An Experimental Study of Submerged Entry Nozzles (SEN) Focusing on Decarburization and Clogging

Arashk Memarpour

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Department of Materials Science and Engineering
Division of Applied Process Metallurgy
Royal Institute of Technology
SE-100 44 Stockholm
Sweden

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Arashk Memarpour: *An experimental study of Submerged Entry Nozzles (SEN) focusing on decarburization and clogging*

KTH School of Industrial Engineering and Management  
Division of Applied Process Metallurgy  
Royal Institute of Technology  
SE-100 44 Stockholm  
Sweden

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To my son
Sam
Abstract

The submerged entry nozzle (SEN) is used to transport the molten steel from a tundish to a mould. The main purpose of its usage is to prevent oxygen and nitrogen pick-up by molten steel from the gas. Furthermore, to achieve the desired flow conditions in the mould. Therefore, the SEN can be considered as a vital factor for a stable casting process and the steel quality. In addition, the steelmaking processes occur at high temperatures around 1873 K, so the interaction between the refractory materials of the SEN and molten steel is unavoidable. Therefore, the knowledge of the SEN behaviors during preheating and casting processes is necessary for the design of the steelmaking processes.

The internal surfaces of modern SENs are coated with a glass/silicon powder layer to prevent the SEN graphite oxidation during preheating. The effects of the interaction between the coating layer and the SEN base refractory materials on clogging were studied. A large number of accretion samples formed inside alumina-graphite clogged SENs were examined using FEG-SEM-EDS and Feature analysis. The internal coated SENs were used for continuous casting of stainless steel grades alloyed with Rare Earth Metals (REM). The post-mortem study results clearly revealed the formation of a multi-layer accretion. A harmful effect of the SENs decarburization on the accretion thickness was also indicated. In addition, the results indicated a penetration of the formed alkaline-rich glaze into the alumina-graphite base refractory. More specifically, the alkaline-rich glaze reacts with graphite to form a carbon monoxide gas. Thereafter, dissociation of CO at the interface between SEN and molten metal takes place. This leads to reoxidation of dissolved alloying elements such as REM (Rare Earth Metal). This reoxidation forms the “In Situ” REM oxides at the interface between the SEN and the REM alloyed molten steel. Also, the interaction of the penetrated glaze with alumina in the SEN base refractory materials leads to the formation of a high-viscous alumina-rich glaze during the SEN preheating process. This, in turn, creates a very uneven surface at the SEN internal surface. Furthermore, these uneven areas react with dissolved REM in molten steel to form REM aluminates, REM silicates and REM alumina-silicates.

The formation of the large “in-situ” REM oxides and the reaction of the REM alloying elements with the previously mentioned SEN’s uneven areas may provide a large REM-rich surface in contact with the primary inclusions in molten steel. This may facilitate the attraction and agglomeration of the primary REM oxide inclusions on the SEN internal surface and thereafter the clogging.

The study revealed the disadvantages of the glass/silicon powder coating applications and the SEN decarburization.

The decarburization behaviors of Al₂O₃-C, ZrO₂-C and MgO-C refractory materials from a commercial Submerged Entry Nozzle (SEN), were also investigated for different gas atmospheres consisting of CO₂, O₂ and Ar. The gas
ratio values were kept the same as it is in a propane combustion flue gas at
different Air-Fuel-Ratio (AFR) values for both Air-Fuel and Oxygen-Fuel
combustion systems. Laboratory experiments were carried out under non-
isothermal conditions followed by isothermal heating. The decarburization ratio
(\(\alpha\)) values of all three refractory types were determined by measuring the real
time weight losses of the samples. The results showed the higher decarburization ratio
(\(\alpha\)) values increasing for MgO-C refractory when changing the Air-Fuel
combustion to Oxygen-Fuel combustion at the same AFR value. It substantiates
the SEN preheating advantage at higher temperatures for shorter holding times
compared to heating at lower temperatures during longer holding times for
\(\text{Al}_2\text{O}_3\)-C samples. Diffusion models were proposed for estimation of the
decarburization rate of an \(\text{Al}_2\text{O}_3\)-C refractory in the SEN.

Two different methods were studied to prevent the SEN decarburization during
preheating: The effect of an ZrSi\(_2\) antioxidant and the coexistence of an
antioxidant additive and a \((4\text{B}_2\text{O}_3 \cdot \text{BaO})\) glass powder on carbon oxidation for
non-isothermal and isothermal heating conditions in a controlled atmosphere.
The coexistence of 8 wt\% ZrSi\(_2\) and 15 wt\% \((4\text{B}_2\text{O}_3 \cdot \text{BaO})\) glass powder of the
total alumina-graphite refractory base materials, presented the most effective
resistance to carbon oxidation. The 121\% volume expansion due to the Zircon
formation during heating and filling up the open pores by a \((4\text{B}_2\text{O}_3 \cdot \text{BaO})\) glaze
during the green body sintering led to an excellent carbon oxidation resistance.

The effects of the plasma spray-PVD coating of the Yttria Stabilized Zirconia
(YSZ) powder on the carbon oxidation of the \(\text{Al}_2\text{O}_3\)-C coated samples were
investigated. Trials were performed at non-isothermal heating conditions in a
controlled atmosphere. Also, the applied temperature profile for the laboratory
trials were defined based on the industrial preheating trials. The controlled
atmospheres consisted of CO\(_2\), O\(_2\) and Ar. The thicknesses of the decarburized
layers were measured and examined using light optic microscopy, FEG-SEM
and EDS. A 250-290 µm YSZ coating is suggested to be an appropriate coating,
as it provides both an even surface as well as prevention of the decarburization
even during heating in air. In addition, the interactions between the YSZ coated
alumina-graphite refractory base materials in contact with a cerium alloyed
molten stainless steel were surveyed. The YSZ coating provided a total
prevention of the alumina reduction by cerium. Therefore, the prevention of the
first clogging product formed on the surface of the SEN refractory base
materials. Therefore, the YSZ plasma-PVD coating can be recommended for
coating of the hot surface of the commercial SENs.

**Key Words:** Refractory, SEN, Clogging, REM, Coating, glaze, alkaline, Post-
Mortem, industrial preheating, ZrSi\(_2\), Graphite, Alumina, Oxidation, \(\text{Al}_2\text{O}_3\)-C,
\(\text{ZrO}_2\)-C, MgO-C, decarburization, reaction mechanism, Yttria Stabilized
Zirconia, plasma spray-PVD coating
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Arashk Memarpour
Sandviken, July 2011
Supplements

The present thesis is based on the following supplements:

**Supplement 1:**
“Studies of effect of glass/silicon powder coatings on clogging behaviour of submerged entry nozzles when using REM alloyed stainless steels”
**Arashk MEMARPOUR, Voicu BRABIE and Pär G. JÖNSSON**
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**Supplement 2:**
“Post-mortem study of the internal coated SENs (Submerged Entry Nozzle) respecting clogging”
**Arashk MEMARPOUR, Voicu BRABIE and Pär G. JÖNSSON**
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**Supplement 3:**
“The Effect of Zirconium Disilicide (ZrSi₂) Additions on the Carbon Oxidation Behavior of Alumina/Graphite Refractory Materials”
**Arashk MEMARPOUR, Voicu BRABIE and Pär G. JÖNSSON**
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**Supplement 4:**
“Studies on the decarburization of commercial submerged entry nozzles”
**Arashk MEMARPOUR, Voicu BRABIE and Pär G. JÖNSSON**
Published in *Steel Grips*, **9** (2011) Plants & Equipment, 121-127.

**Supplement 5:**
“Studies on the decarburization of commercial submerged entry nozzles Studies of Yttria Stabilized Zirconia (YSZ) plasma-PVD coated Al₂O₃-C refractory base materials of a commercial SEN with respect to decarburization and clogging”
**Arashk MEMARPOUR, Voicu BRABIE and Pär G. JÖNSSON**
Submitted for publication in *Steel Grips*, 2011.
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**Supplement 1:** Literature survey, major parts of plant trials, major parts of laboratory trials, thermodynamic calculations, major parts of the FEG-SEM observations and major parts of the writing.

**Supplement 2:** Literature survey, major parts of plant trials, major parts of laboratory trials, thermodynamic calculations, major parts of the FEG-SEM observations and major parts of the writing.

**Supplement 3:** Literature survey, major parts of the heat transfer simulation, major parts of laboratory trials, major parts of the FEG-SEM observations and major parts of the writing.

**Supplement 4:** Literature survey, major parts of laboratory trials, major parts of the FEG-SEM observations and major parts of the writing.

**Supplement 5:** Literature survey, major parts of laboratory trials, thermodynamic calculations, major parts of the FEG-SEM observations and major parts of the writing.
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1. Introduction

Continuous casting is the dominant casting process for crude steel production. More specifically, in 2008 it accounted for 93.1% of the world production.\textsuperscript{1,2) In continuous casting, several ladles in a sequence are cast in a mold by using a tundish as a buffer. Here, the submerged entry nozzle (SEN) is used to transport the molten steel from the tundish to the mould. It is a vital factor for obtaining a stable casting process as well as a good product quality. The casting temperatures are as high as 1873 K, so the interaction between the SEN refractory materials and the molten steel is unavoidable. Therefore, the SEN should have a proper inertness. Moreover, good mechanical properties, such as a high temperature mechanical strength and a high thermal resistance. In general, the interaction between the SEN and molten steel may be categorized into three different mechanisms:\textsuperscript{3)}

- The chemical reactions between refractory base materials and impurities in the nozzle and the molten metal
- The attachment of immersed non-metallic inclusions in the molten steel, to the surface of the nozzle
- The erosion of the nozzle refractory materials.

The first two mechanisms may cause clogging during the casting process, which may limit productivity by interrupting the process. This restricts the number of heats per tundish, which affects the quality of the steel and consequently leads to increasing customer rejections.\textsuperscript{4)} To satisfy customers’ requirements, stainless steelmakers have started to produce more complex steels such as ASTM S35315. This austenitic stainless steel grade resists oxidation at temperatures up to 1423 K. Furthermore, it can provide moderately good service in carbon, nitrogen and sulfur containing atmospheres due to the presence of rare earth metal (REM) alloying elements. However, the addition of the REM alloying elements, such as cerium, may lead to severe nozzle clogging that can interrupt the sequence casting process.\textsuperscript{5)} Katsumata and Todoroki\textsuperscript{6)} investigated the effect of REM alloying elements on inclusion compositions in molten stainless steel and also performed post-mortem studies of SEN accretions. They found that the accretion mainly consisted of solidified steel. This was assumed to be strongly related to the solidification of the delta ferrite due to the presence of REM oxides. In addition, Zhao et al.\textsuperscript{7)} indicated that the reactions between the REM alloying metals and alumina in SEN refractory materials cause an initial clogging. This clogging may continue by agglomeration of REM oxides on the SEN internal surface. As an alternative explanation, Ohyabu et al.\textsuperscript{5)} have suggested that the reaction between the silicon
oxide particles in the nozzle and the REM alloying metals in the molten steel takes place. This may lead to a silica reduction and a REM oxidation. Furthermore, the oxidation products remain at the reaction place. On the other hand, the formation of REM oxides, REM silicates and REM aluminates on the SEN internal surface and inside the SEN pores, according to previous mentioned studies, may lead to attraction forces between these compounds and primary inclusions in the molten steel.8) Furthermore, they show that the attraction forces between REM oxides may vary drastically due to their sizes. Moreover, that less variations of attraction forces occurs due to the chemical composition differences of oxides.

For the new generation of the commercial SENs, a coating with a powder layer is applied inside the SEN. This layer consists of a mixture of glass and silicon powders. It is intended to protect the SEN inside surface from oxidation during the SEN preheating. The effects of this protective layer on the clogging phenomena are not identified; thus, the objectives of supplement 1 were to investigate the interactions between the SEN refractory base materials and the protective glass/silicon powder coating. This was done in laboratory SEN preheating experiments. It was also intended to investigate the interactions between the preheated SEN and molten steel to evaluate the effects of the glass/silicon coated SEN on the clogging during casting of an REM alloyed stainless steel grade. The interaction investigations were also performed using laboratory experiments. In addition, plant trials were performed to evaluate the effects of the glass/ silicon coated SEN on the clogging tendency.

A post-mortem study of used SENs has been the basis of Supplement 2. The study has been focused on a UNS S30815 (253MA) steel grade (20Cr-10Ni-1.4Si-0.05C-0.03Ce, wt %). The post-mortem investigation was performed on the internal coated SENs after casting both by macroscopic and microscopic investigations of the clogging products. In addition, steel samples from the tundish were examined to determine the characteristics of the inclusions flowing through the SENs. Finally, the industrial preheating process of the SENs was surveyed to evaluate the interaction between SENs’ Refractory Base Materials (RBM) and the internal coating of the SENs’ hot surface and its effects on the clogging mechanism.

Graphite in the SEN base refractory materials without glass/silicon powder coating and even with the coating (as Supplement 2 showed) may be oxidized direct in an oxidizing atmosphere such as in an oxygen- or a carbon dioxide-rich atmosphere. Furthermore, by indirect oxidation as reaction 1 presents. More specifically, graphite oxidation starts at 873-973 K in air. This leads to the formation of carbon monoxide or carbon dioxide.9)

\[ C(s) + SiO_2(s) = CO (g) + SiO (g) \] (1)
A method to inhibit the decarburization of Al₂O₃-C refractories is the addition of so-called antioxidants. An antioxidant is an element or a compound with a high oxygen affinity. Aluminum is the most conventional antioxidant. However, the formation of Al₄C₃ after sintering of the green body may be a disadvantage. This is due to that the Al₄C₃ compound may be hydrated even at room temperature to form an Al(OH)₃ compound, as reactions 2 and 3 suggest. This, in turn, may lead to volume expansion and cracking of the refractory bulk.

\[
\begin{align*}
4\text{Al (l)} + 3\text{C(s)} &= \text{Al₄C₃ (s)} \quad (2) \\
\text{Al₄C₃(s)} + 12\text{H₂O (g)} &= 3\text{CH₄(g)} + 4\text{Al(OH)₃ (s)} \quad (3)
\end{align*}
\]

Sunayama et. al. \(^{11}\) have investigated the influence of aluminum additions on the oxidation rate of MgO-graphite refractories. They found a slight improvement of the oxidation resistance at temperatures below 1823 K. Wang and Yamaguchi\(^{12}\) have investigated the influence of Al₈B₄C₇ additions on the decarburization resistance. In addition, Gokce et. al. \(^{10}\) have evaluated the effects of various antioxidants such as Si, Al, B₄C and SiC on the decarburization resistance of MgO-graphite refractory. Overall, only a few researchers such as Youqi et al. \(^{13}\) and Dejiang et. al. \(^{14}\) have investigated the effects of antioxidants on the decarburization resistance of alumina-graphite based refractory materials. More specifically, Youqi et al. \(^{13}\) investigated the effect of a metallic Zn addition on the carbon oxidation and established the severe Zn volatilization during green body sintering. Dejiang et. al. \(^{14}\) established the remarkable carbon oxidation resistance of the refractory due to the silicon-containing boron glass coating. Furthermore, Wang and Yamaguchi \(^{12}\) also have reported on the coexistence effects of a liquid phase and the additives oxidation products to inhibit the oxygen penetration. They reported the positive effects of liquid diboron trioxide on the decarburization resistance. On the other hand, Dejiang et. al. \(^{14}\) have found a severe volatilization of B₂O₃ at temperatures above 1273 K. This may be judged to be an inappropriate glaze during both sintering of the green body and preheating of the SEN, which both are performed at temperatures of about 1473 K.

In **supplement 3**, the effect of ZrSi₂ additions on the carbon oxidation resistance of alumina-graphite base refractory materials used in the SEN is investigated. The advantage of a ZrSi₂ additive compared to a more commonly used aluminum additive is that ZrSi₂ is less sensitive to oxidation during production of green bodies. Furthermore, that the volume expansion of ZrSi₂ after oxidation is higher than for alumina.\(^{15}\) This volume expansion may lead to both inhibition of oxygen ingress during preheating of the SEN as well as filling the open pores which remain after the graphite oxidation. As table 1 \(^{16}\) shows, the oxidation of ZrSi₂ may lead to a 121% relative volume increase. However, the increase is just 29% for aluminum and 71% for dizirconium silicide.
Table 1. Relative volume increase during oxidation of aluminum and other intermetallic compounds\(^{16}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Relative Volume Expansion [Volume percent]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \text{Al} + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{O}_3)</td>
<td>29</td>
</tr>
<tr>
<td>(\text{Zr}_2\text{Si} + 3 \text{O}_2 \rightarrow \text{ZrSiO}_4 + \text{ZrO}_2)</td>
<td>71</td>
</tr>
<tr>
<td>(\text{ZrSi}_2 + 3 \text{O}_2 \rightarrow \text{ZrSiO}_4 + \text{SiO}_2)</td>
<td>121</td>
</tr>
</tbody>
</table>

The usage of a more stable glaze at high temperatures was also studied. The composition with a 64 wt% diboron trioxide and a 36 wt% barium oxide presents the \((4\text{B}_2\text{O}_3 \cdot \text{BaO})\) compound with a melting point of 1162 K (889°C). This value is higher than that for pure \(\text{B}_2\text{O}_3\) and the compound is more stable at higher temperatures.\(^{17}\) This coexistence effects of \(\text{ZrSi}_2\) and \((4\text{B}_2\text{O}_3 \cdot \text{BaO})\) powder on the decarburization resistance of \(\text{Al}_2\text{O}_3\)-C refractory materials used in SEN, was investigated.

It is common to preheat the SEN before the usage to minimize the risks for thermal shocks during introduction of the molten steel into SEN at the casting start. In addition, a commercial SEN may consist of three different materials, namely \(\text{Al}_2\text{O}_3\)-C, \(\text{ZrO}_2\)-C and \(\text{MgO}\)-C. All refractory materials containing graphite have the tendency to be decarburized during the preheating process. There are many articles concerning isothermal decarburization rate of \(\text{MgO}\)-\(\text{C}\)^\(^{18,19,20}\) and just a few concerning isothermal decarburization of \(\text{Al}_2\text{O}_3\)-\(\text{C}\)^\(^{21,22}\). However, articles concerning the decarburization behavior of the commercial SEN different parts are scarce. Studies concerning the kinetic analysis of the decarburization graphite-containing materials exist. These studies are performed concerning an isothermal heating of a graphite-containing sample. A study by Sasai et al.\(^{21}\) showed that the decarburization process proceeded by diffusion of oxygen gas through the pores of the \(\text{Al}_2\text{O}_3\)-C refractory, when heated isothermally. Sunayama et al.\(^{20}\) reported the same result for a \(\text{MgO}\)-\(\text{C}\) refractory, when heated isothermally in an Ar-\(\text{O}_2\) atmosphere. In contrast, Nandy et al.\(^{19}\) showed that the decarburization initially consisted of a chemical reaction mechanism which later was followed by a diffusion mechanism.

In supplement 4, the laboratory decarburizing experiments were performed in an atmosphere containing oxygen and carbon dioxide at a ratio equal to the propane gas combustion flue gas. The reason is that the propane gas torch is commonly used to preheat SENs in Sweden. Two different types of combustion systems (Oxy-Fuel and Air-Fuel combustion) and two different Air-Fuel Ratios (AFR) (1 and 1.5) were investigated. In supplement 4, the decarburization sensitivity for different graphite-containing parts of a commercial SEN was investigated by changing between the two previously mentioned combustion systems. In fact, both non-isothermal and isothermal heating were considered to get a better understanding of the real SEN preheating process. Furthermore, the kinetic analysis was performed to determine the decarburization mechanism(s)
for Al$_2$O$_3$-C materials during non-isothermal heating at temperatures between 873 - 1473 K.

In *supplement 5*, the intention was to investigate the effect of the Yttria Stabilized Zirconia (YSZ) plasma spray-PVD coating$^{23}$ on the carbon oxidation resistance of alumina-graphite refractory base materials used in submerged entry nozzles. In addition, the intention was to investigate the interaction of the coated alumina-graphite refractory base materials in contact with a REM-alloyed molten steel.

Pure zirconia is a polymorphic oxide which has three temperature dependent transition phases.$^{24}$ More specifically, monoclinic at temperatures below 1373 K, tetragonal at temperatures between 1373-2953 K and cubic above 2953 K.$^{24}$ The monoclinic transition to a tetragonal phase may lead to a 3-5% volume expansion.$^{24}$ In addition, this volume expansion may lead to the formation of cracks in the coating layer performed of pure zirconia especially during SEN preheating. These cracks may transport the oxidizing agents present in the ambient region to the graphite. Thereafter, the decarburization may occur. Therefore, it is desirable to apply the YSZ coating.

*The scopes of the present work*

This work is carried out based on both plant- and laboratory-trials. It consists of five supplements and focuses on the following issues:

- An investigation of the interaction between glass/silicon powder coatings and SEN refractory base materials (*supplement 1*)
- An investigation of the interaction between glass/silicon powder coatings, SEN refractory base materials and molten steel (*supplement 1*)
- An investigation of the interaction between glass/silicon powder coated SEN’s and rare earth metals (REM) alloyed stainless steel focusing on clogging (*supplement 1 and supplement 2*)
- A post-mortem study of accretion samples formed inside alumina-graphite clogged Submerged Entry Nozzles (*supplement 2*)
- Industrial preheating trials of the internally coated SENs (*supplement 2*)
- The carbon oxidation behavior of the Zirconium Disilicide (ZrSi$_2$)-containing alumina-graphite refractory materials (*supplement 3*)
- Preheating simulations of the commercial SEN (*supplement 3*)
- Industrial preheating surveys of the commercial SEN (*supplement 2 and supplement 5*)
- The decarburization of the commercial Submerged Entry Nozzles consisting of Al$_2$O$_3$-C, ZrO$_2$-C and MgO-C refractory materials (*supplement 4*)
• An investigation respecting the decarburization of Yttria Stabilized Zirconia (YSZ) plasma-PVD coated Al₂O₃-C from a commercial Submerged Entry Nozzle refractory base materials (supplement 5)
• An investigation of the interaction between an Yttria Stabilized Zirconia (YSZ) plasma-PVD coated Al₂O₃-C and a REM alloyed molten stainless steel (supplement 5)

The main objectives of this work are to provide new results, which may lead to a better understanding of the relation between the SEN usage and the clogging mechanism during the continuous casting process. More specifically, this work was intended to illustrate the vital effect of the SEN base refractory materials, its internal coating and the SEN preheating process on a stable continuous casting process.

The common factor in all supplements is that they focus on the SEN. More specifically, figure 1 illustrates what parts of the SEN that are the focus in the different supplements.

Figure 1. A schematic figure of the structure in this work including an explanation of where in the SEN are studied in the different supplements
2. Experimental methods

Different categories of laboratory experiments and industrial trials have been performed in the supplements. These are described below:

2.1. Interaction between glass/silicon powder coating and SEN refractory base materials during preheating, Laboratory experiments (supplement 1)

The specimens for the preheating experiments were cut from a commercial unused alumina-graphite SEN. The internal surface of the SEN was coated with a mixture of glass powder and 10 wt% metallic silicon, with a thickness of 200-400 µm.

Table 2 presents the chemical composition of the Al₂O₃-C part of the as fabricated SEN. The same commercial SEN was used in both the laboratory and the industrial experiments.

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight percent (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>55.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.8</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2</td>
</tr>
<tr>
<td>MgO</td>
<td>0.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>ZrO₂+ HfO₂</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.2</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>31.6</td>
</tr>
</tbody>
</table>

Table 3 shows the chemical analysis of the glass powder of the coating.
Table 3. Glass chemical compositions in glass/silicon powder coating.

<table>
<thead>
<tr>
<th>Glass Powder components</th>
<th>Weight Percent (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>19.09</td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.14</td>
</tr>
<tr>
<td>CaO</td>
<td>1.89</td>
</tr>
<tr>
<td>Na₂O</td>
<td>15.30</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.47</td>
</tr>
<tr>
<td>ZrO₂+ HfO₂</td>
<td>1.34</td>
</tr>
<tr>
<td>MgO</td>
<td>0.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.62</td>
</tr>
</tbody>
</table>

The specimens were heated in an electrical furnace at a rate of 15 K·min⁻¹ to a temperature of 1473 K. Thereafter, they were held for 20 min under a controlled atmosphere at a total flow rate of 8 nL·min⁻¹. Figure 2 shows the experimental apparatus. The samples were suspended by a platinum wire inside the alumina tube of the electrical furnace. The Pt–10%Rh/Pt thermocouple showed the real time temperature near the suspended samples with an accuracy of ±1 K.

![Figure 2. Experimental apparatus for preheating simulation](image)

The injected gas compositions for the laboratory experiments are illustrated in table 4.
Table 4. Composition of controlled atmosphere in furnace during preheating

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Ar (nL·min⁻¹)</th>
<th>CO₂ (nL·min⁻¹)</th>
<th>O₂ (nL·min⁻¹)</th>
<th>Nliter Injected CO₂</th>
<th>Nliter Injected O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>373-773 K (15K·min⁻¹)</td>
<td>7.83</td>
<td>0.09</td>
<td>0.08</td>
<td>2.40</td>
<td>2.13</td>
</tr>
<tr>
<td>773-973 K (15K·min⁻¹)</td>
<td>7.72</td>
<td>0.15</td>
<td>0.13</td>
<td>2.00</td>
<td>1.73</td>
</tr>
<tr>
<td>973-1273 K (15K·min⁻¹)</td>
<td>7.59</td>
<td>0.22</td>
<td>0.19</td>
<td>4.40</td>
<td>3.80</td>
</tr>
<tr>
<td>1273-1473 K (15K·min⁻¹)</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8.53</td>
<td>7.46</td>
</tr>
<tr>
<td>1473 K</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>6.40</td>
<td>5.60</td>
</tr>
</tbody>
</table>

2.2. Interaction between glass/silicon powder coating, SEN refractory base materials and molten steel, Laboratory experiments (supplement 1)

Two test rod series with different chemical compositions were also prepared to investigate the interactions between refractory base materials, glass/silicon powder coatings and molten steel. They were drilled out of two commercial SENs made of two different refractory base materials, namely alumina-graphite and zirconia-graphite. The samples were cylindrical with a 0.013 m diameter and a 0.10 m height. The rods were coated by the same glass/silicon powder coating as the coating of the commercial SEN, with respect to the chemical compositions and thicknesses. Five test rods were prepared out of each nozzle. The zirconia-graphite base refractory rod was chosen to distinguish between the coating and the base materials. This is due to the fact that the zirconia-graphite base materials contained almost no alumina or alkalis.

After preparation, the rods were preheated, immersed and rotated in molten steel. The experimental set-up was a high temperature furnace equipped with graphite resistance heating elements, as illustrated in figure 3.

The furnace consists of an alumina tube inside, which an argon flow passes through. There are two different crucibles inside the alumina tube. A graphite crucible with a 0.050 m outer diameter, a 0.030 m inner diameter and a 0.048 m depth. Furthermore, an alumina crucible with a 0.030 m outer diameter, a 0.026 m inner diameter and a 0.038 m depth. The alumina crucible was charged with 80 g of an ASTM S30400 steel (18.5Cr–9Ni–0.04C, wt%), which was heated to 1873 K. Furthermore, it was held for 30 min during argon flushing at 5 nL·min⁻¹ through the furnace chamber to ensure the chemical homogeneity. Traces of carbon dioxide, oxygen and moisture in the commercial argon gas were removed by passing the gas through a gas cleaning system. The test rods were situated at the furnace chamber so that they were preheated to 1473 K and held for 20 min before being immersed in the molten steel to a depth of 0.025 m. The
experiments were accomplished by rotating the rods at a speed of 100 rev·min\(^{-1}\) for 10 and 30 min. Then, the test rods were pulled out of the furnace chamber and cooled at room temperature.

![Experimental apparatus](image)

Table 5 summarizes the above mentioned experimental conditions for two tests.

**Table 5. Experimental conditions**

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Rod</td>
<td>Zirconia</td>
<td>Alumina</td>
</tr>
<tr>
<td></td>
<td>-Graphite</td>
<td>-Graphite</td>
</tr>
<tr>
<td>Glass/silicon powder Coating</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Rod Rotation speed</td>
<td>100 rev·min(^{-1})</td>
<td>100 rev·min(^{-1})</td>
</tr>
<tr>
<td>Molten steel Temperature</td>
<td>1873 K</td>
<td>1873 K</td>
</tr>
<tr>
<td>Duration of immersion</td>
<td>10 min</td>
<td>30 min</td>
</tr>
<tr>
<td>Rod pre-heating Temperature</td>
<td>1473 K</td>
<td>1473 K</td>
</tr>
<tr>
<td>Rod pre-heating duration</td>
<td>20 min</td>
<td>20 min</td>
</tr>
<tr>
<td>Argon flushing</td>
<td>5 (nL·min(^{-1}))</td>
<td>5 (nL·min(^{-1}))</td>
</tr>
<tr>
<td>Molten steel grade (ASTM)</td>
<td>S30400</td>
<td>S30400</td>
</tr>
</tbody>
</table>

After the experiments, the immersed parts of the test rods were mounted in a conductive epoxy. They were cut into 0.001 m thick discs to investigate the interface between the refractory base material, the glass/silicon powder coating
and the molten steel. Finally, observation investigations and chemical compositions evaluations were performed for all samples.

2.3. *Post-mortem study and interaction between glass/silicon powder coated SEN and a rare earth metals (REM) alloyed stainless steel, Plant description (supplement 1 and supplement 2)*

Industrial trials were performed for three heats with a clogging tendency under industrial production conditions. The trials were carried out for ASTM S35315 steel grade heats in a 100 ton ladle furnace. The steel was cast at an average casting speed of 0.79 m·min⁻¹ at a 1713 K temperature into a 1608*200 mm² copper mould. The gap between a stopper and the SEN entrance determined the flow rate of molten metal. It was essential to apply a constant flow rate of molten steel to the mould to sustain the previously mentioned constant casting rate during the process. This constant flow rate may be controlled by adjusting the previously mentioned gap size. A pneumatic machine performed the adjusting. The relative stopper position changings were also registered every second during casting.

Macroscopic and microscopic examinations of samples from unused SEN, used SENs, preheated SENs and molten steel in the tundish were performed. It should be mentioned that all investigated used SENs in these supplements were preheated by an industrial preheating process as describes later. The used SENs were cut with a special diamond cutting tool at eight different levels after continuous casting, as figure 4 shows. Thereafter, the accretion characteristics survey was performed for these eight slices.

![Figure 4. Marked cutting levels on longitudinal section of the used SEN](image)

In total, 60 accretion samples of alumina-graphite clogged Submerged Entry Nozzles (SEN) were examined.
2.4. The carbon oxidation behavior of the Zirconium Disilicide (ZrSi₂)-containing alumina-Graphite refractory materials (supplement 3)

2.4.1. Materials

The raw materials used in supplement 3 were crystalline flake graphite (99.9% purity, ≤ 5 µm), tabular corundum (99.4% Al₂O₃ and 0.12% Fe₂O₃, ≤ 300 µm), silica (99.9% purity, ≤ 45 µm), diboron trioxide (99.98% purity, ≤ 45 µm), barium oxide (99.5% purity, ≤ 45 µm) and zirconium disilicide (99.5% purity, ≤ 45 µm).

The usage of a more stable glaze at high temperatures was also studied. Figure 5 presents the binary phase diagram for B₂O₃-BaO. The composition with a 64 wt% diboron trioxide and a 36 wt% barium oxide presents the (4B₂O₃ · BaO) compound with a melting point of 1162 K (889°C). This value is higher than that for pure B₂O₃ and the compound is more stable at higher temperatures. The coexistence effects of ZrSi₂ and (4B₂O₃ · BaO) powder on the decarburization resistance of alumina-graphite refractory materials used in SEN, were investigated.

To produce the (4B₂O₃ · BaO) glass powder, 64 wt% B₂O₃ and 36 wt% BaO powders were weighted using a balance with a ±1 mg weight accuracy. Thereafter, powders were mixed and ground in a ball mill grinding for 24 h. The mixture was uniaxially pressed at 100 MPa. In addition, the green body was heated in a graphite crucible to 1223 K and at a rate of 9 K·min⁻¹. This was done for 1 h using argon to provide an inert atmosphere at a flow rate of 3 nL·min⁻¹.
The formed glaze was first crushed in a mortar to powder. Thereafter, milled in a ball mill grinding operation for 48 h by using corundum balls. 60 wt% alumina, 10 wt% silica and 30 wt% flake graphite powders were mixed in a ball mill using corundum balls for 24 h to prepare the Refractory Base Material (RBM). Different samples were prepared by addition of different amounts of ZrSi2 and (4B2O3·BaO) glass powder into the RBM, as Table 6 shows. Poly Vinyl alcohol (PVA) which is a conventional organic binder in alumina mixtures was used as a binder. More specifically, about 30 vol% of the mixture was finally added as a binder material. Each Powder mixture was then ground for 24 h in a corundum ball mill.

The powder mixture was uniaxially pressed at 215 MPa to form a cylinder with a 17 mm diameter and approximately a 17 mm height. Then, the green body was embedded by active graphite powder in a graphite crucible. Thereafter, the graphite crucible was heated to 513 K in an electrical box furnace in air for 5 h to obtain a degradation of PVA. Finally, the crucible was heated at a rate of 9 K·min⁻¹ to 1373 K in a high-temperature graphite resistance furnace. This was done during 8 h in an argon atmosphere, at a flow rate of 3 nL·min⁻¹.

Table 6. Samples chemical compositions and preparation conditions

<table>
<thead>
<tr>
<th>Test No.</th>
<th>RBM wt%</th>
<th>ZrSi2 wt%</th>
<th>(4B2O3·BaO) wt%</th>
<th>B2O3 wt%</th>
<th>PVA Removal</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>15</td>
<td>10</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>15</td>
<td>5</td>
<td>5</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>5</td>
<td>92</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>6</td>
<td>82</td>
<td>8</td>
<td>10</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>7</td>
<td>77</td>
<td>8</td>
<td>15</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>8</td>
<td>96</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>9</td>
<td>86</td>
<td>4</td>
<td>10</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>10</td>
<td>98</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>11</td>
<td>88</td>
<td>2</td>
<td>10</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
<tr>
<td>12</td>
<td>75</td>
<td>15</td>
<td>10</td>
<td>-</td>
<td>513K-6hr</td>
<td>Un-sintered</td>
</tr>
<tr>
<td>13, 14</td>
<td>70</td>
<td>15</td>
<td>15</td>
<td>-</td>
<td>513K-6hr</td>
<td>1373 K-8hr</td>
</tr>
</tbody>
</table>

2.4.2. Experimental set-up

Figure 6 shows the experimental apparatus used to perform the carbon oxidation experiments. The sample was suspended by a platinum wire inside the alumina tube of the electrical furnace. Here, the sample weight was measured with a thermobalance with an accuracy of ±0.01 g. The thermobalance was connected
to a computer equipped with a Balance-Win software (version 3.0.13), which gathered the real time sample weight every second. The Pt-10% Rh/Pt thermocouple showed the real time temperature near the suspended sample with an accuracy of ±1 K.

It should be noticed that the carbon oxidation resistance evaluation of the antioxidant containing alumina-graphite used in Submerged Entry Nozzle (SEN) refractory base materials, during preheating was the most important aspect of this work. Therefore, the temperature profile which the samples were supposed to follow during heating had to be similar to that found during industrial conditions. In addition, a commercial alumina-graphite refractory preheating simulation was performed from 373 K to 1773 K to suggest the temperature profile for the laboratory trials.

The weight loss in percent was calculated for each sample using equation 4. This was done at a one second interval at a controlled temperature and atmosphere consisting of 6.8 nL·min⁻¹ argon, 0.64 nL·min⁻¹ carbon dioxide and 0.56 nL·min⁻¹ oxygen.

\[
\text{Weight loss percent (wt\%) = \left( \frac{m_i - m_a}{m_i} \right) \times 100}
\]

(4)

where \( m_i \) is the initial mass and \( m_a \) is the actual mass of the investigated sample. The diagram of both weight loss percent and temperature versus time
was plotted for each sample. Moreover, the thickness of the decarburized layer was measured.

2.5. The decarburization of the commercial Submerged Entry Nozzles (supplement 4)

Laboratory samples were drilled out of a commercial SEN into cylinders of a 0.013 m diameter and a 0.036 m length. The specimens were heated in the furnace shown in figure 6. Furthermore, the sample weight was measured with a thermobalance with an accuracy of ±0.01 g. The thermobalance was also connected to a computer equipped with a Balance-Win software (version 3.0.13), which gathered the real time weight of the sample every second. The Pt-10% Rh/Pt thermocouple showed and registered the real time temperature near the suspended sample every second, with an accuracy of ±1 K. Carbon dioxide, oxygen and argon were mixed and injected into the alumina tube by using different amounts and flow rates. The flow rates and gas mixture compositions were adjusted using three brooks Sho-rate flow meters with R-2-15-B tubes (glass and Tantalum float) and R-2-15-AAA tubes (carboloy float). All samples were heated at a constant heating rate of 15 K·min⁻¹ from 298 K up to 1473 K. Thereafter, they were held at this temperature for 60 min. In addition, all samples were heated from 298 K to 873 K at an argon flow rate of 8 nL·min⁻¹ to prevent the decarburization. Table 7 illustrates the chemical compositions of the injected gas related to their AFR, flow rates of the injected gas, refractory materials, combustion type and the performed temperature profile for all experiments. After the decarburization test accomplishment each sample was cooled to room temperature. Furthermore, each sample was placed in an alumina crucible and heated at 1173 K in air for 5 h until it reached a constant weight. The weight loss of the sample during carbon burning-out together with the carbon weight loss during decarburization test may present the total amount of the carbon content in each original sample. The decarburization ratio ($\alpha$) was calculated at different time intervals using equation 5.

$$\alpha = \left(\frac{w_i-w_f}{w_i-w_t}\right)$$

where $w_i$, $w_t$, $w_f$ are the initial weight at 873 K, the real time weight and the final weight after carbon burning-out respectively.
Table 7. Materials, gas mixtures, temperature profiles and combustion properties for experimental tests

<table>
<thead>
<tr>
<th>Tests</th>
<th>Material</th>
<th>CO₂ (vol%)</th>
<th>O₂ (vol%)</th>
<th>Ar (vol%)</th>
<th>Flow rate Nl/min</th>
<th>Non-isothermal Heating 15 K/min</th>
<th>Isothermal Heating 60 min</th>
<th>Oxy-fuel Air-fuel</th>
<th>(AFR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₂O₃-C</td>
<td>8</td>
<td>7</td>
<td>85</td>
<td>8</td>
<td>873-1473 K</td>
<td>1473 K</td>
<td>Air-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃-C</td>
<td>8</td>
<td>7</td>
<td>85</td>
<td>8</td>
<td>-</td>
<td>1473 K</td>
<td>Air-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>Al₂O₃-C</td>
<td>8</td>
<td>7</td>
<td>85</td>
<td>8</td>
<td>873-1,773 K</td>
<td>1773 K</td>
<td>Air-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>ZrO₂-C</td>
<td>8</td>
<td>7</td>
<td>85</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Air-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>MgO-C</td>
<td>8</td>
<td>7</td>
<td>85</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Air-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>6</td>
<td>Al₂O₃-C</td>
<td>32</td>
<td>26</td>
<td>42</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>Al₂O₃-C</td>
<td>32</td>
<td>26</td>
<td>42</td>
<td>2</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>8</td>
<td>ZrO₂-C</td>
<td>32</td>
<td>26</td>
<td>42</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>9</td>
<td>MgO-C</td>
<td>32</td>
<td>26</td>
<td>42</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>Al₂O₃-C</td>
<td>43</td>
<td>-</td>
<td>57</td>
<td>8</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>Al₂O₃-C</td>
<td>43</td>
<td>-</td>
<td>57</td>
<td>3</td>
<td>873-1,473 K</td>
<td>1473 K</td>
<td>Oxy-fuel</td>
<td>1</td>
</tr>
</tbody>
</table>

2.6. Yttria Stabilized Zirconia (YSZ) plasma-PVD coated Al₂O₃-C refractory base materials of a commercial SEN (submerged entry nozzle) (supplement 5)

Two different laboratory trials were performed to evaluate the function of the YSZ coating of the SEN refractory base materials. More specifically, the decarburization resistance of the coated materials and the protection of the coated materials in contact with a REM alloyed molten steel. The trial samples were cylindrical test rods with a 0.013 m diameter and a 0.13 m height. These test rods were drilled out of a commercial SEN made of alumina-graphite refractory base materials. Table 2 shows the chemical composition for the test rods. As the table shows, the test rods contain 31.6 wt % graphite. Moreover, the alkalis content was aimed to be less than 1 wt% to prevent the reduction possibility by graphite. In addition, the substrate consisted of about 10 wt% silica.

The Low Pressure Plasma Spraying (LPPS) vacuum technology$^{23}$ was used to produce different thicknesses of Yttria Stabilized Zirconia (YSZ) layers on test
rods. Due to the presence of the graphite, the coating process was supposed to be performed in a controlled atmosphere. The coating process was performed at Sulzer Metco Wohlen.

The LPPS-Hybrid R&D / prototype system\(^{23}\) was used at a higher working pressure than used for normal coating procedures. Figure 7 illustrates the LPPS-Hybrid apparatus.

![Figure 7. LPPS-Hybrid R&D / prototype system at Sulzer Metco Wohlen](image)

The apparatus consisted of a large vacuum chamber for an increased plasma gun movement flexibility (4-axis gun drive) and an adjustable spray distance of about 1.3 m. The apparatus was also equipped with a multiple powder feed system (4×60C + 4×Twin) with a 4-fold injection capability. Moreover, with a linear string substrate holder with a large transfer chamber, preheating and reversed transfer arc capability. Furthermore, with multiple viewports and diagnostics for on-line monitoring (CCD Camera, Spectroscopy, DPV2000, IR-Pyrometer, IR-Camera). There were some challenges during the plasma spray-PVD coating of the substrates such as coating performances on very porous rods containing graphite, to obtain a good adhesion of the coating on the test rods and preserve the structure of the rods. The high enthalpy plasma jet expanding at lower pressures could sublime the graphite. Therefore, a standard 100 mbar vacuum plasma made of an Argon/Helium gas mixture and a 90 kW input electrical power was used to produce the coating by using Metco 6700 powder material (Yttria (8 wt%) Stabilized Zirconia) with a particle size below 25 µm. The coating was done on alumina-graphite (30 wt% C) rods. The process was performed by producing sweep movements of the plasma jet over the substrate combined with a rotation of the test rods (20 rev·min\(^{-1}\)) using the sting manipulator at a spray distance of 0.4 m. Due to the presence of about 30 wt% graphite in the substrate, it was possible to obtain a high heating rate during the preheating process. More specifically, the test rods were heated to a temperature of between 673-873 K at a heating rate of 144 K·min\(^{-1}\). Figure 8 shows the
surface of a test rod before and after plasma spray-PVD coating. As the figure shows, the test rod is placed in a sting manipulator.

![Image of Alumina-graphite rod mounted in a sting manipulator (before and after coating)]

It should be mentioned that a 0.07 m long piece of each test rod was coated with YSZ. Furthermore, a 0.06 m long piece was left uncoated. This could enable the comparison between the decarburization thickness layers of the YSZ coated substrate and an uncoated substrate for exactly the same trial conditions. Three Rods were coated with an YSZ thickness of 400-480 μm, two with a 500 μm thickness, and three rods with lower coating thicknesses (160 μm, 250 μm and 290 μm). The coating thicknesses may deviate from the planned thickness, due to the high porosity and the surface roughness of the test rods. Table 8 shows the YSZ plasma-PVD coating thicknesses, YSZ powder weights of applied coatings, number of sweeps, applied power and chamber pressure for each sample.

**Table 8. YSZ plasma-PVD coating conditions**

<table>
<thead>
<tr>
<th>Sample Nr</th>
<th>Pressure (mbar)</th>
<th>Sweep Nr</th>
<th>Power (kW)</th>
<th>Weight (g)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1000</td>
<td>94.2</td>
<td>1.86</td>
<td>160</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2500</td>
<td>94.2</td>
<td>5.36</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>2500</td>
<td>94.1</td>
<td>3.16</td>
<td>290</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>2500</td>
<td>94.4</td>
<td>5.77</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>2500</td>
<td>94.2</td>
<td>7.59</td>
<td>480</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>2500</td>
<td>93.3</td>
<td>7.84</td>
<td>500</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>2500</td>
<td>94.1</td>
<td>4.24</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 2 shows the experimental apparatus to perform the carbon oxidation experiments. It should be noticed that the carbon oxidation resistance evaluation of the plasma spray-PVD coated alumina-graphite used in the submerged entry nozzle refractory base materials, during the industrial preheating was the most important aspect of this work. Therefore, the sample temperature profiles during the laboratory preheating trials had to be similar to those found for industrial conditions. Therefore, industrial preheating trials of the commercial SENs alumina-graphite refractory base materials preheating were performed at
Sandvik Materials Technology (SMT) to obtain the temperature profile data. Sample 6 (table 8) with a planned YSZ coating thickness of 500 µm and an alumina-graphite test rod without coating were used to investigate the interactions between the refractory base materials and the YSZ plasma-PVD coating with a cerium alloyed molten steel. The test rod without coating was also drilled out of the same commercial submerged entry nozzle, which was used to prepare the coated test rods. The rods were preheated, immersed and rotated in molten steel. The experimental set-up was a high-temperature furnace equipped with graphite resistance-heating elements, as illustrated in Figure 9.

![Figure 9. Experimental apparatus](image)

The furnace consists of an alumina tube inside which an argon flow passes through. Two different crucibles are placed inside the alumina tube. A graphite crucible with a 0.050 m outer diameter, a 0.038 m inner diameter and a 0.070 m depth. Furthermore, an MgO-2wt% Y₂O₃ crucible with a 0.038 m outer diameter, a 0.031 m inner diameter and a 0.051 m depth. The MgO-2 wt% Y₂O₃ crucible was charged with 150 grams of stainless steel (20.78 wt% Cr - 10.86 wt% Ni - 0.099 wt% C - 1.63 wt% Si - 0.003 wt% Ce), which was heated to 1728 K. Furthermore, it was held for 30 minutes during argon flushing at 5 nL·min⁻¹ through the furnace chamber, to ensure the chemical homogeneity. Traces of carbon dioxide, oxygen and moisture in the commercial argon gas were removed by passing the gas through a gas cleaning system. Thereafter, the molten steel was alloyed by addition of a 0.3 gram cerium foil (99.9% purity, 0.62 mm thick) applied by Alfa Aesar GmbH & Co KG. The test rods were situated in the furnace chamber so that they were preheated at 1473 K and held for 20 minutes before being immersed into the molten steel. A 0.025 m length of the test rods were immersed into the molten
steel. Experiments were accomplished by rotating the rods at a speed of 100 \text{rev·min}^{-1} for 40 minutes. Then, the test rods were pulled out of the furnace chamber and cooled at room temperature. After the experiments, the immersed parts of the experimented test rods and molten steel were mounted in a conductive epoxy. The test rods were cut into 0.003 m thick discs to investigate the interface between the coated refractory base materials and the molten steel. Furthermore, the characteristics of the inclusions in the molten steel were investigated in a FEG-SEM.

2.7. Argon gas cleaning station

The commercial argon gas flushed through the furnaces at the previously mentioned laboratory trials was supplied by AGA with a purity of 99.99%. Traces of oxygen, moisture and carbon dioxide were removed by passing the argon gas through a gas cleaning station. Figure 10 shows the gas cleaning station schematically. The cleaning station consisted of three glass columns and one stainless steel column repleted by silica gel, ascarite, magnesium perchlorate and magnesium chips, respectively. In addition, the stainless steel column was heated to 773 K.

![Figure 10. Ar gas cleaning station](image)

2.8. Observations and chemical compositions analysis

The observations and chemical compositions of the samples were determined using an Ultra 55 Field Emission Gun Scanning Electron Microscope, FEG-SEM, (Carl Zeiss equipped with an EDS Inca Penta FETX3 Oxford Instrument) equipped with an energy dispersive X-ray spectrometry (EDS). All samples were mounted in a specific electrical conducting epoxy material and ground and diamond-polished. Thereafter, the microscopic examinations were carried out using the FEG-SEM using a backscattered detector on both etched and un-etched samples. The FEG-SEM-EDS determinations were performed using a
working distance of 8.5 mm and an acceleration voltage of 20 kV. The FEG-SEM-EDS calibration was performed using the Co standard for each sample. In supplement 1 and supplement 2, the samples were etched by a solution containing five volume percents bromine in methanol. In supplement 3, X-ray diffraction (XRD) analyses were also performed for samples to survey the existence of different compounds. The thickness of the decarburized layers in supplement 4 and supplement 5 were measured using a calibrated Olympus SZX16 light optic microscopy equipped with a 3CCD Color Version Camera Module and Image-Pro Plus software with measurement accuracy of ± 10 µm. Furthermore, the chemical composition analysis of the steel samples in supplement 5 performed using X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS).

2.9. Feature Analysis

An Automated Electron Beam Inclusion Analyzer is the most sophisticated method which is capable to evaluate size, shape and chemistry of non-metallic inclusions. In supplement 1 and supplement 2, INCA Feature was applied for analysis and classification of the features in the samples from the molten steel. The feature analysis has been performed for samples from each steel charge in supplement 2. The analyzes were performed to evaluate the presence and source of inclusions in molten steel in both supplements.
3. Preheating simulation

The temperature profile for heating of samples has been decided by the commercial Submerged Entry Nozzle (SEN) preheating simulation using COMSOL Multiphysics® software (version 3.5). It assumed that the inside diameter of the SEN has a constant value of 0.036 m. Furthermore, that its shape is symmetrical so that simulations can be performed in two dimensions (2D). The selected commercial SEN, alumina-graphite refractory, had a heat conduction coefficient of 18 \( \text{w} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \) at 973 K, a density of 2430 kg m\(^{-3}\) and a specific heat capacity of 1416.56 \( \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \). The heating source is assumed to be a propane combustion torch with a fuel consumption rate of about 10 kg hr\(^{-1}\). The propane flue gas volume for combustion was assumed to be 13.11 Nm\(^3\) Kg\(^{-1}\) with a temperature of 1773 K\(^{27)}\). The propane flue gas velocity is calculated as 35 m s\(^{-1}\), while the nozzle cross section area assumed to be 1018\times10^{-6} m\(^2\) and the propane flue gas flow rate is 0.036 Nm\(^3\) s\(^{-1}\).

The Reynolds number of propane flue gas is calculated using equation 6, where the propane flue gas density (\( \rho_p \)), viscosity (\( \mu_p \)), flow velocity (\( U_p \)) and the SEN diameter (\( d_N \)) assumed to be 0.89 kg m\(^{-3}\)\(^{27)}\), 375.10\(^{-7}\) kg m\(^{-1}\) s\(^{-1}\)\(^{28)}\), 35 m s\(^{-1}\) and 0.036 m, respectively.

\[
Re = \frac{\rho_p U_p d_N}{\mu_p} \tag{6}
\]

The calculated Reynolds number is 29 904. It defines that the propane flue gas flow in the SEN is turbulent\(^{28)}\). The Petukhov equation\(^{28)}\) (equation 7) has been performed to calculate the Nusselt number by assuming both a fully developed turbulent flow in the SEN and a smooth tube with a fraction factor (f) of 0.06\(^{28)}\).

The calculated Nusselt number was 186, when \( n \) in equation 7 was assumed to be zero for gases and Prandtl number (\( Pr \)) was 0.67\(^{28)}\).

\[
Nu = \frac{(f/8)^{Re Pr} (\mu_b / \mu_w)^n}{1.07 + 12.7(f/8)^2 (Pr^{3/2} - 1)} \tag{7}
\]

The propane flue gas heat convection coefficient \( h_p \) was 222.16 w m\(^{-2}\) K\(^{-1}\). This was calculated using the general form of Nusselt number (equation 8), where the propane flue gas heat conduction coefficient (\( k_p \)) assumed to be 0.043 w m\(^{-1}\) K\(^{-1}\)\(^{28)}\).

\[
Nu = \frac{h_p d_N}{k_p} \tag{8}
\]
The simulation has been performed for five points (A, B, C, D and E shown in figure 11) of SEN refractory materials from the inside surface (Point A) to the outside surface (Point E) with a 6.75mm interval during two hours.

Figure 11. The Submerged Entry Nozzle (SEN) cross section and corresponding heat transfer simulated points (A, B, C, D and E)
4. Industrial Preheating Trials

During the performed industrial trials at Outokumpu stainless steel (supplement 2), two FY 6 oxy-propane torches\textsuperscript{27) were used for preheating of the SENs. They were situated at the outlets of the SENs as shown in figure 12.

![Figure 12. Thermocouples and oxy-fuel torches arrangements](image)

The Air-Fuel Ratio (AFR) for the combustion system may decide the flue gas chemical analysis. Thus, the flue gas was analyzed using a M&C Analysentechnik instrument, type PMA 25, equipped with a paramagnetic detector. Furthermore, the CO and CO\textsubscript{2} concentration were measured using a Maihak analyzer of type MULTOR 610 equipped with a Non-Dispersive Infra Red detector (NDIR). Table 9 shows the measurements ranges and accuracies for the previously mentioned gas analyzers.

<table>
<thead>
<tr>
<th>Type of analyzer</th>
<th>Gas</th>
<th>Measurement range</th>
<th>Accuracy</th>
<th>Detector type</th>
</tr>
</thead>
<tbody>
<tr>
<td>M&amp;C Analysentechnik type PMA 25</td>
<td>O\textsubscript{2}</td>
<td>0-10% 0-25% 0-50%</td>
<td>0-100% &lt; 0,5% measuring range</td>
<td>Paramagnetic Detector</td>
</tr>
<tr>
<td>Maihak analyzer type MULTOR 610</td>
<td>CO\textsubscript{2}</td>
<td>0-30%</td>
<td>&lt; 1% measuring range</td>
<td>Non-Dispersive Infrared Detector</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0-50%</td>
<td>&lt; 1% measuring range</td>
<td>Non-Dispersive Infrared Detector</td>
</tr>
</tbody>
</table>
As figure 12 illustrates, six thermocouples (channel 1, 2, 3, 4, 5 and 6) were placed inside the SEN to register the real time temperatures every second. More specifically, the thermocouples were of a S-type for channel 1-5 and a K-type for channel 6. The industrial preheating trials were carried out during 4500 seconds. In addition, the microscopic examinations were performed for preheated SENs sampled after preheating. According to the SEN manufacturer recommendation, the optimal preheating temperatures for the SENs are between 1273 K and 1473 K. Moreover, with a heating rate of 0.63 K·s⁻¹ from room temperature up to 1373 K. The glass/silicon powder coating may form a dense and protecting layer at temperature above 1373 K. Below this temperature the decarburization may take place if the ambient gas contains oxidizing agents such as oxygen or carbon dioxide. In addition, graphite oxidation can be initiated at 873 K. Thus, overall the decarburization inside the coated SENs may occur at temperatures between 873-1373 K.

Industrial preheating trials of the commercial SENs alumina-graphite refractory base materials preheating were also performed at Sandvik Materials Technology (SMT) to obtain the temperature profile data (supplement 5). During the industrial preheating trials, three commercial SENs were assembled in a tundish while one air-propane torch was used for preheating of each SEN. The fuel consumption of each torch was about 22.5 kg·h⁻¹ propane. In addition, two air-propane torches were situated at the tundish cap with a consumption of 78.5 kg·h⁻¹ propane. The torches were situated at the outlets of the SENs. As Figure 13 (to the left) illustrates, six thermocouples (channel 1, 2, 3, 4, 5 and 6) were placed inside the SEN to register the real time temperatures every second. Thermocouples placed at channel 1, 2, 3, 4 and 5 were of an N-type, while channel 6 was of a K-type. In addition, channels 1, 2, 3, 4 and 5 were situated at 100, 180, 260, 340 and 440 mm respectively, from the outlet of the SEN.

Figure 13. SEN and thermocouples arrangements during industrial preheating trials
The Air-Fuel Ratio (AFR) for the combustion system may decide the flue gas chemical composition. Thus, the flue gas was analyzed using a testo 300 M/XL flue gas analyzer equipped with an O₂ and a CO measuring cell and a CO₂ level and AFR calculation function. The analyzer was able to measure oxygen and carbon monoxide in the ranges of (0-21 vol%) and (0-8000 ppm) with an accuracy of ±0.2 vol% and ±20 ppm, respectively. In addition, Figure 13 (to the right) shows the flue gas probe situation, which was placed at a 440 mm from the SEN outlet.
5. **Decarburization mechanisms determinations**

The differential method \(^{30}\) was applied to determine the reaction kinetics for the decarburization experiments during the non-isothermal heating step in the temperature range 873 K to 1473 K. Equation 9 defines the general decarburization rate as follows \(^{30}\):

\[
-J = \frac{d\alpha}{dt} = f(\alpha) \cdot K
\]  

(9)

where \(J\) is the decarburization rate, \(\alpha\) is the decarburization ratio, \(t\) is the reaction time, \(f(\alpha)\) is a function depending on the reaction mechanism and \(K\) is a constant. When the decarburization ratio and time vary, a new function namely \(g(\alpha)\) can be expressed by integration of equation 9 as equation 10 shows.

\[
g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{0}^{t} K \cdot dt
\]

(10)

According to the Arrhenius law, \(K\) is temperature and pressure dependent. In this case study, the laboratory experiments were performed at a constant standard atmospheric pressure. Therefore equation 10 can be transformed into equation 11.

\[
g(\alpha) = \int_{0}^{t} A \cdot e^{-\frac{E}{RT}} \cdot dt
\]

(11)

where \(E\) (KJ·mol\(^{-1}\)) is the activation energy of the decarburization, \(T\) is the temperature (K) and \(R\) is the gas constant (J·K\(^{-1}\)·mol\(^{-1}\)). If the system is heated at a constant heating rate \((\beta\) (K·min\(^{-1}\))\) and the initial temperature is \(T_0\), then the real time temperature \((T)\) of the system can be expressed as equation 12:

\[
T = T_0 + \beta \cdot t
\]

(12)

In addition, Lu et al. \(^{30}\) presented equation 13 for different reaction mechanisms.

\[
\ln\left(\frac{dg(\alpha)}{dt}\right) = \ln A - \frac{E}{RT} - \ln \beta
\]

(13)

where \(A\) is constant, \(\beta\) is the heating rate, \(g(\alpha)\) is the function defined for solid state reactions, \(E\) is the activation energy of the reaction, \(t\) is the reaction real time and \(R\) is the gas constant. Table 10 shows the different mechanisms and their corresponding functional form of \(g(\alpha)\) for solid state reactions. \(^{31}\) As equation 13 illustrates, the correlation between \(\ln(dg(\alpha)/dt)\) and \((1/T)\) is linear.
for a constant heating rate. Therefore, the experimental values of \(\ln(dg(\alpha)/dt)\) vs. \((1/T)\) were plotted in form of curves for each theoretical \(g(\alpha)\) function shown in Table 10. The linear correlation coefficient for each curve was calculated using the ordinary least squares (OLS) method.

### Table 10. Solid state reaction functions.\(^{31}\)

<table>
<thead>
<tr>
<th>Model</th>
<th>Name of the function</th>
<th>(g(\alpha))</th>
<th>Rate controlling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPL(^1)</td>
<td>Mampel power law, (n=1)</td>
<td>-(\ln(1-\alpha))</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>MPL(^0)</td>
<td>Mampel power law, (n=0)</td>
<td>(\alpha)</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>MPL(^2)</td>
<td>Mampel power law, (n=2)</td>
<td>((1-\alpha)^1)-1</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>(R_2)</td>
<td>Contracting cylinder</td>
<td>(1-(1-\alpha)^{1/2})</td>
<td>Phase-boundary reaction, cylindrical symmetry</td>
</tr>
<tr>
<td>(R_3)</td>
<td>Contracting sphere</td>
<td>(1-(1-\alpha)^{1/3})</td>
<td>Phase-boundary reaction, spherical symmetry</td>
</tr>
<tr>
<td>(D_2)</td>
<td>Valensi (Barrer) equation</td>
<td>(\alpha+(1-\alpha)\ln(1-\alpha))</td>
<td>Two-dimensional diffusion, cylindrical symmetry</td>
</tr>
<tr>
<td>(D_3)</td>
<td>Jander Equation</td>
<td>([1-(1-\alpha)^{1/3}]^2)</td>
<td>Three-dimensional diffusion</td>
</tr>
<tr>
<td>(D_4)</td>
<td>Ginstling –Brounshtein equation</td>
<td>(1-2\alpha/3-(1-\alpha)^{2/3})</td>
<td>Three-dimensional diffusion, spherical symmetry</td>
</tr>
</tbody>
</table>
6. Results

6.1. Interaction between glass/silicon powder coating and SEN refractory base materials, Laboratory experiments (supplement 1)

Figure 14 shows the FEG-SEM images of a specimen after a preheating trial. The images illustrate how the glass/silicon powder coating makes a dense layer to protect the base refractory materials from decarburization during the laboratory preheating trail.

![Figure 14. SEM images of glass/silicon powder coating and alumina/graphite refractory after preheating at 1473 K](image)

Table 11 presents the SEM-EDS chemical composition determinations performed for regions A and C shown figure 14. Even if the preheating process was performed in an oxidizing atmosphere, much metallic silicon powder still remained inside the glass/silicon powder coating layer. This is illustrated in region B in figure 14. Region A represent a region where the Al$_2$O$_3$/SiO$_2$ ratio is 0.83 and where the alkaline (Na$_2$O+K$_2$O) content is 6.4 wt%. Furthermore, the Al$_2$O$_3$/SiO$_2$ ratio is 5.40 for the SEN with an alkaline content of 1 wt% (Table 2). The Al$_2$O$_3$/SiO$_2$ ratio is 0.29 for the glaze formed during preheating (figure 14, region C, Table 11) with an alkaline content of 9.3 wt%. A comparison between these chemical composition determinations clearly show that region A is where the SEN refractory base material and glass/silicon coating have interacted during SEN preheating. The interaction led to an increased silica and alkaline concentrations in the SEN base refractory materials. In addition, it can be concluded that the penetrated coating materials have become alumina enriched.
Table 21. SEM-EDS chemical analysis for regions A and C shown in figure 14

<table>
<thead>
<tr>
<th>Compound</th>
<th>Region A-wt%</th>
<th>Region C-wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>4.57</td>
<td>6.18</td>
</tr>
<tr>
<td>MgO</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>38.93</td>
<td>19.67</td>
</tr>
<tr>
<td>SiO₂</td>
<td>46.69</td>
<td>68.54</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.83</td>
<td>3.12</td>
</tr>
<tr>
<td>CaO</td>
<td>1.58</td>
<td>1.89</td>
</tr>
<tr>
<td>TiO₂</td>
<td>6.13</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-</td>
<td>0.61</td>
</tr>
</tbody>
</table>

6.2. Interaction between glass/silicon powder coating, SEN refractory base materials and molten steel, Laboratory experiments (supplement 1)

Figure 15 shows the region at the interface between a preheated zirconia-graphite rod (test 1, table 5) at 1473 K immersed and rotated in molten steel for 10 min.

![Image of zirconia-graphite rod surface](image)

Figure 15. Zirconia-graphite rod surface after preheating at 1473 K and immersion in molten steel at 1873 K

The EDS chemical composition analysis for region A between zirconia particles in the zirconia-graphite refractory was performed. The Al₂O₃/SiO₂ ratio for region A is 0.19 with an alkaline (Na₂O+K₂O) content of 12.78 wt%. However, this ratio is 0.04 for commercial zirconia-graphite refractory with almost no
alkaline content. The high concentration of alumina and alkaline in this area may indicate that the source is the glass/silicon powder coating. However, the zirconia concentration value in region A is 17.7 times higher in comparison to the formed glaze during preheating (Table 11, region C). These results confirm that penetration of the glaze occurs during preheating. Furthermore, they indicate that an interaction between the glaze and the zirconia particles in the refractory occurs. In addition, the penetrated glaze has become zirconia rich due to the interaction. This zirconia rich glaze has a higher viscosity in comparison to the glaze with a lower zirconia concentration. Figure 16 shows FEG-SEM images at the interface of the alumina-graphite and zirconia-graphite rod in the molten steel (tests 1 and 2, table 5). It clearly shows the formation of an uneven surface on the refractory base materials due to the penetration of the glass/silicon powder coating. It has led to the formation of surface irregularities, which protrude a distance of about 187.2 µm and 600 µm in test 1. Furthermore, 178 µm in test 2 at the interface of the test rods in contact with the molten steel.

Figure 16. zirconia-graphite rods (top) and alumina-graphite rod (bottom) interfaces after preheating at 1473 K and immersion in molten steel at 1873 K

Figure 17 clearly shows the penetration of the glaze in test 1, 218 µm into the zirconia-graphite refractory materials. This penetration has also provided a contact region between the penetrated glaze and the graphite in the refractory base materials.
6.3. Post-mortem study of the internal coated SENs respecting clogging phenomena (supplement 2) and Interaction between glass/silicon powder coated SEN and a rare earth metals (REM) alloyed stainless steel, Plant description (supplement 1)

In an ideal situation the diagram of the relative stopper position changing versus time should be a straight line without any tilt for a constant casting rate. As soon as the curve goes up during time it means that the SEN has been clogged. The accretion formation decreases the SEN’s active area inside the SEN. To adjust the flow rate, the stopper has to be lifted up to increase the active area. Figure 18 illustrates the stoppers positions versus time during casting for the three industrial trials. As the figure shows all of the surveyed charges had clogging problem identified by the increased stopper positions.

6.3.1. Macroscopic examination
The macroscopic examination of the transverse sections showed a presence of an accretion inside the SEN along the whole longitudinal section, even in the part immersed in the mould. In addition, with different thicknesses. Figure 19 shows the transverse section of both the SEN and the accretion at level 5 shown in figure 4. As the figure illustrates, a two millimeter layer, formed inside the SEN region, has led to a 10 mm excessive accretion in comparison to regions without this two millimeters thick layer. The accretion thicknesses showed no significant variation above and below the mould molten powder level.

![Figure 19. Transverse section of a clogged nozzle](image)

6.3.2. **Microscopic Examination**

Figure 20 shows an un-etched accretion region (Left) and an etched region (Right). The microscopic observations revealed the formation of four different layers from the SEN refractory materials to the tail of the nozzle blockage. Layers 1, 2, 3 and 4 with a thickness of about 1-2 mm (inside the SEN region), 120-300 µm, 100-500 µm and 7-17 mm respectively, could be distinguished.

![Figure 20. SEM accretion observations, un-etched (left) and etched (right) sample](image)
6.3.3. **Layer 1**

Figure 21 shows a SEM image of layer 1, defined in figure 20. The SEM observations and chemical analysis show that this layer consists of steel spots and large alumina particles present in the matrix. In addition, no trace of graphite could be found in this layer. This despite that this region is a part of the SEN, which contains about 30 wt% graphite.

![Figure 21. SEM image of layer 1 shown in figure 20](image)

The microscopic examinations of the unused SEN confirmed the presence of oxide particles and graphite. However, no matrix could be identified. It can be concluded that the matrix is a material that has penetrated into the SEN’s refractory base materials. The chemical composition analysis was performed to identify this phase. Figure 22 shows the region at the interface between a steel spot and an alumina particle in the matrix in this layer.

![Figure 22. SEM image at the interface between a steel spot and an alumina particle in layer 1](image)

Table 12 shows the chemical composition analysis of the matrix region (A) in figure 22. It can clearly be seen that this region contains 45 wt% SiO$_2$ and 9.16 wt% alkaline materials (Na$_2$O-K$_2$O). This clearly substantiates that they do not
originate from the SEN commercial alumina-graphite base refractory materials, which contains just 10 wt% SiO\textsubscript{2} and almost no alkaline (table 2).

Table 12. SEM-EDS chemical analysis of region A in figure 22

<table>
<thead>
<tr>
<th>Formula</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{2}O</td>
<td>8.35</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>26.99</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>44.87</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>0.81</td>
</tr>
<tr>
<td>CaO</td>
<td>2.66</td>
</tr>
<tr>
<td>La\textsubscript{2}O\textsubscript{3}</td>
<td>3.47</td>
</tr>
<tr>
<td>Ce\textsubscript{2}O\textsubscript{3}</td>
<td>12.39</td>
</tr>
<tr>
<td>Nd\textsubscript{2}O\textsubscript{3}</td>
<td>0.45</td>
</tr>
</tbody>
</table>

6.3.4. Layer 2

Figure 23 shows a SEM image of layer 2 defined in figure 20 for an etched sample. This layer consists of white particles containing a high REM concentration present in a darker matrix. The chemical composition analysis performed for three points (A, B and C) is shown in figure 23. The un-etched sample of this layer also contained steel spots.

![Figure 23. SEM image of layer 2](image)

The stoichiometric ratio of elements in atom for points A and C in analyzed region agrees with the theoretical ratio for REAlO\textsubscript{3} and RE\textsubscript{4.67} (SiO\textsubscript{4})\textsubscript{3}O. Also, point B represents a high alkaline content region with almost equal concentrations of alumina and silica.
Figure 24 shows an etched sample from layer 2 (defined in figure 20) at the interface between layer 2 and 3. This figure clearly substantiates that layer 2 represents a very uneven layer which thickness may vary from just few micrometers, or as seen in this figure, up to 153 µm.

![Figure 24. SEM image of an etched sample at the interface between SEN and the accretion](image)

6.3.5. **Layer 3**

Layer 3 defined in figure 20 consists of large inclusions present in a matrix of solidified steel. Figure 25 shows an etched sample of this layer, before grinding (left) and after grinding (right). The inclusions in this region had a dendritic morphology and the interfaces between the large inclusions were not distinguishable.

![Figure 25. SEM images of layer 3, sample without grinding (left) and with grinding (right)](image)

The chemical composition analysis of the inclusions in this region indicated an existence of three different types of inclusions. This layer generally consisted of large inclusions of type RE$_2$SiO$_5$, RE$_{4.67}$ (SiO$_4$)$_3$O and some large RE$_2$O$_2$S inclusions. Furthermore, a few RE$_2$O$_3$ inclusions could also be observed. Figure 26 shows a 34.25 µm inclusion of RE$_2$O$_2$S in this layer.
Figure 26. SEM image of a RE₂O₂S inclusion in layer 3

Figure 27 shows an etched sample from layer 3 at the interface between layer 3 and 4. Region A in layer 3 consists mostly of large RE₂SiO₅, RE ₄.₆₇(SiO₄)₂O and RE₂O₂S (≥10µm) inclusions. While region B is a thin region located between layer 3 and 4, which consists of agglomerated small RE₂O₃ inclusions (200nm-5µm) present in molten steel. The chemical composition analysis of inclusions in region B indicated that they contain almost no aluminum and silicon.

Figure 27. SEM images of an etched sample from layer 3 and regions A and B in this layer

6.3.6. Layer 4

Figure 28 shows the final accretion layer, identified in figure 20. It constitutes the most part of the accretion. Two pictures on top show two ground and polished un-etched samples. The pictures in the bottom show two etched samples from the same layer. The accretion in this layer contains small cerium oxide particles (white particles) embedded in solidified stainless steel (grey matrix).
Figure 28. SEM images of REM oxide inclusions in layer 4 for un-etched samples (top) and etched samples (bottom)

The inclusions contain almost no aluminum and silicon. The stoichiometric atom ratio for inclusions in this region agrees with the theoretical ratio for RE$_2$O$_3$.

The characteristics of the primary inclusions in molten steel flowing through the SEN were investigated using a feature analysis. The results may facilitate the comparison between the primary inclusions and the inclusions in clogging products to establish whether they originate from primary inclusions or if they were formed “In Situ”.

6.4. Feature Analysis

Tables 13 and 14 illustrate the inclusion characteristics and size distribution for one of the surveyed samples taken in the tundish during the industrial trials. Table 13 shows those inclusions, which were found to consist of REM, oxygen and other elements.

<table>
<thead>
<tr>
<th>Class</th>
<th>&lt; 2.00 µm</th>
<th>2-5 µm</th>
<th>5-20 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Features</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Inclusions (Si, Al)</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Inclusions (Al, Si, Ca, Mg)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Inclusions (Al, Si, Mg)</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Inclusions (Al, Si, Ca)</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 14 shows those inclusions consisting of REM elements and oxygen. It can be concluded that the quantity of large inclusions containing REM, Al and Si is just 2, while the total number of the analyzed inclusions is 175.

<table>
<thead>
<tr>
<th>Class</th>
<th>&lt; 4 µm</th>
<th>4-6 µm</th>
<th>6-8 µm</th>
<th>8-10 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Features</td>
<td>94</td>
<td>55</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>Inclusions (Ce)</td>
<td>83</td>
<td>46</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Inclusions (La)</td>
<td>11</td>
<td>9</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

6.5. Outokumpu Stainless steel Industrial preheating trials

The results were evaluated to establish the possibility of decarburization. The Air-Fuel Ratio (AFR) for the combustion system was adjusted so that the flue gas chemical analysis obtained partial pressure for CO$_2$, CO and O$_2$ of about 0.07 atm, 0.27 atm and 0.0016 atm, respectively. It was assumed that the oxygen concentration is equal to zero, due to the very low concentration of oxygen in the flue gas passing through the nozzles. In addition, a high concentration of carbon monoxide was used to form of a reducing atmosphere dominating inside the nozzles. The carbon dioxide is the only oxidizing agent in the flue gas, which may cause graphite oxidation as reaction 14 illustrates:

$$C (s) + CO_2 (g) = 2CO (g) \quad \Delta G = (169008 - 172.192T) + RT \ln \left( \frac{p_{CO}^2}{p_{CO_2} a_c} \right)$$ (14)

The Gibbs free energy values may be decided by four parameters; namely the carbon monoxide partial pressure, the carbon dioxide partial pressure, the temperature and the graphite activity. The preheating trials substantiated that the partial pressures of gases passing through the nozzles during preheating are almost constant. However, the temperatures for different regions inside the SENs were found to vary with time. When the Gibbs free energy values (reaction 14) for regions around different channels, shown in figure 12 become negative, the graphite oxidation reaction is thermodynamically possible.

Figure 29 shows the real time temperatures registered by different channels during an industrial preheating trial.
Figure 29. Temperature vs. time for six different channels inside the SEN during preheating trial.

The curves shown in figure 29 have been divided into small segments with almost constant heating rates. Table 15 shows these temperature intervals and the corresponding heating rates for each segment.

Table 15. Temperature intervals and constant heating rates for different channels extracted from figure 29

<table>
<thead>
<tr>
<th>Channel Number</th>
<th>Temperature interval(K)</th>
<th>[Heating rate] (K·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel 1</td>
<td>298-1313 [1.69]</td>
<td>1313-1533 [0.13]</td>
</tr>
<tr>
<td>Channel 2</td>
<td>298-1153 [1.425]</td>
<td>1153-1393 [0.67]</td>
</tr>
<tr>
<td>Channel 3</td>
<td>298-1073 [1.12]</td>
<td>1073-1273 [0.67]</td>
</tr>
<tr>
<td>Channel 4</td>
<td>298-993 [0.83]</td>
<td>993-1213 [0.31]</td>
</tr>
<tr>
<td>Channel 5</td>
<td>298-893 [0.66]</td>
<td>893-1093 [0.30]</td>
</tr>
<tr>
<td>Channel 6</td>
<td>298-873 [4.79]</td>
<td>873-1033 [0.53]</td>
</tr>
</tbody>
</table>

Figure 30 shows Gibbs free energy values for regions at channels shown in figure 29. The values are calculated by using reaction 14.
As the figure illustrates, the graphite oxidation reaction (reaction 14) is thermodynamically possible for channel 1, 2, 3 and 4 after 1080, 1500, 1920 and 2760 seconds from the preheating start regarding reaction 14 and figure 29. In addition, the real time temperatures for regions around channels 1, 2, 3 and 4 at the previous mentioned times are 1533, 1533, 1473 and 1273 K respectively. At these temperatures, a dense protective coating may form that may prevent SEN oxidation. Furthermore, the Gibbs free energy never becomes negative for the regions around channel 5. Therefore, there exist no chance for graphite oxidation. In addition, the maximum reachable temperature in these regions is 1153 K, which may prevent the formation of a proper protective coating inside the nozzles. The regions around channel 5 have the potential to be decarburized if the nozzles come into contact with the atmospheric air after the preheating and before the casting start. The glass/silicon powder coating temperature is 1193 K for the regions around channel 6, when the Gibbs free energy of the graphite oxidation reaction becomes negative (900 seconds after the preheating start). As table 15 illustrates, the heating rate for the regions around channel 6, at temperatures between 1193-1293 K, is just 0.15 K·s⁻¹. Therefore, these regions have a very high thermodynamic potential to be decarburized before formation of the glaze at temperatures above 1373 K.

Figure 31 shows SEM observations of regions around channel 1 before preheating (left) and after the industrial preheating trial (right).
As table 15 shows, the maximum preheating temperature at this channel is 1593 K, which is higher than the recommended preheating temperature. The formation of a dense protecting glaze is confirmed by the formation of a 135µm thick layer from a 387µm thick as-fabricated powder coating. Table 16 illustrates alumina and silica concentrations for point A, B, C, D and E shown in figure 31. Furthermore, the unused SEN’s Refractory Base Material (RBM). The comparison between these chemical composition analyses for different points with the SEN refractory base material’s RBM analysis may clearly substantiate that the high silica concentration in these points originates from the penetrated glaze into the refractory base materials. The penetrated glaze could be detected at the maximum distance of 337 µm from the SEN/glaze interface.

Table 16. Chemical analysis for point A, B, C, D, E and SEN’s RBM shown in figure 31

<table>
<thead>
<tr>
<th>Point</th>
<th>SiO₂ (wt %)</th>
<th>Al₂O₃ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>B</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>E</td>
<td>47</td>
<td>53</td>
</tr>
<tr>
<td>RBM</td>
<td>10</td>
<td>55</td>
</tr>
</tbody>
</table>

Furthermore, SEM observations and chemical composition analysis of regions around channel 6 (before and after preheating shown in figure 32) may clearly substantiate the penetration of the glaze into the refractory base materials at about a 2.236 mm distance. The thickness of the formed glaze layer is 503 µm, which is thicker than the original glass/silicon powder coating. In addition, the chemical composition analysis of the black regions in the glaze region confirmed the presence of flake graphite. This originates from the refractory base materials and not the glaze. Therefore, it can be concluded that the decarburization started in this region during preheating. Thereafter, it proceeded before the glass powder coating started to form a glaze layer.
above 1273 K, the glaze started to penetrate into the SEN’s pores after the decarburization. Therefore, small amounts of the remained flake graphite could be detected in this layer.

6.6. The carbon oxidation behavior of the Zirconium Disilicide (ZrSi$_2$)-containing alumina-Graphite refractory materials (supplement 2)

The simulated temperature profiles for points A, B, C, D and E (figure 11) are shown in figure 33.

The simulation revealed the following results:
• The temperature profiles are almost the same for points A, B, C, D and E inside the SEN alumina-graphite refractory for the studied time of 7200 seconds. This is due to that the graphite has a high thermal conductivity.

• At point A, the temperature increases from 298 K to 1473 K (a 1172 K temperature increase) in 1140 seconds. Furthermore, it takes 4320 seconds for the same point to be heated from 1473 K to 1626 K (a 153 K temperature increase).

• The maximum reached temperature is 1626.5 K.

The determined temperature profile between 398 K – 1473 K for sample heating is presented in figure 34, as the continuous curve shows. The experimental apparatus in figure 2 was capable to perform different heating programs (ramp) using a constant heating rate. Therefore, the simulated temperature profile (continuous curve) has been divided into four sections. Each one with a constant heating rate, as the dashed lines shows in figure 34.

![Figure 34. The temperature profile simulated using ComSol software (continuous curve) and corresponding line with four constant heating rate segments (dashed line)](image)

The four temperature sections and their related injected gases are shown in table 17.

Table 17. Different segments with constant heating rate shown by dashed line in figure 34

<table>
<thead>
<tr>
<th>Temperature Interval (K)</th>
<th>Ramp K·min⁻¹</th>
<th>Ar (nL·min⁻¹)</th>
<th>CO₂ (nL·min⁻¹)</th>
<th>O₂ (nL·min⁻¹)</th>
<th>Total Flow (nL·min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373-773</td>
<td>100</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8</td>
</tr>
<tr>
<td>773-973</td>
<td>63</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8</td>
</tr>
<tr>
<td>973-1273</td>
<td>42</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8</td>
</tr>
<tr>
<td>1273-1473</td>
<td>15</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8</td>
</tr>
</tbody>
</table>
The alumina tube situated inside the furnace in figure 2 can just tolerate a heating rate of about 15 K·min⁻¹. Also, it may crack at higher heating rates. Therefore, the partial pressure of injected oxygen and carbon dioxide were adjusted so that the total oxidizing components amounts, which the refractory materials were exposed to, were the same at both high and low heating rates. This is shown in table 18. The heating rate during the laboratory trials was 15 K·min⁻¹.

Table 18. The flow rate calculated for the injected gas components of for both simulations and trials

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Ar (nL·min⁻¹)</th>
<th>CO₂ (nL·min⁻¹)</th>
<th>O₂ (nL·min⁻¹)</th>
<th>Nliter Injected CO₂</th>
<th>Nliter Injected O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>373-773 K (100 K·min⁻¹) simulation</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>2.56</td>
<td>2.24</td>
</tr>
<tr>
<td>373-773 K (15 K·min⁻¹) Trial</td>
<td>7.83</td>
<td>0.09</td>
<td>0.08</td>
<td>2.40</td>
<td>2.13</td>
</tr>
<tr>
<td>773-973 K (63 K·min⁻¹) simulation</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>2.02</td>
<td>1.77</td>
</tr>
<tr>
<td>773-973 K (15 K·min⁻¹) Trial</td>
<td>7.72</td>
<td>0.15</td>
<td>0.13</td>
<td>2.00</td>
<td>1.73</td>
</tr>
<tr>
<td>973-1273 K (42 K·min⁻¹) simulation</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>4.57</td>
<td>3.99</td>
</tr>
<tr>
<td>973-1273 K (15 K·min⁻¹) Trial</td>
<td>7.59</td>
<td>0.22</td>
<td>0.19</td>
<td>4.40</td>
<td>3.80</td>
</tr>
<tr>
<td>1273-1473 K (15 K·min⁻¹) Trial - simulation</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>8.53</td>
<td>7.46</td>
</tr>
<tr>
<td>373-1473 K simulation</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.68</td>
<td>15.46</td>
</tr>
<tr>
<td>373-1473 K Trial</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.33</td>
<td>15.12</td>
</tr>
<tr>
<td>1473 K (10 min) Trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>6.40</td>
<td>5.60</td>
</tr>
</tbody>
</table>

6.7. The carbon oxidation behavior of the Zirconium Disilicide (ZrSi₂)-containing alumina-Graphite refractory materials (supplement 3)

The decarburized thickness layer of each specimen was measured by using a light optic microscope. The measured thickness was compared to the decarburization thickness layers of the Refractory Base Material (RBM).
Equation 15 defines the Decarburization Resistance Improvement in percent (DRI %).

Decarburization Resistance Improvement % (DRI, %) = 100 \times \left(1 - \frac{a}{b}\right) \quad (15)

where \(a\) is the decarburization layer thickness of the antioxidant-containing sample and \(b\) is the decarburization layer thickness of the base refractory materials (RBM). Figure 35 shows the decarburization resistance improvement (DRI%) for Tests 2-11 (table 6).

![Figure 35. The Decarburization Resistance Improvement % (DRI %) for Tests 2-11](image)

The sample with 8 wt% ZrSi\(_2\) and 15 wt% (4B\(_2\)O\(_3\) ·BaO) glass powder (Test 7) showed a carbon oxidation resistance improvement of 46.3 DRI%. This was the highest value. Test 4, which contained both B\(_2\)O\(_3\) powder and (4B\(_2\)O\(_3\) ·BaO) glass powder, showed less resistance in comparison to Test 3, which contained only a (4B\(_2\)O\(_3\) ·BaO) glass powder. Also, the addition of (4B\(_2\)O\(_3\) ·BaO) glass powder mostly enhanced the decarburization resistance for specimens containing higher than 8 wt% of ZrSi\(_2\). The addition of a (4B\(_2\)O\(_3\) ·BaO) glass powder showed almost no effect on the decarburization resistance for samples containing between 2 and 4 wt% ZrSi\(_2\).

Figure 36 shows the weight loss% versus time for samples containing 15 wt% ZrSi\(_2\) and 15 wt% (4B\(_2\)O\(_3\) ·BaO) glass powder. These had been heated isothermally for 25 minutes at constant temperatures of 1473 K (Test 13) and 1773 K (Test 14). A slight weight loss percent increase of about one percent was observed for a temperature increase of 300 K. The less sensitivity to temperature of the ZrSi\(_2\) containing refractory materials can be attributed to the higher driving forces for a ZrSiO\(_4\) formation at higher temperatures.
6.8. The decarburization of the commercial Submerged Entry Nozzles (supplement 4)

Figure 37 shows plots of the decarburization ratio ($\alpha$) as a function of time for the non-isothermal heating of tests 1, 4, 5, 6, 8 and 9 at a heating rate of 15 (K·min$^{-1}$). This was done from 873 K to 1473 K followed by isothermal heating for 60 min at 1473 K (table 7). As plot a) illustrates, the decarburization ratios of the Al$_2$O$_3$-C, ZrO$_2$-C and MgO-C samples reached 0.40, 0.50 and 0.32 respectively after the non-isothermally heating completion. This for an atmosphere consisting of 8 vol% CO$_2$, 7 vol% O$_2$ and 85 vol% Ar. In addition, the decarburization ratios of the Al$_2$O$_3$-C, ZrO$_2$-C and MgO-C samples reached 1, 1 and 0.88 after 60 min, 46 min and 60 min respectively during isothermal heating at 1473 K. Furthermore, as plot b) illustrates, the decarburization ratios of the Al$_2$O$_3$-C, ZrO$_2$-C and MgO-C samples reached 0.76, 0.92 and 1 respectively after the non-isothermal heating completion in an atmosphere consisting of 32 vol% CO$_2$, 26 vol% O$_2$ and 42 vol% Ar. In addition, the decarburization ratios of the Al$_2$O$_3$-C and ZrO$_2$-C samples increased to unity after 28 min and 6 min respectively during isothermally heating at 1473 K.
Figure 37. Decarburization behaviors of Al₂O₃-C, ZrO₂-C and MgO-C with AFR=1.5 for a) Air-fuel combustion and b) oxygen-fuel combustion

Figure 38 shows plots of the decarburization ratio ($\alpha$) as a function of time for non-isothermal heating of tests 6, 7, 10 and 11 at 15 (K·min⁻¹) from 873 K to 1473 K followed by isothermal heating for 60 min at 1473 K. As plot a) shows, the decarburization ratios for the Al₂O₃-C samples reached 0.76 and 0.66 for gas flowing rates of 8 (nL·min⁻¹) and 2 (nL·min⁻¹), respectively. These values were obtained after completion of the non-isothermal heating in an atmosphere consisting of 32 vol% CO₂, 26 vol% O₂ and 42 vol% Ar. In addition, the decarburization ratios of the Al₂O₃-C samples exposed to 8 (nL·min⁻¹) and 2 (nL·min⁻¹) gas mixtures reached unity after 28 min and 32 min respectively during isothermal heating at 1473 K. Plot b) demonstrates that the decarburization ratios of the Al₂O₃-C samples became 0.10 and 0.06 with gas flowing rates of 8 (nL·min⁻¹) and 3 (nL·min⁻¹), respectively. This after the non-isothermal heating completion in an atmosphere consisting of 43 vol% CO₂ and 57 vol% Ar. The decarburization ratios of these samples reached 0.42 and 0.32 after 60 min, during isothermal heating at 1473 K when exposed to 8 (nL·min⁻¹) and 3 (nL·min⁻¹) gas mixtures respectively.

Figure 38. Decarburization behaviors of Al₂O₃-C Oxygen-Fuel combustion a) AFR=1.5, at 8 (nL·min⁻¹) and 2 (nL·min⁻¹) b) AFR=1, 3 (nL·min⁻¹) and 8 (nL·min⁻¹)
Figure 39 shows plots of the decarburization ratio ($\alpha$) as a function of time for four $\text{Al}_2\text{O}_3$-$\text{C}$ samples exposed to an atmosphere consisting of 8 vol\% CO$_2$, 7 vol\% O$_2$ and 85 vol\% Ar. Plot a) illustrates the test results for two $\text{Al}_2\text{O}_3$-$\text{C}$ samples both heated non-isothermally with a 15 (K·min$^{-1}$) heating rate from 873 K to 1473 K (test 1). Furthermore, one continued to 1773 K (test 3). Thereafter, test 1 and test 3 were heated isothermally for 60 min at 1473 K and 1773 K, respectively. The decarburization values for both samples reached 0.38 during heating between 873 K-1473 K. In addition, the decarburization ratio for test 1 became 0.64 after 20 min of isothermal heating at 1473. Furthermore, the decarburization ratio for test 3 was 0.60 for 20 min during non-isothermal heating from 1473 K to 1773 K at 15 (K·min$^{-1}$). After 40 min both samples were completely decarburized. It can be concluded that when using the same heating rate of 15 (K·min$^{-1}$), the samples in test 1 and test 3 were totally decarburized during isothermal heating at 1473 K and 1773 K after 60.5 min and 40.5 min respectively. It should be mentioned that the total carbon loss during the first 20 min of the isothermal heating at 1473 K in test 1 and the 20 min non-isothermal heating from 1473 K to 1773 K in test 3 were almost the same.

Plot b) compares the oxidation behavior of two $\text{Al}_2\text{O}_3$-$\text{C}$ samples, namely test 1 and test 2. Test 1 was heated non-isothermally from 873 K to 1473 K followed by isothermal heating at 1473 K for 60 min. However, test 2 was just heated isothermally at 1473 K for 60 min. This plot demonstrates that the decarburization ratio reached almost 0.40 in test 1 before the temperature reached 1473 K. After isothermal heating of both tests at 1473 K for 60 min, the decarburization ratios for test 1 and test 2 reached 0.98 and 0.68, respectively. These results clearly indicate that the decarburization ratios differ between test 1 and test 2. More specifically, decreases from 0.40 to 0.30. It can be concluded that the decarburization rate for test 1 at 1473 K is lower than the decarburization rate for test 2 at the same temperature.
The temperatures registration of channels 1-6 shown in figure 40 proceeded in 40 min. It shows the temperature versus time for these channels. As this figure shows, the maximum reachable temperatures during the 40 min preheating processes are 1293 K, 1153 K, 993 K, 873 K, 793 K and 893 K for channels 1, 2, 3, 4, 5 and 6, respectively.

A chemical composition analysis of the flue gas inside the preheating SEN was also performed. The analysis substantiated the presence of 3.6 vol% oxygen and 11.3 vol% carbon dioxide in the flue gas. Furthermore, an AFR value of about 1.21 was measured for the surveyed combustion system in this study. The temperature profile of the industrial preheating trial between 298-1293K of channel 1 was selected as the temperature profile for the laboratory preheating trials of the YSZ coated alumina-graphite test rods. In addition, the experimental apparatus shown in figure 2 was capable to perform different heating programs (ramp) with a constant heating rate. Therefore, the temperature profile of the industrial preheating trial has been divided into six sections. Each one with a constant heating of 177, 80, 70, 30, 20 and 10 (K·min\(^{-1}\)), respectively. Furthermore, the alumina tube situated inside the furnace shown in figure 2 can just tolerate a maximum heating rate of about 10 K·min\(^{-1}\). Moreover, it may crack at higher heating rates. It was assumed that the flue gas passing through the SEN during the industrial heating and the laboratory trials have the same flow rate, namely 8 nL·min\(^{-1}\). The total amount of oxidizing components (oxygen and carbon dioxide) in the
injected gases were designed to be the same for both the industrial preheating trials and the laboratory trials carried out with a constant heating rate at 10 K·min⁻¹. Therefore, the total amount of the oxidizing components, which the samples were exposed to, was the same. Table 19 presents the oxidizing components amount and temperature profiles for both the industrial preheating trials and the laboratory trials for constant heating rates.

Table 19. Materials, gas mixtures, temperature profiles and combustion properties for experimental tests

<table>
<thead>
<tr>
<th>Section #</th>
<th>Temperature K (Heating rate K·min⁻¹)</th>
<th>Ar (nL·min⁻¹)</th>
<th>CO₂ (nL·min⁻¹)</th>
<th>O₂ (nL·min⁻¹)</th>
<th>Nliter Injected CO₂</th>
<th>Nliter Injected O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298-653 (177) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>1</td>
<td>298-653 (10) Laboratory Trial</td>
<td>7.94</td>
<td>0.03</td>
<td>0.03</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>653-813 (80) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>653-813 (10) Laboratory Trial</td>
<td>7.85</td>
<td>0.08</td>
<td>0.07</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>3</td>
<td>813-953 (70) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>3</td>
<td>813-953 (10) Laboratory Trial</td>
<td>7.83</td>
<td>0.09</td>
<td>0.08</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>4</td>
<td>813-1073 (30) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>2.56</td>
<td>2.24</td>
</tr>
<tr>
<td>4</td>
<td>813-1073 (10) Laboratory Trial</td>
<td>7.60</td>
<td>0.21</td>
<td>0.19</td>
<td>2.56</td>
<td>2.24</td>
</tr>
<tr>
<td>5</td>
<td>1073-1113 (20) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>5</td>
<td>1073-1113 (10) Laboratory Trial</td>
<td>7.40</td>
<td>0.32</td>
<td>0.28</td>
<td>1.28</td>
<td>1.12</td>
</tr>
<tr>
<td>6</td>
<td>1113-1293 (10) Industrial trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>11.52</td>
<td>10.08</td>
</tr>
<tr>
<td>6</td>
<td>1113-1293 (10) Laboratory Trial</td>
<td>6.8</td>
<td>0.64</td>
<td>0.56</td>
<td>11.52</td>
<td>10.08</td>
</tr>
</tbody>
</table>

The concentration of the oxidizing components in the injected gases were adjusted using four brooks Sho-rate flow meters equipped with R-2-15-B tubes (glass and Tantalum float) and R-2-15-AAA tubes (carboloy float). As table 19 illustrates, the total amount of oxidizing components (oxygen and carbon dioxide) in the injected gases are the same for both the industrial preheating trials and the planned laboratory trials with constant heating rates at each section.
Table 20 shows five laboratory decarburization trails (test 1-5) for different samples (table 8) performed using the experimental apparatus shown in figure 2. Here, a heating rate of 10 K·min⁻¹ and a controlled atmosphere (table 19) was used.

<table>
<thead>
<tr>
<th>Test Nr</th>
<th>Sample Nr</th>
<th>AFR</th>
<th>Max. Temperature (K)</th>
<th>Holding time at max. temperature (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>2</td>
<td>1.5</td>
<td>1293</td>
<td>30</td>
</tr>
<tr>
<td>Test 2</td>
<td>4</td>
<td>1.5</td>
<td>1473</td>
<td>30</td>
</tr>
<tr>
<td>Test 3</td>
<td>1</td>
<td>1.5</td>
<td>1293</td>
<td>30</td>
</tr>
<tr>
<td>Test 4</td>
<td>3</td>
<td>Air</td>
<td>1293</td>
<td>30</td>
</tr>
<tr>
<td>Test 5</td>
<td>7</td>
<td>1.5</td>
<td>1293</td>
<td>7200</td>
</tr>
</tbody>
</table>

The laboratory trials were performed in an atmosphere containing oxygen, argon and carbon dioxide at a ratio equal to the propane gas combustion flue gas. Two different types of combustion systems were investigated: air-fuel combustion at Air-Fuel Ratios (AFR) of 1.5 and preheating in air. The industrial preheating trials showed the existence of an AFR value of 1.2, which corresponds to an oxidizing atmosphere. This value was supposed to be 1.5 for the laboratory trials. This value is even more oxidizing in comparison to the industrial preheating trials. The maximum applied temperature for test 1, 3, 4 and 5 was 1293 K and 1473 K for test 2. The heating rate was 10 K·min⁻¹ for test 2 at the temperature interval between 1293-1473K. Furthermore, with Ar, CO₂ and O₂ flow rates of 6.8, 0.64 and 0.56 nL·min⁻¹, respectively within this temperature interval. Test 4 was performed at a heating rate of 10 K·min⁻¹ from 298 K to 1293 K in a controlled atmosphere containing 20 vol % (1.6 nL·min⁻¹) of oxygen and 80 vol% (6.4 nL·min⁻¹) of argon. This to simulate the heating using air with the same total gas flow rate of 8 nL·min⁻¹.

The decarburized layer thickness for alumina-30 wt% graphite refractory base materials without YSZ coating for tests 1, 2, 4 and 5 were 1, 2.5, 2 and 4 mm, respectively. However, no decarburized layers could be detected for tests 1-5 with an YSZ coating. The macroscopic observation of an YSZ coated sample with a 160 μm coating thickness (sample 1, table 8) in an oxidizing atmosphere of an AFR value equal to 1.5 (test 3) and a maximum temperature of 1293K showed no existence of a decarburization layer. Figure 41 shows the SEM-EDS elements mapping of an YSZ sample of this test. This was performed at the interface between the YSZ coating and SEN refractory base materials. The figure illustrates the existence of graphite in both the alumina-graphite substrate and at the interface. Thus, these results substantiate the effect of the YSZ coating on the decarburization prevention.
Figure 41. X-ray chemical element mapping at the interface between alumina-graphite and YSZ coating (test 3)

Figure 42 shows a macroscopic image of two samples, the 290μm YSZ coated sample (sample to the left) and the uncoated sample (sample to the right). Both samples were heated in a controlled atmosphere containing 20 vol% of oxygen and 80 vol% of argon. Furthermore, at a maximum temperature of 1293 K (test 4).

Figure 42. Macroscopic image of cross-section samples of YSZ coated (sample to the left) and uncoated (sample to the right) of test 4 (Air, 30 seconds holding time)

The decarburized layer is marked with arrows (2 mm) in the uncoated sample. However, no decarburization layer could be detected in the YSZ coated sample. Figure 43 shows a macroscopic image of two samples. More specifically, the YSZ coated sample (the left sample) and the uncoated sample (the right sample) of test with sample with a 250μm YSZ coating thickness heated in an oxidizing atmosphere. Furthermore, with an AFR value equal to 1.5 at a maximum
temperature of 1293 K and a holding time of 7200 seconds at the maximum
temperature (test 5). This YSZ coating is slightly thinner (40µm) than the
previously mentioned sample with a 290µm thickness (figure 42). The
decarburized layer is marked with arrows in the uncoated sample (4mm).
However, similar to the results in figure 42 no decarburization layer could be
detected in the YSZ coated sample.

Figure 43. Macroscopic image of cross-section samples of YSZ coated (sample to the left) and
uncoated (sample to the right) of test 5 (AFR=1.5, 7200 seconds holding time)

6.11. The interaction survey between the YSZ plasma-PVD coated
Al$_2$O$_3$-C refractory base materials and a Ce alloyed molten
stainless steel (supplement 5)

Figure 44 shows the SEM image and X-ray chemical elements mapping at the
interface between the non-coated alumina-graphite test rod and the molten steel.
As the Ce mapping may illustrate, cerium in the molten steel has interacted with
alumina particles in the test rod refractory base materials. The chemical analysis
of the interacted region showed the formation of compounds containing 45.7
wt% alumina, 49.4 wt % cerium oxide and 4.7 wt% silica. The added cerium
may lead to a formation of the cerium aluminates. In addition, the cerium has
been penetrated 413µm into the SEN refractory base materials from the interface
between the SEN and molten steel.
Figure 44. X-ray chemical element mapping for un-coated SEN, interface and molten steel

Figure 45 shows the SEM image and X-ray chemical elements mapping at the interface between an alumina-graphite test rod with a 500µm thick plasma-PVD YSZ coating in the contact with a molten steel containing 20.53 wt% Cr, 10.96 wt% Ni, 0.13 wt% C, 1.58 wt% Si, and 0.04 wt% Ce. As the mapping for cerium shows, the YSZ coating has totally prevented the interaction between cerium and alumina in the SEN refractory base materials. Thus, there is no sign of an interaction between the alumina particles of the SEN refractory base materials and the alloyed cerium in molten steel. As the SEM image shows, the YSZ coating surface in contact with the molten steel is still smooth after the rotation of the test rods in the molten steel.

Figure 45. X-ray chemical element mapping for plasma-PVD YSZ coated SEN, interface and molten steel

Figure 46 shows a SEM image of the steel and the inclusions. Three different inclusion types marked by A, B and C, as the arrows illustrate, were detected.

Figure 46. X-ray chemical element mapping for plasma-PVD YSZ coated SEN, interface and molten steel
Table 21 shows the chemical compositions of these three types. As the table illustrates, all inclusions contain almost just cerium oxide and no alumina or silica. The inclusion analyses were performed for a large quantity of inclusions. Almost the same chemical compositions were detected for them as for inclusions A, B and C shown in Figure 46.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Inclusion A (wt%)</th>
<th>Inclusion B (wt%)</th>
<th>Inclusion C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.23</td>
<td>0.47</td>
<td>0.33</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.28</td>
<td>0.51</td>
<td>0.03</td>
</tr>
<tr>
<td>Ce&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>99.49</td>
<td>99.03</td>
<td>99.64</td>
</tr>
</tbody>
</table>
7. Discussion

A sufficient thickness of the glass/silicon coating on the SEN internal surface is intended to supply a protective glaze-coating. This can prevent the diffusion of oxygen and thereafter a decrease of the decarburization during the SEN preheating. On the other hand, the glaze can penetrate into the SEN refractory base materials, as the laboratory experiments showed (figure 17). Thereafter, the penetrated glaze can react with the SEN alumina-graphite refractory base materials to form an alumina-rich glaze. This was shown in the laboratory preheating experiment and for the zirconia-graphite test rod (figure 3). This alumina-rich glaze has a much higher viscosity compared to the original glaze. Therefore, the SEN alumina and silica particles may adhere to each other to form an uneven surface at the interface between the SEN and the molten steel. This was shown in both the laboratory rotating experiments and the industrial trials. On the other hand, this uneven region which contains alumina, silica and glaze may react with dissolved REM in molten steel. This reaction results in the formation of REM aluminates, REM silicates and REM alumina silicates as shown in Figure 23 and Table 12. This may lead to the formation of a REM-rich layer at the glaze-penetrated areas. This, in turn, may lead to the formation of an uneven internal surface at the interface between the SEN and molten steel.

The transportation rate of the primary inclusions to the nozzle wall has been considered as a key parameter for the clogging rate evaluation. This transportation leads to an agglomeration of primary inclusions. It has also been stated that the presence of a turbulent fluid flow in the nozzle has an important influence on the transportation rate of inclusions. The study showed that the mass transfer coefficient of inclusions from the liquid to the nozzle wall (unit length unit time\(^{-1}\)) has a reversed relationship with the viscous sub-layer thickness (\(\delta\)). It can be concluded that a thinner viscous sub-layer will result in a higher mass transfer coefficient for inclusions. These can deposit on the nozzle wall and thereafter increase the clogging rate. The viscous sub-layer thickness can be calculated by using equation 16:

\[
\delta = 25. \, d \cdot (N_{Re})^{-7/8}
\]  

(16)

where \(d\) is the nozzle diameter, \(N_{Re}\) is the Reynolds number in the nozzle and \(\delta\) is the thickness of the viscous sub-layer. The thickness of viscous sub-layer has been calculated for the SEN used in industrial trials with a casting rate of 0.79 (m\(\cdot\)min\(^{-1}\)) when casting 1.608*0.200 m\(^2\) slabs. The sub-layer thickness calculations were performed for a SEN with a smooth internal surface to compare the calculated sub-layer thicknesses to the height of the irregularities shown in figure 16. As figure 47 illustrates, the viscous sub-layer thickness may vary between 2.5-1.4 µm for the studied case. The comparison between the
calculated sub-layer thicknesses and the heights of the formed irregularities shown in figure 16 may clearly substantiate the fact that uneven areas caused by penetrated glaze may end up long outside the viscous sub-layer.

![Figure 47. Viscous sublayer thickness for commercial SEN used in this study at different centre axis lengths in nozzle](image)

In this region, the turbulence flow region dominates. These protruding areas facilitate the accumulation of the primary inclusions in the molten steel, on the SEN internal surface as figure 48 shows.

![Figure 48. Image (SEM) of SEN internal surface, which ended up in turbulence flow region](image)

The laboratory results also indicated a penetration of the glaze containing high amounts of alkalis (Na$_2$O and K$_2$O) into the SEN refractory base materials. The alkalis can be reduced by graphite to supply oxygen in form of carbon monoxide at the interface between the SEN and the molten steel. To confirm the possibility of this reaction, the alkalis activity in the penetrated glaze was calculated using the Thermo-Calc software and using the Slag 2 database. The penetrated glaze chemical composition was the same as the preheating
laboratory simulation results (Table 11 region A). The calculated alkalis activity was $4.84 \times 10^{-8}$.

The alkalis reduction and carbon monoxide formation can be defined by reaction 19. The standard Gibbs free energy for reaction 19 is reached using reactions 17 and 18.  

\[ \text{Na}_2\text{O} (l) = 2\text{Na} (g) + \frac{1}{2} \text{O}_2 (g) \quad \Delta G^0 = 519000 - 235T \text{ (J·mol}^{-1}) \quad (17) \]
\[ \text{C} (s) + \frac{1}{2} \text{O}_2 (g) = \text{CO} (g) \quad \Delta G^0 = -114400 - 85.77T \text{ (J·mol}^{-1}) \quad (18) \]

\[ \text{Na}_2\text{O} (l) + \text{C} (s) = 2 \text{Na} (g) + \text{CO} (g) \quad \Delta G^0 = 404600 - 320.77T \text{ (J·mol}^{-1}) \quad (19) \]

The molten steel temperature in the tundish was measured to be 1713 K. By inserting this value into equation 19 the standard Gibbs free energy can be calculated as -144879 (J·mol$^{-1}$). The equilibrium state can be reached when the carbon monoxide partial pressure is 0.9992 atm. In addition, the carbon monoxide may dissociate at the interface between the SEN and the molten steel, which may lead to REM reoxidation as reaction 24 shows. The standard Gibbs free energy for reaction 24 is calculated using equations (20)$^{33}$, (21)$^{35}$, (22)$^{36}$ and (23)$^{33}$.

\[ 2 \text{Ce} (l) + \frac{3}{2} \text{O}_2 (g) = \text{Ce}_2\text{O}_3(s) \quad \Delta G^0 = -1775439 + 271.75T \text{ (J·mol}^{-1}) \quad (20) \]
\[ 2 \text{[Ce]} = 2 \text{Ce} (l) \quad \Delta G^0 = -469064 + 395.47T \text{ (J·mol}^{-1}) \quad (21) \]
\[ 3 \text{C} (s) = 3 \text{[C]} \quad \Delta G^0 = 67782 - 126.774T \text{ (J·mol}^{-1}) \quad (22) \]
\[ 3 \text{CO} (g) = 3 \text{C} (s) + \frac{3}{2} \text{O}_2 (g) \quad \Delta G^0 = 343200 + 257.31T \text{ (J·mol}^{-1}) \]

(23)

\[ 2 \text{[Ce]} + 3 \text{CO} (g) = 3 \text{[C]} + \text{Ce}_2\text{O}_3(s) \quad \Delta G^0 = -1833521 + 797.69T \text{ (J·mol}^{-1}) \quad (24) \]

In addition, the standard free energy of -467078 (J·mol$^{-1}$) at 1713 K was calculated using reaction 24. The equilibrium carbon monoxide partial pressure was $1.37 \times 10^{-5}$ atm, if it was assumed that the cerium oxide activity is equal to unity. It should be noted that, the activity of carbon and cerium in molten steel were calculated for a stainless steel grade containing 0.091 wt% C, 1.64 wt% Si, 20.92 wt% Cr, 10.86 wt% Ni, 0.033 wt% Ce and 0.005 wt% Al.

In conclusion, the higher equilibrium carbon monoxide partial pressure (0.9992 atm) for reaction 19 in comparison to the equilibrium carbon monoxide partial
pressure for reaction 24 \((1.37 \times 10^{-5} \text{ atm})\) may illustrate the possibility of a carbon monoxide dissociation at the interface between SEN and molten steel. It can be concluded that alkaline (Na\(_2\)O and K\(_2\)O) can be reduced by graphite at high temperatures. Furthermore, that the carbon monoxide may transfer into the interface between SEN and molten steel, due to the negative pressure in the SEN cross section outside in.\(^{37}\)

At the interface, the carbon monoxide may dissociate to dissolved carbon and oxygen in molten steel. The dissociation increases the oxygen concentration at the interface. On the other hand, the SEN preheating experiments and the industrial trials revealed that a high concentration of metallic silicon remained in the glaze layer (figure 24, region B). This metallic silicon may be dissolved at the interface between the SEN and the molten steel after the casting start. This may lead to enrichment of silicon in the molten steel. In this area the steel is already both carbon- and oxygen-rich due to the dissociation of carbon monoxide in the molten steel at the interface.

The interaction parameters for REM, carbon and silicon 
\[
\varepsilon_{Ce}^C = -16.5, \quad \varepsilon_{Si}^C = -7.7, \quad \varepsilon_{Si}^C = 9.7 \]

may clearly reveal the tendency of a REM activity reduction and an increased Si activity at the presence of the carbon. The presence of a high activity Si, REM and oxygen may define the existence of the RE\(_{4.67}\) (SiO\(_4\))\(_3\)O compound in the accretion (figure 25). Figure 49 shows the x-ray chemical elements mapping for the SEN, the interface and an accretion from an industrial trial. The image clearly shows the coexistence of REM and silicon just at the interface region. Only REM oxides are present from the interface towards the inside of the accretion.

The molten steel sampling was also performed from the tundish at the SEN entrance for industrial trials to evaluate the inclusions type and quantity which flow through the SEN during casting. Figure 50 shows a feature determination result, which was performed by a FEG-SEM operating in the automatic mode. There were 80 inclusions detected in this test. However, there was just one inclusion consisting of REM, Al, Si and Ca with a size of 5-10 \(\mu\)m. Furthermore, two inclusions consisting of REM, Al and Si and the remaining were REM oxides. The Feature study reveals the very low quantity of a RE\(_{4.67}\) (SiO\(_4\))\(_3\)O compound in the molten steel flowing through the SEN. It can also be concluded that the 100 \(\mu\)m continuous layer consisting of RE\(_{4.67}\) (SiO\(_4\))\(_3\)O compound is formed “in-situ” at the interface between the SEN and the accretion.
The interaction between dissolved REM in molten steel and the SEN alumina and silica on one hand and the “in-situ” formation of the RE<sub>4.67</sub> (SiO<sub>4</sub>)<sub>3</sub>O compound on the other hand, supply large surfaces containing high amounts of REM at the interface between the SEN and the molten steel. Figure 51 shows the inclusions size variations of an etched accretion along the accretion propagation direction. The figure illustrates that larger primary REM oxide inclusions are adhered earlier to the REM-rich surfaces, most likely due to the high attraction forces. The clogging continues by agglomeration of smaller primary inclusions.

There are some studies<sup>4,38,39</sup> which also emphasize that clogging takes place by “in-situ” formation of an initial reaction layer and the agglomeration of primary
inclusions in molten steel. This reaction layer is formed by a reaction between dissolved Al in aluminum-killed molten steel with oxygen. The oxygen source is shown to be CO, which is formed due to the reduction reaction between the SEN impurities (alkalis and silica) and graphite.

In addition, the macroscopic and microscopic investigations in post-mortem studies revealed the existence of both a solidified stainless steel and a multi-layer accretion. These layers together may lead to clogging phenomena. These investigations also revealed the harmful effect of the SEN decarburization. As figure 19 shows the SEN decarburization may result in the formation of a 2.4 times thicker accretion layer compared to when a 2 mm thick decarburized layer existed inside the SEN without decarburization. This fact may be attributed to the higher heat conduction of the steel in the penetrated region, the higher interaction area between REM and SEN’s RBM, and more penetration of the glaze into the decarburized region with higher porosity. In addition, the industrial preheating process survey reveals the thermodynamically possibility for the SEN decarburization inside the SEN at the regions around channel 6 (Figure 30). SEN decarburization never occurs for regions around channel 5 during the preheating process due to their low preheating temperatures and therefore positive Gibbs free energy values (Figure 30). But after the preheating process accomplishment, these regions of the preheated SEN may be exposed to the air before the casting start. Thereafter, the decarburization may occur. This can define the formation of a 2 mm decarburization layer shown in figure 19. Furthermore, the industrial preheating survey revealed the decarburization of regions around channel 6 during the preheating process (figure 32). This is due to the reaction between graphite and carbon dioxide in the flue gas and the glaze penetrated to the graphite vacancies. The industrial preheating also revealed the glaze penetration into the SEN for regions exposed to high temperatures such as the regions around channel 1 (figure 31). It can be concluded that the penetration of the glaze into the SEN’s refractory base materials may occur at regions around channel 3, 2 and 1 (table 15, figures 29 and 31). Here, the local temperature reaches temperatures above 1473 K, which is the maximum
recommended SEN’s preheating temperature. The industrial preheating survey substantiated even the glaze penetration up to 2.236 mm in regions around channel 6 (figure 32).

There are large REM silicates inclusions present in layer 3 (Figure 25). However, the feature analysis of the molten steel in the tundish showed the existence of very low quantities of inclusions consisting of REM, Si and Al in samples from the tundish. More specifically, one percent of the primary inclusions passing through the SEN were REM-silicate containing Al. This quantity is not enough to form a 100-500 µm thick layer 3 with just a few REM oxides. This fact together with the dendritic morphology of the inclusions in this layer, may suggest that these inclusions have been formed “In Situ”.

Figure 52 summarizes the mechanism of REM silicate inclusion formation at the SEN/molten steel interface (layer 3). The dissociation of CO gas increases the oxygen concentration at the interface where dissolved REM as alloying element and metallic silicon from the glaze, already existed. The existence of these three elements may lead to formation of the “In Situ” REM silicates seen in layer 3.

Figure 52. “In Situ” formation of REM silicate inclusions by reoxidation

7.1. The mechanisms of the additive oxidation and decarburization

Gebwein et al.⁴⁰ have studied the oxidation kinetics of ZrSi₂ powder in flowing air using non-isothermal thermogravimetric (TG) analysis with heating rate at 10 K/min. The results showed that the oxidation may lead to formation of elemental silicon and an intermediate reaction product at temperatures above 737 K. Thereafter, the oxidation of the elemental silicon at temperatures above 1073 K. Finally, the formation of Zircon takes place at temperatures above 1373K. The following reactions may proceed when the sintered refractory specimens are exposed to an oxidizing atmosphere:
\[
\begin{align*}
ZrSi_2 (s) + (x-(x,y/2)+1) O_2 (g) & \rightarrow ZrO_2 + (2-y) SiO_x (s) + y Si (s) \quad \text{at } T \geq 737 K \quad (25) \\
ZrO_2 (s) + (2-y) SiO_x (s) + y Si (s) + O_2 (g) & \rightarrow ZrO_2 (s) + 2 SiO_2 (s) \quad \text{at } T \geq 1073 K \quad (26) \\
C(s) + O_2 (g) & \rightarrow CO_2 (g) \quad \text{at } T = 873-973 K \quad (27) \\
C(s) + 1/2O_2 (g) & \rightarrow CO (g) \quad \text{at } T = 873-973 K \quad (28) \\
SiC (s) + 2 O_2 (g) & \rightarrow SiO_2 (s) + CO_2 (g) \quad (29) \\
C(s) + CO_2 (g) & \rightarrow 2CO (g) \quad (30) \\
ZrO_2 (s) + SiO_2 (s) & \rightarrow ZrSiO_4 (s) \quad \text{at } T \geq 1373 K \quad (31)
\end{align*}
\]

The reaction interface between the samples and the gas phase may be assumed to be a circle for the cylindrical samples used in this study. Therefore, alumina, silica, graphite and zirconium disilicide may come into contact with the gas atmosphere at the reaction interface. Initially, oxygen reacts instantly with zirconium disilicide at 737 K to form ZrO₂, SiOₓ and metallic silicon as reaction 25 shows. The reaction proceeds as long as the zirconium disilicide amount becomes zero at the reaction interface. In the absence of the zirconium disilicide, the carbon oxidation may be assumed to proceed at temperatures from 873 K to 1073 K as reactions 27, 28 and 30 show. The oxidation of metallic silicon may proceed at temperatures above 1073 K as reaction 26 shows. Finally, the zircon formation may proceed at temperatures above 1373 K. The zirconia formation may be judged as the most important stage during which the volume expansion is considered to prevent the oxygen ingress. Furthermore, reaction 29 presents the oxidation of SiC formed during the green body sintering.

An X-Ray Diffraction Analysis (XRD) was performed for the sample containing 8 wt% ZrSi₂ and 10 wt% (4B₂O₃ ·BaO) glass powder (Test 6, table 6) after the decarburization laboratory trial completion at 1473 K. The results revealed the existence of both a ZrSiO₄ and a (4B₂O₃ ·BaO) glaze. The formation of ZrSiO₄ indicates the efficiency of ZrSi₂ as an antioxidant to react with oxygen and a volume increase due to zircon formation. Figure 53 a) shows the FEG-SEM image of the ZrSi₂ powder used as an antioxidant additive in this paper. As the figure shows, the particles sizes may vary between 5.9 µm and 21.5 µm. Figure 53 b) shows the image of a sample containing 15 wt% ZrSi₂ and 10 wt% (4B₂O₃ ·BaO) glass powder after decarburization at 1473 K. The ZrSi₂ particles sizes after oxidation may vary between 25 µm to 68 µm. The comparison between particles sizes in figures a) and b) may illustrate the oxidation and volume increase of ZrSi₂ particles, which had been situated between alumina particles. This mechanism may lead to a closing of the refractory open pores and thereafter an oxygen ingress prevention.
7.2. Decarburization mechanisms and reaction kinetic between $\text{Al}_2\text{O}_3$-$\text{C}$ and gas phase

The experimental values of $\ln(\frac{dg(\alpha)}{dt})$ vs. $(1/T)$ were plotted in form of curves for each theoretical $g(\alpha)$ function shown in table 10. These curves are presented in figure 54 for an $\text{Al}_2\text{O}_3$-$\text{C}$ sample heated non-isothermally at 15 (K·min$^{-1}$) heating rate. Furthermore, in the temperature range 873 K to 1473 K exposed to an atmosphere consisting of 8 vol% CO$_2$, 7 vol% O$_2$ and 85 vol% Ar (test 1, table 7).

![Figure 54. Ln(dg(\alpha)/dt) vs. (1/T) for different solid state reaction mechanisms (table 3) plotted using the differential method](image-url)
The linear correlation coefficient for each curve in figure 54 was calculated. The same approach was applied for an Al$_2$O$_3$-C sample heated non-isothermally at a 15 (K·min$^{-1}$) heating rate. Furthermore, in the temperature range 873 K to 1473 K in an atmosphere consisting of 32 vol% CO$_2$, 26 vol% O$_2$ and 42 vol% Ar (test 6, table 7).

The linear correlation coefficients for test 1 are higher than 0.990 for diffusion rate controlling mechanisms, while it is under 0.960 for both chemical reaction and phase-boundary reaction rate controlling mechanisms. In addition, the linear correlations for test 6 are higher than 0.980 for diffusion rate controlling mechanisms. In addition, it is under 0.890 for both chemical reaction and phase-boundary reaction rate controlling mechanisms. The comparison of linear correlation coefficients may suggest diffusion models (Valensi Barrer’s, Jander’s or Ginstling’s diffusion model) as the most probable reaction models for decarburization during non-isothermal heating of test 1 and test 6. It can be concluded that neither chemical reactions nor phase boundary reactions may be proposed as the controlling mechanisms of decarburization.

The difference between Jander’s, Ginstling’s and Valensi Barrer’s diffusion models is related to the assumptions of their reaction areas. Jander’s diffusion model assumes a constant reaction area, while Ginstling’s and Valensi Barrer’s model assume decreasing reaction areas. The graphite flake used in the graphite-containing refractory materials was investigated using the FEG-SEM. Figure 55 shows the FEG-SEM images of a graphite flake at two magnifications.

As the figure to the right illustrates, the ratio of length to the thickness (L/t) of the flake is 8.40. Then, it is reasonable to assume that the reaction areas between the oxidizing atmosphere and graphite flakes are constants. It can be concluded that Jander’s model can be assumed to be more suitable to use to determine the reaction controlling mechanism at this reaction area. On the other hand, the geometry of the samples must be taken into consideration. For a cylindrical sample, the total interaction area between the sample and the oxidizing gas mixture decreases when the radius of the un-reacted area decreases. Therefore, Valensi Barrer’s model may be supposed as the controlling reaction mechanism.
of the decarburization during the non-isothermal heating. Equations 32 and 33 show these two models as a function of the decarburization ratio: 21

\[ \alpha + (1 - \alpha) \cdot \ln(1 - \alpha) = K_{pValensiBarrer} \cdot t \]  
\[ 1 - (1 - \alpha)^{3/2} = K_{pJander} \cdot t \]

where \( K_{pValensi-Barrer} \) (s\(^{-1}\)) and \( K_{pJander} \) (s\(^{-1}\)) are the rate constants and \( t \) is time (s). Furthermore, the decarburization reaction may involve the following steps:

1. Diffusion of oxygen/carbon dioxide through the gas boundary layer
2. Diffusion of oxidizing gases through the decarburized layer of the sample (A decreasing interface area)
3. Diffusion of oxidizing gases through the decarburized layer of the flake graphite (A constant interface area)
4. Chemical reaction at the interface
5. Diffusion of carbon monoxide/carbon dioxide from the reaction area towards the sample outer surface

The differential method approved the diffusion steps as controlling steps for the decarburization process. The coexistence of a decreasing reaction area and a constant reaction area may suppose the addition of Valensi Barrer’s and Jander’s diffusion models as the modified reaction kinetic model for the decarburization. Then, the decarburization rate controlling can be calculated as equation 34 shows.

\[ \alpha + (1 - \alpha) \cdot \ln(1 - \alpha) + \left[ 1 - (1 - \alpha)^{3/2} \right]^2 = (K_{pValensiBarrer} + K_{pJander}) \cdot t \]  

The addition of the rate constants of two diffusion models may be replaced by a new constant, \( K_p \), as shown in equation 35.

\[ \alpha + (1 - \alpha) \cdot \ln(1 - \alpha) + \left[ 1 - (1 - \alpha)^{3/2} \right]^2 = K_p \cdot t \]  

To evaluate the validity of this hypothesis, the left side of equation 35 was assumed to be a new \( g(\alpha) \) function. As defined for equation 13, the correlation between \( \ln(dg(\alpha)/dt) \) and \( (1/T) \) should also be linearly for a constant heating rate for equation 35. Therefore, the experimental values of \( \ln(dg(\alpha)/dt) \) vs. \( (1/T) \)
were plotted for the new theoretical g(α) function. These curves are presented in figure 56 for two Al₂O₃-C samples heated non-isothermally at a 15 (K·min⁻¹) heating rate. Furthermore, for the temperature range 873 K to 1473 K and using atmospheres consisting of 8 vol% CO₂, 7 vol% O₂ and 85 vol% Ar (test 1) and 32 vol% CO₂, 26 vol% O₂ and 42 vol% Ar (test 6). The calculated linear correlation coefficients for test 1 and test 6 are 0.992 and 0.988, which may establish the validity of the hypothesis.

Figure 56. Ln(dg(α)/dt) vs. (1/T) for solid state reaction mechanism (equation) plotted using the differential method

The value of the activation energy (E) can be calculated from the straight line slope (-E/R) in the plots for ln(dg(α)/dt) vs. (1/T) for a constant heating rate. The value of activation energy calculated for test 1 and test 6 were 81.8 (KJ·mol⁻¹) and 88.8 (KJ·mol⁻¹), respectively. The values are found to be in the near range that Jansson et al. 41) reported (87-101 KJ·mol⁻¹) for commercial MgO-C refractories.

7.3. Chemical reactions during decarburization

Reaction 36, 37 and 38 may proceed during the decarburization of the carbon-containing refractories.

\[ \text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) \]  \hspace{1cm} (36)

\[ 2\text{C(s)} + \text{O}_2(\text{g}) = 2\text{CO}(\text{g}) \]  \hspace{1cm} (37)

\[ \text{C(s)} + \text{CO}_2(\text{g}) = 2\text{CO}(\text{g}) \]  \hspace{1cm} (38)

The thermodynamic of the reactions were considered to determine which reaction(s) is dominant during non-isothermal and isothermal heating of carbon-containing refractories. The relationship between the equilibrium partial
pressures for O2, CO and CO2 at different temperatures were calculated by using the changes in the standard free energy of formations \(^{36}\) for reactions 36, 37 and 38. The activity of carbon was assumed to be equal to unity. The equilibrium partial pressure for O2 was calculated as \(4.62 \times 10^{-23}\) (bar) at 873 K and \(1.10 \times 10^{-14}\) (bar) at 1473 K. Therefore, the equilibrium partial pressure was assumed to be zero. Figure 57 shows the equilibrium partial pressures for O2, CO and CO2 versus the temperature.

![Figure 57. Relationship between equilibrium partial pressure of O2, CO and CO2, temperature and CO2 concentrations for Air-Fuel and Oxygen-Fuel combustion systems](image)

The horizontal lines show CO2 concentrations in the injected gases for both Air-Fuel and Oxy-Fuel combustion systems and AFR values equal to 1 and 1.5. The diagram clearly shows that reaction 38 may proceed at 1103 K, 998 K and 968 K for Air-Fuel combustion (AFR=1.5), Oxy-Fuel combustion (AFR=1.5) and Oxy-Fuel combustion (AFR=1), respectively. Moreover, it is clear that the equilibrium partial pressure of CO2 becomes negligible at temperatures above 1273 K. It can be concluded that reaction 37 proceeds mainly at temperature over 1273 K. In addition, the thermodynamic calculations for the changes in standard free energy of formation for equations 36 and 37 showed that reaction 36 may proceed under 1103 K, 998 K and 968 K for Air-Fuel combustion (AFR=1.5), Oxy-Fuel combustion (AFR=1.5) and Oxy-Fuel combustion (AFR=1), respectively.

Furthermore, the oxidation rate of the carbon-containing refractories is determined to be controlled by the diffusion of oxidizing gases through the pores. Therefore, equation 35 may be applied and equation 39 may define the constant rate.\(^{21}\)

\[
K_p = A \cdot M_c \cdot D_{eff} \cdot \left[ \frac{(P_{\text{ox,at}} - P_{\text{ox,in}})}{(\gamma \cdot F_c \cdot r_c^2 \cdot R \cdot T)} \right]
\] (39)
where \( A \) is constant, \( M_C \) is molecular weight of carbon (g·mol\(^{-1}\)), \( D_{\text{eff}} \) is the effective diffusion coefficient of oxidizing gases through the pores in the refractory and flake graphite (cm\(^2\)·s\(^{-1}\)), \( P_{\text{ox,a}} \) is the partial pressure of oxidizing gases at the interface between the refractory and the injected gases (Pa), \( P_{\text{ox,i}} \) is the partial pressure of the oxidizing gases at the reaction interface (Pa), \( \gamma \) is the refractory bulk density, \( F_C \) is the refractory carbon content, \( r_0 \) is the refractory radius (cm), \( R \) is the gas constant (Pa·cm\(^3\)·K\(^{-1}\)·mol\(^{-1}\)) and \( T \) is the temperature (K). The effective diffusion coefficient of oxidizing gas mixture, diffusing through the carbon-containing refractory is given by equation 40.

\[
D_{\text{eff}} = D \cdot \varepsilon^{1.5}
\]  

where \( D \) is the diffusion coefficient for a O\(_2\)-CO-CO\(_2\) gas mixture (cm\(^2\)·s\(^{-1}\)) and \( \varepsilon \) is the porosity of the refractory oxidized zone. The substitution of the effective diffusion coefficient shown in equation 40 into the equation 39 may result in equation 41 for the carbon-containing refractories investigated in this study. This equation shows that the rate constant is correlated to the porosity and the reciprocal of the carbon content.

\[
K_p \propto \left( \frac{\varepsilon^{1.5}}{F_C} \right)
\]

Furthermore, table 22 shows the apparent porosity, average grain size, carbon content and bulk density for the commercial Al\(_2\)O\(_3\)-C, ZrO\(_2\)-C and MgO-C refractory materials used in commercial SENs. The average particle size and the total carbon content of the base refractory materials were decided by the FEG-SEM observations. Furthermore, by the carbon-burning out performed for these three refractory types.

### Table 22. Physical properties of the SEN graphite containing parts

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Al(_2)O(_3)-C</th>
<th>MgO-C</th>
<th>ZrO(_2)-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent Porosity (%)</td>
<td>14.5</td>
<td>16.3</td>
<td>15.7</td>
</tr>
<tr>
<td>Mean grain size (µm)</td>
<td>399</td>
<td>533</td>
<td>220</td>
</tr>
<tr>
<td>Carbon Content Fc (wt %)</td>
<td>25</td>
<td>17.5</td>
<td>12</td>
</tr>
<tr>
<td>Bulk Density (g/cm(^3))</td>
<td>2.69</td>
<td>2.52</td>
<td>4.09</td>
</tr>
</tbody>
</table>

The highest decarburization rate of ZrO\(_2\)-C in test 4 and test 8 (Figure 37 a and 37 b) may be attributed to the lowest carbon contents (F\(_C\)). It can be concluded that these tests have the highest rate constant due to the lowest carbon contents, as equation 41 and table 22 shows.
The apparent porosity for Al₂O₃-C is 14.5 %, which is just slightly larger than 16.5 % for MgO-C. In addition, the carbon content of the MgO-C samples are 17.5 wt%, which is less in comparison to 25 wt% for the Al₂O₃-C samples. The calculated (ε₁.5/Fc) ratios for Al₂O₃-C and MgO-C are 12.11 and 12.50, respectively. The higher value for the constant rate of MgO-C samples may propose higher decarburization rates for this type of refractory material in comparison to Al₂O₃-C. In contrast, Figure 37 a) clearly shows that MgO-C samples have the lowest decarburization rate for an Air-Fuel combustion system at an AFR equal to 1.5. However, the Al₂O₃-C samples in Oxy-Fuel combustion system (Figure 37 b) have a lower decarburization rate than the MgO-C samples, as equation 16 had predicted.

It should be mentioned that Lin et al. 42) showed that the cold isostatic pressing of alumina particles with a larger mean size may lead to a formation of larger pores. As table 22 shows the mean grain size of MgO particles is 533 µm while it is just 399 µm for Al₂O₃ particles. It can be concluded that the average volume for accumulated flake graphite for MgO-C samples are higher than for Al₂O₃-C and ZrO₂-C samples. In addition, the flake graphite in this case study contains 3.2 wt% ashes. It can be concluded that a large volume of flake graphite may decline the total diffusion coefficient for oxidizing gases. The larger flake graphite volume region may lead to the introduction of a larger reaction interface between oxidizing gases and graphite. Therefore, more formation of CO gas due to reactions 37 and 38. In addition, Riguard et al. 43) showed that CO gas may act as a gaseous antioxidant. It can be concluded that MgO-C samples in an Air-Fuel combustion system (test 5) showed the lowest decarburization rate. This is due to the high concentration formation of CO at the interface, especially at temperatures where both reactions 37 and 38 are dominating. Furthermore, the diffusion coefficient value for oxidizing gases declines for larger accumulated flake graphite regions due to the formation of an ash-rich region around the graphite region.

The higher concentration of oxygen for Oxygen-Fuel combustion with an AFR value equal to 1.5 for test 9 has compensated the effect of the CO formation. Therefore, the MgO-C (test 9) showed the highest decarburization rate for a Oxygen-Fuel combustion system (Fig. 37 b).

7.4. Yttria Stabilized Zirconia (YSZ) plasma-PVD coated Al₂O₃ refractory base materials

Figure 58 shows a SEM image of an YSZ sample from test 3, table 20 at the interface between SEN refractory base materials and the plasma-PVD coating.
As the figure may illustrate, the thickness of the plasma spray-PVD coated YSZ was 160 µm. It clearly shows that the surface of the alumina-graphite test rods before plasma coating was uneven. As Figure shows, a 100 µm irregularity at the interface between the alumina-graphite test rod and the YSZ plasma spray-PVD coating has just slightly been reduced to a 60 µm irregularity after coating. It can be concluded that for a thinner YSZ plasma coating layer such as 160 µm, the uneven surface of the substrate may be reflected more than it could be reflected for a thicker coating. Furthermore, Memarpour et. al. \textsuperscript{44} showed that these irregularities may end up a long way outside the viscous sublayer at the interface between the SEN internal hot surface and the molten steel during casting. These regions are highly turbulent. Thus, these protruding areas may facilitate the accumulation of primary inclusions in the molten steel, on the SEN internal surface. It can be concluded that a 160 µm YSZ coating layer may not be accounted for as an appropriate coating, even if it totally could prevent the decarburization.

Figure 59 shows the SEM image of test 4 (table 20) with 290µm YSZ coating layer after decarburization trial.
It also shows that the surface of the alumina-graphite test rod before the plasma spray-PVD coating was uneven. As the figure shows, a 120 µm irregularity at the interface between the alumina-graphite test rod and the YSZ plasma coating has been drastically reduced to a 55 µm irregularity after coating. Thus, it can be concluded that for the YSZ plasma coating, with a coating layer with a 290 µm thickness, the uneven surface of the substrate may be reflected much less than it could be reflected for thinner coatings such as a 160µm thickness (Figure 58). Thus, a 290 µm YSZ coating thickness may be suggested as an appropriate coating thickness. This since it provides both an even surface and prevention of the decarburization, even during heating in air.

It can be concluded that the plasma-spray PVD coating of the commercial SEN refractory base materials with the YSZ is favorable with respect to the decarburization prevention. In addition, there was no sign of decarburization for coatings with 160, 250, 290 and 400µm thicknesses. The 290µm coating showed no sign of the decarburization at the heating in air. Furthermore, it had an even surface on the top of the coating. In addition, the sample with a 250 µm coating thickness showed no sign of decarburization at longer heating times at the maximum temperature in an oxidizing atmosphere. Therefore, the usage of coating thicknesses between 250-290µm may be recommended for YSZ coatings of the commercial SEN internal surface.

The other important property expected to be fulfilled with the coating is a decreased reaction between the SEN refractory base materials (alumina-graphite) and the REM alloyed molten stainless steel during casting. The chemical reaction possibility of the cerium alloying element with a zirconium oxide coating layer in contact with a stainless steel type containing Ce (0.09 wt% C, 1.64 wt% Si, 20.92 wt% Cr, 10.86 wt% Ni, 0.033 wt% Ce, 0.005 wt% Al and 0.001 wt% Zr) was evaluated using thermodynamic data. Reaction 42 shows the standard free Gibbs energy$^{36}$ for the reduction of the zirconia and oxidation of solute cerium. Equation 43 was applied to calculate the Gibbs free energy of the reaction at 1713 K. Furthermore, the Gibbs free energy for alumina reduction by solute cerium was calculated to compare to the value for zirconia. Equation 45 was applied to calculate the Gibbs free energy of reaction 44 at 1713 K. It was assumed that the activity of zirconium oxide and cerium oxide were equal to unity. In addition, the activity for solute cerium and zirconium were calculated using Wagner’s equation. In addition, the solute zirconium concentration in the molten steel was assumed to be 0.001 wt%. The constant activity coefficient ($\gamma^0$) for Ce, Zr and Al are 0.034, 0.037 and 0.029, respectively.$^{36}$ Table 23 shows all interaction coefficients used in the calculations.$^{35}$
Table 23. Interaction coefficients of elements in liquid iron at 1600°C[^35]

<table>
<thead>
<tr>
<th>( e_j )</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ce</th>
<th>Al</th>
<th>Zr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>-0.05</td>
<td>-0.06</td>
<td>0.02</td>
<td>0.02</td>
<td>-0.02</td>
<td>0.06</td>
<td>-0.03</td>
</tr>
<tr>
<td>Ce</td>
<td>-0.43</td>
<td>-0.07</td>
<td>0.02</td>
<td>0.01</td>
<td>-2.58</td>
<td>0.03</td>
<td>-0.02</td>
</tr>
<tr>
<td>Al</td>
<td>0.09</td>
<td>0.0056</td>
<td>0.003</td>
<td>-0.01</td>
<td>0.045</td>
<td>-0.002</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

The calculated values of the free Gibbs energy for reactions 42 and 44 at 1713 K were -131383 J and -235515 J, respectively. The calculations substantiate that both alumina and zirconia may be reduced by solute cerium in the molten stainless steel. However, the driving force of this reduction reaction is 104132 J higher for alumina than zirconia.

\[
2 [\text{Ce}] + \frac{3}{2} \text{ZrO}_2 (s) = \text{Ce}_2\text{O}_3 (s) + \frac{3}{2} [\text{Zr}] \quad \Delta G^0 = -592934.5 + 284.62 \cdot T
\]  

(42)

\[
\Delta G = \Delta G^0 + R \cdot T \cdot \ln \left( \frac{a_{\text{Zr}}^{3/2} \cdot a_{\text{Ce}_2\text{O}_3}^{3/2}}{a_{\text{Ce}} \cdot a_{\text{ZrO}_2}} \right) \\
\Delta G = -131383.48 \text{ J}
\]  

(43)

\[
2 [\text{Ce}] + \text{Al}_2\text{O}_3 (s) = \text{Ce}_2\text{O}_3 (s) + 2[\text{Al}] \quad \Delta G^0 = -630136 + 266.13 \cdot T
\]  

(44)

\[
\Delta G = \Delta G^0 + R \cdot T \cdot \ln \left( \frac{a_{\text{Al}}^{2} \cdot a_{\text{Ce}_2\text{O}_3}}{a_{\text{Ce}} \cdot a_{\text{Al}_2\text{O}_3}} \right) \\
\Delta G = -235515.47 \text{ J}
\]  

(45)

The cerium penetrated zone shown in figure 44 may be attributed to the penetration of the molten steel into the test rod without coating. This is due to the existence of the 18 vol% apparent porosity of the commercial SEN refractory base materials. It should be mentioned that the volume fraction of the refractory base materials porosity may increase during rotation of the immersed test rods in molten steel by graphite dissolution. Memarpour et al.\[^{44,45}\] substantiated the formation of the cerium aluminates inside the SEN during industrial continuous casting of Rare Earth Metals (REM) alloyed steel grades. Furthermore, Kojola et al.\[^{8}\] substantiated the existence of an attraction force between these phases and primary cerium inclusions in molten steel. This mechanism may lead to the formation of accretions inside the SEN. In addition, the study\[^{7}\] showed that the formation of cerium aluminates may lead to an initial clogging. It can be concluded that the prevention of this interaction between alumina particles in the SEN refractory base materials and the alloyed Ce in molten steel is favourable with respect to clogging prevention.

To confirm the ‘in situ’ formation of the cerium aluminates at the interface between the un-coated test rods and the Ce alloyed molten steel, the characteristics of the inclusions in the molten steel were determined. Furthermore, the reaction between cerium oxide and alumina may not take place.
at temperatures below 1943 K. It can be concluded that the molten steel did not contain cerium aluminates. Moreover, that they were formed ‘in situ’ due to the interaction between the alloyed cerium and alumina particles of the SEN refractory base materials. However, the chemical interaction of the YSZ coating with the solute cerium is possible, according to the thermodynamic calculations. To evaluate the extent of this interaction area, an X-ray chemical elements mapping at the interface between the plasma-PVD YSZ coating and the molten steel was performed. Figure 60 shows the SEM image and the mapping of this area.

It seems to be impossible to point out the interaction layer in this figure. To decide the thickness of the interaction area a line mapping was performed for a 200 µm line at the interface between the 500 µm YSZ coating and molten steel. Figure 61 shows the SEM image of the interface and line A along which the mapping was performed.
A region can be detected between the dashed lines where the zirconium concentration decreases while the cerium concentration increases. This transition area containing both cerium and zirconium may be determined to be the interaction region between the solute cerium in molten steel and zirconia in the YSZ coating. As Figure 61 illustrates, the thickness of this interaction interface is 40 µm. As a comparison, the interface thickness was 413 µm for the test rod without an YSZ coating. The formation of a very thin interaction layer for YSZ coated rods may be attributed to the applied Low Pressure Plasma Spraying (LPPS) process. The high kinetic energy transferred to the spray particles may lead to the formation of a very dense coating with a very low porosity. Therefore, the molten steel containing cerium may not penetrate as easy into the SEN refractory base materials. Therefore, the interaction may be drastically restricted to a very thin interaction layer at the interface between the YSZ coating and the molten steel.

It can be concluded that plasma-PVD coating of the SEN internal hot surface with the Yttria Stabilized Zirconia (YSZ) powder may be suggested as an alternative to the traditional glass/silicon powder coating. The YSZ coating may not penetrate to the SEN refractory base materials during preheating, as the traditional glass/silicon coating does. In addition, the plasma-PVD YSZ coating contains no alkalis that can be reduced by graphite to apply an oxygen source inside the SEN hot surface. Furthermore, the appropriate thickness of the YSZ coating may change the SEN internal hot surface to a smooth surface, even if the substrate surface has some irregularities. In addition, the YSZ coating may prevent the interaction between the alumina and silica in the SEN refractory base materials with cerium in the molten steel. Thereafter, formation of the first clogging product is prevented.
### 8. Concluding discussions

The submerged entry nozzle (SEN) is used to transport the molten steel from a tundish to a mould. The main purpose of the SEN usage is both to prevent oxygen and nitrogen pick-up by molten steel from the gas. Furthermore, to achieve the desired flow conditions in the mould. Therefore, the SEN can be considered as a vital factor for a stable casting process and the steel quality. In addition, the steelmaking processes occur at high temperatures around 1873 K, so the interaction between the refractory materials of the SEN and molten steel is unavoidable. Therefore, the knowledge of the SEN behaviors during preheating and casting processes is necessary for the design of the steelmaking processes (Figure 1).

The internal surfaces of modern SENs are coated with a glass/silicon powder layer to prevent the SEN graphite oxidation during preheating. The effects of the interaction between the coating layer and the SEN base refractory materials on clogging were studied in **supplement 1**. The results of the laboratory preheating experiments indicated a penetration of the formed alkaline-rich glaze into the alumina-graphite base refractory. The industrial preheating trials performed in **supplement 2** also confirmed the penetration of the formed alkaline-rich glaze into the alumina-graphite base refractory. More specifically, the alkaline-rich glaze reacts with graphite to form a carbon monoxide gas. Thereafter, dissociation of CO at the interface between SEN and molten metal takes place. This leads to reoxidation of dissolved alloying elements such as REM (Rare Earth Metal). This reoxidation forms the “In Situ” REM oxides at the interface between the SEN and the REM alloyed molten steel. Also, the interaction of the penetrated glaze with alumina in the SEN base refractory materials leads to the formation of a high-viscous alumina-rich glaze during the SEN preheating process. This, in turn, creates a very uneven surface at the SEN internal surface. A large number of accretion samples formed inside alumina-graphite clogged SENs were examined using FEG-SEM-EDS and Feature analysis in **supplement 2**. The internal coated SENs were used for continuous casting of stainless steel grades alloyed with Rare Earth Metals (REM). The internal surfaces of the SENs were coated by the same glass/silicon powder layer as studied in **supplement 1**. The results indicated a harmful effect of the SENs decarburization on the accretion thickness. In addition, the post-mortem study results clearly revealed the formation of a multi-layer accretion. Furthermore, (supplement 2) the presence of the uneven surfaces at the SEN internal surface. These areas consist of alumina particles, silica particles and the penetrated glaze in between. The results showed that these areas have reacted with dissolved REM in molten steel to form REM aluminates, REM silicates and REM alumina-silicates. The formation of the large “in-situ” REM oxides and the
reaction of the REM alloying elements with the previously mentioned SEN’s uneven areas may provide a large REM-rich surface in contact with the primary inclusions in molten steel. This may facilitate the attraction and agglomeration of the primary REM oxide inclusions on the SEN internal surface and thereafter the clogging.

**Supplement 1** revealed the disadvantages of the glass/silicon powder layer. **Supplement 2** revealed that decarburization may occur even for an internally coated SEN during an inappropriate industrial preheating process. In addition, **Supplement 2** revealed the harmful effect of the SENs decarburization on the accretion thickness. This led to the proposal of a new refractory material for the commercial SENs. **Supplement 3**, the effect of a ZrSi2 antioxidant and the coexistence of an antioxidant additive and a (4B2O3 ·BaO) glass powder on carbon oxidation were investigated at simulated non-isothermal heating conditions in a controlled atmosphere. Also, the effect of an ZrSi2 antioxidant on the carbon oxidation was investigated at isothermal temperatures at 1473 K and 1773 K. The specimens’ weight losses and temperatures were plotted versus time and compared to each other. The thickness of the oxide areas were measured and also examined using XRD, FEG-SEM and EDS. The coexistence of 8 wt% ZrSi2 and 15 wt% (4B2O3 ·BaO) glass powder of the total alumina-graphite refractory base materials, presented the most effective resistance to carbon oxidation. The 121% volume expansion due to the Zircon formation during heating and filling up the open pores by (4B2O3 ·BaO) glaze during green body sintering led to an excellent carbon oxidation resistance.

**Supplement 4**, the decarburization behaviors of Al2O3-C, ZrO2-C and MgO-C refractory materials from a commercial Submerged Entry Nozzle (SEN), were investigated for different gas atmospheres consisting of CO2, O2 and Ar. The (CO2/O2) ratio values were kept the same as it is in a propane combustion flue gas at Air-Fuel-Ratio (AFR) values equal to 1.5 and 1 for both Air-Fuel and Oxygen-Fuel combustion systems. Laboratory experiments were carried out under non-isothermal conditions in the temperature range 873 K to 1473 K at a heating rate of 15 (K·min⁻¹) followed by isothermal heating at 1473 K for 60 min. The decarburization ratio \( \alpha \) values of all three refractory types were determined by measuring the real time weight losses of the samples. The results showed that the decarburization ratio \( \alpha \) values of the MgO-C refractory became 3.1 times higher for Oxygen-Fuel combustion compared to Air-Fuel combustion at an AFR equal to 1.5 in the temperature range 873 K to 1473 K. The decarburization ratio \( \alpha \) values for Al2O3-C samples were the same as for the isothermal heating at 1473 K and non-isothermal heating in the temperature range 1473 K to 1773 K with a 15 (K·min⁻¹) heating rate. It substantiates the SEN preheating advantage at higher temperatures for shorter holding times compared to heating at lower temperatures for longer holding times. Diffusion models were proposed for estimating the decarburization rate of an Al2O3-C
refractory in the SEN. The activation energy for Al$_2$O$_3$-C samples heated at an AFR equal to 1.5, for Air-Fuel and Oxygen-Fuel combustions were found to be 81.8 (KJ·mol$^{-1}$) and 88.8 (KJ·mol$^{-1}$), respectively for a non-isothermal heating in the temperature range 873 K to 1473 K.

In supplement 5, the effects of the plasma spray-PVD coating of the Yttria Stabilized Zirconia (YSZ) powder on the carbon oxidation of the Al$_2$O$_3$-C coated samples were investigated. Laboratory preheating trials were performed at non-isothermal heating conditions in a controlled atmosphere. Also, the applied temperature profile for the laboratory trials were defined based on the industrial preheating trials. The controlled atmospheres consisted of CO$_2$, O$_2$ and Ar. The (CO$_2$/O$_2$) ratios were kept the same as for a propane combustion flue gas at an Air-Fuel-Ratio (AFR) value equal to 1.5, for heating in an air-fuel mixture and in air. The thicknesses of the decarburized layers were measured and examined using light optic microscopy, FEG-SEM and EDS. The YSZ plasma-PVD coated alumina-graphite refractory base materials, presented the effective resistance to carbon oxidation at different coating thicknesses from 160-480 μm in both combustion flue gas and air atmospheres. For the YSZ plasma coating that contained a thinner coating layer such as 160 μm, the uneven surface of the substrate may be reflected more than it could be reflected for a thicker coating. However, for the YSZ plasma coating with a coating thickness of 290 μm, the uneven surface of the substrate may be reflected much less than it could be reflected for thinner coatings. A 250μm and a 290μm YSZ coating may prevent the decarburization of an alumina-graphite refractory base materials during preheating in air at a maximum heating temperature of 1293 K. Moreover, in an oxidizing atmosphere with an AFR value equal to 1.5 at a maximum temperature of 1293 K and a holding time of 7200 seconds. A 250-290 μm YSZ coating is suggested to be an appropriate coating, as it provides both an even surface and prevention of the decarburization even during heating in air. In addition, the interactions between the YSZ coated alumina-graphite refractory base materials in contact with a cerium alloyed molten stainless steel were surveyed. The YSZ coating provided a total prevention of the alumina reduction by cerium. Therefore, the prevention of the first clogging product formed on the surface of the SEN refractory base materials. Therefore, the YSZ plasma-PVD coating can be recommended for coating of the hot surface of commercial submerged entry nozzles.
9. Conclusions

The performance of both laboratory and industrial trials in supplement 1 and supplements 2 have led to a better understanding of the SEN glass/silicon powder coating effects on clogging during casting of the REM alloyed stainless steel grades. The laboratory trails revealed the following information:

- The post-mortem study revealed the formation of an accretion layer where SENs’ hot surface were decarburized. This layer was thicker in comparison to those surfaces which had not been decarburized.
- The industrial preheating trials revealed that decarburization of the SEN is possible both during the preheating and after the preheating accomplishment as well as before the casting start.
- A multi-layer accretion was formed inside the SEN during casting.
- The formed glaze layer may penetrate into the SEN base refractory materials between alumina and silica particles. This penetration may lead to the reaction between the glaze and the SEN base refractory materials to form a high-viscous alumina-rich glaze.
- The high-viscous glaze may lead to a formation of an uneven and corrosion-resistance surface inside the SEN after the casting start. It is related to the heterogeneous corrosion rate of the SEN internal surface. The calculation showed that uneven surfaces are proper places where primary inclusions in molten steel can be agglomerated. This is due to that they may end up in the turbulent flow region.
- The penetration of the glaze may lead to reactions between alkaline in the glaze and graphite to supply a carbon monoxide source at the interface between the SEN and the molten steel. The carbon monoxide may be dissociated to oxygen and carbon at the interface. The carbon and oxygen may be dissolved in the molten steel.

The industrial trials showed the following important information:

- The formation of an uneven surface inside the SEN, the formation of the large “in-situ” cerium silicates and the reaction of dissolved REM with the SEN base refractory materials supply a large REM-rich surface in contact with the primary inclusion containing molten steel. This may facilitate the attraction and agglomeration of the primary REM oxides inclusions on the SEN internal surface and thereafter the clogging.
The study showed the vital effect of the glass/silicon powder coating on clogging mechanisms and it led to suggest the usage of a modified SEN refractory base material (supplement 3).

The effects of ZrSi₂ additive on the carbon oxidation resistance of the Alumina/Graphite refractory materials were studied in supplement 3. The main findings in this supplement are the following:

- The simulation results suggested an optimized pre-heating temperature of 1473K for an alumina/graphite refractory when the maximum reachable temperature is 1773K.
- The ZrSi₂ acts as an antioxidant, to restrict the alumina/graphite carbon oxidation by reacting with the oxidizing components such as oxygen and carbon dioxide. The 121 vol% expansion due to the formation of the zircon (ZrSiO₄) from the ZrSi₂ during oxidation can close open pores of the refractory formed during oxidation of the graphite.
- The highest carbon oxidation resistance of the refractory was achieved by addition of 8 wt% ZrSi₂ to the Refractory Base Material (RBM). The addition led to a 36% decrease of the decarburized layer thickness compared to the refractory base material without antioxidant additions.
- The antioxidant addition showed almost no effect at 4 wt% and 2 wt% addition of RBM.
- The coexistence of ZrSi₂ and (4B₂O₃·BaO) glass powder presented a remarkable improvement of the decarburization resistance for those samples containing 8 wt% and 15 wt% antioxidant of the RBM. The melting of the added glass powder led to filling of the refractory open pores formed during the green body sintering. The glaze acts as an oxidizing gas barrier.
- The (4B₂O₃·BaO) glaze showed a better stability than a pure B₂O₃ glaze during sintering at temperatures higher than 1273 K.
- The best result was achieved by additions of 8 wt% ZrSi₂ and 15 wt% (4B₂O₃·BaO) glass powder to the RBM. The addition led to a 46% decrease of the decarburized layer thickness compared to the refractory base material without antioxidant additions.
- The isothermal decarburization trials at 1473 K and 1773 K during 25 minutes revealed a less temperature sensitivity of the ZrSi₂-containing refractory materials at temperatures between 1473 K -1773 K.

The decarburization behaviors of Al₂O₃-C, ZrO₂-C and MgO-C commercial SEN refractory materials were investigated in laboratory-scale experiments (supplement 4).

The primary outcomes of the investigations are summarized below:

- The decarburization ratio (α) values for Al₂O₃-C, ZrO₂-C and MgO-C refractories were 1.8, 1.9 and 3.1 times higher respectively for oxygen-fuel
combustion compared to air-fuel combustion. These values are valid for an AFR value equal to 1.5 in the temperature range 873 K to 1473 K. Overall, MgO-C refractory materials show the highest decarburization ratio increase in this combustion system change.

- The decarburization ratio ($\alpha$) values for Al$_2$O$_3$-C became just 1.1 times higher when the gas mixture volume flux inlet became 4 times higher (from 2 Nl/min to 8 Nl/min at 298 K) for tests with an AFR equal to 1.5. Furthermore, for oxygen-fuel combustion when heated non-isothermally from 873 K to 1473 K. In both volume flux cases, the samples were totally decarburized after almost 30 min of isothermal heating at 1473 K.

- For the stoichiometric oxygen-fuel combustion of propane, the decarburization ratio ($\alpha$) values for Al$_2$O$_3$-C samples were almost the same during non-isothermal heating in the temperature range 873 K to 1473 K. Even if the gas mixture volume flux inlet became 2.7 times higher. The decarburization ratio ($\alpha$) values for both Al$_2$O$_3$-C samples were below 0.50 after isothermal heating at 1473 K for 60 min.

- The decarburization ratio ($\alpha$) values for Al$_2$O$_3$-C samples were almost the same as for the isothermal heating of a sample at 1473 and for non-isothermal heating of another sample in the temperature range 1473K to 1773 K with 15 K/min heating rate. This result may illustrate that it is more advantageous to heat the refractories to higher temperatures at shorter holding times instead of heating at low temperatures and at longer holding times.

- The isothermal heating of the Al$_2$O$_3$-C refractory at 1473 K for 60 min showed a 30% less decarburization ratio ($\alpha$) value in comparison to the same sample heated at 15 K/min in the temperature range 873 K to 1473 K followed by isothermal heating at 1473 K for 60 min. It can be concluded that at the maximum heating rate during the SEN pre-heating a 30 wt% graphite saving is possible.

- Both Jander’s and Ginstling’s diffusion models were supposed to be probable reaction models to predict the decarburization rates during non-isothermal in the temperature range 873 K to 1474 K. The FEG-SEM observations of the graphite flake morphology substantiated the assumption validity of a constant reaction area between reactants. Therefore, Jander’s diffusion model was deemed more suitable for the current experiments.

- The activation energy for Al$_2$O$_3$-C samples heated at AFR equal to 1.5, for air-fuel and oxygen-fuel were found to be 84.5 KJ/mol and 95.5 KJ/mol respectively during non-isothermal heating in the temperature range 873 K to 1473 K.

In supplement 5, decarburization trials were performed in a laboratory scale using plasma spray-PVD coated alumina-graphite test rods. The coating material was an Yttria Stabilized Zirconia (YSZ) powder. The low pressure plasma spraying (LPPS) vacuum technology was applied to perform the coating. The
trials were performed in a controlled atmosphere, using a pre-set temperature profile, a maximum heating temperature and a specific holding time for this temperature. Furthermore, the behavior of the plasma-PVD YSZ coated test rods in contact with a molten steel containing Ce were determined using microscopy and thermodynamic calculations.

The following findings are the primary results from the performed investigations:

- The YSZ coating may prevent the decarburization of the alumina-graphite during heating in an oxidizing atmosphere.
- The YSZ coating of about 160µm may prevent the decarburization in an oxidizing atmosphere containing both oxygen and carbon dioxide.
- The roughness of the alumina-graphite substrate may be reflected in form of a rough YSZ coating surface when applying a thin plasma spray-PVD coating such as a 160 µm thickness.
- The roughness of the alumina-graphite substrate showed the least reflection in form of a rough YSZ coating surface when applying a 480µm thick plasma spray-PVD coating.
- The laboratory trials substantiate the formation of a very thin interaction layer between the YSZ coating and a Ce alloyed molten stainless steel.
- The laboratory trials substantiate the prevention of the interaction between solute cerium in molten steel and alumina in SEN refractory base materials.
- The plasma-PVD coatings with 250-290µm thicknesses showed a very good decarburization prevention both in an air atmosphere and during long holding times at maximum temperatures. Furthermore, the reflection of the roughness of the alumina-graphite substrate has been reduced drastically.
- The YSZ plasma-PVD coating can be recommended for the coating of the hot surface of the commercial SENs as an alternative for the traditional glass/silicon powder coating.
10. Future work

Clogging of the SEN may limit the productivity during casting by interrupting the casting process, restricting the number of charges per tundish and affecting the steel quality. From the experiences and results of this work, the vital roles of the SEN-base refractory materials, internal coatings and preheating are revealed. In order to improve the quality of the commercial SENs with respect to the clogging, the following suggestions are made for future work:

- SEN double internal coatings, the conventional glass/silicon powder coating and an extra alkalines-free glass coating. This extra coating is intended to form a glaze preventing the penetration of the conventional alkalines-rich coating into the SEN base refractory materials.

- The chemical composition adjustment of the previous mentioned extra coating. This coating is also intended to have a high temperature melting point, so that it would be remained on the SEN internal surface during casting.

- Plasma spray-PVD coating of the internal surface of the commercial SENs using a 43 wt% mullite and 57 wt% silica powder. The composition of (3 Ce₂O₃-24 SiO₂- 5 Al₂O₃) may form a liquid phase at casting temperatures. The formation of this liquid may prevent the accumulation of primary cerium oxide inclusions in molten steel when passing through the SEN.
11. References

45. A. Memarpour, V. Brabie and P.G. Jönsson: 7th European Continuous Casting Conference (ECCC2011), the METEC InSteelCon® 2011.