

ELECTROCHEMICAL METHODS FOR THE PREVENTION OF CLOGGING IN SUBMERGED ENTRY NOZZLES

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INTRODUCTION

The quality of steel produced with continuous casting is mainly influenced by the steel cleanliness. The amount and size of non-metallic inclusions is crucial for modern quality aspects. One source of inclusions can be the alumina build-up in the submerged entry nozzle and its removal through the steel flow. Big inclusions or inclusion clusters can get into the mould and rest in the strand when not properly separated into the mould slag. It is therefore important to find measures for prevention or reduction of clogging in continuous casting.

Alumina build-up is generated in several ways. It can be composed of non-metallic inclusions from secondary steelmaking which get attached to the nozzle wall and form clusters called clogging [1, 2]. As both inclusions and nozzle refractory are oxide compounds it is hardly possible to prevent the sticking of each other in case of contact. The inclusions will be held in the surface roughness and sinter. Liquid inclusions as calcium-aluminates will wet the nozzle surface as the interfacial tension between slags and solid oxides is very low. After several hours of casting this build-up can form layers of some cm thick.

Graphite in the nozzle refractory, usually necessary for good resistance to thermal fatigue, lowers the wettability of the nozzle. Nevertheless after a certain time of preheating in oxidizing atmosphere a decarburized surface layer will form which behaves almost as pure oxides in terms of wettability.

In this sense it would be helpful to reduce the inclusion build-up through a reduced wettability of the nozzle refractory by slags (equivalent to liquid inclusions). Additionally a reduced wettability of the nozzle refractory by liquid steel would be of advantage. In this way a smaller interface area provides fewer possibilities for reaction between the nozzle and steel. Additionally inclusions would have less chance to attach the nozzle wall and form a clogging layer.

Another important source of clogging material is the in-situ formation of mostly alumina at the interface between steel and nozzle refractory. Several mechanisms are known to be responsible for this phenomenon. As the nozzle refractory is porous and steel is flowing inside with high velocity, air can be sucked into the steel stream where it partly dissolves. Aluminium which is solved in the steel to reach low oxygen contents combines with the oxygen of the air to form alumina [3]. Additionally so-called suboxides in

the form of SiO, AlO and Al₂O can form inside the nozzle refractory between oxides and bonding graphite at high temperatures [4, 5]. These gaseous substances are also sucked to the interface where they recombine with solved oxygen from the steel to their original oxide form – alumina or silica [6, 7].

All these processes take place just at the interface where alumina forms tight build-up layers. Because of solid inclusions as reaction products it is not possible in this case to diminish clogging through wetting control. On the other hand a reduction of the oxygen activity at the interface would change the thermodynamic equilibrium making alumina less stable. This process is possible through the application of an electrochemical cell. To remove oxygen from the steel melt an oxygen ion conducting material as zirconia is used [8]. Usually such a solid electrolyte is used to measure the oxygen activity of steel melts through the electromotive force (EMF). A zirconia probe is inserted into the melt and the EMF between the steel and a reference point (usually a mixture of metal and metal oxide) with a known oxygen partial pressure is measured. On the steel side the following reaction takes place (1),



while on the reference side oxygen ions recombine to gaseous oxygen (2):



The principle can also be returned which means an electrolytic deoxidation. For this purpose a voltage is applied to the system. It is composed of the EMF – as defined by the difference of oxygen potentials between the steel melt and the reference side - and potential drops on the electric resistances of electronic and ionic conduction in zirconia material [9]:

$$U = EMF + I_{ion}R_{ion} + I_{El}R_{El} = \frac{RT}{4F} \ln \frac{p_{\text{O}_2}(\text{Ref})}{p_{\text{O}_2}(\text{Metall})} + I_{ion}R_{ion} + I_{El}R_{El} \quad (3)$$

In order to reduce clogging an oxygen activity as low as possible in the steel would be preferential. To transport it to the reference side a negative potential must be applied to the steel melt. In a continuous system as the steel flow through the submerged entry nozzle oxygen has to be continuously pumped out of the steel. The amount must be sufficient to keep the oxygen activity at the interface below the solubility product for alumina

formation which is about 20 to 30 ppm at 1580°C depending on the aluminium content.

Experiments which deal with these two methods – influence of direct current on wettability and electrochemical deoxidation – are presented here to investigate which possibilities they offer for reducing the clogging phenomenon.

EXPERIMENTAL PROCEDURE

Wetting experiments

In wetting experiments the influence of an applied voltage on the wetting behaviour of nozzle refractory by liquid slag and steel has been investigated. All experiments were performed with industrial nozzle refractory material. Rough compositions are given in **Table 1**. The refractory was graphite-bonded alumina with different contents of silica and other oxides at low amounts. Disks of about 4 mm thickness were cut from the nozzles and separated into plates of about 2 x 2 cm. They were carefully grinded to remove coarse roughness.

Tab. 1. Chemical composition of nozzle materials.

	Al_2O_3	SiO_2	CaO	MgO	TiO_2	SiC	ZrO_2	C
<i>M1</i>	63	1.3	0.2	0.2	0.3	4.9	0.2	bal.
<i>M2</i>	51	9.0	0.2	0.8	0.8	0.4	1.7	bal.

Nevertheless it was impossible to polish their surface perfectly as the bond strength between the refractory grains and the graphite is limited. As a result the surface exhibited a certain roughness which was kept as uniform as possible having a maximum roughness depth of about 0.2 mm. The plates were cleaned with ethanol to remove dust and dried for several hours. After drying they were placed on an alumina holder which can be pushed horizontally into the furnace of a heating microscope. Below the plate a molybdenum wire served as the reference electrode. All voltages given here refer to this electrode. Another electrode in form of a molybdenum rod with wire tip was placed above the plate. In case of wetting experiments with slag this molybdenum wire was immersed into the droplet. In case of steel droplets the electrode was made of thicker molybdenum wire. Additionally experiments with a titanium boride electrode mounted on the molybdenum wire were made.

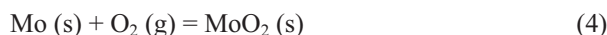
The wetting angle of steel and slag samples was determined with the sessile drop method. Argon was flushed through through the furnace for 20 min before heating. Experimental temperature was 1580°C for steel and 1450°C for slag samples which was controlled by a thermocouple just below the sample plate. 10 min after reaching the experimental temperature the upper electrode was moved down to contact the sample properly, but without disturbing the contact angle. A voltage between -2 V and +2 V was switched on 10 min

later for 30 min of time. After this time the contact angle was found to be stable.

Pictures were taken every 5 min by a camera through a quartz glass and manipulated with image processing to measure the contact angle between the droplet and the sample plate.

Deoxidation experiments

Deoxidation experiments were conducted in a vacuum induction furnace with argon atmosphere. Samples of about 2 x 2 x 4 cm were cut from the lower part of a nozzle wall of M1. The meniscus region and the nozzle part which are immersed into liquid steel were composed of graphite-bonded zirconia in nozzles of this type. A hole in the middle of the sample was partly filled with molybdenum oxide, which was contacted by a molybdenum wire (electrode 1) and held by a small ceramic pipe. This pipe was mounted on a steel pipe sample holder and installed in the furnace. Air was blown through the sample holder and the ceramic pipe into the sample hole. This formed the reference side with a constant oxygen potential according to:



The second electrode contacted the steel melt through a ceramic pipe. Melt and the outer surface of the sample can be regarded as a reaction side in terms of an electrochemical cell (electrode 2). During the test a voltage was applied with steel melt being the negative potential. Two samples of this type were held in the steel melt. Only one was equipped with an electrode while the other one served as a reference sample.

A low alloyed steel melt was held at 1580°C for three hours while adding aluminium every 30 min to keep an aluminium content of about 800 ppm. This high content was necessary to ensure a sufficient formation of alumina inclusions at the sample surface.

After the experiment the samples were embedded under vacuum to stabilize the refractory microstructure. The samples were cut to analyze the surface structure in the cross section with optical microscopy and secondary electron microscopy (SEM).

DISCUSSION

Wetting experiments

First results of wetting experiments of nozzle refractory by CaO-Al₂O₃-slag (mass 1:1) with applied voltages are presented in **Figure 1**. There is some tendency that in case of positive potential on the slag side the wetting angle slightly increases. The opposite occurs in case of negative potential on slag side. The change in wetting angle is quite small which makes it a not very pronounced effect. Nevertheless such behaviour is predicted from electrocapillary theory. In fact one must find the electrocapillary maximum where the highest

interfacial energy exists between the two phases refractory and steel or slag. In slags this increase is caused by desorption of ions from the interface through electric potential which are normally surface active. In our case it can be stated as a first result that more cations might be present at the interface which desorb into the bulk of slag at a positive slag side potential.

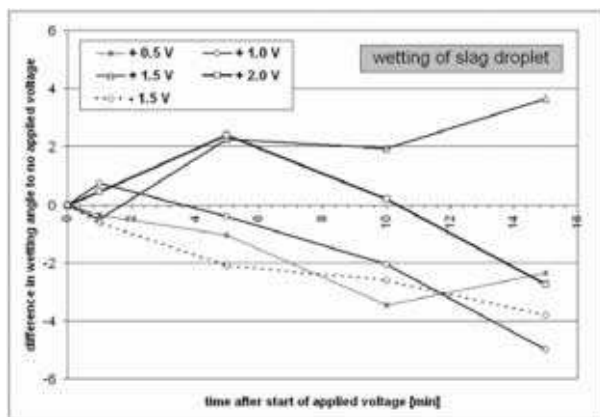


Fig.1. Wetting angles between slag droplet and nozzle refractory M1 after voltage application.

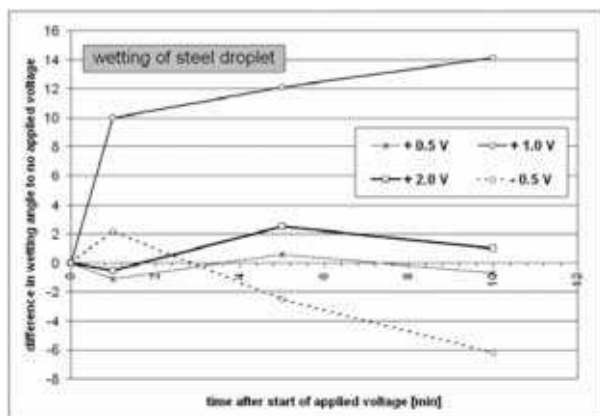


Fig.2. Wetting angles between steel droplet and nozzle refractory M2 after voltage application.

With steel a less significant effect was observed (Figure 2). Only in the case of +1 V an increase of the contact angle could be measured while in other cases the contact angle remained almost stable or decreased slightly. Obviously the electrocapillary effect between steel and refractory material is weak or other voltages must be applied to find the minimum in wettability. In further experiments voltages outside of the range -2 V to 2 V will be analyzed.

To summarize the effect of electrowetting between steel or slag and nozzle refractory is quite weak and could only be measured with some uncertainties. The roughness of the sample plates might prevent the wetting or dewetting by holding the droplet. In the case

of steel droplets a carbon pickup was unavoidable which caused the wetting angle to increase slightly.

Deoxidation experiments

Because of soft air bubbling through the refractory sample for oxygen feeding and the continuous adding of aluminium - alumina inclusions were formed at the surface of the samples. After three hours an alumina layer of up to 1 mm thickness was grown on the samples which simulated clogging in the nozzle during continuous casting. In real process oxygen gets to the interface through air flow, gaseous suboxide formation and solution of non-stable oxides from refractory material into steel.

The thickness of the alumina layer on the reference sample (without voltage) and the electrode sample (with voltage) was compared to measure the effect of electrochemical deoxidation on clogging. Results of these measurements are shown in Figure 3.

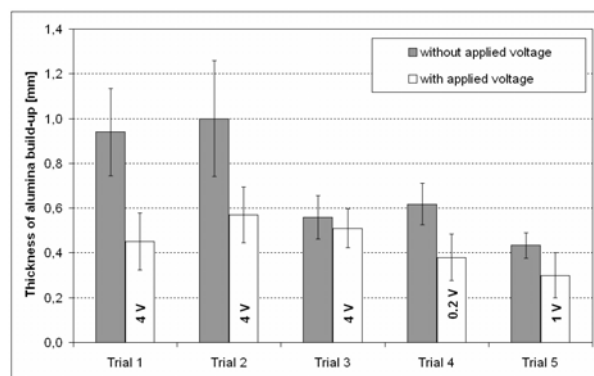


Fig.3. Thickness of alumina layers on reference sample and electrode sample with applied voltage.

Each value is a mean value of at least ten measurements around the circumference of the sample. To prove the nature of these layers SEM pictures have been taken with microprobe analysis. The results of the partition of alumina as build-up layer and zirconia as base material are shown in Figure 4 together with SEM pictures. As can be seen an applied voltage reduces the thickness of the grown alumina layer markedly. This can be explained in two ways: Oxygen which is dissolved in the melt is transported in form of ions through the zirconia to the reference side. If the oxygen activity is kept below the solubility product of alumina, no alumina forms. Second possibility is that alumina already present at the interface can dissolve into the melt again if the oxygen activity locally drops below the solubility product. It is for sure that with this method no deoxidation of a whole steel melt is possible, but for the prevention of clogging oxygen activities must only be lowered locally at the interface between refractory and steel melt. It has been shown in this study that this is obviously possible even with industrial

materials. Nevertheless these experiments were done on laboratory scale. There should be further work to apply this technique in practice with real nozzles. Additionally it is necessary to find the optimal current in order to surely reduce clogging but also to prevent electrochemical reactions because of too high voltages.

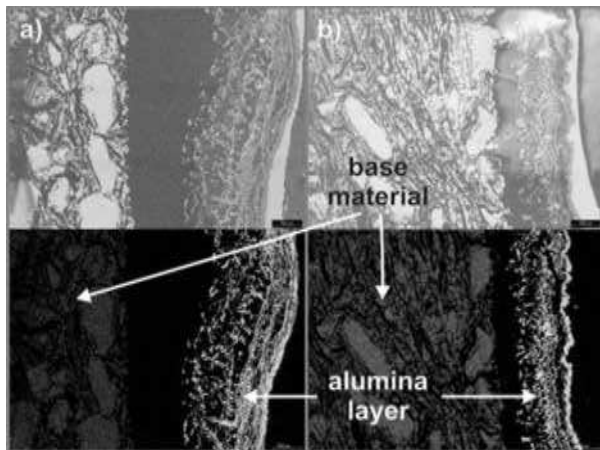


Fig.4. SEM pictures with partition of alumina (white) and zirconia (grey) after trial 4

The voltage necessary to hold the oxygen activity below 10 ppm was calculated to be about 1.2 V with pure zirconia. On the other hand bonding graphite is an electronic conductor which lowers the efficiency of applied voltage through electrical current through the samples without transporting oxygen ions. As no data exists for conduction of oxygen ions in graphite bonded zirconia, the amount of electrical current loss is unknown. Nevertheless it is believed that enough bridges between zirconia grains exist in the refractory material which offers paths for conduction of oxygen ions. Additionally carbon is burned during heating of refractory nozzles in air atmosphere and dissolves into steel melt at the interface. As a result a surface layer with reduced or no carbon content is generated which can be regarded as almost pure zirconia layer capable of conducting oxygen ions.

SUMMARY

Experiments have been done to explore the possibility of preventing clogging in submerged entry nozzles during continuous casting of steel with the help of electric current. With the first method - known as electrowetting or electrocapillarity - the adsorption of species at the interfaces and therefore wettability of refractory materials by slag and steel melts can be influenced by electric current. Regarding the clogging phenomenon the adhesion of non-metallic inclusions and the steel melt on the nozzle wall should be reduced. Experiments studying the wettability of carbon-bonded refractory materials by slags with an applied electrical current in the range between -2 V and +2 V have been

done in a heating microscope. The results showed weak effect but the possibility to further study this phenomenon on a laboratory scale. A second way is to use electric current in an electrochemical deoxidation process. The oxygen activity is crucial for the in-situ formation of non-metallic inclusions near the nozzle wall. With electrochemical deoxidation an electric current is applied to a zirconia-based refractory material to lower the oxygen activity in the vicinity of the nozzle wall. By doing this in-situ formation of non-metallic inclusions is prevented and clogging build-up is retarded. Experiments on carbon-bonded zirconia samples dipped into a steel melt in a vacuum induction furnace were carried out. It was found that under laboratory conditions it is possible to decrease the thickness of the build-alumina layer on a laboratory scale.

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