>Morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>Ce52La33</td>
<td>Ce51La35</td>
</tr>
<tr>
<td></td>
<td>Average size</td>
<td>2.9</td>
<td>3.9</td>
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<tr>
<td></td>
<td>Type D</td>
<td>Morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>Ce26La59</td>
<td>Ce28La57</td>
</tr>
<tr>
<td></td>
<td>Average size</td>
<td>10.6</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>Type E</td>
<td>Morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Composition</td>
<td>-</td>
<td>Ce55La30</td>
</tr>
<tr>
<td></td>
<td>Average size</td>
<td>-</td>
<td>3.5</td>
</tr>
</tbody>
</table>
3.4 Statistical Analysis of the Maximum size of Inclusion

The typical SEM images with inclusions found in the 2D and 3D studies were shown in Fig. 3-29. As can be seen, the morphology of most of the inclusions is spherical. In addition, the inclusions observed in this study are single inclusions and not clusters. The typical inclusion from the 2D and 3D determinations are shown in Fig. 3-30 at large magnifications. The composition of inclusions is mainly Al$_2$O$_3$-CaO. More specifically, 32±4 CaO and 65±7 Al$_2$O$_3$ in the inclusions of sizes ranging from of 1 to 6 µm. For the inclusions in the size range of 6-14 µm, the value is 34±2 CaO and 63±5 Al$_2$O$_3$. This indicated that the inclusion belongs to one type in the present study. In addition, the distribution of the main elements is almost homogenous, as shown in Fig. 3-31.

Fig. 3-29 Typical SEM images with inclusions in (a) 2D and (b) 3D determinations

Fig. 3-30 Typical inclusion in metal samples in (a) 2D and (b) 3D determinations
3.4.1 Size evaluation of inclusions in 2D and 3D measurements

The comparison of the statistical analysis between the 2D and 3D determinations was done by using the SEV method. A magnification of 500 was used in both the 2D and 3D studies. In addition, the number of measurements was 50, 100, 150, 200 and 250. Also, similar unit volumes were used to enable an equivalent comparison. The unit volumes ($V_0$) for 2D and 3D measurements were $1.5928 \times 10^{-4}$ mm$^3$ and $1.62 \times 10^{-4}$ mm$^3$, as shown in Table 3-15. The EVD regression lines for inclusions in the S1 sample obtained from 2D and 3D methods are plotted in Fig. 3-32. Data are given for 50 and 250 measurements to exemplify the influence of this variable. As can be seen, the 3D data are located on the right side of the 2D data for the 50 measurements. This phenomenon can be explained by one of the disadvantage of the 2D measurements. Namely, the sectioned diameter is smaller than the real size of the spherical inclusion. However, the true size of the inclusion can be easily investigated in 3D after an electrolytic extraction of a steel sample. For the results obtained from 250 measurements, the 2D data and 3D data are mostly overlapped with each other except for the large size inclusions. The reason for this is not clear now and further studies are needed.

The regression lines for the 2D and 3D determinations are almost parallel to each other for each number of measurements. The slopes of the EVD lines are similar. The largest discrepancy is 0.0378 for 100 measurements and the smallest discrepancy is 0.0121 for 150 measurements, as can be seen from Table 3-15. The estimated inclusion size in a large volume is plotted for the 2D and 3D determinations in Fig. 3-33. The slope of the estimated inclusion size (EIS) for the 2D methods is similar to that for the 3D methods. The difference between 2D and 3D is small for both small and large volumes of steel. For example, for 10 t of steel, the smallest discrepancy is 0.3627 µm for 50 measurements. Moreover, the biggest discrepancy is 0.9000 µm for 100 measurements. All those discrepancies are in the range of a 95% confidence interval for all the number of measurements.

The $n\%$ value in Table 3-15 represents the percentage of the inclusions located outside of the 95% confidence interval of the EVD lines. In addition, the $\Delta$ value represents the average distance between the experiment data and the predicted value of these inclusions. It is obvious
that the n% and Δ values obtained from 3D measurements are smaller than the values from the 2D measurements. This phenomenon is also clearly shown in Fig. 3-32, especially for the big size inclusions. Furthermore, the R² (correlation coefficient) values obtained from the 3D determinations are larger than those from the 2D determinations for all the samples. It can be concluded from the observed result that, although the predicted maximum size of inclusions is similar for 2D and 3D measurements for the spherical inclusion in the size range of 1-14 µm, the 3D methods is more accurate and receivable than the 2D method.

Table 3-15. Parameters for S1 sample at different number of measurements and unit volume in 2D and 3D methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimension</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>h₀ (µm)</td>
<td>2D</td>
<td>3.5257</td>
</tr>
<tr>
<td>Unit volume (x10^-4 mm³)</td>
<td>2D</td>
<td>1.5928</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>2D</td>
<td>0.9665</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>0.9868</td>
</tr>
<tr>
<td>Slope (EVD)</td>
<td>2D</td>
<td>0.9050</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>0.9242</td>
</tr>
<tr>
<td>Slope (EIS)</td>
<td>2D</td>
<td>2.5443</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>2.4776</td>
</tr>
<tr>
<td>95% CI</td>
<td>2D</td>
<td>1.8514</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>1.8028</td>
</tr>
<tr>
<td>n%</td>
<td>2D</td>
<td>8.3333</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>4.1667</td>
</tr>
<tr>
<td>Δ (µm)</td>
<td>2D</td>
<td>1.74±0.75</td>
</tr>
<tr>
<td></td>
<td>3D</td>
<td>1.24±0.61</td>
</tr>
<tr>
<td>L_max (µm)</td>
<td>2D</td>
<td>35.3873</td>
</tr>
<tr>
<td>(10 t)</td>
<td>3D</td>
<td>35.0246</td>
</tr>
</tbody>
</table>

Fig. 3-32 EVD lines for inclusions in the S1 Sample for (a) 50 and (b) 250 of measurements
Fig. 3-33 Comparison of the estimated inclusion size in a large volume of steel for (a) 50 and (b) measurements between 2D and 3D determinations

In order to transform the unit area to a unit volume, the thickness term \( h_0 \) is used. However, this value is changed from 3.5257 µm to 3.9871 µm for different number of measurements, which lead to unit volume values ranging from \( 1.5928 \times 10^{-4} \) to \( 1.8026 \times 10^{-4} \) mm\(^3\). However, this value should be a fixed value. The effect of different \( h_0 \) (1, 2, 6, 8 µm) values on the estimated maximum inclusion size is plotted in Fig. 3-34. The data is calculated for the S1 sample when 250 measurements were used. As can be seen, the estimated inclusion size line moves downward as the \( h_0 \) value is increased. The \( h_0 \) value calculated from the equation (2-8) is 3.9871 µm. The predicted maximum size of inclusion for 2 and 6 µm is within the 95% confidence interval with the 3.9871 µm for 10 t steel. However, the 1 and 8 µm is not in this interval. The above results indicated that the thickness term \( h_0 \) and a small range of variance are acceptable for the prediction of the spherical inclusions in the present study.

Fig. 3-34 Effect of \( h_0 \) value on the estimated maximum size of inclusions in 2D measurements
3.4.2 Number of measurements

The number of measurements is also an important factor in the statistics analysis. It is always necessary to know the minimum number of measurements in order to obtain a good estimate of the extreme sizes. 50, 100, 150, 200 and 250 measurements were carried out to detect the effect of number on the predicted sizes. The EVD lines for different number of measurements are plotted in Fig. 3-35 for 2D and 3D methods. The lines are almost overlapped with each other for 2D and 3D methods except the 50 number of measurements. The slopes of the EVD lines are similar. As shown in Table 3-15, the R² value tends to increase and the SE value tends to decrease with an increased number of measurements for both the 2D and 3D measurements. However, the n% and Δ value do not show any tendency as the number of measurements increase.

![Graphs showing EVD regression lines for different number of measurements.](image)

**Fig. 3-35** Effect of number of measurements on the EVD regression lines on (a) 2D and (b) 3D methods

The predicted maximum size of inclusions in a large amount of steel is compared for the 50 to 250 measurements. For example, the biggest difference between the estimated largest sizes of inclusions is 2.0699 µm for the 10 t steel in a 2D determination. This value is 2.0419 µm as for a 3D measurement. The deviation is located outside of the 95% confidence interval for both the 2D and 3D measurements. The smallest predicted value is 50 measurements in both methods. Then for the 100 to 250 measurements, the largest difference is 1.4425 µm for 2D methods and 1.3093 µm for 3D methods. These deviations are within the 95% confidence interval for the 100 measurement for both 2D and 3D determinations. Therefore, it is concluded that the number of measurements from 100 to 250 has no big effect on the predicted maximum size of inclusion. However, the more number of measurements, the more
accurate results would be. This also implies that 100 measurements are enough to obtain a reliable statistical analysis of the spherical inclusions studied in the present study.

3.4.3 Unit volume

S. Beretta et al. [44] pointed out that the predicted maximum size of inclusions is not accurate if the unit volume too small. Therefore, the effect of the unit volume on the SEV method was analyzed based on a 3D measurement. The number of measurements for all the samples is 100. The EVD regression lines for different samples are plotted in Fig. 3-36 and the parameters are given in Table 3-16 for different unit volumes from the 3D data. As can be seen, the regression lines representing a big unit volume are located on the right hand side of the small unit volume values for all the samples. This is because the size of the inclusions investigated by the big unit volume approach is larger than that for the small unit volume approach. The larger observed volume, the larger opportunity to find the big size inclusion. The R² value obtained from a 4 V₀ unit volume is larger than that from a 2 V₀ for most samples. This implies that a big unit volume is more suitable to use to determine the characteristic of inclusions in the present study. The slope of the EVD lines from both unit volumes is almost similar, except for sample S4. In addition, the discrepancy for the S1 and S3 samples is smaller than that for the S2 sample.

Fig. 3-37 gives the comparison of the predicted biggest size of inclusions with different unit volumes for inclusion from samples S1 to S4. The predicted maximum size of inclusions is similar for the S1 and S3 samples when different unit volumes were used. However, this value is different and the difference increases with an increased weight of steel for both the S2 and S4 samples. In addition, the predicted difference for the S2 sample is smaller than that for the S4 sample. For 10 t of steel, the discrepancy of the predicted largest size of inclusion for the S2 sample is 0.9331 µm, which is within the 95% confidence interval. However, this value is 5.1681 µm for the S4 sample, which is outside the 95% confidence interval.

Therefore, the unit volume is an important factor that affects the predicted maximum size of inclusions in the present study. It is recommended that for large size ranges of inclusions, large unit volumes should be used in order to obtain an enough number of large size inclusions. For small size ranges of inclusions, small unit volumes should be used to obtain accurate measurements of small size inclusions.
**Fig. 3-36.** Comparison of unit volumes for (a) S1, (b) S2, (c) S3 and (d) S4

**Table 3-16.** Parameters for different samples with different unit volume

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Volume</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>2 V₀</td>
<td>0.9767</td>
<td>0.9702</td>
<td>0.9954</td>
<td>0.9716</td>
</tr>
<tr>
<td></td>
<td>4 V₀</td>
<td>0.9922</td>
<td>0.9952</td>
<td>0.9898</td>
<td>0.9960</td>
</tr>
<tr>
<td>Slope (EVD)</td>
<td>2 V₀</td>
<td>0.7859</td>
<td>0.8999</td>
<td>0.9686</td>
<td>1.2926</td>
</tr>
<tr>
<td></td>
<td>4 V₀</td>
<td>0.7761</td>
<td>0.9649</td>
<td>0.9490</td>
<td>1.0529</td>
</tr>
<tr>
<td>Slope</td>
<td>2 V₀</td>
<td>2.9299</td>
<td>2.5590</td>
<td>2.3773</td>
<td>1.7814</td>
</tr>
<tr>
<td></td>
<td>4 V₀</td>
<td>3.9670</td>
<td>2.3866</td>
<td>2.4265</td>
<td>2.1870</td>
</tr>
<tr>
<td>SE</td>
<td>2 V₀</td>
<td>1.5075</td>
<td>1.1367</td>
<td>1.2232</td>
<td>0.9166</td>
</tr>
<tr>
<td></td>
<td>4 V₀</td>
<td>1.5266</td>
<td>1.2280</td>
<td>1.2485</td>
<td>1.1253</td>
</tr>
<tr>
<td>L_max (µm) (10 t)</td>
<td>2 V₀</td>
<td>41.6481</td>
<td>35.3198</td>
<td>33.8376</td>
<td>25.8973</td>
</tr>
<tr>
<td></td>
<td>4 V₀</td>
<td>42.0171</td>
<td>34.3867</td>
<td>34.2479</td>
<td>31.0654</td>
</tr>
</tbody>
</table>
Fig. 3-37. Predicted maximum size of inclusions with $4V_0$ and $2V_0$ for different samples
4. Conclusions

The inclusion contents in the ferroalloys and metal samples were investigated in this study. More specifically, the characteristics (such as morphology, size, composition and number) of inclusions were studied in 3D after electrolytic extraction. The following main conclusions were obtained.

1. Inclusions in Ferroalloys (Supplements I and II)

   (1) The inclusions in ferroalloys (FeTi, FeNb, FeSi, SiMn, LC and HCFeCr) can be successfully analyzed after a separation of the inclusions from the matrix using the electrolytic extraction method.

   (2) Both metallic and non-metallic inclusions were investigated in the ferroalloys. Some inclusions, like REM oxides, which are not reported in previous studies, were found in the ferroalloys after electrolytic extraction.

   (3) Overall, the inclusions can be divided into two categories depending on the melting point. The characteristics of the inclusions in ferroalloys should be known before their additions to the liquid steel, for a better controlled steelmaking process.

2. Inclusions in high-silicon non-calcium treated stainless steels (Supplement III)

   (1) The samples of the stainless steel with low Al content (LAl) contain 96-98% of spherical inclusions (SP), 1-2% of regular and irregular inclusions (IR) and 1-2% of clusters (CL). Most of these spherical inclusions are homogeneous CaO-SiO₂-MgO-Al₂O₃ slag inclusions (SP1). The IR inclusions and clusters consisted of pure MgO oxides and some were partially covered by a SiO₂-Al₂O₃-MgO-CaO layer.

   (2) The samples of the stainless steel with high Al content (HAl) contain SP (75-76%), IR (12-17%) inclusions and clusters (7-15%). Most of spherical inclusions are heterogeneous (SP2 and SP3). The Al₂O₃ content in the spherical inclusions increased from 47 mass% to 53 mass%. During the same period, the SiO₂ content decreased from 42 mass% to 26 mass%. The IR inclusions and clusters consisted of homogeneous MgO·Al₂O₃ inclusions.

   (3) The frequency of clusters in the HAl steel increased from 3% to 15%. Moreover, the number of large size clusters (> 4 µm) increased significantly during casting when the Al₂O₃ contents in surface layer of inclusions reached the maximum values.
(4) An increased soluble Al content in liquid steel in the ladle and an decreased of temperature during casting promote the formation of MgO·Al₂O₃ spinel inclusions.

3. Inclusions in REM treated stainless steel (Supplement IV)

(1) Typical clusters with regular and irregular inclusions were the main types of clusters (69-98%) in all PT and IH steel samples.

(2) The composition of inclusions in clusters of all PT and IH steel samples corresponded mostly to REM oxides. The clusters in all the PT samples and Type D clusters in IH sample were La rich while the Type C and Type E clusters in IH samples were Ce rich REM oxides.

(3) The evolution of the size and number of main type of clusters followed the same trend in the PT and IH samples. However, the number of the main type of clusters per unit volume in PT samples was larger than that in IH samples for both the small and large size ranges.

4. Statistical Analysis of the Maximum size of Inclusion (Supplement V)

(1) The predicted maximum size of inclusions was similar for 2D and 3D measurements for the spherical inclusion, but the 3D methods was more accurate and reliable than the 2D method. The thickness term h₀ and small range of variance was acceptable for the prediction of the inclusions in this study.

(2) The deviations of the predicted maximum size of inclusions from 100 to 250 measurements were within the 95% confidence interval for the 100 measurement for both 2D and 3D determinations. However, an increase of the number of measurements, will lead to an increased accuracy of the predictions.

(3) The unit volume is an important factor that affects the predicted maximum size of inclusions. It is recommended that large unit volumes should be used in order to obtain an enough number of large size inclusions.
5. Future Work

The present work is focused on three dimensional determinations of inclusions in the ferroalloys and steel samples. The following work is suggested for the future work:

1. The metallic inclusions in the ferroalloys, which have a melting point that is higher than the steelmaking temperature, should be studied more in depth in the future. In addition, the solubility of them in steel at steelmaking conditions should also be considered.

2. The effect of different kinds of ferroalloy additions on the inclusion characteristics in specific steel grades should be studied in the future.

3. The inclusions in the nozzle clogging part should be analyzed in order to study the clogging mechanism.

4. Modifications of spinel inclusions and REM cluster in liquid steel during the refining process should be studied for avoiding the nozzle clogging.

5. The predicted maximum size of inclusions should be compared to the experimental results for confirmation.
6. References


Appendix

In this study, the following equations obtained based on a Redlich-Kister type polynomial were used for determination of the partial molar excess for the free energy change of Si, Al, Mg and O:

\[ RTln^{Y_{Si}} = X_{Fe}(1 - X_{Si})^{0} \Omega_{Fe-Si} + X_{Fe}(X_{Fe} - 2X_{Si} - 2X_{Fe}X_{Si} + 2X_{Si}^2)^{1} \Omega_{Fe-Si} \]
\[ + X_{Cr}(1 - X_{Si})^{0} \Omega_{Cr-Si} + X_{Cr}(X_{Cr} - 2X_{Si} - 2X_{Cr}X_{Si} + 2X_{Si}^2)^{1} \Omega_{Cr-Si} \]
\[ + X_{Ni}(1 - X_{Si})^{0} \Omega_{Ni-Si} + X_{Ni}(X_{Ni} - 2X_{Si} - 2X_{Ni}X_{Si} + 2X_{Si}^2)^{1} \Omega_{Ni-Si} \]
\[ + X_{O}(1 - X_{Si})^{0} \Omega_{O-Si} \]
\[ -X_{Fe}[X_{Cr}^{0} \Omega_{Fe-Cr} + 2X_{Cr}(X_{Fe} - X_{Cr})^{1} \Omega_{Fe-Cr}] \]
\[ -X_{Fe}[X_{Ni}^{0} \Omega_{Fe-Ni} + 2X_{Ni}(X_{Fe} - X_{Ni})^{1} \Omega_{Fe-Ni}] \]
\[ -X_{Fe}[X_{Al}^{0} \Omega_{Fe-Al} + 2X_{Al}(X_{Fe} - X_{Al})^{1} \Omega_{Fe-Al}] \]
\[ -X_{Fe}\left[ X_{Mg}^{0} \Omega_{Fe-Mg} + 2X_{Mg}(X_{Fe} - X_{Mg})^{1} \Omega_{Fe-Mg} \right] \]
\[ -X_{Fe}\left[ X_{O}^{0} \Omega_{Fe-O} + 2X_{O}(X_{Fe} - X_{O})^{1} \Omega_{Fe-O} \right] \]
\[ -X_{Cr}\left[ X_{Ni}^{0} \Omega_{Cr-Ni} + 2X_{Ni}(X_{Cr} - X_{Ni})^{1} \Omega_{Cr-Ni} \right] \]
\[ -X_{Cr}\left[ X_{Al}^{0} \Omega_{Cr-Al} + 2X_{Al}(X_{Cr} - X_{Al})^{1} \Omega_{Cr-Al} \right] \]
\[ -X_{Cr}\left[ X_{O}^{0} \Omega_{Cr-O} + 2X_{O}(X_{Cr} - X_{O})^{1} \Omega_{Cr-O} \right] \]
\[ -X_{Ni}\left[ X_{Al}^{0} \Omega_{Ni-Al} + 2X_{Al}(X_{Ni} - X_{Al})^{1} \Omega_{Ni-Al} \right] \]
\[ -X_{Ni}\left[ X_{Mg}^{0} \Omega_{Ni-Mg} + 2X_{Mg}(X_{Ni} - X_{Mg})^{1} \Omega_{Ni-Mg} \right] \]
\[ -X_{Ni}\left[ X_{O}^{0} \Omega_{Ni-O} + 2X_{O}(X_{Ni} - X_{O})^{1} \Omega_{Ni-O} \right] \]
\[ -X_{Al}\left[ X_{O}^{0} \Omega_{Al-O} + X_{Mg}X_{O}^{0} \Omega_{Mg-O} \right] \]
\[ -2X_{Fe}X_{Cr}X_{Ni}^{0} \Omega_{Fe-Cr-Ni} - 3X_{Fe}^{2}X_{Cr}X_{Ni}^{1} \Omega_{Fe-Cr-Ni} \]
\[ -3X_{Fe}X_{Cr}X_{Ni}^{2}X_{Fe-Cr-Ni} - 3X_{Fe}X_{Cr}X_{Ni}^{2}X_{Ni}^{1} \Omega_{Fe-Cr-Ni} \] (A-1)

\[ RTln^{Y_{Al}} = X_{Fe}(1 - X_{Al})^{0} \Omega_{Fe-Al} + X_{Fe}(X_{Fe} - 2X_{Al} - 2X_{Fe}X_{Al} + 2X_{Al}^2)^{1} \Omega_{Fe-Al} \]
\[ + X_{Cr}(1 - X_{Al})^{0} \Omega_{Cr-Al} + X_{Cr}(X_{Cr} - 2X_{Al} - 2X_{Cr}X_{Al} + 2X_{Al}^2)^{1} \Omega_{Cr-Al} \]
\[ + X_{Ni}(1 - X_{Al})^{0} \Omega_{Ni-Al} + X_{Ni}(X_{Ni} - 2X_{Al} - 2X_{Ni}X_{Al} + 2X_{Al}^2)^{1} \Omega_{Ni-Al} \]
\[ + X_{O}(1 - X_{Al})^{0} \Omega_{O-Al} \]
\[ -X_{Fe}[X_{Cr}^{0} \Omega_{Fe-Cr} + 2X_{Cr}(X_{Fe} - X_{Cr})^{1} \Omega_{Fe-Cr}] \]
\[ -X_{Fe}[X_{Ni}^{0} \Omega_{Fe-Ni} + 2X_{Ni}(X_{Fe} - X_{Ni})^{1} \Omega_{Fe-Ni}] \]

65
-X_{Fe}[X_{Si}^{0} \Omega_{Fe-Si} + 2X_{Si}(X_{Fe} - X_{Si})^{1}\Omega_{Fe-Si}]
-X_{Fe}[X_{Mg}^{0} \Omega_{Fe-Mg} + 2X_{Mg}(X_{Fe} - X_{Mg})^{1}\Omega_{Fe-Mg}]
-X_{Fe}[X_{O}^{0} \Omega_{Fe-O} + 2X_{O}(X_{Fe} - X_{O})^{1}\Omega_{Fe-O}]
-X_{Cr}[X_{Ni}^{0} \Omega_{Cr-Ni} + 2X_{Ni}(X_{Cr} - X_{Ni})^{1}\Omega_{Cr-Ni}]
-X_{Cr}[X_{Si}^{0} \Omega_{Cr-Si} + 2X_{Si}(X_{Cr} - X_{Si})^{1}\Omega_{Cr-Si}]
-X_{Cr}[X_{O}^{0} \Omega_{Cr-O} + 2X_{O}(X_{Cr} - X_{O})^{1}\Omega_{Cr-O}]
-X_{Ni}[X_{Si}^{0} \Omega_{Ni-Si} + 2X_{Si}(X_{Ni} - X_{Si})^{1}\Omega_{Ni-Si}]
-X_{Ni}[X_{Mg}^{0} \Omega_{Ni-Mg} + 2X_{Mg}(X_{Ni} - X_{Mg})^{1}\Omega_{Ni-Mg}]
-X_{Ni}[X_{O}^{0} \Omega_{Ni-O} + 2X_{O}(X_{Ni} - X_{O})^{1}\Omega_{Ni-O}]
-X_{Si}[X_{O}^{0} \Omega_{Si-O} + 2X_{O}(X_{Si} - X_{O})^{1}\Omega_{Si-O}]
-X_{Mg}[X_{O}^{0} \Omega_{Mg-O} + 2X_{O}(X_{Mg} - X_{O})^{1}\Omega_{Mg-O}]
-2X_{Fe}X_{Cr}X_{Ni}^{0} \Omega_{Fe-Cr-Ni} - 3X_{Fe}^{2}X_{Cr}X_{Ni}^{1} \Omega_{Fe-Cr-Ni}
-3X_{Fe}X_{Cr}^{2}X_{Ni}^{1} \Omega_{Fe-Cr-Ni} - 3X_{Fe}X_{Cr}X_{Ni}^{2} \Omega_{Fe-Cr-Ni}^{1}

(A-2)

RTIn^{y_{Mg}} = X_{Fe}(1 - X_{Mg})^{0} \Omega_{Fe-Mg} + X_{Fe}(X_{Fe} - 2X_{Mg} - 2X_{Fe}X_{Mg} + 2X_{Mg}^{2})^{1} \Omega_{Fe-Mg}
+X_{Ni}(1 - X_{Mg})^{0} \Omega_{Ni-Mg} + X_{Ni}(X_{Ni} - 2X_{Mg} - 2X_{Ni}X_{Mg} + 2X_{Mg}^{2})^{1} \Omega_{Ni-Mg}
+X_{O}(1 - X_{Mg})^{0} \Omega_{O-Mg}
-X_{Fe}[X_{Cr}^{0} \Omega_{Fe-Cr} + 2X_{Cr}(X_{Fe} - X_{Cr})^{1}\Omega_{Fe-Cr}]
-X_{Fe}[X_{Ni}^{0} \Omega_{Fe-Ni} + 2X_{Ni}(X_{Fe} - X_{Ni})^{1}\Omega_{Fe-Ni}]
-X_{Fe}[X_{Si}^{0} \Omega_{Fe-Si} + 2X_{Si}(X_{Fe} - X_{Si})^{1}\Omega_{Fe-Si}]
-X_{Fe}[X_{Al}^{0} \Omega_{Fe-Al} + 2X_{Al}(X_{Fe} - X_{Al})^{1}\Omega_{Fe-Al}]
-X_{Fe}[X_{O}^{0} \Omega_{Fe-O} + 2X_{O}(X_{Fe} - X_{O})^{1}\Omega_{Fe-O}]
-X_{Cr}[X_{Ni}^{0} \Omega_{Cr-Ni} + 2X_{Ni}(X_{Cr} - X_{Ni})^{1}\Omega_{Cr-Ni}]
-X_{Cr}[X_{Si}^{0} \Omega_{Cr-Si} + 2X_{Si}(X_{Cr} - X_{Si})^{1}\Omega_{Cr-Si}]
-X_{Cr}[X_{Al}^{0} \Omega_{Cr-Al} + 2X_{Al}(X_{Cr} - X_{Al})^{1}\Omega_{Cr-Al}]
-X_{Cr}[X_{O}^{0} \Omega_{Cr-O} + 2X_{O}(X_{Cr} - X_{O})^{1}\Omega_{Cr-O}]
-X_{Ni}[X_{Si}^{0} \Omega_{Ni-Si} + 2X_{Si}(X_{Ni} - X_{Si})^{1}\Omega_{Ni-Si}]
-X_{Ni}[X_{Al}^{0} \Omega_{Ni-Al} + 2X_{Al}(X_{Ni} - X_{Al})^{1}\Omega_{Ni-Al}]
-X_{Ni}[X_{O}^{0} \Omega_{Ni-O} + 2X_{O}(X_{Ni} - X_{O})^{1}\Omega_{Ni-O}]

66
\[ -X_{Si}[X_S^{0} \Omega_{Si-O} + 2X_O(X_{Si} - X_O)^{1} \Omega_{Si-O}] \]
\[ -X_{Al}[X_S^{0} \Omega_{Al-O} + 2X_O(X_{Al} - X_O)^{1} \Omega_{Al-O}] \]
\[ -2X_{Fe}X_{Cr}X_{Ni}^{0} \Omega_{Fe-Cr-Ni} - 3X_{Fe}^{2}X_{Cr}X_{Ni}^{1} \Omega_{Fe-Cr-Ni} \]
\[ -3X_{Fe}X_{Cr}^{2}X_{Ni}^{1} \Omega_{Fe-Cr-Ni} - 3X_{Fe}X_{Cr}X_{Ni}^{2} \Omega_{Fe-Cr-Ni} \]

\[ \text{RTln}^{y_0} = X_{Fe}(1 - X_O)^{0} \Omega_{Fe-O} + X_{Fe}(X_{Fe} - 2X_O - 2X_{Fe}X_O + 2X_O^{2})^{1} \Omega_{Fe-O} \]
\[ +X_{Cr}(1 - X_O)^{0} \Omega_{Cr-O} + X_{Cr}(X_{Cr} - 2X_O - 2X_{Cr}X_O + 2X_O^{2})^{1} \Omega_{Cr-O} \]
\[ +X_{Ni}(1 - X_O)^{0} \Omega_{Ni-O} + X_{Ni}(X_{Ni} - 2X_O - 2X_{Ni}X_O + 2X_O^{2})^{1} \Omega_{Ni-O} \]
\[ +X_{Si}(1 - X_O)^{0} \Omega_{Si-O} + X_{Si}(X_{Si} - 2X_O - 2X_{Si}X_O + 2X_O^{2})^{1} \Omega_{Si-O} \]
\[ +X_{Al}(1 - X_O)^{0} \Omega_{Al-O} + x_{Mg}(1 - X_O)^{0} \Omega_{Mg-O} \]
\[ -X_{Fe}[X_{Cr}^{0} \Omega_{Fe-Cr} + 2X_{Cr}(X_{Fe} - X_{Cr})^{1} \Omega_{Fe-Cr}] \]
\[ -X_{Fe}[X_{Ni}^{0} \Omega_{Fe-Ni} + 2X_{Ni}(X_{Fe} - X_{Ni})^{1} \Omega_{Fe-Ni}] \]
\[ -X_{Fe}[X_{Si}^{0} \Omega_{Fe-Si} + 2X_{Si}(X_{Fe} - X_{Si})^{1} \Omega_{Fe-Si}] \]
\[ -X_{Fe}[X_{Al}^{0} \Omega_{Fe-Al} + 2X_{Al}(X_{Fe} - X_{Al})^{1} \Omega_{Fe-Al}] \]
\[ -X_{Fe}[X_{Mg}^{0} \Omega_{Fe-Mg} + 2X_{Mg}(X_{Fe} - X_{Mg})^{1} \Omega_{Fe-Mg}] \]
\[ X_i: \text{mole fraction of component } i, \ y_i: \text{activity coefficient of component } i, R: \text{gas constant}, T: \text{temperature (K)}, \ \Omega: \text{interaction parameter}. \]