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Examination of nozzle clogging in continuous casting

B. Harcsik[1], P. Tardy[2] and G. Karoly[1]

[1] *Institute of Metallurgy and Foundry Engineering, University of Miskolc, Hungary*
e-mail: harcsik.bela@uni-miskolc.hu
[2] *Association of the Hungarian Steel Industry*

Key words:
Continuous casting; inclusions; clogging; calcium treatment; aluminates

Abstract – Formation of deposits inside the submerged entry nozzles used in continuous casting of especially low-silicon Al-killed mild steels may often cause nozzle clogging and casting disorder. Technological experience has shown that the application of Ca-treatment before casting usually eliminates this phenomenon. In order to understand deposit formation and the way it can be avoided, we have carried out detailed mineralogical analyses of the deposits formed on the inner and outer surfaces of the nozzles by different techniques. Results obtained from deposits formed during the casting of only Al-killed and subsequently Ca-treated steels show that the results obtained from deposits formed during the casting of only Al-killed and subsequently Ca-treated steels show that the alumina inclusions carried to the wall of the nozzle form the matrix of the dangerous deposits. Application of Ca-treatment resulted in mostly liquid aluminates compounds and almost negligible deposit formation. The outer surface of the nozzles however showed similar deposit formation because of possible reoxidation of dissolved aluminium.

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The casting disorder caused by nozzle clogging has become a widely used term in steel production, although in a broader sense, deposit formation resulting from adhesion of solid inclusions [1–3] may occur on any parts of the casting equipment shown in Figure 1: in the ladle/tundish nozzle, on the slide-gate, in the submerged entry nozzle (SEN). This phenomenon has represented a technical problem for steel makers ever since continuous casting was introduced. If the problem is temporarily solved, either by increasing the inner size of the casting equipment parts or by giving oxygen cleaning to the ladle or to the tundish, the product quality may be adversely affected.

Nozzle clogging primarily occurs in the production of steels where non-metallic inclusions with a higher melting temperature than that of the steel (1530–1570 °C) are formed (e.g. Al_2O_3, CaS) [4]. In Hungary, nozzle clogging can primarily be observed in the casting of aluminium-killed, low-silicon mild steel grades, which is a widely produced steel grade. The steel grade (RRSt 13, St24, etc.) is mostly used for cold rolling, the main requirement for which is enhanced resistance to ageing. These steels have accounted for the major part of the product range of ISD Dunaferr for several decades.

In order to ensure resistance to ageing, nitrogen – responsible for this phenomenon – is bound in the form of AlN, therefore, the specification requires that the Al content should be between 0.020 and 0.060% (200–600 ppm). Due to their small amount, Mn and Si do not take part in the deoxidation of these steels, therefore, aluminium simultaneously serves for setting the remaining dissolved oxygen content.

In practice, this can be implemented – with more or less success – in the course of a so called stepwise deoxidation process, which lasts from the tapping to the beginning of casting. How successful it is, depends on the given conditions and the technological discipline. In the first phase, that is during tapping, an efficient pre-deoxidation process takes place by the addition of Al blocks, whereby a considerable part of the free and active oxygen reacts with Al and

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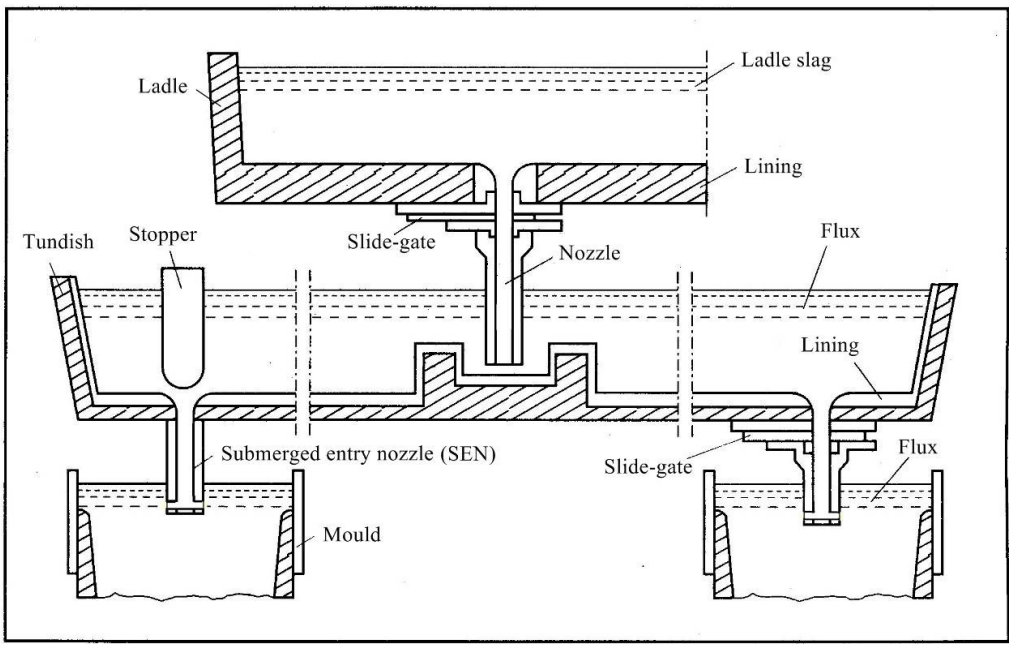


Fig. 1. The position of deposits causing nozzle clogging in continuous casting.

forms Al_2O_3. In the subsequent phase, the active oxygen concentration is reduced below 3–4 ppm ($3–4 \times 10^{-4}$%) by Al-wire addition, thus ensuring a preferable 0.020–0.060% dissolved Al concentration before casting with a relatively small loss. Naturally, it should also be ensured that all the Al_2O_3 inclusions formed in the stepwise deoxidation process could disappear from the melt to the greatest possible extent. Otherwise, nozzle clogging will adversely affect castability [5, 6].

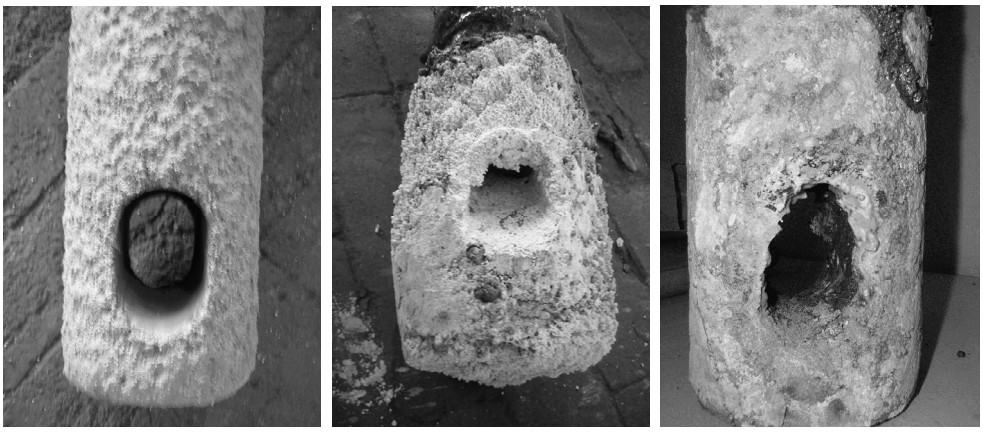
The relationship between the factors influencing the formation of Al_2O_3 and entrapment in the melt has been studied by several researchers, including experts working for Dunaferr as well, for the past decades. The Clean Steel conference series starting in the 1970s in Hungary, has been given so much attention, because the formation, controlling of inclusions, together with their adverse and beneficial effects in casting technology are still an open field of investigation nowadays, however, a lot of new information has been found recently. It has been proved that there are at least 30 factors influencing the formation of Al_2O_3 and in its entrapment in the melt [7, 8], but if we consider the sources of reaction, there are even more factors affecting the alumina deposit formation, which reduces castability through nozzle clogging. In order to reduce the incidence of casting disorder, through technological modification of steel production, the composition of the deposits causing nozzle clogging should be explored first by up-to-date instruments and methods and define the deposit structures whose formation should be prevented.

1 Examination of deposits occurring on the SEN

According to Rackers and Thomas [2], deposits formed during casting (causing clogging in an extreme case) can be classified into the following categories: deoxidation products, solidified steel, some complex exogenous or endogenous inclusions, or endogeneous inclusions formed as a result of a reoxidation process. Whichever the cause of deposit formation is, it decreases productivity (through the effect on casting speed and the extra time required for intervention), increases production costs (through the need for maintenance or replacements) and can significantly spoil quality.

In the scope of a recent research (commissioned by ISD Dunaferr Co.), a joint team of

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(a) (b) (c)

Fig. 2. Deposit occurring outside the submerged nozzle in producing low-silicon, Al-killed steel ((a) new, (b) used, no Ca added, (c) used, Ca treated).

experts from University of Miskolc and ISD Dunaferr Co. have been collaborating to find out the possible methods to eliminate nozzle clogging. Obviously, this program started with finding out the causes of deposits under the circumstances at ISD Dunaferr, and defining what deposits should be prevented by modifying the parameters of production technology. Although technical literature provides a lot of useful information on this phenomenon, we cannot avoid examining the structure of deposits formed at a definite place.

In order to examine the deposits, we have conducted two series of experiments simultaneously monitoring and checking a number of technological parameters [3]. In the two series of experiments comprising 54 and 46 heats respectively, we produced low-silicon, Al-killed steel, but while in the first series only Al-deoxidation took place, in the second series Ca-treatment was also applied following the Al-deoxidation. One sequence consisted of 4–6 heats of 140 tons each. The SEN is replaced after each sequence. It is evident that in the first series, the major part of endogenous inclusions, formed as a result of deoxidation, are Al_2O_3 particles, whereas in the latter, the inclusions can be made up of Ca-based aluminates. The question arises: what can be observed in the deposits leading to nozzle clogging after Al-deoxidation and what are the effects of Ca-treatment?

The analysis of the deposits is based on the examination of submerged nozzles removed at the end of the first three sequences in both series of experiments. The investigation has revealed that there is a greater extent of clogging detected when only Al-deoxidation takes place (Fig. 2), while in the case of Ca-treatment, the size of deposit outside the submerged nozzle is not significant although, identical submerged nozzles and flux were used in both series of experiments.

For the purpose of comparison, also the composition of the new SEN needed to be examined. The submerged nozzle (Vesuvius BK2416) was analysed by taking a sample from the main material and from the original inner coating (Fig. 3). The analysis was done with the Bruker D8 Advente type X-ray powder diffractometer (Tab. 1) at the Department of Mineralogy and Petrography, University of Miskolc, while in the case of flux (PROSIMET SINTHESIS D7S AT), the analysis of the supplier – shown in Table 2 – was accepted.

1.1 The examination of deposit surface

In order to determine the mineral structure and composition of the deposits on the SEN used in producing low-silicon steel treated only with Al, we took samples of the deposit detected inside the submerged nozzle as shown in Figure 4 and applied X-ray powder diffractometry.

The samples taken from the surface portions indicated in Figure 4 were examined

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Table 1. The mineral composition of the submerged nozzle used in the experiments.

Portion 1 (black)		Portion 2 (brown)	
ZrO_2	4.80%	ZrO_2	2.80%
Al_2O_3	41.90%	Al_2O_3	16.60%
$NaAl_{11}O_{17}$	0.30%	$NaAl_{11}O_{17}$	0.00%
C	41.40%	C	41.20%
SiC	0.00%	SiC	6.80%
SiO_2	10.60%	SiO_2	10.30%
Si	0.90%	Si	22.30%

Table 2. The composition of the flux used in the experiments.

C_{tot}	C_{free}	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	H_2O 120℃	Na_2O+K_2O	CaO/SiO_2
9.68	7.83	35.7	0.47	7.66	32.6	0.73	0.34	4.99	0.91

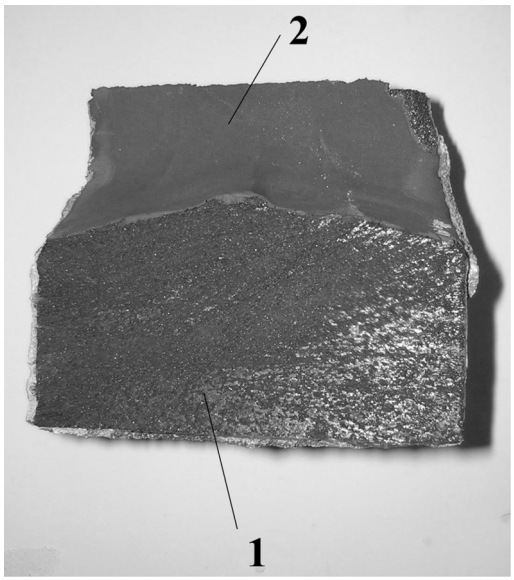


Fig. 3. The analysed portions of the new submerged nozzle (1 – black material of the submerged nozzle, 2 – brown inner coating).

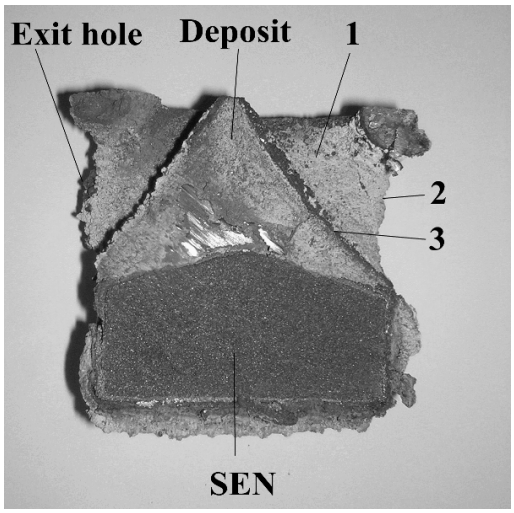


Fig. 4. Deposits in the cross-section of the submerged entry nozzle casting low-silicon, Al-killed steel (1 – hole surface, 2 – rim surface, 3 – deposit surface).

in the same way at the end of all three sequences, and similar compositions were found. The average values are listed in Table 3.

Data in Table 3 show that the inner surfaces of the submerged nozzles used for casting only Al-treated steels are typically covered by a layer consisting of alumina (~62–69%), Mg-Al oxide spinnel (16–22%), hematite type ferric-oxide (2–6%) and Ca-aluminate (5–11%) almost uniformly independent from the location of the surface portion within the SEN. The hematite type ferric-oxide comes from steel grains included in the porous structure oxidized when the nozzle is removed from the mould. The MgO may come from the applied refractory materials (ladle lining, tundish lining). Since Ca-treatment was not applied in this series of steel production, Ca-aluminate can be generated from the slag physically mixing with the steel due to over-intensive argon bubbling.

Hardly any deposit could be detected inside the submerged nozzles if the steels received Ca-treatment in the ladle prior to casting. Deposit samples could hardly be taken from any surface of the SEN. It can be accepted that the partial areas around the exit hole and the inner surface were quite similar in this case too. There were surface samples taken from three SEN nozzles from three different casting sequences for analysis (Tab. 4).

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Table 3. Average mineral compositions in samples taken from different surfaces of the SEN used in the production of only Al-treated steels.

Hole surface		Rim surface		Deposit surface	
Fe_2O_3	2.83%	Fe_2O_3	3.97%	Fe_2O_3	6.13%
Al_2O_3	64.33%	Al_2O_3	69.63%	Al_2O_3	61.77%
$NaAl_{11}O_{17}$	5.50%	$NaAl_{11}O_{17}$	0.60%	$NaAl_{11}O_{17}$	3.03%
$CaAl_4O_7$	1.13%	$CaAl_4O_7$	0.90%	$CaAl_4O_7$	5.07%
$CaO(Al_2O_3)_6$	4.57%	$CaO(Al_2O_3)_6$	8.33%	$CaO(Al_2O_3)_6$	5.93%
$(Mg_{0.527}Al_{0.473})$ $(Al_{1.758}Mg_{0.126})O_4$	21.60%	$(Mg_{0.462}Al_{0.538})$ $(Al_{1.764}Mg_{0.084})O_4$	16.63%	$(Mg_{0.527}Al_{0.473})$ $(Al_{1.758}Mg_{0.126})O_4$	18.07%

Table 4. Average mineral compositions in samples taken from the hole surfaces on the inside of three different submerged nozzles in the production of Ca-treated steel.

SEN No.1		SEN No.2		SEN No.3	
$CaO(Al_2O_3)_2$	12.10%	$CaO(Al_2O_3)_2$	20.30%	$CaO(Al_2O_3)_2$	36.50%
$CaOAl_2O_3$	52.30%	$CaOAl_2O_3$	42.00%	$CaOAl_2O_3$	34.30%
$CaFe(Si_2O_6)$	1.00%	$Ca_3Al_2Si_3O_{12}$	0.90%	$Ca_3Al_2Si_3O_{12}$	2.80%
$FeMn(SiO_4)$	1.30%	$CaO(Al_2O_3)_6$	10.90%	$CaMgAl_{10}O_{17}$	2.40%
$MgOAl_2O_3$	31.40%	$MgOAl_2O_3$	26.20%	$MgOAl_2O_3$	19.00%

Here we found mainly calcium aluminates. The amount of Mg-Al oxide spinnel was found higher, which may be simply attributed to the larger exit holes resulting from the lack of clogging, which may allow the influx of more slag on removing the SEN. The images of Figure 2 clearly show that the amount of deposit is fairly negligible here.

In order to get more information on the reasons of nozzle clogging, the inner structure of the deposit found in the region of the exit holes at the bottom of the SEN needs to be analysed. For this purpose, cross-sectional surfaces were examined by SEM and micro X-ray probe analysis allowing also phase determination.

1.2 The examination of deposit structure

In order to see the structure of the deposits shown in Figure 4, we cut the submerged nozzles – three of which were used in each series of castings – along their longitudinal axis, and created a polished surface (Fig. 5). A 1 mm wide strip of the polished surface was selected along the marked central radial line and at right angles to it for SEM examination. The corresponding micro-photos are jointly presented in Figure 6.

The composed image of Figure 6 shows the bottom wall of the nozzle on the far right end side. Each phase is represented by a different shade of grey. The SEM images are created by backscattered electrons sensitive to the atomic number, thus the phases containing different elements have different grey values. The colour differences were analysed in each case with an image analysis software at the Innovation Management, ISD Dunaferr Co. The observed phases, ranging from the darkest to the white, are noted in Table 5, and the typical components of the deposits found in the examined three used SEN samples are shown in Table 6.

Table 5. The detected phases in the deposit according to their grey values.

Grey value	Phases
black	cavities, synthetic resin
	alumina
	Ca-aluminates
	iron-silicate
	ferric-oxide (hematite)
white	steel

The three examined submerged nozzles used in the production of Ca-treated steel were also cut along their longitudinal axis. Although just a small amount of deposit was detected inside the used SEN (see Fig. 2c), a polished surface was made also in this case to produce SEM images (Fig. 7).

Due to the smaller extent of deposit formation after Ca treatment – compared to nozzles used with only Al-killed steels – we examined approximately two-thirds of

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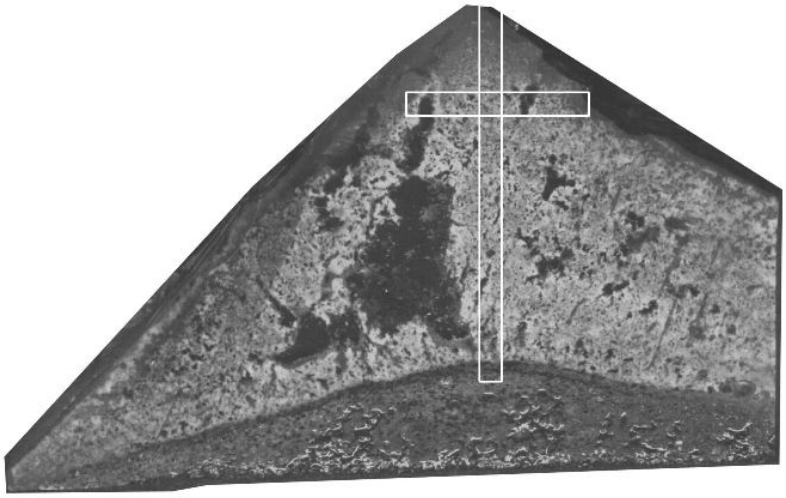


Fig. 5. Polished cross-sectional surface of the deposit found in the SEN after casting only Al treated steel, indicating the location of SEM images.

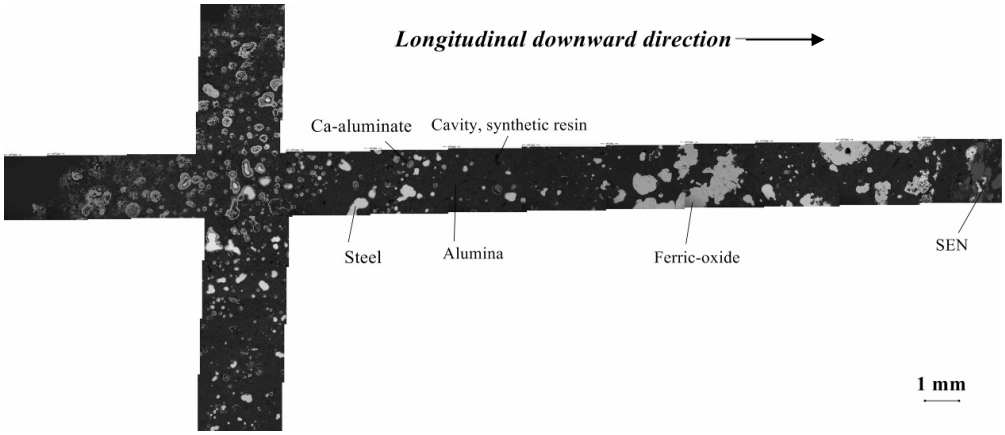


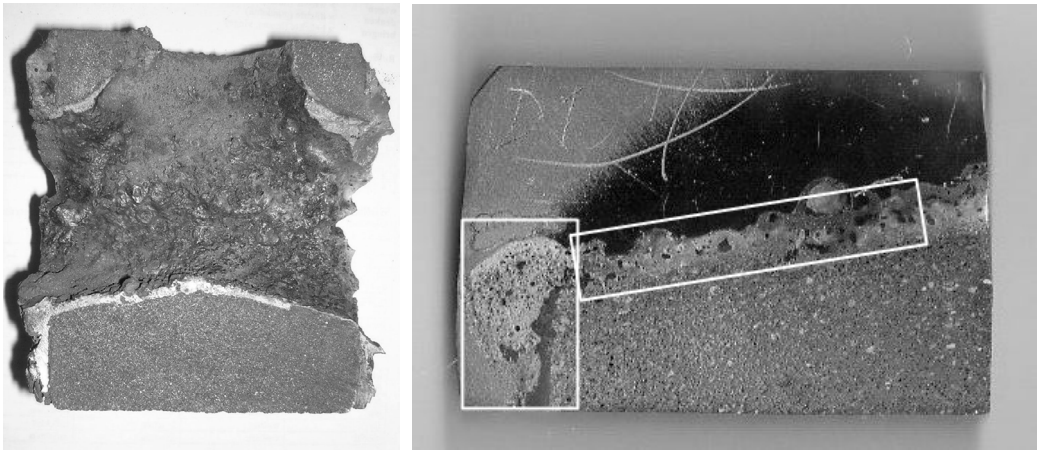
Fig. 6. SEM images of the cross-section made (longitudinally and at right angle to it) across the deposit in a SEN used for casting steel treated with only Al.

Table 6. The main components of deposits found in SEN samples used for casting low Si steels given only Al-treatment.

Origin of sample	Components, per cent			
	Al_2O_3	Ca-aluminate	Fe	Cavity
SEN No.1	84.56	9.54	9.77	0.23
SEN No.2	87.48	4.35	8.98	0.24
SEN No.3	81.50	9.88	13.35	0.67

the polished surface instead of analysing only a strip along a transverse line. This examination also found the phases ranging from the darkest to the white as summarised in Table 5. The white colour deposit seen in the backscattered electron images of Figure 8 is mainly composed of steel drops and hematite at the outside of the SEN exit hole. The approximate phase composition of the different components in the internal thin layer at the surface of the SEN was analysed during the testing by electron microscopy. According to Table 7, the grey colour base matrix contains vitreous calcium-aluminium silicates and calcium aluminates. The slight amount of

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(a) (b)

Fig. 7. Cross-section of the submerged entry nozzle after casting calcium treated low-silicon, Al-killed steel (a), polished surface (b) indicating the location of SEM image.

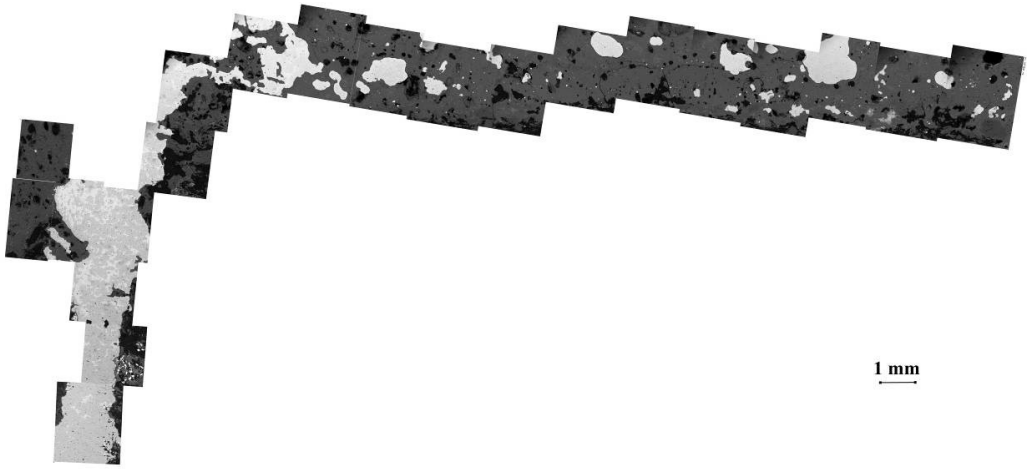


Fig. 8. SEM images of the cross-section in the deposit (along the inner surface of the bottom wall in the SEN used for casting steel given Ca treatment).

calcium-aluminate (mostly $CaO.6Al_2O_3$) found in the deposit corresponds to those compounds which are solid at the temperature of casting.

2 Discussion

The continuous casting of low-silicon, aluminium-killed steels features significant deposit formation particularly in the lower, narrow section of the submerged nozzle. The flow of the melt slows down, and carries inclusions to the wall, where various forms of solid alumina (Al_2O_3 type, or solid aluminates) tend to adhere to the inner lining of the submerged nozzle and grow during casting. On the outside wall of the SEN, deposits may also form depending on the cleanness of the continuously flowing melt around it.

The deposit formed in the production of low-silicon, only Al-killed steel features a base matrix of alumina, which – according to Table 6 – includes a slight amount (5–10%) of Ca-aluminates together with entrapped steel drops. A surprising result of the examinations is that Ca also appears in the deposit from the casting of steel where Ca-treatment had not been applied. The detailed analysis of the calcium aluminate phase shown in Figure 6 and Table 6 is given in Table 8.

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Table 7. Results of image analysis in steel produced with Ca-treatment.

Phases by colour	Average amount [%]	Main components [%]			
White	10.59	FeO: 94.49	MnO: 3.9	SiO_2:1.61	
Greyish white	19.58	FeO: 95.58	MnO: 4.33		
Medium grey	58.50	Al_2O_3: 39.65	CaO:35.63	SiO_2:21.03	MgO: 1.09
Dark grey	10.55	Al_2O_3: 78.35	CaO: 18.43		
Black	0.83	cavity			

Table 8. The composition of Ca- aluminate type inclusions found in SEN samples used for casting low Si steels given only Al-treatment.

Composition, %	SEN No.1	SEN No.2	SEN No.3
MgO	1.48	0.92	2.76
Al_2O_3	85.39	90.3	87.62
SiO_2	2.37	–	–
CaO	9.4	7.75	9.61
FeO	0.55	1.02	–
ZrO_2	0.8	–	–

According to Table 8 and Figure 9, the composition of the calcium aluminate found in the deposit from only Al treated heats corresponds to the $CaO.6Al_2O_3$ aluminate compound, which is solid at the temperature of casting. Obviously, its source is partly the flux, and the final slag physically mixing in the melt. The smallest droplets or particles of the CaO rich slag containing 4 ~ 7% FeO may react with the dissolved aluminium and alumina content of the melt, thus Ca-aluminates are produced. The calcium content of the deposit indicates that the extent of reoxidation – which is hard to measure – cannot be neglected even if air contact is eliminated. The entrapped slag having increased the active oxygen level in the melt causes further generation of alumina or solid aluminate inclusions.

The deposit formation in the production of steel given Ca-treatment is significantly smaller and virtually no accretion build-up was seen, as demonstrated in Figure 7. As a result of intensive Ca treatment, most of the aluminium used for killing steel must have formed liquid Ca-aluminates at the temperature of casting. Thus, serious Al_2O_3 deposition and the frequently observed clogging of the SEN in casting only Al-treated steels can be prevented. In order to avoid deposit formation at the temperature of steel casting, the optimum range of aluminate composition lies in the 40–60% Al_2O_3 range in the CaO- Al_2O_3 system shown in Figure 9.

It can also be seen from Table 7 that the relatively small amount of this deposit contains mainly vitreous aluminium-calcium silicates and oxidized steel drops. The latter comes from steel entrapped in the porous structure and it is oxidised as the SEN is removed from the bath. The former probably originates from the flux solidified in the tundish at the end of casting or from the slag formed in the mould.

Both in the case of steels treated only with aluminium and in the case of treatment with aluminium and calcium, high FeO concentration can be detected in the layer adhering to the outside of the nozzle around the exit hole (Tab. 7 and Fig. 8). This outer deposit formation is obviously due to slag accretion and reoxidation of entrapped liquid iron. At the outer surface, iron drops may act as adhesive material, but these deposits do not result in nozzle clogging. The alumina and aluminate inclusions – although scarce if Ca treatment is also included – can be found inside the nozzle and at the surface of the exit hole.

The importance of nozzle clogging and the effect of including Ca treatment in the ladle metallurgical procedure can be demonstrated by the interventions required to ensure the continuity of casting. Technological data collected at the ISD Dunaferr Ltd., Hungary point out that Ca treatment results in a definitely reduced frequency of casting disturbances. Table 9 shows the

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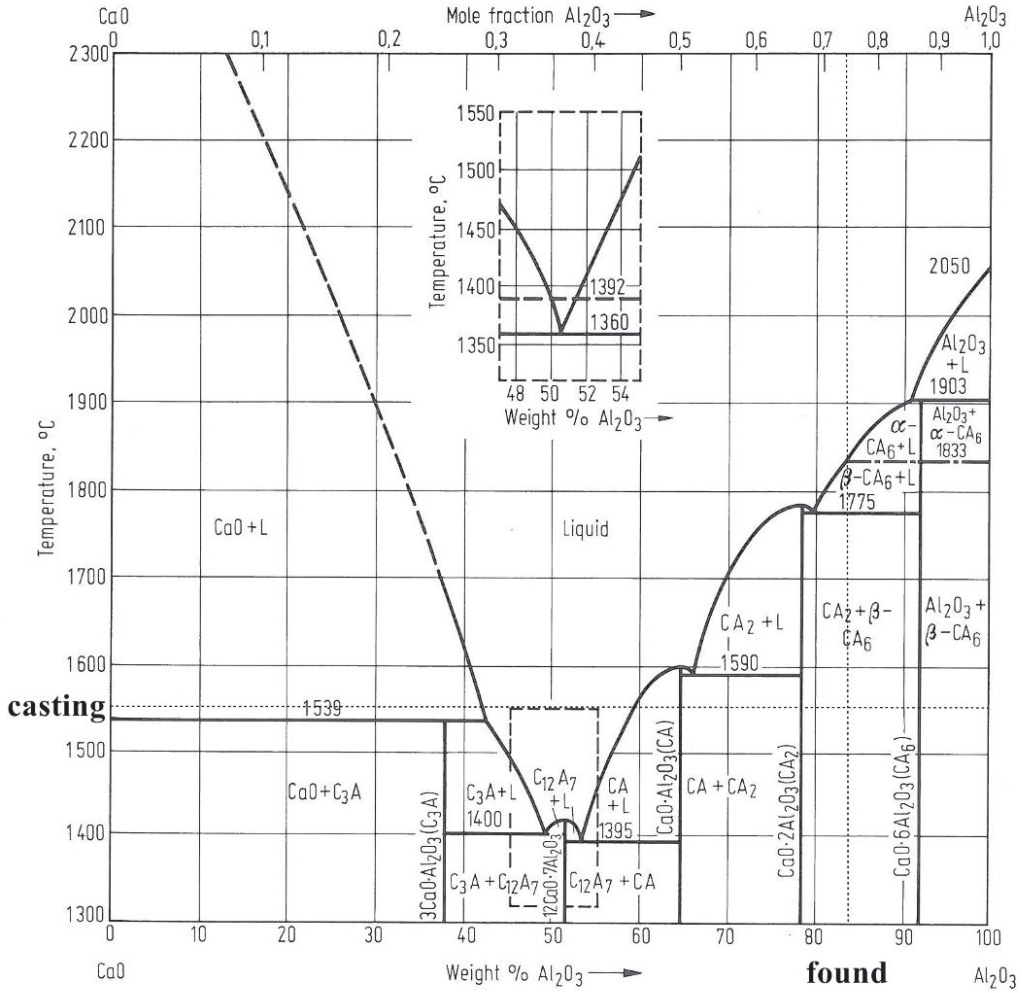


Fig. 9. The CaO-Al_2O_3 equilibrium phase diagram (temperature of casting and composition of calcium aluminate found in the deposit marked with dotted lines) [9].

Table 9. Occurrence of casting disorder and the frequency of technological interventions in cases of only Al-killed and Ca treated heats.

Interventions to eliminate casting disorder	Occurrence			
	Only Al killed heats (54 heats)		Al killed and Ca treated heats (46 heats)	
Stopper opening	3	5.56%	0	0
Oxygen cleaning of ladle nozzle	14	25.93%	2	4.35%
Oxygen cleaning of SEN	4	7.41%	1	2.17%
Total		38.9%		6.52%

different types of technological interventions applied to eliminate casting disorder.

Approximately 50 heats of only Al killed and Al+Ca treated steel were examined with regard to the tendency of nozzle clogging. The frequency of necessary technological interventions could be reduced by including the Ca treatment to one sixth compared to the cases where no Ca treatment was applied.

It has been confirmed that deposit formation – a certain degree clogging – is inevitable in conventional continuous casting of Al killed low silicon steel grades. Deposit

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formation can only be reduced to an acceptable minimum through refining technologies and tightening technological discipline or by increasing perfection, as long as the Σ oxygen content is above 10 ppm, and we can must take into account the possible occurrence of re-oxidation. Comparison of our technological findings to the results of analysing the SEN samples verified that clogging is caused by the deposition of solid inclusions and that their modification by Ca treatment may virtually eliminate this harmful phenomenon. Another way of avoiding this type of casting disorder may be the enhancement of removing inclusions by an optimised method of argon flushing. This aspect will be examined in our further investigations.

3 Conclusions

The findings of the deposit formation analysis show that excessive amounts of Al_2O_3 inclusions may result in the build-up of deposits at the exit holes of SEN used in continuous casting. There are limited possibilities of changing the flow conditions, so the most important way to prevent deposit formation is by preventing a larger amount of Al_2O_3 from getting inside the submerged nozzle through applying metallurgical methods and preventing reoxidation. The appearance of solid calcium aluminate in the deposit inside the SEN used in the casting of only Al killed steel indicates that the FeO-rich ladle slag can be mixed with steel before casting and reoxidation can occur causing Al_2O_3 formation and deposition in the nozzle. Argon flushing may be efficient, although it needs careful optimization. Vacuum treatment and induction stirring are other – although rather expensive – methods of reducing inclusion content. If sophisticated technology is not available and argon flushing cannot be applied reliably, Ca treatment may be the only way to avoid nozzle clogging during the casting of Al killed low silicon steels. If the given conditions do not prevent alumina inclusions from getting inside the submerged nozzle in large quantities, then lower melting calcium aluminate compounds should be formed through Ca-treatment, which do not result in nozzle clogging.

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