

Investigating the influence of Ti and P on the clogging of ULC steels in the continuous casting process

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Abstract

In the casting of Ti-bearing ULC steels, clogging of the submerged entry nozzle (SEN) affects both the productivity of the caster and the quality of cast products. The plant experience shows a negative influence of increasing Ti and P contents on the clogging tendency of ULC steel grades. Analytical investigations on samples from the process and laboratory experiments have been carried out in order to gain a better understanding of the influence of Ti and P on the clogging phenomenon of ULC steel grades.

After casting Ti and P alloyed ULC steels, the deposits from clogged SEN have been analysed. The results indicate that the particles consist mainly of alumina ($\text{Al}_2\text{O}_3 > 90$ mass%), while the Ti content makes up only a very small portion (0.58 – 3.58 mass%). An automated inclusion analysis by OES-PDA shows that the size of oxide inclusions decreases with increasing Ti content. The determination of the influence of Ti and P solutes on the wetting in the liquid Fe/ Al_2O_3 system by the sessile drop method indicates that both elements lower the wetting angle and reduce the melt surface tension. Concerning Ti, the decrease of the wetting angle occurs only in the case of reactive wetting. The effects of Ti and P on clogging are found to be significantly different: Ti lowers the size of Al_2O_3 inclusions only if an interfacial wettable surface layer forms. Small alumina inclusions enhance the clogging proneness. The time between Al deoxidation and Ti addition is thus an essential process variable in order to prevent clogging. As for P, it increases the Ti activity if both solutes are added to the melt. Moreover, it lowers the melt viscosity, thus increasing the wettability in the Fe-Ti-P system. The negative effect of P on clogging is, therefore, less pronounced than that of Ti and presumably harder to influence.

Key words: contact angle, continuous casting, drop shape analysis, interstitial free steel, non-metallic inclusions, nozzle clogging, pulse discrimination analysis, sessile drop, ultra low carbon steel, wetting

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1 Introduction

In the history of continuous casting, clogging of the submerged entry nozzle has always been one of the biggest problems facing steelmakers. Indeed, SEN clogging is a complex phenomenon mainly resulting from alumina buildup and which can occur anywhere inside the nozzle, especially on the upper well, bore, and ports [1]. The accretion of Al_2O_3 on the casting pouring system not only decreases the productivity of the caster by reducing casting throughput and causing unscheduled nozzle exchanges, but also worsens the steel quality by giving rise to a change in the nozzle flow pattern and jet characteristics exiting the nozzle, thus leading to mould level fluctuations which increase the risk of slag entrainment and surface defects (slivers). Furthermore, dislodged clogs can become trapped in the steel, increasing the inclusion population in the strand [1 - 4].

Rackers and Thomas [2] classify SEN clogging into four different types according to their formation mechanism: the agglomeration and sintering at the nozzle wall of deoxidation products, air aspiration into the nozzle, chemical reaction between the nozzle refractory and the steel, and steel solidified in the nozzle. In practice, however, a given nozzle deposit is often a combination of two or more of these types, which makes the identification of its root cause a delicate task.

Several studies have been conducted to elucidate the mechanisms of nozzle deposits, and various adhesion theories have been proposed. They were mainly based on the reaction between the molten steel and the SEN refractory [4 - 7], the interfacial tension between alumina and molten steel [8, 9] and the interfacial tension gradient near the nozzle boundary surface [10, 11]. The most generally accepted theory is that SEN clogging is caused by the attachment of solid inclusions (principally Al_2O_3 , TiO_2 , rare earth oxides, ...), already present in the steel melt, to the wall of the nozzle [1 - 7]. The adhesion of the Al_2O_3 inclusions and their subsequent sintering to form a network are explained by the achieved reduction in surface energy of the system [1, 8, 9]. Other investigations [3, 12] focused on the influence of hydrodynamic conditions in the SEN. Accordingly, turbulence increases the potential to deposit, because this intensifies the transverse component of the inclusion flow in the SEN. In this regard, Wilson *et al.* [12] demonstrated that small inclusions are more sensitive to turbulence than larger ones. Furthermore, the surface roughness was found to increase turbulence and heighten the probability for inclusions to contact and stick to the wall [3]. As Wang *et al.* [11] have shown, chemical reactions between the SEN and liquid steel generate a concentration gradient near the interface. As a result, a boundary layer is formed near the SEN wall.

Once inclusions enter that layer, they are forced to move to the SEN wall due to the interfacial tension gradient (*Marangoni* effect) generated by the local concentration change.

Although the mechanism which contributes most to SEN clogging is still debatable, it is widely accepted that a higher steel cleanliness is the key for the prevention of the occurrence of severe clogging [13].

At voestalpine Stahl GmbH, the tundish flow control is conducted using a stopper rod system, and clogging, which is frequently experienced during the casting of IF-ULC steel grades, occurs mainly in the stopper area and at the exit port of the SEN. **Figure 1** shows a typical clogged SEN which was used for casting Ti-bearing ULC steels. A substantial reduction of the inner section of the nozzle due to the deposition of clogging materials is registered.

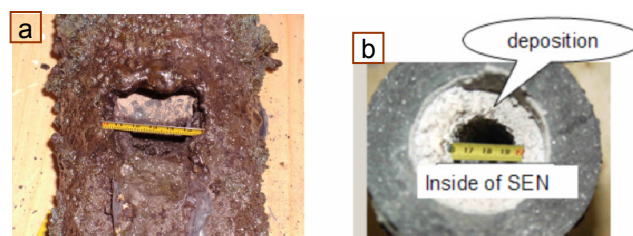


Figure 1: Typical nozzle clogging: deposits (a) at the exit port and (b) on the inner wall of the SEN

An evaluation of the clogging potential for an ULC steel grade containing different Ti contents carried out at the caster No.3 showed that an increase in [Ti] concentration leads to more clogging, **Figure 2** [14]. This observation is consistent with the viewpoint shared by many researchers [15 - 19], viz.: SEN clogging is more severe in the case of Ti-bearing Al-killed steels than in those without Ti.

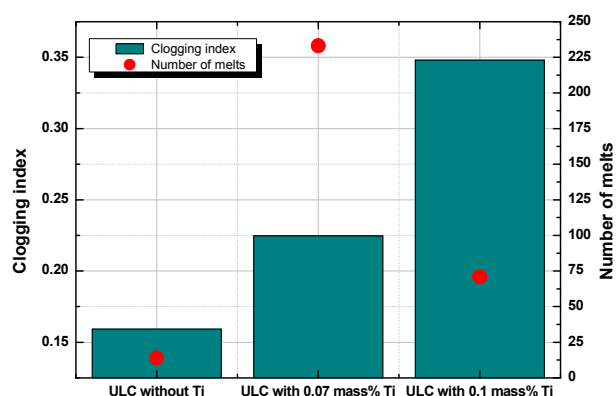


Figure 2: Influence of Ti content on the clogging behavior of ULC steels

As a matter of fact, the influence of Ti on the nozzle clogging phenomenon has been thoroughly investigated [13, 15 - 19] and several theories have been put forward:

According to Kawashima *et al.* [20], the exacerbated clogging experienced during the casting of Fe-Al-Ti alloys is a combined effect of: (a) the Ti-induced increase of wettability between the nozzle refractory and molten steel resulting in an acceleration of the SiO₂ reduction in the refractory by [Al] and a change of nozzle surface quality; (b) the decrease of the oxygen activity in the steel melt causing the decomposition of Al₂O₃ particles and thereby increasing the number of finer inclusions.

Kimura [21] postulated that the reaction between the SEN refractory and alloyed Ti favours the adhesion of Al₂O₃ inclusions to the nozzle wall. Recently, Cui *et al.* [18] showed the existence in clogging deposits of FeO·TiO₂ phases which hold those deposits together firmly enough to lead to the inferior castability of Ti-bearing ULC steels.

The formation of Al-Ti-O inclusions has been given as one of the major reasons for the severity of SEN clogging during the casting of Ti-bearing Al-killed steels [13, 15 - 19]. Ruby-Meyer *et al.* [22] showed that Ti exists in the form of a binary TiO_x-Al₂O₃ phase in the inclusions observed in Ti-bearing Al-killed low carbon steels. Those TiO_x-Al₂O₃ inclusions are reported to be wetted more easily by the liquid steel compared to the pure Al₂O₃ inclusions [23]. As a result, the separation of TiO_x-Al₂O₃ inclusions at the steel/slag interface is unlikely. Basu *et al.* [17] laid particular emphasis on the existence of Al-Ti-O inclusions covering Al₂O₃ core oxides. Those complex oxides are also wetted by liquid steel.

In a work by Matsuura *et al.* [15], the evolution of non-metallic inclusions (NMIs) as a result of Al and Ti additions to molten Fe was investigated. It was asserted that when Al₂O₃ is thermodynamically stable, adding Ti has the effect of temporally modifying the inclusions morphologically and chemically as a result of local super-saturation. The morphology of Al₂O₃ inclusions would then change from spherical to polygonal shapes, which could be the cause of more SEN clogging. Wang *et al.* [24] investigated the effect of gradual increase of Ti additions on the inclusion evolution after Al deoxidation. They found out that the Ti/Al ratio is a controlling factor for the inclusion shape change and that a critical value exists between 1/4 and 1/2, which promotes the morphology to be dominated by irregularly shaped inclusions after Ti addition.

Despite the considerable number of fundamental and applied research studies carried out on this topic, the clogging mechanisms have not yet been explicitly explained; and most notably there is no fundamental answer about the relationship between Ti alloying and clogging. The present work addresses this issue.

Therefore, the goal of this study is to characterise the SEN deposits that are typically encountered during the casting of Ti-bearing steels at the continuous casting machine No. 3 operated by voestalpine Stahl in Linz, and relate them to the occurrence of nozzle clogging. P was included in the study, as operational experience shows that the addition of that element to Ti-bearing steels tends to exacerbate the problem of nozzle clogging during the continuous casting process. In addition to the investigations performed on plant samples, laboratory studies were also carried out in order to shed light on the role played by additions of Ti and P on the wetting properties in the Fe-based alloy/Al₂O₃ system. The ultimate objective of those investigations was to determine the relationship between the wetting characteristics and the clogging behaviour of Al₂O₃-based refractories during the casting of steels containing Ti and P.

2 Experimental Methods

2.1 Nozzle sampling and characterisation of SEN deposits

In order to identify the root cause of clogging in Ti-bearing ULC steels, an analysis of the clog material is the first step. For that purpose, several nozzles were collected after the sequences had finished. Those nozzles were submitted to the following investigating methods:

- The morphologies and compositions of SEN deposits were analysed using an SEM equipped with an energy dispersive spectroscopy (EDS) system.
- To study the influence of Ti and P on the inclusion behaviour in ULC steel grades, a detailed characterisation of the various NMI types was carried out with help of an automated SEM [25] and optical emission spectrometry with pulse discrimination analysis (OES-PDA).

With help of OES-PDA, the size of inclusions can be estimated [26]. The optical spark emission spectroscopy is used for bulk analysis of steel samples during steel production. Each measurement of OES consists of some thousand single sparks, with which the concentration of all elements of main interest are determined. The technical modification of pulse discrimination analysis (PDA) makes it possible to gain the information with which one can evaluate the concentration of the solved elements in the steel as well as the element concentrations in the non-metallic inclusions. With new mathematical algorithms, it is possible to compute different inclusion parameters. First, one can calculate the

amount of various elements within NMIs in mass %. Second, the number of detected inclusions can be determined. Finally, the size index of NMIs for a specific element within the sample is calculated as the ratio between the amount of that element and the total number of NMIs.

2.2 Laboratory studies

The laboratory studies consisted in the determination of the influence of Ti and P contents on the wetting behaviour in the binary and ternary systems: Fe-Ti(P)/Al₂O₃ and Fe-Ti-P/Al₂O₃, respectively.

Materials

The master alloys for wetting tests were prepared using a novel method combining vacuum induction melting and air induction melting with a CaO-SiO₂-Al₂O₃ protective slag, as well as a sampling performed under inert gas atmosphere [27]. The chemical composition of the Fe alloys was in the following range for the Fe-Ti series:

- [C]: 0.02 to 0.03 mass%
- [S]: 0.002 to 0.005 mass%
- [Ti]: 0.003 to 0.175 mass%
- O_{tot}: 0.0025 to 0.0080 mass%.

For the Fe-P series, a similar composition was used, except for Ti which was replaced by P in the range between 0.0030 and 0.105 mass%.

To avoid the influence of surface roughness, high purity alumina substrates (99.98 mass % Al₂O₃, R_a = 0.2 μm) were used throughout the experiments.

Experimental set-up and procedure

The sessile drop technique was used in the present study to measure the wetting angles of molten Fe-Ti, Fe-P and Fe-Ti-P alloys on solid Al₂O₃ substrates as a function of the steel chemistry at temperatures ranging from 1550 to 1620°C. The experiments were conducted in a horizontal tube furnace (**Figure 3**) with a linear heating process (rate: 15°C/min). A holding time of 10 min at 1620°C was followed by cooling down at a rate of 10°C/min.

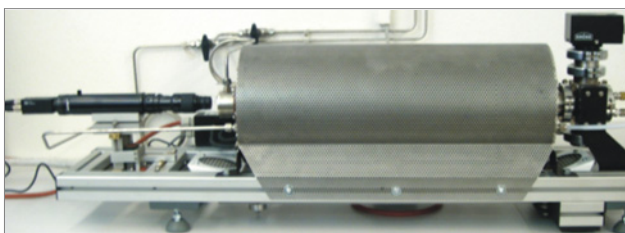


Figure 3: Drop Shape Analysis apparatus at the Chair of Metallurav

Once the sample was melted, the measurements of the contact angle as a function of temperature and time started. They consisted in a continuous monitoring of the shape of the sessile drop by a digital video camera connected to a computer, enabling automatic image analysis using a commercial software. The characteristic dimensions of the droplet (contact angle θ , drop base radius R and height H) were extracted with an accuracy of $\pm 2^\circ$ for θ and $\pm 2\%$ for R and H.

Microscopic analysis of the interface

At the end of the wetting experiments, the samples were taken out of the furnace and the interfacial region was analysed microscopically in order to obtain information on the nature of interaction between the substrate and the liquid melt, and the possible formation of reaction products. The chemistry, morphology and microstructure of both sides (metal and substrate) of the interface were determined by means of SEM-EDS.

3 Results

3.1 SEN clogging deposits characterisation by means of SEM-EDS analysis

The investigation of SEN clogging deposition material from 5 casting sequences for ULC steels shows that the deposits consist of small-sized particles (< 5 μm) with different shapes, predominantly dendritic. It is worth pointing out that those small, friable particles were loosely hold, and could be easily removed by the touch of fingers, as already noted by Dawson [3]. **Figure 4** shows the morphology of typical clogging deposition materials from two different locations.

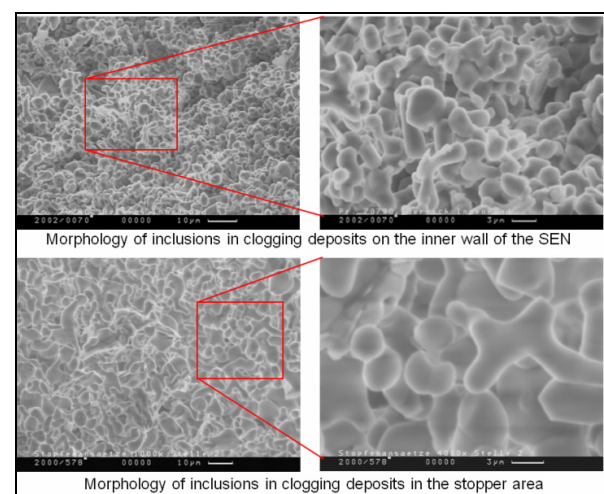


Figure 4: SEN images showing the morphology of clogging deposits

For the chemical analysis of SEN clogging deposits, all five samples were selected and SEM/EDS was first applied to an area equal to $22 \times 33 \mu\text{m}^2$. The buildup material consists of between 87 and 98% Al_2O_3 , 0.58 and 3.58% TiO_2 (balance: MgO, Fe and FeO) in the case of Ti- and Ti-P-ULC steel grades and solely Al_2O_3 in case of P-bearing ULC steels. The actual composition of the clogging deposits is given in **Table 1**.

Sample No.	Steel analysis, mass%			Clogging deposition analysis, mass%				
	Ti	P	Ti/Al	Al_2O_3	TiO_2	MgO	Fe	Ti/Al
1	0.067	0.008	1.9	91	2.3	1	5.34	0.028
2	0.024	0.049	-	98	0.58	0.9	0.4	-
3	0.002	0.079	-	100	-	-	-	-
4	0.071	0.005	2	93	2.53	0.87	3.16	0.031
5	0.054	0.007	1.4	87	3.58	1.05	8	0.047

Table 1: Chemical analysis of steel samples and SEN clogging deposits

3.2 Inclusion characterisation by means of an automated SEM-EDS analysis

To determine the inclusion composition in the steel bulk, samples from four different ULC steel grades with variable Ti and Al contents were taken from the tundish and analysed by means of an automated SEM-EDS. The chemical composition of the steel samples was as follows:

- [C]: < 0.0033 mass%
- [Si]: < 0.05 mass%
- [Mn]: 0.1 to 0.6 mass%
- [Al]: 0.035 to 0.043 mass%.

For the analytical study, a 100 mm^2 steel surface area was metallographically prepared and for each steel sample, 600 to 1000 particles were characterised at a $600\times$ magnification. The inclusion types found were mainly pure Al_2O_3 or Al-Ti-O complex oxides. No pure TiO_2 particles were detected. The automated SEM analysis results are presented in **Figure 5**. It is seen that with increasing Ti/Al ratio in the steel sample, the composition ratio of Ti/Al for the inclusions increases as well. As the Al content in these inclusions dominates, the resulting Ti/Al ratio is very low.

The comparison between the Ti/Al ratio of the clogging deposits and that of inclusions in the steel sample shows approximately similar values. This result indicates that the clogging buildup material presumably stems from the inclusions present in the liquid steel.

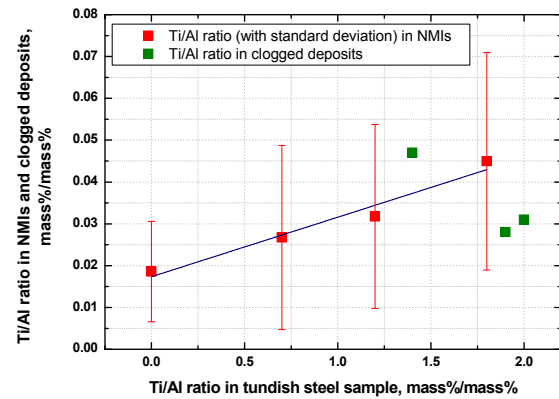


Figure 5: Influence of the Ti/Al ratio in the steel sample on the Ti/Al-ratio in micro-inclusions

3.3 Influence of the Ti content on the size of Al_2O_3 inclusions

The size of alumina inclusions was determined by means of two methods: automated SEM/EDS and OES-PDA. Using the automated SEM on metallographically prepared steel specimen, it was seen that the average inclusion size decreases with increasing Ti/Al ratio in the steel sample. The average inclusion diameter of the alumina particles was found to vary between 2.1 and 3.1 micrometers (**Figure 6**).

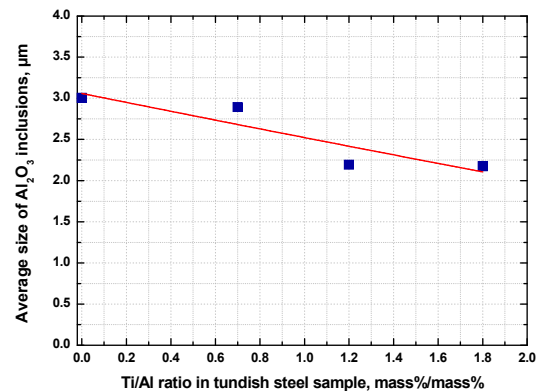


Figure 6: Variation of inclusion size as a function of the Ti/Al ratio in the steel sample

Next to the analysis with the automated SEM, more than 5000 melts from the ULC steel grade with different Ti contents were investigated by OES-PDA. In this case, the Al_2O_3 size index was measured. The analysis results presented in **Figure 7** show that the size of Al_2O_3 inclusions decreases with higher Ti contents in the melt. This result is consistent with the outcome of the SEM measurements.

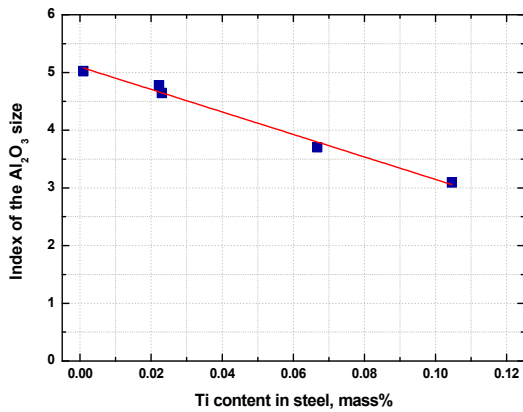


Figure 7: Influence of the Ti content in the steel on the size of alumina inclusions

3.4 Wetting Measurements

The results of the wetting experiments in the Fe-Ti/Al₂O₃ system are presented in **Figure 8**. It is seen that the wetting angle decreases greatly with increasing Ti content, most notably in the low concentration range. This is in good agreement with the results of works by Kishimoto [28] and Ueda et al. [29], but is not in accord with investigations by Zhong et al. [30] who found the effect of Ti on the wettability of steels to be weak at 1575°C and 1600°C and even negligible at 1550°C. It is worth mentioning that the situation, where Ti does not affect the wettability only occurs in the case of a non-reactive system [8, 20].

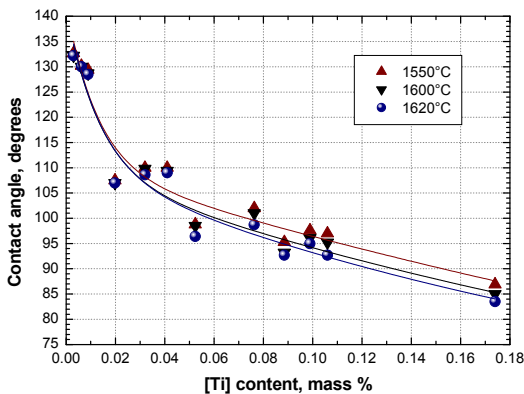


Figure 8: Effect of [Ti] content on the contact angle between Fe-Ti alloys and Al₂O₃ substrates as a function of temperature

Wetting angles measured in the Fe-P/Al₂O₃ system showed a marked decrease with increasing [P] concentration in the steel melt, **Figure 9**. However, the improvement of wettability was moderate as compared to that observed in the Fe-Ti series. Additional alloying to [P] contents above 0.10 mass% did not contribute to any further decrease of the

contact angle which remained above 90° in the investigated concentration range. As for the temperature influence on the wetting behaviour, it was found to be practically constant.

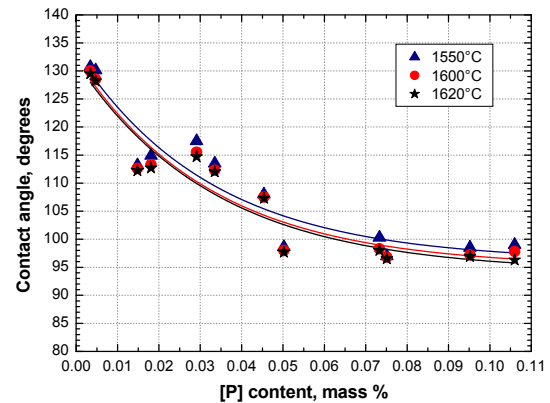


Figure 9: Effect of [P] content on the contact angle between Fe alloys and Al₂O₃ substrates as a function of temperature

Finally, the combined effect of Ti and P on the wetting behaviour in steel melts was found not to be additive, but at best partially synergetic. The curves in **Figure 10** show that at low [P] contents in the Fe alloy, the θ values decrease exponentially with increasing [Ti] content irrespective of the [P] concentration. At high P contents, however, the wettability depends largely on the [P] concentration.

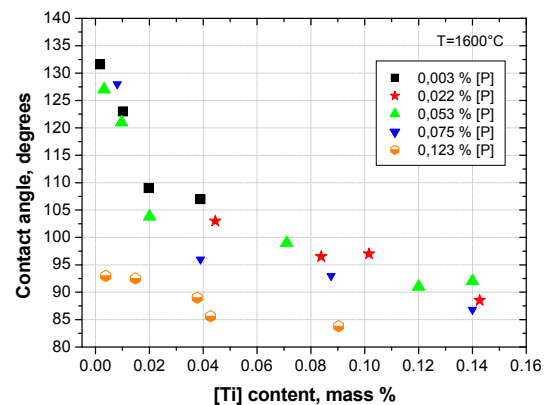


Figure 10: Combined effect of [Ti] and [P] contents on the wetting behaviour in the Fe alloys/Al₂O₃ system at 1600°C

3.5 Interfacial characterisation after wetting tests

After the wetting experiments, the alumina surface under the droplet was completely covered with the reaction product layer, **Figure 11**. Nevertheless, the solidified droplet detached easily from the substrate.

This implies that the formed layer is not wetted by liquid steel. An SEM examination of the contact surfaces revealed that after experiments on Fe-Ti alloys with Ti contents < 0.1 mass% and low [O] contents, the reaction layer between the droplet and the substrate was rather very thin and consisted only of FeAl_2O_4 , while in the case of the experiments under high [Ti] contents this layer was thicker and rich in Al, O, Fe and Ti. In the latter case, the Fe-Ti droplet adhered firmly to the underlying substrate, which is an indication of an improvement in the melt wetting behaviour.

The SEM analysis of the P samples after the wetting experiments showed that, unlike in the case of Ti, there was no hercynite reaction layer between the droplet and the substrate.

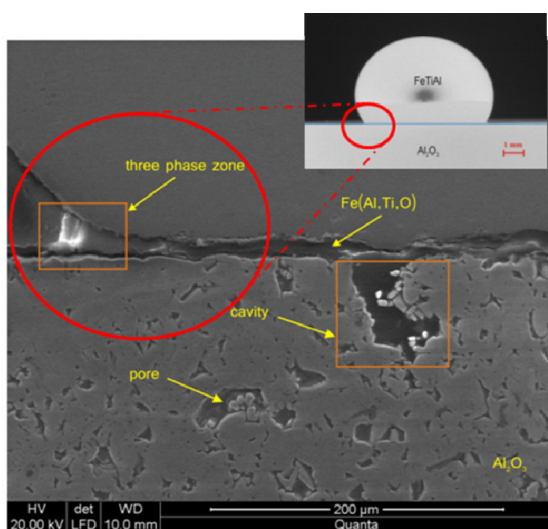


Figure 11: SEM image of a cross-section of the interfacial zone after a wetting experiment on a sample with 60 ppm O_{tot} and 65 ppm [Ti] showing the formation of a relatively thick interfacial layer composed of complex oxides. The spreading melt penetrated and filled the surface cavity, which means that the intrinsic wetting angle $\theta < 90^\circ$, i.e. the Al_2O_3 substrate is wetted by the Fe-Ti alloy.

4 Discussion

4.1 Morphology of clogging deposits

In order to understand the clogging mechanisms, it is important to clarify two fundamental points:

- Why do clogging buildups mainly consist of small particles?
- How is it possible for those loosely bound and friable particles to withstand the force of steel

flow [3] and not to be flushed away from the SEN wall?

In a simulation of the behaviour of solid inclusions, Mukai and Zeze [31] showed that the attachment probability between inclusions and SEN wall depends on the inclusion size. Due to a lift force (so-called *Magnus* force) [32], inclusions larger than 50 μm are not entrapped, but the probability for smaller inclusions ($< 20 \mu\text{m}$) to get entrapped lies above 30%. As for Long *et al.* [33], they developed a kinetic model to study the entrapment of inclusions in the molten steel flowing through a SEN during the continuous casting process. They concluded that inclusions with a diameter larger than 100 μm cannot get entrapped by the nozzle wall, and the entrapment probability increases significantly with a decreasing inclusion size for inclusions smaller than 15 μm .

In his work [5], Singh proposed an explanation to the question in (b) by suggesting the existence of a thin boundary layer along the SEN wall within which the flow velocity increases from 0 m/s at the wall to free stream values at some distance from the wall. If the Al_2O_3 particles pass through that boundary layer and attach to the wall, they have no tendency to move because the flow velocity is almost zero. Dawson [3] supplemented Singh's boundary theory by introducing his separation theory to account for the forces acting in the traverse direction and which could cause the inclusion to contact the SEN wall. In a series of water modelling and steel casting experiments, it was confirmed that SEN clogging is caused by the existence of a separated zone with a highly turbulent flow. Moreover, the frequent flow reversals and stalls prevailing in that zone allow eddies to carry inclusions directly to the SEN wall. The separation theory helps to understand why the loose particles do not get washed away by steel flowing at velocities in excess of 3 m/s [3].

4.2 Chemical analysis of clogging deposits and inclusions in steel samples

In the production of IF ULC steels, Ti is added in the ladle a few minutes after Al deoxidation. Normally, the Al/Ti ratio is such that Al_2O_3 is the thermodynamically stable phase. Practically, additions to liquid steel of Ti with a content in the range of 0.06 – 0.07 mass% should not induce a chemical reaction between Al_2O_3 and Ti. However, Ti is a surface active element and its content on the surface of Al_2O_3 particles is expected to be higher than in the bulk of the melt. That local increase of the Ti content in the vicinity of alumina inclusions induces a chemical reaction between Al_2O_3 and Ti. The existence of Ti in the clogging deposition material and in the inclusions

present in the steel samples confirms the occurrence of that chemical reaction.

SEN clogging deposits encountered in Ti-bearing ULC steels contain minutes of Ti, but they consist almost completely of Al_2O_3 (87 – 98 mass%). Ti is also found in clogged SENs during the casting of P-Ti-ULC steels, whereas Al_2O_3 is the only constituent of clogging deposits for P-bearing ULC steels.

4.3 Influence of Ti on inclusion size

An investigation conducted at voestalpine to follow the change of total oxygen (O_{tot}) in the liquid steel after Al-deoxidation showed that the amount of O_{tot} decreased from 350 to 100 ppm in 3 min and from 100 to 30 ppm in 4 min during the RH degassing process [34]. In about 7 min after deoxidation, the FeTi addition is carried out. Thereafter, no further decrease of O_{tot} is observed. The rapid drop of O_{tot} is caused by the high turbulence which boosts the coalescence of Al_2O_3 inclusions and the formation of large clusters. The reasons for the cessation of the change in O_{tot} could be as follows:

- Due to the addition of FeTi to the melt, the agglomeration process of Al_2O_3 will be slowed down; consequently the inclusions size remains small.
- The removal rate of Al_2O_3 inclusions from the steel melt is balanced by the reoxidation.

According to Olette [35], the agglomeration of NMIs is influenced by the contact angle between inclusion and liquid steel. A small contact angle means a good wettability between steel and inclusion, and this hinders the agglomeration of NMIs. The agglomeration behaviour of several types of inclusions in liquid steel has been investigated using a laser scanning confocal microscope [36]. While alumina inclusions tended to agglomerate and grow very quickly, none of the other types of inclusions, such as spinel and calcium aluminate was observed to agglomerate. This implies that the interfacial tension between solid calcium alumina or spinel inclusions and liquid steel is lower than that between alumina and steel. Those calcium aluminates and spinels may behave similarly to the Ti-bearing inclusions covering Al_2O_3 core oxides which were found by Basu *et al.* [17] and which were wetted by liquid steel, because of the low interfacial tension between both phases. As Ti decreases the contact angle (**Figure 8**) and in further consequence the interfacial tension between Fe and Al_2O_3 , the alumina size remains small with higher Ti contents.

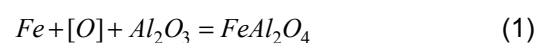
As for the severe clogging experienced during the casting of ULC steels containing P, the most likely

reason could be, as observed by Kaushik *et al.* [18], the formation of smaller alumina inclusions that are retained in the liquid steel and contribute towards the increased deposition. The analytical study of industrial clogging materials could not, however, corroborate the findings of Kaushik *et al.*: the effect of P on the inclusion size was found to be rather negligible.

4.4 Wetting experiments

Depending on the reactivity and stability of the solid substrate in contact with the spreading liquid metal, two different classes of systems are distinguished, namely: non-reactive and reactive. In a non-reactive system, the nature of the ceramic substrate is not significantly modified by its contact with a metal melt. The wettability is only the result of chemical bonds, which are achieved by the mutual saturation of the free valences of the contacting surfaces and acting *van der Waals* forces [37]. Therefore, the interaction of liquid metal with the ceramic does not lead to the formation of new phases. In reactive systems, however, wetting, chemical reactions, and solute segregation are interactively coupled. In this case, the liquid metal is not in direct contact with the initial unreacted substrate, but with the new compound formed at the metal/ceramic interface due to the chemical reaction accompanying the wetting process [37]. Generally, a change in the wetting characteristics of the system Fe alloy/ Al_2O_3 , which is a reactive one [37], can be brought about by one or a combination of the following factors [8, 37, 38]: Adsorption or segregation of surface active solutes at interfaces, and interfacial reactions resulting in the formation of a new compound which is more wettable than the original substrate.

As observed during the measurements in the Fe-Ti/ Al_2O_3 system, droplets of Fe alloys without Ti did not wet alumina, the measured contact angles being greater than 130° . However, additions of up to 0.10 mass% Ti led to a remarkable decrease in the steady contact angle to about 90° , and at [Ti] contents greater than 0.15 mass% the Fe alloys were found to become wetting (i.e., $\theta < 90^\circ$). The non-wetting behaviour observed at very low [Ti] contents is a consequence of the formation at the Fe-Ti/ Al_2O_3 interface of an oxide layer. For the oxygen contents expected in the Fe drop, the stable interfacial phase will be hercynite ($FeAl_2O_4$) which is formed according to the reaction [39]:

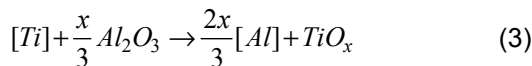


The Gibbs free energy of formation for above reaction is given by:

$$\Delta G^0 = -328.348 + 82.044 \cdot T \quad [J \cdot mole^{-1}] \quad (2)$$

At steelmaking temperatures, $\Delta G^0 < 0$ and, therefore, reaction (1) proceeds spontaneously.

In the metallurgical practice, the addition of Ti to a steel melt in contact with an Al_2O_3 -based refractory results in reactions involving the dissolution of Al_2O_3 according to the following general equation [22]:



Reaction (3), which is the cornerstone of the so-called *Ti-induced reactive wetting*, results in the formation of various Ti-bearing oxides, some of which are wetted by liquid Fe and in the enrichment of the melt with the interface active Al. In both cases, it comes to a considerable improvement of the wetting behaviour of the metal/refractory system.

Thus, at low [Ti] concentrations, reactivity involves a limited dissolution of Al into the Fe alloy, whereas at high [Ti] contents, Ti reacts with Al_2O_3 to form wettable TiO_x layers of the order of some micrometers in thickness at the interface. The change in the type of alloy-substrate interface, from Fe-Ti/ Al_2O_3 to Fe-Ti/ TiO_x , leads to a pronounced change in wetting (from wetting angles higher than 130° to those in the range of $80 - 90^\circ$). The experimental results are in good agreement with the approach to reactive wetting proposed by Eustathopoulos *et al.* [37] according to which the final degree of wetting is only controlled by the nature of the interfacial reaction product.

The results of SEM analysis revealed that the Ti oxides segregated at the surface of the steel droplet as well as at the interface between the droplet and the Al_2O_3 substrate, thus causing dramatic decreases in the wetting angle. This suggests that these oxides are surface active with respect to Fe melts.

The current findings help to better understand the reasons of the frequent nozzle clogging experienced during the casting of Al-killed Ti-alloyed steels. Accordingly, under the condition where the reoxidation rate is controlled at a very low level, the effect of Ti additions to liquid steel is to increase the wetting of alumina by the steel melt, which in turn results in a better contact between the Al_2O_3 -based ceramic surface and the liquid steel, and therefore to

a decreased interfacial resistance to heat transfer. This leads to increased cooling rates at the steel-SEN interface, and subsequently in the occurrence of the *thermal clogging* manifested by freezing of steel at the melt-refractory interface. Furthermore, the Ti-induced wetting between the liquid steel and Al_2O_3 inclusions hinders the agglomeration of those inclusions and hence, small particles are retained in the melt. These observations are consistent with the results of other researchers [13, 17, 29].

In the case of Fe-P samples, it was found that the wetting angles exhibited a marked decrease with increasing [P] contents in the melt composition, but this improvement of wettability was moderate as compared to that observed in the Fe-Ti series. Additional alloying to [P] contents above 0.10 mass% did not contribute to any further decrease of the contact angle which remained above 90° in the investigated concentration range.

The improvement in the wetting behaviour of P-containing Fe alloys on alumina substrates can be explained by the adsorption effect of P at the melt surface. This finding is supported by the work of Xue *et al.* [40], in which P in liquid Fe was found to act as a surface active element and to segregate extensively on the surface of Fe alloys. Moreover, P is known to considerably enhance the oxygen activity in the Fe melt [41]. Thus, P additions to Fe-based melts do modify significantly the liquid-vapour surface tension. Following Young's equation [42]:

$$\gamma_{lv} \cdot \cos \theta = (\gamma_{sv} - \gamma_{sl}) \quad (4)$$

where γ_{ij} denotes the interfacial tension of the interface ij and l , v and s designate the liquid, gas and solid phase, respectively, an improvement in wetting can result either from a decrease of the values of γ_{sl} only or of both γ_{sl} and γ_{lv} .

During the experiments on Fe-Ti-P melts, it was found that the effect of Ti and P on the wetting behaviour is not additive. Ti, being the most surface active element, enriches itself at the interfaces and contributes, consequently, to a decrease of solid-liquid interfacial tension and/or the liquid-vapour surface tension of the system. As the experimental results showed, at least at high [P] contents (> 0.1 mass%) an increase in [Ti] content does not contribute significantly to wetting in spite of the precipitation of Ti at the interface. The positive effect of P on wetting is due to its role in enhancing the Ti activity and lowering the viscosity of the steel melt, thus increasing the wetting kinetics, and hence the wettability [37, 43].

5 Conclusions

In the present study, several methods have been used to investigate the clogging behaviour of ULC steels bearing Ti and P. The salient findings are as follows:

- The investigation of the clogging deposition material shows that it consists of small sized particles (diameter < 5 μm) with different shapes, mostly dendritic.
- During the casting of Ti-bearing ULC steels, SEN clogging deposits contain minutes of Ti, but they consist almost completely of Al_2O_3 (87 – 98 mass%). Ti is also found in clogged SENs during the casting of P-Ti-ULC steels, whereas Al_2O_3 is the only constituent of clogging deposits for P-alloyed ULC steels.
- The comparison between the Ti/Al ratio of clogging deposits and that of inclusions in the steel sample shows similar values. This result indicates that the SEN buildup originates primarily from deoxidation products.
- The size of Al_2O_3 inclusions decreases with a high Ti/Al ratio or higher Ti contents in the melt. This finding suggests that the small size of alumina in the liquid steel is the main reason for the increased proneness to clogging observed in Ti bearing ULC steels.
- The continuous decrease in the contact angle with Ti concentration as measured using the sessile drop method in the binary Fe-Ti alloys can be safely attributed to Ti adsorption at the steel/alumina interface. It is noticeable that more Ti additions lead to the formation at the interface of Ti-bearing oxides resulting in a further decrease in the contact angle.
- The observed improvement of wettability in the Fe-P/ Al_2O_3 system is due to the surface adsorption effect of P which contributes to a decrease in liquid steel surface tension.
- The effect of P on Ti-bearing steels consists mainly in enhancing the activity of Ti in the melt, thus giving rise to a reduction of the threshold Ti concentration needed to obtain a given level of wetting.
- The wetting improvement between alumina-based substrates and liquid steel containing Ti and P leads to a decrease of the potential for the removal of Al_2O_3 -rich inclusions from the melt.

Clearly, the present work has only been able to touch on some aspects of the complex topic of nozzle clogging during the continuous casting of steels. In order to gain a better understanding of the mechanisms and factors affecting that phenomenon, more extensive theoretical and experimental investigations are needed. Specifically, the agglomeration and separation behaviours of various oxides commonly found in liquid steel will be systematically examined by means of a newly acquired high-temperature laser scanning confocal microscope (HTLSCM) at the Montanuniversitaet Leoben.

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