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SUBMERGED ENTRY NOZZLE CLOGGING DURING CONTINUOUS CASTING OF Al-KILLED STEEL

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Nozzle clogging is a common problem in the production of continuously cast Al-killed steels. Clogging occurs when there are solid inclusions in molten steel at casting temperatures. SENs (Submerged entry nozzles) from continuous casting of Al-killed low alloy steel grades with increased content of sulfur (0,020 to 0,035 % S) were examined. The examinations revealed that the deposits are mainly alumina based, with spinel and sulfur inclusions and some entrapped steel melt. It was concluded that the process of clogging begins when the steel melt infiltrates the refractory and removes the protective zirconia surface, thus allowing the adhesion of fine solid aluminates, which form the deposits.

Keywords: continuous casting, non-metallic inclusions, SEN (submerged entry nozzle) clogging, reoxidation of steel melt

INTRODUCTION

Nozzle clogging is a common problem in the production of continuously cast Al-killed steels [1–4]. Clogging occurs when solid inclusions are present in molten steel at casting temperatures. Steels with increased content of aluminum are particularly at risk to deposit formation. Titanium steels are also susceptible to deposit formation [5]. Sun et al. [6] report that the combination of TiAl oxide inclusions is even more susceptible to deposit formation in SEN (submerged entry nozzle) than pure aluminates, because of better wettability. The origin of such inclusions is mostly reoxidation. Another group of steels that are susceptible to clogging are Ca treated steels with an increased level of sulfur (above 0,012 %) [2]. L. Zhang et al. [7] classified clogging into four different formation processes: agglomeration of deoxidation products, solid steel build up, the agglomeration of complex oxides and buildup of reaction products.

Aluminum oxide network morphology, found in clogging deposits is very similar to that of the clusters observed in liquid steel after deoxidation of the steel. Therefore, it has been suggested that the clusters observed in the clogging deposit are formed as a result of reoxidation in the tundish [8].

Catastrophic clogging of calcium treated steel can be correlated to reoxidation of the steel during tundish fill. Reoxidation results in additional formation of aluminium oxide, which transforms the liquid calcium aluminates into solid aluminium oxide-rich calcium aluminate particles that caused clogging [8].

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A number of studies describe the effect of tundish fluxes with different basicity on steel reoxidation [8]. Fluxes with FeO, MnO and SiO_2 are reduced, which results in aluminium loss and manganese and silicon pickup.

R. Dekkers [8] noticed that particles in a clogging deposit formed during casting of low carbon aluminium – killed steel are mainly (coral-shaped) clusters, dendritic clusters and irregular plates. These particles are definitely formed during the reoxidation of the steel after the ladle metallurgy process and most probably in the SEN. The agglomeration of solid alumina particles in molten steel is generally dealt with by inclusion modification. Alumina inclusion modification is most commonly performed by CaSi additions [3,9]. Calcium forms CaO in the steel melt and binds with alumina particles to form lower melting oxides. As the content of CaO is lowered the melting point rises, therefore sufficient amounts of CaSi additions are needed to modify the inclusions and provide a low melting point. Calcium aluminates that have high melting points (above the casting temperatures) also form deposits and are therefore as troublesome as the pure aluminates. Al_2O_3 – CaO inclusions have a high sulfide affinity, CaS is formed during the cooling of the steel melt, resulting in a complex inclusion of CaS and calcium aluminates [10]. Clogging of SEN can not only affects casting speed, which is directly related to the productivity, [11] but can also cause casting termination due to the complete plugging of the SEN [3]. These kinds of problems are of great importance in steel plants that produce many different steel grades. The deposits that form during continuous casting of Al-killed steels are fine alumina particles that stick to the inner wall of the SEN. These fine particles are then sintered into a mass that obstructs the metal flow. K. N. Vdovin et al. [12] report that a coat of pure alumina or ZrO_2 reduces deposit formation on SEN in Al killed steels.

EXPERIMENTAL

Clogged SEN samples from the production of continuously cast Al- killed, low alloy steel grades with increased content of sulfur (0,020 to 0,035 % S) were analyzed. SEN samples were embedded in bakelite, grinded and polished for light observation microscope (Microphot FXA, Nikon). Carbon was evaporated on the surface of the specimens for electron microscope (SEM, Jeol – JSM6500F) observations. The SEN sample is shown in Figure 1. The SEN refractory was zirconia based and it composition is given in Table 1.

Table 1 **Chemical composition of SEN refractory / wt%**

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	ZrO_2	HfO_2
9,81	0,13	0,65	0,07	3,33	0,05	84,9	1,69

Figure 1 SEN with deposit

RESULTS AND DISCUSSION

The SEN had a layer of sintered alumina deposited on the zirconia refractory. The section of the deposit is shown in Figure 2 with steel melt infiltrating the surface layer of zirconia refractory. Then alumina deposits form on the infiltrated layer combined with zirconia grains loosened by the steel melt. The alumina deposits then grow, entrapping different kinds of non-metallic inclusions present in the melt, and steel droplets as well. CaS particles can also be found among the alumina agglomerates, because of the high sulfur content in the steel melt. The structure of the deposit changes from the bottom of the SEN towards the top. The unaffected zirconia refractory, with zirconia grains is shown in Figure 2.

Alumina inclusions that agglomerated between the loosened zirconia grains are shown in Figure 3. The mapping shows areas of increased content of calcium oxide in the agglomerated deposit between zirconia grains. This suggests that the inclusions that first stuck to the refractory were partially modified with CaSi. EDS analysis of the calcium rich area give the approximate composition of $CaO \cdot 3Al_2O_3$. This layer is the most crucial, because it shows the start of the growth of the deposit.

If the steel reoxidizes, calcium treatment cannot maintain effective inclusion modification because more alumina is formed. The alumina reacts with the liquid calcium aluminate inclusions forming a solid alumina-rich calcium aluminate, which then agglomerates. When the liquid steel flows through nozzles, the temperature drop causes a decrease of solubility of oxygen in steel, which drives the $Al – O – Al_2O_3$ equilibrium towards the alumina side and the formation of alumina depositions on the nozzle wall. Atmospheric oxygen is transported through pores to the nozzle interface due to the pressure

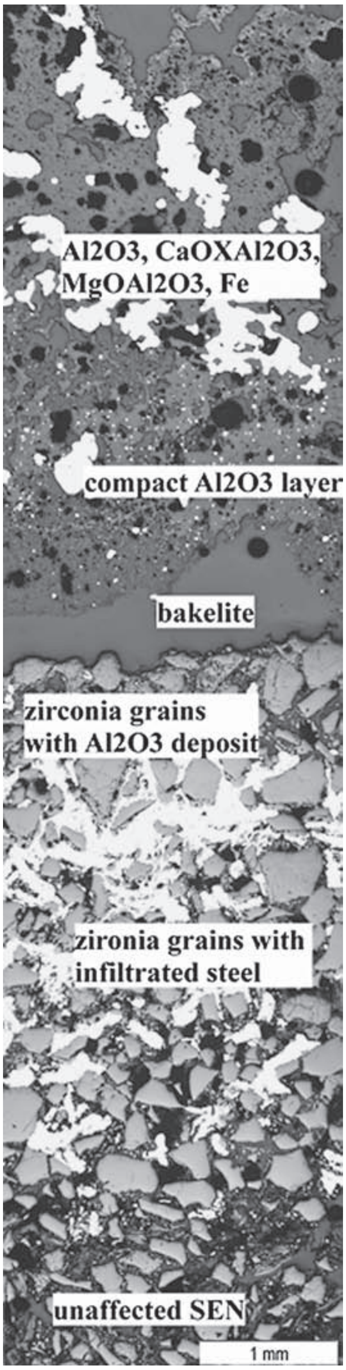

Figure 2 SEN deposit profile

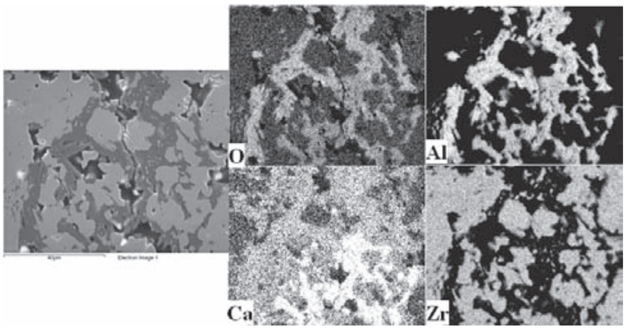

Figure 3 Mapping of zirconia refractory with alumina inclusions

gradient. The results are solid alumina inclusions, as described by the equation [13]:

$$2(Al) + 3(O) = Al_2O_{3(s)} \quad (1)$$

$$\Delta G_1^0 = -1205115 + 386,7T \;/\; \frac{J}{mol} \quad (2)$$

$$a_O = \sqrt[3]{\frac{a_{Al_2O_3}}{a_{Al}^2 \cdot e^{\frac{-\Delta G_1^0}{RT}}}} \quad (3)$$

When the steel solidifies, the solubility of oxygen approaches zero. The remaining oxygen in the melt will end up as oxide inclusions. In the Figure 4 are oxygen activity is plotted as a function of steel temperature.

Calcium treatment is a countermeasure to avoid harmful alumina or spinel inclusions by modifying them to harmless liquid calcium aluminate inclusions [14] By normal steelmaking conditions, calcium aluminates compared to spinel inclusions are thermodynamically favored to form, the dissolved Ca can than reduce spinel inclusions and convert them into calcium aluminates. Considering the effect of dissolved Ca in steel, the stable region of spinel phase was moved to greater contents of dissolved Mg and Al. Partially reduced $MgO \cdot Al_2O_3$ spinels are visible in the compact alumina layer of the deposit in Figure 5. The formation of spinel occurs continuously because of steady supply of Mg from the reduction of MgO in slags or refractories.

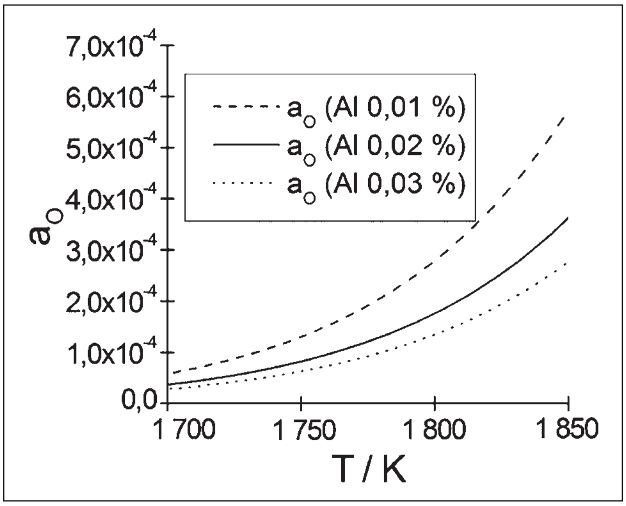

Figure 4 Oxygen activity in steel melt for different temperatures

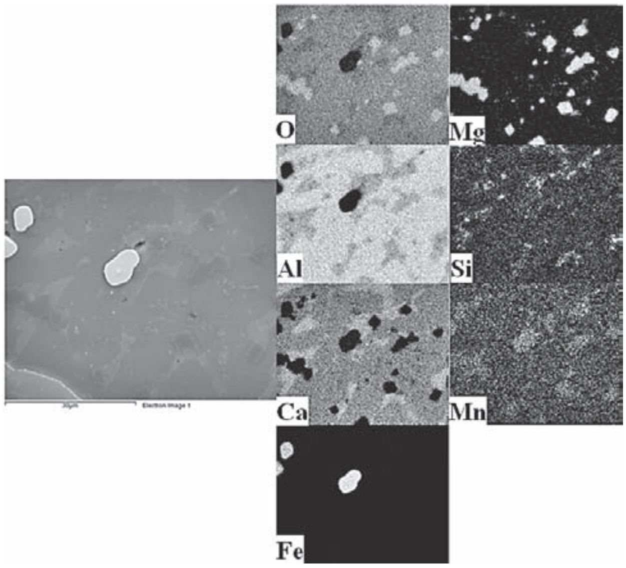

Figure 5 Mapping of dense alumina based nozzle deposit

$MgO \cdot Al_2O_3$ spinel inclusions are harmful to both the quality of products and steel castability because of their high melting point and high hardness. Because $MgO \cdot Al_2O_3$ spinel inclusions are solid at the temperature of the molten steel, the core of the spinel inclusions is always solid even with calcium treatment. Therefore, the calcium treatment does not fully modify the $MgO \cdot Al_2O_3$ inclusions into uniform $CaO \cdot MgO \cdot Al_2O_3$ inclusions or $CaO \cdot Al_2O_3$ inclusions.

As is shown in Figure 6, the most outer layer of the SEN deposit that was in contact with the steel melt has the most loosely formed alumina deposit. Magnesium spinels and sulfide inclusions are also entrapped in the deposit that consists of mostly alumina and steel. The main difference between the compact and loose alumina layer, is the presence of iron, and EDS shows 10 to 20 % of iron in alumina. The content of silicon has been increased also and EDS analysis shows up to 5 % of Si.

The low FeO concentrations in the ladle slags result in significantly higher levels of $MgO \cdot Al_2O_3$ spinel-type inclusions in steel. In the steels with high S content, the

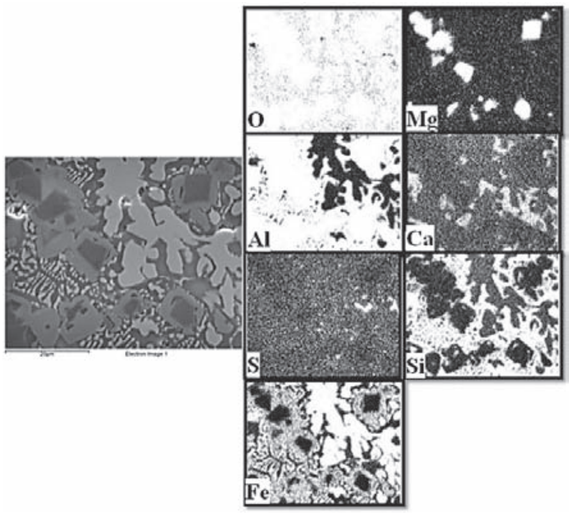

Figure 6 Mapping of the alumina based deposit and entrapped steel

formation of liquid inclusions is not possible without some CaS precipitation. The process in which the formation of CaS is avoided by incomplete modification of alumina is thermodynamically preferred to complete modification of alumina with the formation of CaS. On the order hand, is important to avoid excessive CaS precipitation, because of its high tendency to clogging.

EDS analysis results show the presence of mostly $CaO·2Al_2O_3$ and $CaO·6Al_2O_3$, with the occasional by magnesium spinel in the deposit which is consistent with the analysis that L.M. Aksel'rod et al. [15].

CONCLUSIONS

Mappings of the nozzle deposit layers indicate the base of deposit consists of alumina inclusions and that the growth on the refractory wall started with calcium aluminate inclusions sticking to the zirconia refractory surface, eroded by the steel melt. The steel melt infiltrated the refractory and removed the protective surface from the zirconia, allowing the adhesion of fine aluminates. The larger spinel type inclusions did not stick directly to the refractory alumina based deposit, but get entrapped during the deposit growth.

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