Optimization of Rare Earth Metals (REM) addition in high temperature stainless steel grade 253MA

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ABSTRACT

The focus of this thesis work is to optimize rare earth metal (REM) addition in Therma 253MA, an austenitic stainless-steel grade in order to get a good trade-off between oxidation resistance property and the amount of big REM inclusions formed. Big REM inclusions are detrimental to material properties and REM is required to be dissolved in the matrix for improving the oxidation resistance. REM optimization can also lead to economical savings for Outokumpu. The distribution of REM between matrix and inclusion is affected by factors such as REM addition, initial oxygen and sulphur contents and time to casting of the melt. The re-oxidation of melt in the tundish also affects the REM distribution. Hence, the effect of these factors on the inclusion characteristics is investigated by analysing samples with different REM additions, using light optical microscope (LOM) and scanning electron microscope (SEM). LOM analysis focussed on stringer inclusion characteristics. SEM+EDS analysis is done using automated “INCA Feature” software with focus on overall inclusion characteristics. Oxidation and creep tests are also performed to study the effect of different REM additions on oxidation and creep behaviour. The results from inclusion analysis show that increasing REM addition and time to casting has a bad effect on stringer and overall inclusion characteristics. The re-oxidation in the tundish influences the inclusion formation, but does not affect the stringer characteristics. The resistance to oxidation of the samples is also compared and is observed to increase within increasing REM addition. Finally, this works suggests an optimal REM addition for Therma 253MA to get a good balance between oxidation resistance and amount of big inclusions.

Keywords: REM addition, non-metallic inclusions, oxidation, austenitic, optimization

**Nyckelord:** REM-tillägg, icke-metalliska inneslutningar, oxidation, austenitisk, optimering
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1 INTRODUCTION

The discovery of stainless steel, more than a century ago has revolutionised the modern world as we know it today. Ever since its first commercial production started in the early 1900s as a “rust free” material for cutlery, stainless steel has found its application in almost every manufacturing sector today. Initially known for its “rust free” property, stainless steel over the years, were soon recognised for its excellent physical and mechanical properties in demanding applications. Today, stainless steel is considered as iron-based family of alloys, comprising of various grades, catering to very specific requirements. With the automotive and the construction sector growing, the demand for stainless steel has been increasing steadily. With the increasing demand for high performance stainless steel, metallurgists all over the world have been constantly working towards improving the properties of stainless steel with good quality.

Outokumpu stainless steel AB is a leading producer of various grades of stainless steel, with a strong footprint in Europe and America. Therma 253 MA is one of the many special grades, designed and produced by Outokumpu for high temperature applications. Apart from the main alloying elements chromium and nickel, this grade is alloyed with nitrogen, silicon and rare earth metal (REM). REMs improve oxidation, erosion-corrosion and oxide spallation resistances. Cold rolled 253 MA is mainly used to manufacture manifold and other critical parts in automotive industry. In recent years, there are reports of delamination and cracking, observed in very thin sections after deep drawing and other severe deformation processes in 253MA, as shown in Figure 1 [1, 2]. Analysis by Outokumpu shows that these defects are caused by REM oxide stringer inclusions[1, 2] in thin sections after severe forming processes. Figure 2 shows the presence of REM oxide stringer inclusions in delamination. This creates a need to optimise the REM addition in this grade to maintain a proper balance between the amount of big REM oxide stringers and the oxidation resistance property of the material.
A recent study done at Avesta Research Centre (ARC) briefly discussed the effect of different REM additions. A light optical microscope analysis of samples obtained from different heats with different heat addition was believed to show a reduction in amount of REM inclusions with decreasing amount of REM addition as shown in Figure 3. It is also believed that the level of oxygen and sulphur present in steel also affects the REM distribution between matrix and inclusions. Hence, a detailed quantitative study on REM inclusions is warranted to optimise the REM addition. Such optimization can result in economical savings for Outokumpu.
Figure 3: LOM images showing microstructure with decreasing REM additions from (a) to (d)

### 1.1 Ethical and social aspects

This thesis work is carried out at Avesta Research centre in the most ethical way possible. Certain data in this report have been removed or replaced with alternative notations, as they are deemed confidential by Outokumpu. Avesta Research centre can be approached for the complete report. There is certainly no bias in conducting the experiment and assumptions for analysing the results are considered with proper justification. Previous studies related to this work have been given due credit, wherever required, upholding the ethics of doing this thesis work.

The social aspects of this work cannot be understood completely from the results of this work. This work provides a start towards optimizing the REM addition in 253MA and has lot of future scope in it. In the long run, this work has the scope for giving Outokumpu and its stakeholders a competitive edge in the production of 253MA in the global market. This work also aims at educating the operators about the effect of different factors in the formation of
non-metallic REM inclusions. Hence, optimization of REM addition may give better control on the formation of big non-metallic inclusions, thereby improving the quality of stainless steel.

1.2 Aims
The aim and purpose of this experimental work is threefold. The first is to investigate REM inclusions quantitatively for different heats of 253 MA with different REM additions. The results from this investigation will be further used to estimate the REM content dissolved in the matrix. The second part of this work is to investigate how different factors like REM content, oxygen and sulphur contents and casting time influence characteristics of REM inclusions. The final part of this work will be to summarise the effect of different REM additions on inclusion characteristics and oxidation resistance property of 253MA. The overall goal of this experimental work is to suggest an optimal REM addition for this grade, 253MA to get a good trade-off between amount of big inclusions or stringers and better properties.
2 BACKGROUND

2.1 Stainless Steel in general

Stainless steel is a family of iron-based alloys, commonly known for exceptional resistance to corrosion. These alloys generally contain a minimum of 10.5% chromium (Cr) and a maximum of 1.2% carbon (C) [3]. The rust-free property is attributed to the chromium content, which forms a passive, adherent and self-healing oxide layer, that covers the entire surface, inhibiting further corrosion. Better corrosion resistance is achieved by increasing the chromium content in the steel beyond 10.5% or by adding other elements like molybdenum and nickel [4]. Additions of molybdenum enhances resistance to pitting corrosion, in particular [4]. Nickel increases ductility and toughness by promoting an austenitic structure. Other elements are also added to enhance the properties of stainless steel. These elements affect the microstructure of stainless steel by either promoting a ferritic structure or austenitic structure and therefore classified as ferrite and austenite stabilizers respectively. Based on microstructure, stainless steel is broadly classified as: Ferritic, Austenitic, Duplex and Martensitic stainless steel.

2.2 Austenitic stainless steel

Among the above, austenitic stainless steel is the largest group with formability and corrosion resistance, superior to other groups. Nickel (Ni), manganese (Mn) and nitrogen (N) are the main elements added to form the austenitic structure in this alloy. This group is classified into two sub-groups: 200 series and 300 series [5]. The 300 series are Ni-based stainless steel, containing a minimum of 6% Ni. The widely known grade in this series is 304, otherwise known as 18-8 (18% Cr 8% Ni). The 200 series grades have relatively higher content of Mn and N, but lower amount of Ni. Apart from these two major series, certain austenitic grades are also designed for demanding applications. There are super-austenitic grades like Outokumpu’s 254 SMO with high amounts of Cr between 17 and 25%, Ni between 14 and 25% and Mo between 3% and 7% [5].

Outokumpu’s Therma 253 MA is a high temperature austenitic grade, micro-alloyed with REM, designed for high temperature applications with service temperature up to 1150°C [5]. This grade exhibits excellent creep properties and oxidation resistance under cyclic conditions at high temperature, better than the ferritic grades. The typical composition of 253MA is shown in Table 1.
Table 1: Chemical composition of austenitic stainless-steel grade Therma 253MA (mass %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>N</th>
<th>Si</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.09</td>
<td>21.00</td>
<td>11.00</td>
<td>0.17</td>
<td>1.6</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### 2.3 Production of 253MA at Avesta works

The production of 253MA is typical of any stainless grade, produced at Avesta works. The production of all the grades of stainless steel at Avesta works is scrap based. Outokumpu uses 85-90% of recycled scrap (mainly stainless steel) for the production along with the alloying elements as the remaining virgin materials [5]. The scrap along with the different alloying elements and slag formers are charged into the electric arc furnace (EAF) using baskets, based on a particular recipe for each grade. The charge is melted by the spark between the carbon electrodes in the EAF. Once the melting is completed, de-slagging is done. The melt is then transferred to Argon oxygen decarburization (AOD) converter or vessel. This step is primarily for reducing the carbon content in the melt by blowing mixture of argon and oxygen through the bottom tuyeres. Moreover, some alloys are also added at this stage to the melt. After decarburization, desulphurization of melt is carried out in the vessel using basic slag. High quality requirements for stainless steel grades demand secondary refining process. The melt is tapped from AOD vessel into ladle and transferred to ladle refining station. At this stage, final adjustments to composition are done. In the case of 253MA grade, REM is added in the form of misch metal into the ladle furnace. Misch metal is an alloy of REM, with cerium (Ce) as the major constituent. The content of Ce is analysed and taken to be the representative of all the REMs added to 253MA. Temperature adjustment is also done at this stage by electrode heating to ensure a suitable casting temperature. Ladle refining process is equipped with electromagnetic stirrer and porous plugs at the bottom of the ladle to facilitate constant stirring for temperature and composition homogenization. The molten steel is then transferred to the continuous casting machine, where it is cast into slabs. These slabs are cut and then sent to the rolling mill for further processing.

### 2.4 Brief introduction to REM

International Union of Pure and Applied Chemistry (IUPAC) defines rare earth metals as the elements that comprise the lanthanide series in the periodic table (atomic numbers starting from 57 to 71), including scandium and yttrium. These rare earth elements have a unique electronic
configuration, with valence electrons occupying the 6s sub-shell completely and start filling the 4f sub shell, instead of filling the corresponding 5d sub-shell. Their electronic configuration is represented by [X]4fn-15d16s2 or [X]4fn6s2. This makes the rare earth metal highly reactive [6].

REM are being widely used in steel-making, since the early 19th century to meet very specific requirements. The most common way of adding REM to steel is through misch metal. Misch metal is an alloy of rare earth elements, typically containing around 55% cerium, 25% lanthanum and other rare earth elements like neodymium, praseodymium, etc. Misch metal has remarkable qualities like low melting point, low vapour pressure and high reactivity making them favourable as steel additives [7]. Due to high chemical activity of REM, they have high affinity for oxygen (O) and sulphur (S) present in steel, making them useful in purifying steel.

2.5 Thermodynamics of REM in steel-making

REM, owing to its strong activity, reacts with oxygen and sulphur to form various oxides, sulphides and oxysulfides. Wilson and Vahed used thermodynamic data to study the formation of various cerium compounds in steel. They came up with precipitation diagrams for Ce-O-S system in steel, as shown in Figure 4[8, 9].

It was theoretically observed that Cerium (IV) oxide (CeO₂) formation requires a very high oxygen activity and hence its formation is not favourable under normal steel making conditions. Cerium (III) oxide (Ce₂O₃) is the stable oxide, that is formed under normal steel making conditions. Figure 4(a) represents the equilibrium of Ce₂O₃ with steel with respect to the henrian activity coefficients of cerium (hCe) and oxygen (hO). Figure 4(b) represents the equilibrium of different Cerium sulphides: Cerium(II) sulphide (CeS), Cerium(III) sulphide (Ce₂S₃) and Cerium(IV) sulphide (CeS₂) with steel, with respect to the henrian activity coefficients of cerium (hCe) and sulphur (hS). Figure 4(a) and Figure 4(b) are combined to construct the precipitation diagram of Ce-O-S system as shown in Figure 4(c), which also contains the equilibrium of Cerium oxysulfide (Ce₂O₂S) with steel.

Based on Figure 4(c), the following predictions were made:

- The oxygen to sulphur ratio is crucial in determining the formation and also the precipitation sequence between Ce₂O₃ and Ce₂O₂S. Generally, in Al-killed steel, Ce₂O₃ precipitate first.
• Oxygen activity must be very low for cerium sulphides to precipitate first. Hence, normally Ce$_2$O$_2$S are formed before any of the cerium sulphides are formed.

• Normally, Cerium oxy sulphides are also enriched with lanthanum.

![Diagram of Ce-O-S system in steel](image)

Figure 4: Precipitation diagram of Ce-O-S system in steel

It is clear from the above theoretical predictions that the contents of oxygen and sulphur have a strong influence on type and the amount of REM inclusions formed and thereby controls the amount of REM dissolved in the matrix. Figure 5 shows a schematic representation of the amount of REM inclusions at a given REM, O and S content, illustrated by Outokumpu in ARC 20160042 [10]. Figure 5 can also be considered as a different version of that developed by Wilson and Vahed. It is shown that there is always some amount of slag (inclusions) present for any given amount of REM, O and S contents. More importantly, it must be noted that the
amount of slag increases with increasing REM for the same amount of O and S. The same trend is observed with increasing O and S content for the same amount of REM addition.

![Figure 5: Schematic relation of REM addition, sulphur and oxygen content, and slag amount](image)

### 2.6 REM functions

#### 2.6.1 De-oxidation and Desulphurization

The strong chemical activity of REM is exploited in purifying steel by reducing oxygen and sulphur content to a very low level by forming stable oxides and sulphides, with high melting points. Refer 2.5 for the different oxides and sulphides formed by Ce in steel. Purification is completed when these non-metallic inclusions are later removed as slag. REM has a tendency to form oxide clusters in molten steel, with irregular shape and large density, comparable to steel [11, 12]. Examples of typical REM clusters are shown in Figure 6. REM sulphides are spherical and form only when the oxygen content is very low [8, 9, 13]. It must be noted that the REM oxide clusters have posed a serious challenge to the castability of steel. These clusters tend to stick with each other and get agglomerated on the inside walls of the nozzle, causing clogging. Such clogging issues can lead to shutdown of the entire process for many hours. Nozzle clogging is a serious issue in steel grades deoxidised with REM [11, 14].
2.6.2 Inclusion modification

Non-metallic inclusions have a profound effect on the quality of stainless steel, in particular [15]. The physical and the mechanical properties are greatly influenced by the characteristics of non-metallic inclusions. Manganese sulphide (MnS) inclusions are also known to be initiating sites for pitting corrosion in stainless steel [13, 15]. REM has the ability to alter the characteristics and distribution of inclusions by forming very stable oxides, sulphides and oxy-sulphides. The properties of steel are greatly improved by the improved inclusion distribution. According to free energy, REM can modify and suppress the formation of detrimental MnS [13]. It has been experimentally observed that REM addition improved the pitting corrosion resistance of super duplex stainless steel by eliminating MnS inclusions [13]. It was also observed in the same study that REM addition created a considerable reduction in interfacial area of inclusions, which eventually resulted in improvement of pitting corrosion resistance. The positive effect of Ce on pitting corrosion resistance of hyper duplex steel was studied by Jeon et.al [16]. It was observed that the Ce modified the inclusion characteristics by forming stable oxides, which reduced the formation of micro-crevices by generating Cr-rich zones around them. Hence, the formation of stable Ce oxides improved the resistance to pitting corrosion in hyper duplex steel [16]. The ability of REM to reduce the mean size of the inclusion distribution was already observed in [13]. The same trend was also observed in 25% duplex stainless steel by Ha et.al, resulting in better resistance to pitting corrosion [17].

2.6.3 Grain refinement

The microstructure of steel is also influenced by REM inclusions. Fine inclusions of REM can act as heterogenous nucleation sites and can also segregate at grain boundaries and pin them.
This hinders the grain growth and results in a fine grain structure [6]. The strength and ductility of duplex stainless steel was increased due to grain refinement by fine REM inclusions, as they pinned the grain boundaries, hindering the grain growth [18]. Grain refinement was also observed in as cast structure of ultra-low carbon steel, alloyed with REM, which resulted in improved yield strength [6].

2.6.4 Alloying

The microstructure of the steel is also greatly influenced and the properties are improved, when REM is dissolved in the matrix. Tiny amounts of REM, with its higher atomic radii distort the crystal lattice and therefore increase the strength of steel [6]. REM tend to segregate at grain boundaries, resulting in grain boundary strengthening [6]. It is believed that REM, because of its higher atomic radii, blocks the diffusion of chromium, molybdenum and tungsten in duplex stainless steel by occupying voids and vacancies, and therefore suppresses the formation of inter-metallic phases [18]. Micro-alloying of REM improves the oxidation resistance of heat-resistant stainless steel like Outokumpu’s Therma 253MA through “reactive element effect”. The phenomenon of high temperature oxidation is really crucial in understanding the effect of REM on the oxidation resistance.

2.7 High temperature oxidation

This is a very important phenomenon, which needs to be considered when designing materials for high temperature application. It is one form of corrosion at high temperature along with sulphidation, carburization and nitridation [5]. When exposed to oxidizing atmosphere, a protective layer of chromium oxide is formed on the surface, which prevents further oxidation. In the initial stages of oxidation, oxides of all elements are formed. Due to superior stability, Chromium oxide tends to grow laterally over others and cover the entire surface of the metal. This phase is called the transient oxidation [5]. Thereafter, the rate of oxidation is dependent on the growth of this protective layer. The growth of this layer is dependent on the transport of cations and anions through this layer. In the case of chromium oxide, the growth rate is dominated by the outward diffusion of chromium cations [19]. It must also be noted that the adhesion of this protective layer affects the oxidation resistance significantly. Many factors like growth induced stresses inside the scale and thermal shocks can lead to oxide spallation [5]. Lack of adhesion can also be caused by rapid outward diffusion of chromium ions too.
Therefore, oxidation resistance can be improved in the following ways:

- Sufficient amount of Chromium so that material can form a stable protective layer
- Reducing the growth rate of scale
- Improving scale adhesion

### 2.8 Reactive Element effect

Addition of rare earth metals is proven to have a very strong positive effect on the above ways in improving the oxidation resistance. This is the reactive element effect. This effect can be summarised with theories as follows:

- **Enhance selective oxidation of Cr**
  REM and its oxides, as mentioned before, act as heterogenous nucleation sites and stabilise fine alloy grain size. This increases the dislocation or sub grain boundary densities, providing a path for the diffusion of scale forming Cr to the surface. This reduces the transient oxidation stage and allows for fast formation of chromium oxide layer [19, 20].

- **Reduce scale growth rate**
  The reduction in growth rate is closely related to the diffusion properties of anions and cations through the oxide scale. REM occupies the grain boundary in the oxide scale also at the metal/scale interface. The presence of REM at these locations blocks the diffusion of chromium, thereby changing growth mechanism of oxide layer to oxygen transport. Since diffusion of oxygen is much slower than that of chromium, the growth rate of scale is greatly reduced [19, 20].

- **Improve scale adhesion**
  Lack of adhesion can arise from creation of vacancies by rapid diffusion of Cr from the metal/scale interface. This can be suppressed by REM segregation at the metal/scale interface to inhibit Cr diffusion and changing the growth mechanism to inward oxygen diffusion [19].

Several studies have been done to explain the above theories with experimental evidence [19]. The change in scale growth mechanism is a commonly accepted theory [18]. However, it must be noted that there is no clear explanation as to why REM blocks the diffusion of cations and not anions [19]. Hence, further studies are warranted to come up with a single model that could explain the effect of REM on oxidation behaviour of stainless steel.
2.9 Effect of REM addition on oxidation behaviour of 253 MA

Several studies have been conducted at Avesta Research Centre to investigate the effect of different REM additions on oxidation behaviour of Therma 253 MA. Cyclic oxidation and isothermal oxidation tests were done for mill samples produced with the different REM additions in approx. 100ton of steel. Rui Wu and Rita Lindstrom have summarised the findings in the ARC20160042[10].

Under both cyclic and isothermal tests, the sample with lowest REM addition exhibited poor oxidation resistance at higher temperatures of more than 1000°C. Overall, the oxidation resistance of samples was observed to decrease with decreasing REM addition.

2.10 Effect of REM addition on creep strength of austenitic steel grades

The effect of REM addition on creep behaviour of high temperature grades is not very clear. Any effect of Ce on creep strength of such grades is probably indirect. Unlike carbon and nitrogen, cerium does not strengthen the austenitic matrix through solid-solution strengthening[21]. However, cerium can remove or modify detrimental non-metallic inclusions like oxides and sulphides, which precipitate at grain boundaries and reduce the creep strength[21, 22]. A significant improvement in creep strength is observed for type-347H austenitic steel when Ce addition is done with Boron[23, 24]. Micro alloying of Ce removes traces of sulphur and oxygen in the grain boundary by forming oxy-sulphides, thus facilitating the precipitation of Boron in elemental form at the grain boundaries[24]. Hence, the positive effect of B on the creep strength of type-347H is amplified by Ce addition. Due to this indirect effect, it is believed that the effect of different REM addition to 253MA is also insignificant.


3 EXPERIMENT

This chapter covers the various analysis and tests carried out in this experimental work. The major part of the experimental work is to investigate inclusion characteristics in austenitic grade 253 MA using Light optical microscope (LOM) and Scanning electron microscope (SEM) for different amounts of REM additions in steel. The different REM additions considered are: REM-1, REM-2, REM-3, REM-4 and REM-5 of misch metal per approximately 100ton of steel

1. The REM additions are increased from REM-1 to REM-5, with REM-5 nearly two times that of REM-1.

The oxidation test results for REM-1, REM-3, REM-4 and REM-5 samples are already reported in ARC20160042[10]. For REM-2 addition, cyclic and isothermal oxidation tests are done and the results are compared with those obtained for other REM addition samples. Creep tests are also conducted for two REM-1 samples at different stress levels.

3.1 Sampling

The samples for this experimental work are provided by Outokumpu Stainless AB. They are cut from the ends of final rolled plates, near to the tensile test specimen location. Each sample is denoted by its heat and slab number. Refer Figure 7 for sample Id terminology.

Table 2 gives for the list of prepared samples and various inclusions investigations preformed for each sample (as denoted by ‘X’ in Table 2) in this work. Table 2 also contains the contents of Cerium (Ce) and Sulphur (S) in each sample, as measured in the tundish before casting. It must be mentioned that there is no information available regarding the specific slab end from which each sample has been cut. Hence, it is not known whether the sample represents the beginning or the end of the slab. The oxygen content is not measured at any stage during the

1 The actual values of REM additions are not mentioned in this report, as they are deemed as confidential data of Outokumpu Stainless AB.
steel-making process. Hence, additional samples were cut and separately analyzed for cerium, oxygen, sulphur and nitrogen using Optical emission spectroscopy (OES) and LECO gas analyzers respectively, in addition to the heat analysis.

<table>
<thead>
<tr>
<th>Sample Id2</th>
<th>REM addition</th>
<th>thickness (mm)</th>
<th>Ce (wt %)</th>
<th>S (wt %)</th>
<th>LOM3</th>
<th>SEM (INCA Feature)4</th>
</tr>
</thead>
<tbody>
<tr>
<td>442039-2</td>
<td>REM-5</td>
<td>10</td>
<td>0.05</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>585013-1a</td>
<td>REM-4</td>
<td>5</td>
<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>585013-1b</td>
<td>REM-4</td>
<td>5</td>
<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>585013-2a</td>
<td>REM-4</td>
<td>8</td>
<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>585013-2b</td>
<td>REM-4</td>
<td>8</td>
<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td></td>
</tr>
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<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>585013-3b</td>
<td>REM-4</td>
<td>8</td>
<td>0.042</td>
<td>0.001</td>
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<td>0.001</td>
<td>X</td>
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<tr>
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<td>0.001</td>
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<td>X</td>
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<td>442266-3</td>
<td>REM-3</td>
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<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>584643-1</td>
<td>REM-1</td>
<td>2</td>
<td>0.03</td>
<td>0.001</td>
<td>X</td>
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<td>584778-2</td>
<td>REM-1</td>
<td>2.5</td>
<td>0.03</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>582145-3</td>
<td>REM-1</td>
<td>2.5</td>
<td>0.042</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>560915-4</td>
<td>REM-1</td>
<td>1.5</td>
<td>0.036</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>590695-1</td>
<td>REM-2</td>
<td>2</td>
<td>0.031</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>590904-2</td>
<td>REM-2</td>
<td>4</td>
<td>0.036</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>590450-3</td>
<td>REM-2</td>
<td>2</td>
<td>0.036</td>
<td>0.001</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

It should be noted that REM inclusions are to be examined on the polished cross-section of these samples, perpendicular to the rolling direction. The area of examination for each specimen is specified in APPENDIX-1. It was observed from a previous study that oxygen content varies along the casting sequence of a particular heat [25]. So, samples are cut from all the slabs belonging to heat 585013 to study the effect of casting sequence on the REM distribution. The thickness of REM-1 and REM-2 samples is small (less than 4 mm). Hence, two to three samples (with same id) are cut from each slab to have a good amount of area for better statistics for inclusion investigation. Sample 590904-2 is selected among the REM-2 addition samples for oxidation (cyclic and isothermal) tests. Apart from the samples mentioned in Table 2, heat 560791 (REM-1 addition) was chosen for creep tests at different stress levels.

2 Letters “a” and “b” denote the two ends of the slab.

3 Multiple areas on 442039-2, 585013-3a, 585013-4a and 442266-3 are selected for LOM for better statistics.

4 Multiple areas on 442049-2, 442266-3, 584778-2 and 582145-3 are selected for SEM for better statistics.
3.2 Sample preparation

For inclusion investigation, each sample is prepared by automatic grinding and polishing in the following steps: stone grinder, 9 µm polishing with diamond suspension, 3 µm polishing with diamond suspension and final 0.2 µm polishing with colloidal silica. The samples are thoroughly washed with soap and water and also kept in ultrasonic bath for 3-5 min in between steps to remove the residual particles. The sample is finally washed with alcohol to remove any grease or dirt present. Before analysis, it is important to ensure that the sample surface is devoid of any scratch marks, dirt or anything that could possibly interfere with the analysis.

The samples for oxidation tests are approximately 20x15 mm and cuboidal. All the surfaces of the sample are wet ground with 80 mesh paper and finished with 180 mesh paper. The opposite surfaces are kept as parallel as possible. It should be noted that ISO21608:2012 is the recommended standard for specimen preparation for oxidation tests, which suggests final grinding with 1200 mesh paper. However, since sample for earlier oxidation tests were finished with 180 mesh paper, the current samples are prepared in the same way in order to compare the results.

3.3 LOM investigation

Each sample is analyzed by using Light optical microscope in bright field mode at a magnification of 200x. Inclusion analysis is done as per standard ASTM E45 using a software called “Inclusion Inspector”. This software is connected to the microscope and automatically detects particles over a defined area on the sample, giving detailed information about the particle characteristics too. Classification of particles is also done by this software as per method A in ASTM E45. The area of observation for each sample, defined using this software, is mentioned in APPENDIX-1. The smallest particle that can be detected has an equivalent circular diameter of 1.05 µm. This investigation focusses on the type-B and type-C stringer type inclusions present in each sample as it is believed that these types of inclusions are more problematic and serve as initiation sites for cracks and delamination during heavy forming processes. The definition of type-B and type-C stringers are slightly modified from the standard to concentrate more on the big stringers. Hence, for this work, stringers are those inclusions with a minimum of 20 particles in them and satisfying the other criteria as per the standard.
\section*{3.4 SEM investigation}

Certain samples, as indicated in Table 2 were analyzed under Zeiss FEG-SEM with an accelerating voltage of 15kV at a higher magnification of 1000x. Inclusion observation was done using back scatter electron (BSE) mode. Inclusion detection and measurements along with EDS analysis are done automatically using INCA Feature software. This software automatically detects particles over a defined area and along with fast EDS analysis, giving detailed information about inclusion characteristics. This software also facilitates the classification of inclusions as per the user’s customized recipe. A surface to surface feature analysis with the area of observation, chosen as per the thickness of the specimen as mentioned in APPENDIX-1 was done. The minimum particle size detection was set to ECD of 0.4 μm.

The results from the INCA Feature analysis are used to calculate the amount of cerium present in inclusions. The Ce present in inclusions is calculated by use of statistical methods and certain assumption, which are listed later in the report. Thereby, the amount of REM, dissolved in the matrix is calculated by assuming the equation 1.

\begin{equation}
\text{Bulk Ce content} = \text{Ce dissolved in matrix} + \text{Ce present in inclusions}
\end{equation}

The bulk Ce content in each sample was obtained from the composition analysis, done at the tundish stage during the melting process of each heat.

\section*{3.5 Oxidation tests}

Isothermal oxidation tests are performed in dry air in Thermogravimetry analyzer (TGA) Setaram TG 96 in dry air at 1000 °C, 1100°C and 1150°C for 250 hours. Cyclic oxidation tests are performed using the same setup in dry air at 1150°C for 90 hours and 1175°C for 50 hours. The temperature cycle for cyclic oxidation is as follows:

- Heating up to the target temperature
- Holding 2 hours at target temperature
- Cooling down to room temperature
- Hold for 10 min at room temperature

Prior to the test, the total surface area and the weight of the sample are measured and noted. The mass change is measured continuously using a microbalance during the test.

The mass change measured from the tests over time for different samples are used to compare their oxidation behaviour. Higher the mass change for a given time, means that the sample
oxidizes more and hence the resistance to oxidation of the corresponding sample is lower. For cyclic oxidation, two other parameters: breakaway time and maximum mass change are obtained from the test results to compare the oxidation behaviour of samples under cyclic conditions. The breakaway time denotes the beginning of oxide spallation. This denotes the time at which the mass change begins to drop after attaining a maximum. Shorter breakaway time suggests poor adhesion of the oxide layer. The maximum mass change is the mass change observed just before the oxide spallation starts. A higher maximum change means that the sample oxidizes more and hence has lower resistance to oxidation.
4 RESULTS

This chapter starts with the results of inclusion analysis using LOM and SEM. The effect of the following factors: REM addition, casting sequence, time to casting and initial sulphur content on inclusion characteristics are covered in this chapter. LOM results focus on the characteristics of stringer inclusions: total number, average stringer length, stringer particle density. SEM results focus on the overall characteristics of inclusions: total number, total inclusion area. The oxidation and creep test results are also presented in this chapter.

4.1 Particle characteristics after LOM investigation

Every sample is analyzed from surface to surface under LOM using “Inclusion Inspector”, which is an automatic image analysis of non-metallic inclusions in steel. The particles detected are classified into different inclusion types as per ASTM E-45 Method A and its characteristics are measured. A typical particle map for each REM addition is shown in Figure 8. Figure 8 shows that inclusions are observed to be present in the form of strings in high REM addition samples (REM-5, REM-4 and REM-3). These stringers are observed to be located towards the centre of the samples. On the contrary, REM-1 and REM-2 samples showed a rather uniform distribution of particles from surface to surface, with nearly no stringers present.

![Particle Maps](image)

*Figure 8: Particle Maps for different REM additions*

The volume fraction of particles \( (f_v) \) of each sample is taken to be equivalent to area fraction.

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5 The particle maps are compressed images, and hence do not correspond to the actual size of the sample.
(fa) of particle section in the cross-section [26]. Equivalent circular diameter (ECD) of each particle is the diameter of circle with the area of the particle section. The volume of each particle is estimated by assuming the particles to be perfect spheres with diameter equivalent to ECD. This assumption, however, underestimates the particle volume by a small amount. This facilitates the calculation of volume of metal analysed (V_m) by equation 2.

$$V_m = \frac{\sum_{i=1}^{n} \left( \frac{4}{3} \pi \left(\frac{d_i}{2}\right)^3 \right)}{f_v}$$  \hspace{1cm} (2)

Where, di is the measured ECD of ith particle and n is the number of measured particles in the sample using “Inclusion inspector” software. The typical particle size distribution graphs with number of particles per volume (Nv) for size intervals of 1μm is shown for all the REM addition samples in Figure 9. Nv for each size interval is calculated using equation 3.

$$Nv = \frac{n_i}{V_m}$$  \hspace{1cm} (3)

Where, ni is the number of particles in ith size interval. Figure 9 shows that the number of small particles (ECD = 1-5 μm) is much larger than big particle (ECD > 5 μm) for all REM addition samples. Therefore, Figure 9(b) is shown for looking at distribution of big particles. Figure 9(a) shows the lowest REM addition, REM-1 sample contains nearly twice the number of small particles (ECD = 1-2 μm), observed in REM-5 sample. On the contrary, it is evident from Figure 9(b) that the number of big particles (ECD> 5μm) in REM-5 sample becomes increasingly more with size when compared to REM-1 samples. This shows that, with higher REM addition, increasing number of bigger particles are expected to be formed in the melt and the particle density of small particles decreases.

Figure 9: Particle-size distribution curves (a) Nv vs ECD (b) Log (Nv) vs ECD
The effect of REM addition on the whole particle density (Nv) and the particle size, represented by the total particle area are better understood by looking at Figure 10. Nv is calculated in the same manner using equation 3, except that the total number of particles in each sample is considered for this calculation. Overall, the particle density tends to decrease with increasing REM addition. The total area of particles per observed area tends to follow the opposite trend. It must be noted that the both particle density and total particle area appear to saturate after REM-4 addition. The total particle area is observed to be the lowest for REM-2 addition.

It is evident from Figure 10, that higher the REM addition, the particle area is more with lesser number of particles present. Therefore, bigger particles are expected to be formed when more than REM-3 of REM is added. Between REM-1 and REM-2 addition, the particle density and total particle area is lower in the latter. However, a higher particle density and lower particle area for REM-1 and REM-2 shows that at these additions, a very large number of small particles are present.

![Figure 10: (a) Nv for different REM additions (b) total area of particles per observed area for different REM additions under LOM](image)

### 4.2 Stringer characteristics after LOM investigation

It is already shown in Figure 8, that stringer type inclusions are more prominent in high REM addition samples. These stringer type inclusions are problematic as they become crack initiation site in thin sections under heavy forming operations. Previous reports have shown that these stringers are mainly composed of REM inclusions[1, 2, 10]. This makes the investigation of stringers and its characteristics (total number, length and stringer particle density) for different REM addition samples crucial in controlling them.

Figure 11 shows the influence of different REM additions on characteristics of stringer type inclusions. Overall, the characteristics are observed to increase with increasing REM addition.
High REM additions of more than REM-3 showed increasingly more stringers per unit volume with increase in REM. The stringers also appeared to be longer and contain a greater number of particles per unit length, when REM addition is increased. The REM-1 and REM-2 samples showed nearly no stringers, with just one sample among the REM-1 samples exhibiting a significant number of stringers per unit volume. The average length of stringers in the REM-1 sample is observed to be more than that for REM-3 sample. This is misleading because it must be noted that there are not enough stringers present for good statistical evaluation. And hence, the probability of stringer forming in REM-1 samples is much less than that observed for REM-3 samples. The REM-2 samples were not considered in Figure 11 (b) and (c) for the same reason. The increased average length for REM-1 sample, compared to the REM-3 samples can also be due to the increased inter-particle distance in the stringer, of REM-1 samples, owing to its lowest particle density.

Previous study has explored the possibility of re-oxidation during initial filling of tundish[25]. It is found that the oxygen level increases by 3-4 times the level observed in ladle furnace during the initial stages of casting[25]. Figure 12 explores the influence of casting sequence on
stringer characteristics of heat 585013 (REM-4). Overall, the stringer features increase along the casting sequence. This shows that re-oxidation phenomenon, which is prominent during the initial stage of casting does not have any influence on the stringers. However, the residence time for the remaining melt in the ladle and the tundish increases along the casting sequence. This residence time is referred to as “time to casting” in this work. So, with increase in time to casting along the casting sequence, the stringer type inclusions in the same heat become increasingly more in number, longer and also contain a greater number of particles.

Figure 12: Stringer characteristics along casting sequence of Heat 585013 (REM-4) (a) Total number of stringers per unit volume (b) Average length of stringer (c) particles density of stringer

The spread of values, observed for REM-4 samples in Figure 11 implied that stringer-type inclusions are influenced by factors other than REM addition. Figure 12 showed the effect of time to casting on stringer characteristics. Table 3 compares the stringer characteristics of samples taken from same slab number of different heats corresponding to REM-4 addition to investigate the influence of the sulphur content before REM addition ($S_{\text{initial}}$). The $S_{\text{initial}}$ for each heat is obtained from the production plant. (Note: The oxygen content is generally not measured at any stage during the steel making process in the plant) It must also be noted that the time to casting for the samples from same slab number in Table 3 are different too. The
influence of sulphur is not very clear with this data due to the overlapping effect of time to casting being present. However, the influence of time to casting on stringers observed in the same slab number of two different heats corresponding to the same REM addition agrees with the results mentioned before in Figure 12.

Table 3: Comparison of stringer characteristics for same slabs of different heats (REM-4)

<table>
<thead>
<tr>
<th>Sample-Id</th>
<th>$S_{\text{initial}}$ (mass %)$^6$</th>
<th>Time to casting (min)</th>
<th>Stringer number, Nv (mm$^{-3}$)</th>
<th>Average stringer length (μm)</th>
<th>Particle density in stringer per unit length (μm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>585013-2</td>
<td>Medium</td>
<td>37.5</td>
<td>44</td>
<td>196</td>
<td>153</td>
</tr>
<tr>
<td>584443-2</td>
<td>Low</td>
<td>46</td>
<td>73</td>
<td>374</td>
<td>203</td>
</tr>
<tr>
<td>585013-3</td>
<td>Medium</td>
<td>49</td>
<td>51</td>
<td>189</td>
<td>151</td>
</tr>
<tr>
<td>441715-3</td>
<td>High</td>
<td>55</td>
<td>66</td>
<td>362</td>
<td>177</td>
</tr>
</tbody>
</table>

4.3 Inclusion characteristics after SEM (Feature) investigation

An automatic inclusion analysis is performed on FEG-SEM using “INCA Feature” software for certain samples, as mentioned in Table 2. The inclusion characteristics such as size, number and composition are measured for each sample using this software and compared.

The particle size distribution curves after SEM investigation are obtained in the same way as in LOM analysis. Each inclusion is considered to be a perfect sphere with diameter equivalent to ECD. Moreover, the volume fraction of inclusions($f_i$) for each sample is assumed to be same as the area fraction of inclusions($f_A$) in the cross-section of the sample analyzed [26]. This allows the calculation of volume of metal ($V_m$) analyzed using equation 2. The particle distribution curves with size interval of 0.2 μm for different REM additions after SEM analysis are shown and compared in Figure 13. $N_v$ for each size interval is calculated using equation 3.

All the samples are shown to contain inclusions smaller than 1 μm ECD in large number. So, the small inclusions (ECD < 2 μm) are so much large in number than that for inclusions with ECD > 2 μm. And for the same reason, the average size of inclusion does not change much with different REM addition. Hence, Figure 13 (b) is referred for looking at size distribution of big inclusions (ECD> 5 μm).

Similar to LOM investigation, the lowest REM addition REM-1 sample contained 2-3 times the number of small inclusions (ECD< 2μm) observed in REM-5 addition sample. The big inclusions (ECD > 5 μm) is observed to follow the opposite trend, with more being observed 2

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$^6$ The sulphur content values not mentioned in this report, as they are deemed as confidential data of Outokumpu Stainless AB.
REM-5 sample with increasing size. This shows that higher the REM addition, increasing number of big inclusions are expected to be formed in the melt and the particle density of small inclusions decreases.

Figure 13: Typical particle-size distribution for different REM additions after SEM (Feature) analysis

Figure 14 compares the inclusion density, Nv and the total inclusion area per observed area for all the sample based on the amount of REM added. Overall, the inclusion density showed a decreasing trend with increasing REM addition under SEM. This is similar to that observed under LOM. The total inclusion area is observed to be highest for REM-1 addition. However, from REM-2 onwards, the inclusion area was observed to increase with increasing REM addition, similar to the trend observed under LOM.

Figure 14: Effect of REM addition on (a) Inclusion density, Nv (b) Total inclusion area per unit area

The influence of casting sequence on inclusion density and total inclusion area is studied by plotting Figure 15. The inclusion density and inclusion area were observed to follow a similar trend along the casting sequence. They decreased along the casting sequence until the third slab and increased in the final slab.
Figure 15: Effect of casting sequence on (a) Inclusion density, \( N_v \) (b) Total inclusion area per unit area of heat 585013

The same parameters, inclusion density and inclusion area from the same slab number of different heats corresponding to the same REM addition were shown and compared in Table 4. This comparison is made to analyse the effect of initial content of sulphur on the said inclusion characteristics. The effect of \( S_{initial} \) is not clear from these results. It must also be noted that even though the samples, considered for this particular analysis are from the same sequence in casting, the time to casting of these slabs is different. The time to casting is observed to exert an increasing effect on inclusion density and total inclusion area.

Table 4: Comparison of \( N_v \) and total inclusion area per observed area for same slabs of different heats (REM-4)

<table>
<thead>
<tr>
<th>Sample-Id</th>
<th>( S_{initial} ) (mass %)</th>
<th>Time to casting (min)</th>
<th>Inclusion density, ( N_v ) (mm(^{-3}))</th>
<th>Total inclusion area in ( \mu m^2 ) per observed area (mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>585013-2a</td>
<td>Medium</td>
<td>37.5</td>
<td>253809</td>
<td>430.69</td>
</tr>
<tr>
<td>584443-2</td>
<td>Low</td>
<td>46</td>
<td>353366</td>
<td>458.77</td>
</tr>
<tr>
<td>585013-3a</td>
<td>Medium</td>
<td>49</td>
<td>220902</td>
<td>419.74</td>
</tr>
<tr>
<td>441715-3</td>
<td>High</td>
<td>55</td>
<td>310246</td>
<td>455.86</td>
</tr>
</tbody>
</table>

4.4 Calculation of Cerium content in matrix

The EDS analysis of each inclusion is obtained from “INCA Feature”. This is used to calculate the cerium content present in each inclusion. The phases present in each inclusion must be known to facilitate this calculation.

APPENDIX-2 shows a ternary diagram between oxides of Ce, La and SI-Al-Ca oxides combined together. The oxides in all the samples are observed to be mainly composed of cerium and lanthanum. The few inclusions SI-Al-Ca oxide inclusions observed in the case of REM-1 sample can be misleading as these inclusions are very small (<1 \( \mu m \)) and hence are heavily influenced by the composition of the matrix. Hence, it is safe to assume that only REM inclusions are present in all the samples.
However, the presence of sulphur cannot be ignored. Table 5 shows the typical inclusion types observed in 253MA. It is observed that oxides of cerium and lanthanum are either present in the form of stringers or observed to be irregular in shape. The third type of inclusion confirms the presence of spherical oxy-sulphides of cerium and lanthanum. Hence the effect of sulphur cannot be ignored. Studies in the past have also reported the presence of REM-oxides and REM-oxy-sulphides in 253MA[27]. Hence, the phases assumed in each inclusion are: cerium oxide (Ce₂O₃), lanthanum oxide (La₂O₃), cerium oxy-sulphide (Ce₂O₂S) and lanthanum oxy-sulphide (La₂O₂S).

<table>
<thead>
<tr>
<th>Types</th>
<th>Morphology</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stringer</td>
<td>Ce-La-O</td>
<td></td>
</tr>
<tr>
<td>Irregular</td>
<td>Ce-La-O</td>
<td></td>
</tr>
<tr>
<td>Spherical</td>
<td>Ce-La-O-S</td>
<td></td>
</tr>
</tbody>
</table>

The weight percentage of each phase in each inclusion can be calculated from the weight percentage of S, Ce, La and O, obtained from EDS (Feature) analysis through stoichiometric calculation. Since, it is assumed that only REM inclusions are present the weight percentage of the REM phases are normalised to 100% in each inclusion. The mass of cerium ($m_{Ce}$) in each inclusion is then calculated by assuming each inclusion to be prefect spheres (with ECD as its diameter). It should be noted that calculated value for $m_{Ce}$ is somewhat lower because of underestimation of volume of each inclusion, resulting from the above assumption. The density of each phase considered for $m_{Ce}$ calculation is mentioned in Table 6.
Table 6: Density of REM phases in g/cm$^3$

<table>
<thead>
<tr>
<th></th>
<th>Ce$_2$O$_3$</th>
<th>La$_2$O$_3$</th>
<th>Ce$_2$O$_2$S</th>
<th>La$_2$O$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.2</td>
<td>6.51</td>
<td>5.99</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The volume of the sample analysed is calculated using equation 2, and subsequently the mass of the sample analysed ($M$) is calculated from the density ($\rho_{\text{stainless steel}} = 8\text{g/cm}^3$). The mass percentage of cerium present in inclusions for each sample is calculated using equation 4.

$$\text{mass percentage of Ce (inclusions)} = \frac{\sum_{i=1}^{n} m_{Ce}}{M}$$  \hspace{1cm} (4)

Where, $m_{Ce}$ is the mass of Ce present in $i^{th}$ inclusion.

Equation 1 is then used to calculate the mass percentage of cerium, dissolved in matrix. Figure 16(a) and Figure 16(b) shows the mass % of cerium (insoluble) and that of cerium (matrix) respectively, for different REM additions. The amount of Ce present in inclusions is observed to be the highest for highest for REM-1 addition. On the contrary, the Ce present in the matrix is shown to be the lowest for REM-1 samples. When the REM addition is increased beyond REM-2, the amount of Ce in inclusion increases with increasing REM addition. The overall trend for the amount of Cerium dissolved in matrix is observed to increase with increasing REM addition. It must be noted that the amount of Ce present in matrix for REM-2 sample is observed to more than higher REM addition samples also.

![Figure 16: Cerium distribution for different REM additions](image)

4.5 Isothermal Oxidation test

Figure 17 to Figure 19 shows the variation in mass change per unit area of the sample over time for the sample 590904-2 (REM-2) at different temperatures$^7$. The results from previous

$^7$ The values of mass change and time are not expressed in the graphs, as they are deemed as confidential data of Outokumpu Stainless AB.
studies [10, 28] are included in the Figure 17 to Figure 19 for comparison. With increasing temperature, the mass change for all the REM addition samples increase for a given amount of time. At all the temperatures, the mass change of REM-1 sample is observed to be the highest at any given time. At 1000°C, the mass change of the other REM addition samples (except REM-1) are observed to be almost the same over the time. At 1100°C, the mass change of REM-2 sample is observed to be more than REM-4 sample at any given time. This difference in mass change between REM-2 and REM-4 samples increased with time at the same temperature. When the temperature is increased to 1150°C, the mass change of REM-2 sample is again observed to be more when compared to REM-4 sample. Moreover, the mass change observed in REM-3 sample is between that of REM-2 and REM-4 samples. The difference between REM-2 and REM-4 samples is also observed to increase when the temperature is increased from 1100°C to 1150°C.

Figure 17: Isothermal oxidation test at 1000°C. Mass change per unit area as a function of time for heat 590904-2 (REM-2). Results from [10, 28] are included for comparison.
Figure 18: Isothermal oxidation test at 1100°C. Mass change per unit area as a function of time for heat 590904-2 (REM-2). Results from [10, 28] are included for comparison.

Figure 19: Isothermal oxidation test at 1150°C. Mass change per unit area as a function of time for heat 590904-2 (REM-2). Results from [10, 28] are included for comparison.
4.6 Cyclic oxidation test

Figure 20 and Figure 21 show the variation in mass change of sample over time for the sample 590904-2 (REM-2) under cyclic conditions. The results from previous studies [10, 28] are included in the Figure 20 and Figure 21 for comparison. The mass change for all the samples is observed to increase up to a certain time and then started to decrease. The time after which the mass changes begins to decrease is the breakaway time and the mass change corresponding to this time is the maximum mass change. The measured breakaway time and the maximum mass change for all the sample are represented in Figure 22 and Figure 23. Overall, the breakaway time is observed to decrease with increasing REM addition. This decreasing trend is shown by a linear trendline in Figure 22. It is also observed that the breakaway time for a given sample decreases when the temperature is increased from 1150°C to 1175°C. The maximum mass change is observed to be highest for REM-1 addition sample. Among the other REM addition samples, the measured maximum mass change is observed to decrease with decreasing REM addition up to REM-3 and then increases with further decrease in REM addition, with the maximum mass change attaining its highest value for REM-1 samples.

Figure 20: Cyclic oxidation test at 1150°C/90h. Mass change per unit area as a function of time for heat 590904-2 (REM-2). Results from [10, 28] are included for comparison.

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8 The oxidation data such as values of breakaway time and maximum mass change are not displayed in the graphs as they are deemed as confidential data of Outokumpu Stainless AB.
Figure 21: Cyclic oxidation test at 1175°C/50h. Mass change per unit area as a function of time for heat 590904-2 (REM-2). Results from [10, 28] are included for comparison.

Figure 22: Measured breakaway time for Therma 253 MA with different REM additions at 1150°C and 1175°C. Trend line is added. Results from [10, 28] are included for comparison.
Figure 23: Measured maximum value of mass change for Therma 253 MA with different REM additions at 1150°C and 1175°C. Trend line is added. Results from [10, 28] are included for comparison.
5 DISCUSSION

5.1 Stringer characteristics

The big stringer type inclusions (minimum 20 particles) are observed to be present when at least REM-3 is added to this grade. Figure 11, Figure 12 and Table 3 show clearly that REM additions and time to casting are important factors that influence the formation of stringers and its characteristics. So, with increasing REM addition, stringers increase in number, with its length and particle density also increasing at the same time. The time to casting is also observed to exert a similar influence on stringer characteristics. The influence of sulphur content in the liquid melt, before REM addition on the stringer characteristics is not clear. This can be due to the overlapping effect of time to casting. So, more sample with better process control is suggested to study this influence. The effect of the former factors is better understood by considering the mechanism behind stringer formation.

Three mechanisms are proposed to explain the formation of stringer type inclusions:

1. Stringers are formed when inclusion clusters, formed in liquid steel are broken down on rolling operation
2. Stringers are formed when hard, brittle inclusion phases in liquid steel are crushed on rolling operation
3. Stringers are formed when fine small inclusions move close to each other due to random movement of steel in ladle and tundish.

It is evident from APPENDIX-2 that most of the particles present in the sample are REM inclusions. So, the breakdown of clusters is considered as the dominant mechanism because of the tendency of REM inclusions to form clusters in liquid steel[11, 12]. Bigger clusters are expected to be formed by turbulent collisions in steel, when REM additions are increased from REM-3 and above, which eventually break down to form big stringers after rolling. The formation and growth of REM clusters also depends on time. It is known that the clusters grow in size with increasing time in ladle[12]. So, with increasing time to casting, cluster are expected to grow in size, which will eventually influence the stringer formation too.
5.2 Inclusion characteristics

The typical inclusion size distribution curves, as shown in Figure 9 and Figure 13, observed after LOM and SEM(Feature) analysis respectively, are consistent with each other. These curves show that the small inclusions (ECD< 2 μm) are greater in number than inclusions with ECD> 2 μm. For the same reason, the average size of the inclusions is the same for all the REM additions. However, it is also shown that the distribution of particles with respect to size changes with increasing REM addition. With higher REM additions, bigger inclusions are observed to be present at the expense of small inclusions. As already mentioned before, REM inclusions tend to collide with each other and form clusters, which grow predominantly by turbulent collisions in liquid melt. So, big clusters of REM inclusions are expected to be formed in when high REM additions of more than REM-3 are added to the melt. On the contrary, a large number of fine uniformly distributed particles are formed when REM-1 and REM-2 are added.

The inclusion density and the total inclusion area are calculated for all the samples and analysed the effect of different factors on these inclusion characteristics. Figure 10(a) and Figure 14(a) show that with increasing REM addition, the number of inclusions per unit volume decreases. This is a logical conclusion, due to the many inclusions colliding with each other and forming clusters. The overall trend observed in the total inclusion area is found to increase with increasing REM addition. However, REM-1 sample showed a deviation from this trend under SEM (Feature analysis). The total inclusion area for these samples is observed to be more than REM-5 samples. The reason for this deviation is not clear, although it is believed that higher magnification in the case of SEM and small observed area for higher REM addition samples could have caused this unexpected trend.

The effect of casting sequence on inclusion density and total inclusion area is observed to follow the same trend, as shown in Figure 15. The higher inclusion density and inclusion area in the initial stages of casting can be related to the phenomenon of re-oxidation during this time. A thesis study, exploring the extend of this phenomenon has shown that the total oxygen content increases 3-4 times in the initial stages of casting sequence, subsequently reducing to the level observed in ladle furnace towards the end of the casting sequence. But, the residence time of the remaining melt, considered as the time to casting increases along the casting sequence. Hence, the inclusion density and inclusion area is supposed to increase because of new inclusions being formed in the ladle with increasing time to casting. But the decreasing trend observed until the third slab suggests that re-oxidation is the dominating parameter,
influencing the inclusion characteristics. The small increase observed in the final slab can be due to the subsiding influence of re-oxidation and the effect of time to casting taking over. REM inclusions are known to cause nozzle clogging by different mechanisms [27]. And sometimes, these clogging structure inside the nozzle can suffer a mechanical collapse due to the inertia of flowing steel, which could alter the inclusion number and area[29]. So, the small increase in inclusion number and inclusion area observed for the final can also suggest the above-mentioned reason. Hence, the effect of casting sequence on the inclusion characteristics is a combination of the effects of phenomenon of re-oxidation, time to casting and nozzle clogging, sometimes. Analysis of more heats is warranted to get a clear picture on which is the dominating influence.

On comparing the inclusion characteristics of same slabs of different heats, corresponding to the same REM addition, it was observed that increasing time to casting increases the inclusion number and area. The influence of time to casting has been explained before. The effect of sulphur content in the liquid melt, before REM addition on the inclusion characteristics is not clear. This can be due to the overlapping effect of time to casting or initial oxygen content. Hence, analysis of more samples, sampled from the same slab no for many heats are warranted to give a better picture about the influence of sulphur content.

### 5.3 Cerium content in the matrix

The amount of cerium present in inclusion was calculated and compared for different REM additions in Figure 16(a). The trend observed for Ce content in inclusion agrees with that observed for the inclusion area for different REM additions, as shown in Figure 14(b). This is a logical conclusion as majority of the inclusions are mainly composed of Ce and La together. The Ce content in the matrix was observed to increase overall with increasing REM addition as shown in Figure 16(b), although the REM-2 sample deviated from the trend. This sample was observed to more Ce in matrix than REM-4 and REM-5 addition samples. This deviation cannot be explained. Hence, analysis of more REM-2 samples must be done to confirm this deviation. Moreover, La content in matrix could not be calculated because information about the bulk content of La was not available.
5.4 Oxidation resistance

At all the temperatures, the mass change was observed to be the highest for REM-1 sample under isothermal conditions. This means REM-1 sample oxidized more for a given time and hence has the lowest isothermal oxidation resistance. Moreover, the REM-1 sample showed the shortest breakaway time and the highest maximum mass change under cyclic oxidation. This means that REM-1 sample oxidized more for a given time and the adhesion of the oxide layer is also poor, suggesting that the cyclic oxidation resistance is the lowest for REM-1 sample. The amount cerium present in matrix is responsible for providing resistance to oxidation. The lowest content of Cerium observed for REM-1 sample, as shown in Figure 16(b) therefore explains the reason behind the lower isothermal and cyclic oxidation resistance observed for the same sample.

The isothermal oxidation resistance of the other REM addition samples is observed to be in this order: REM-4> REM-3>REM-2, when the temperature is at least 1100°C. At 1000°C, the same samples including REM-5 sample showed almost similar oxidation behavior, hence almost same resistance to isothermal oxidation. Under cyclic oxidation, the overall decrease in breakaway time at both the temperatures suggests improved adhesion of the oxide layer with increasing REM addition. However, it must be noted that there is not much difference in breakaway time and maximum mass change between REM-2 and REM-4 samples. The increasing level of Cerium present in matrix with increasing REM addition, as observed in Figure 16(b) explains the increasing resistance to isothermal oxidation for higher REM addition samples. The reason for variation in breakaway time and mass change with different REM additions (except REM-1 sample) under cyclic condition is unclear. However, the overall decreasing trend in breakaway time suggests improved adhesion of the oxide layer because of the increasing Ce content in the matrix with increasing REM addition.
6 CONCLUSIONS

The main focus of this experimental work is to investigate the effect of different factors like REM addition, sulphur content, time to casting, etc on the distribution of REM in 253MA. The objective of this study was to suggest an optimal REM addition to get a good trade-off between inclusion content and better properties. The summary of the experimental findings are as follows:

- Inclusions increase in size and decrease in number with increasing REM addition. Re-oxidation of melt during initial stages of casting and increasing time to casting increase the number and thus total area of inclusions being formed for a given REM addition.
- More big-sized clusters are formed in liquid melt when REM addition is increased to REM-3 or more per 100T of steel. These clusters eventually form more stringers with increased size and particle density in when at least REM-3 of REM are added. On the contrary, a large number of fine inclusions are uniformly distributed in REM-1 and REM-2 samples, with nearly no stringer type inclusions found. Time to casting plays a huge role in stringer formation for a given REM addition. Re-oxidation of melt during initial casting stages does not influence stringer formation.
- The influence of initial content of sulphur before REM addition, on stringers and particle characteristics is unclear. More analysis of samples is warranted.
- Overall, the isothermal and cyclic oxidation resistance increases with increasing REM addition at particularly high temperatures (more than 1100°C) due to increasing amount of cerium present in matrix. REM-1 sample showed significantly poor resistance to both isothermal and cyclic oxidation at all temperatures.
- Based on results from this work, REM-2 sample showed better inclusion characteristics with no stringers, when compared to higher REM addition. Moreover, the isothermal oxidation resistance of REM-2 sample is same as observed for higher REM additions, and its cyclic oxidation resistance is comparable to REM-4 sample. Hence, REM-2 can be suggested as an optimal REM addition sample to get a good balance between big inclusions and oxidation resistance.
7 FUTURE WORK

This experimental work investigated the effect of different factors on the inclusion characteristics. Among the different factors, the effect of oxygen was not considered in this work as information about the initial oxygen content was not available. The scope of this work can be extended to include the effect of oxygen on inclusion characteristics by analysing oxygen content before REM addition.

In this experimental work, water-based solvents could only be used for preparing the specimens. However, it is recommended to prepare specimens with non-aqueous solvent because REM inclusions are observed to water-sensitive.

The volume of inclusions calculated in the work from 2D measurements is certainly underestimated because of the underlying assumption that each inclusion is a perfect sphere (with ECD as diameter). A correction value must be included to account for this underestimation by applying stereological principles in calculating volume of a spherical particle from two dimensional sections. On the contrary, 3D investigation techniques like electrolytic extraction is recommended for studying the inclusion characteristics more accurately[30]. Moreover, experimental measurement techniques can also be explored to measure the content of cerium, dissolved in the matrix. The values obtained from such advanced techniques can be useful for comparison with the calculated values in this work.

The inclusion characteristics are believed to affect the formation and characteristics of stringer characteristics, as mentioned in section 5.1. This correlation between inclusion clusters and stringer inclusions can be further verified by investigating samples taken from tundish. Some results of inclusion analysis could not be explained because of certain limitations. The effect of initial sulphur content is not clear from this work and thus warrants investigation of more samples. Similarly, results of SEM investigation can be further verified by analysing higher REM addition samples over a larger area of observation to explain the deviations observed in sections 5.2 and 5.3.
I would like to express my utmost gratitude to Cecilia Lille and my supervisor Dr. Rui Wu from Outokumpu for providing me with this opportunity to work at the Avesta Research Centre. I am thankful for their invaluable support, which helped me in completing my thesis.

I would like to thank Jan Y Jonson and James Oliver for providing me with the knowledge required for handling advanced microscopy techniques. This work would not have been possible without their constant guidance and suggestions in investigating non-metallic inclusions.

I would also like to thank Daniel Eyzop and Henrik Ahrman for providing me with the expertise required for preparing samples for metallographic examination.

I would also like to offer my deepest thanks to my supervisor, Andrey Karasev and my examiner, Pär Jönsson from KTH, for guiding me and devoting their precious time in answering my queries.
9 Reference


### APPENDIX-1: Examination area (LOM and SEM)

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APPENDIX-2: Ternary plot

(a) REM-5

(b) REM-4

(c) REM-3

(d) REM-2

(e) REM-1