Study of the mould flux film between mould and steel shell.

P.O.Hooli
Outokumpu Polarit, Finland

Abstract

Samples of the mould flux film have been taken during tailout. Location of the samples has been even 40 cm below the meniscus.

Samples have been analysed with SEM/EDS microscopy.

We have observed, that the film structure concerning different slag phases is changing surprisingly from the meniscus area downward.

Results of these investigations are presented in this paper.

Outokumpu Polarit is casting stainless steel slabs about 600 kt annually.

1 Trials and methods used to examine the powder slag layer

1 .1 The sampling of the powder slag layer between mould and shell

In the finishing (tailout) procedure of the cast the steel plate is placed in to the tail of last slab to close the tail without any deslagging (shown schematically in figure 1). This is also possible to do without using any water, and in that case the powder slag layer remains on the walls of the mould and the unveiling powder slag layer is possible to draw up with the clamp. The form of the sample is shown schematically in figure 2. Layer can be up to 40 cm down from meniscus.

1 .2 Examination of the flux layer

Samples token with the clamp was set on the steel plate for cooling and to keep the pieces on their "original" places. When cooling, the original, quite big pieces where breaking up to smaller pieces. Pieces were marked for being identified later when making measurements and samples for microscopy.

Following measures and analyses has been made:

- measurement of thickness
- optical microscope
- SEM/EDS
- melting test in laboratory
- chemical analysis

When taking layer samples from mould, part of the layer remains on the mould wall, and this must be considered, when analysing layers.

1 .3 Tests with tracers

BaO and ZrO2 have been used as tracer elements in the powder. By using two different tracers there is possible to get more information with one trial.
As an example tracers are used as follows: there has been cast last 30 minutes with tracer powder or there has been cast last 45 - 10 minutes before the end of the cast with tracer 1 containing powder and last 10 minutes with tracer 2 containing powder.

Base levels of the tracers used in the powder were also analysed.

2 Results of the study of the powder slag layer

2 .1 Basic features of the sampled layer

Layer can consists of several sub layers, but there is two main sub layers (figure 3):

- a “real” layer, which has been there during the casting
- an extra sub layer formed during the finishing procedure i.e. this layer has not been there during casting and the composition of this layer is the same as the molten flux on the steel in the end of casting i.e. nearly the same as the nominal composition of the flux without carbon.

When sampling, part of the real layer remains on the mould wall, sometimes more, sometimes less. That is why the surface of the sampled layer, which has been against the mould, is not smooth as one could maybe expect. On the mould remaining layer looks white.

The features of the real layer depend on the distance from the meniscus. (See figure 3 and 4 A-H). Near the meniscus (up to 10 cm) it is thin (<0,1 mm), it’s fairly sound and there is not any bigger variation in the content of the elements. Farther off from meniscus (for example over 20 cm) it is thicker (up to 0,7 mm), there can be holes and it can be otherwise inhomogenous and surprising big variations in the contents of the elements. Biggest surprise was the Na and F containing layer against the mould.
The real layer is also thicker and more inhomogenous in the longer cast.

As a summary, the slag film can consist of 4 sub layers (Figure 5):

1. a layer formed during the tailout [1]
2. Thin layer on the shell side from the calcium rich layer in the slag film i.e. possibly the lubricating layer against shell [2]
3. a layer with high calcium content against liquid, lubricating layer [3]
4. a layer with high aluminium content (Al-rich layer) [4] and a layer with high Na and F (NaF-rich layer) contents as a first layer against the mould [4b]

Some features of the layers: Area number 1 is solidified during the tailout i.e. in not more than some minutes. Average composition is same as powder. Main phase is Ca,SiOx in the form of sticks or “dendrite arms”. Between those is Na, F, Al, etc. rich phase, probably this is latest solidified phase. Number 2 is thin layer with coarser structure compared with number 1, which indicates different solidification circumstances. In number 3 dominating phase is Ca,SiOx, and only small amounts of Na,F,Al, etc. In area number 4 Na,F-rich phase is dominating. In area 4b is among Na,F-rich phase some additional, isolated phases. Phase areas are partly circular.
In all areas, except 4b, there is possible to see more or less vertical orientation i.e. from mould side to shell side. The small, light particles are Zr-oxides. The big, roundish holes indicates probably gas generation (CO, Na?).
The compounds of the elements in the different slag layers are shown in table 1.

2 .2 Behaviour of the contents of the elements in the layer.

Point (area 0,1 x 0,1 mm) analyses were made through the layer with SEM/EDS analyser. An example is shown in figure 6. This sample is from the distance of 39 cm below the meniscus and after 5 hours casting (case H in figure 4). In this case the variation of the contents of the elements (compounds) is one of the biggest among the samples, but same principal phenomenon have found also in other samples.

On the mould side, there has found contents of 50 % as highest value of sodium (and rest is mainly F)! Note also the peculiar behaviour of Ca, Al, S. As it is shown in figure 7 the variation of the contents of the elements increases progressively downward from the meniscus.

2 .3 Surface of the powder slag layer ”in contact with mould”

In the figure 9 is shown surface pieces of originally one, bigger flux layer sample. On the surface it is possible to see areas with different colours and thus compositions. Some elements (compounds) are typical: Na, F and surprising high concentrations of Mn. When making analyses through the layer, it is possible to get different results near the mould wall side depending on which kind of place the transversal cut is done.

2 .4 Results from tracer tests

In figure 10 is shown an example of the result of a tracer test (ZrO tracer containing powder used last 30 minutes of the cast). In this figure is shown the thickness of the total layer and the thickness of the layer with very low tracer content (i.e. above the points Zr is high). It is possible to see, that the thickness of the layer not containing tracer is increasing downward from the meniscus. This could mean, that this layer has been there already 30 minutes before the end of casting, maybe anyhow moving.

A thin layer was sometimes (with smaller analysing points i.e. 0,05X0,05 mm) observed next to the calcium rich layer on the shell side (see figure 5). Its width is varied between about 0,05 - 0,15 mm. Concerning case shown in figure 4D, thin layer is located at the distance of 1,7 - 1,8 mm from mould side. In this layer Na, Al and Mn are little higher and Ca little lower. As it is shown in the figure 11, Ba content is nearly zero on the mould side of this thin layer. This indicates, that it is older than 15 minutes (BaO containing powder used last 15 minutes of the cast), in other words it has been solid at least 15 minutes and there has been the border between solid and liquid phases during casting. Also the solidified structure in this layer is different from the extra layer. Maybe this thin layer is the lubricating layer fluid during casting.

2 .5 ”The white layer” remaining on the mould the mould wall

In figure 8 is shown the structure and in table 2 the compositions of the “white layer” remaining mainly on the mould wall. This layer is reactive, as we could see, when spraying water on it: it was “burning” with flames. Explanation could be, that layer contains metallic sodium or potassium!

Carbon is an element, which can thermodynamically reduce sodiumoxide. The white layer contains significantly carbon, but the other parts not.

3 Discussion

When analysing sampled flux layers, we found some surprises. One of those was, that on the mould wall was a layer with high Na and F containing probably some metallic Na.

Main part of the powder slag layer sampled from the mould with our method is formed during the finishing procedure of the cast. There is anyhow possible to find a layer, which has been there during steady state period of the cast. In the distance of a few centimetres below the meniscus this layer is thin and changes in the composition through the layer are small. But the lower part the layer is thicker and there are big variations in the concentration of the elements with some porosity.
We could also find a layer, which probably has been the liquid, lubricating layer during the casting.

How are these layers formed during the casting? There is a Ca rich layer and on the mould side from this is Ca poor, Na rich layer (se fig.6). The solidified structure consist basically of two phases: Ca rich “dendrites” and between those is Ca poor (last solidified) areas. Possibly these Ca poor areas have been partly liquid during the casting and farther off from meniscus ferrostatic pressure causes, that liquid phase is pushed towards the mould and it is freezing against the mould.
Explanation of metallic Na needs reduction reaction. We found out, that in the Na rich layer is containing carbon, which maybe could reduce sodiumoxide.

These results can help us to consider the role of the different compounds in the casting powder. For example the roles of Na, Mn and S are bigger than one could assume from the contents in the powder. With the aid of this sampling method developed by Outokumpu Polarit we hope, that we can develop powders and get better control over the heat flux.

References:
1. Development of high speed casting in conventional CC stainless steel slab production, Draft Final Report, ECSC steel RTD programme.

Tables

Table 1. The compounds of the elements in the different slag layers.

Layer	CaO	SiO_2	Al_2O_3	Na_2O	NaF	K_2O
NaF-rich	13,91	10,1	0,8	12,7	34,6	4,7
Al-rich	28-32	32-37	11-22,5	-	11-16,5	-
Ca-rich	50-60	~32	1-6	-	1-6	-

Table 2. The composition of the different phases from photo 8 of “white layer”. (in w%).

	Ba	C	O	F	Na	Al	Si	K	Ca	Cr	Mn	Fe	Cl
1				47,7	52,3		0,2						
(2)		36,6	8,4	4,8	3,1								0,5
3	2,0	3,1	32,6	13,1	4,2	0,6	12,9	0,9	30,0	0,6	0,8	0,7	

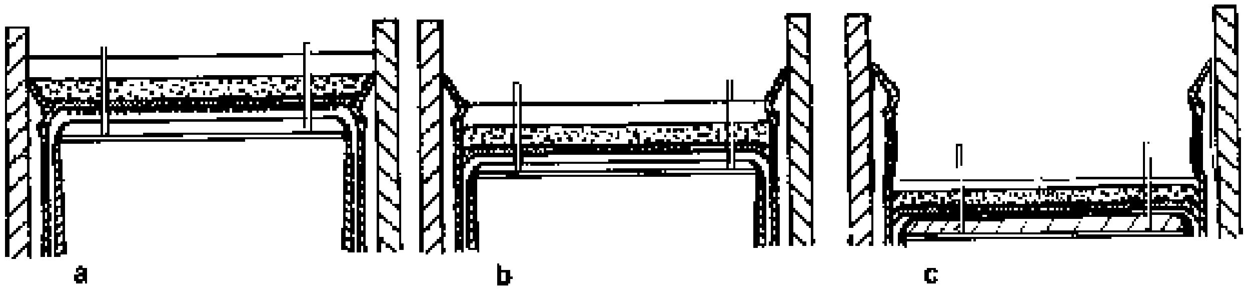


Figure 1. The method to close the tail of the last slab in the finishing procedure schematically a) steel plate is immersed in to the shell, b) shell is drawn down and c) powder slag layer remains on the walls of the mould.

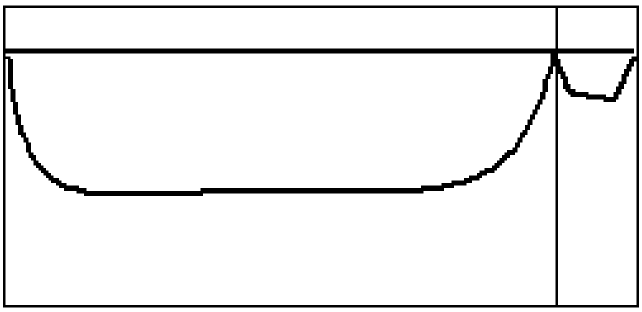


Figure 2. Form of the flux layer schematically on the wide and small faces of the mould. Sampled flux layer can be 40 cm down from meniscus.

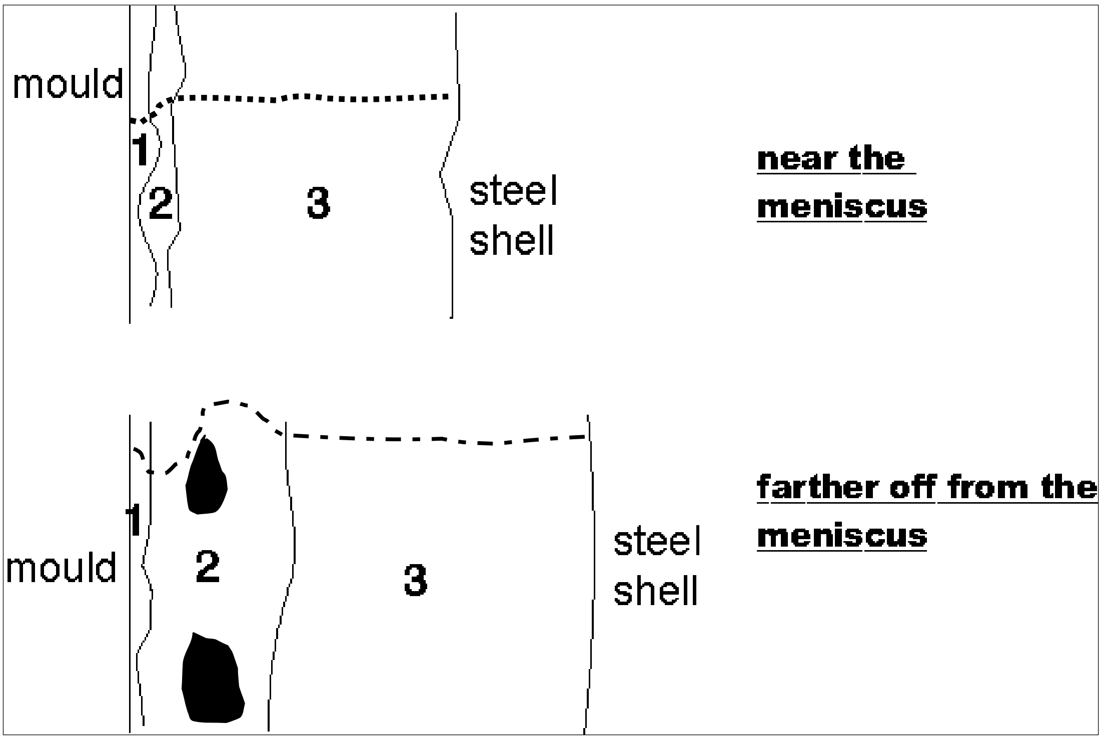
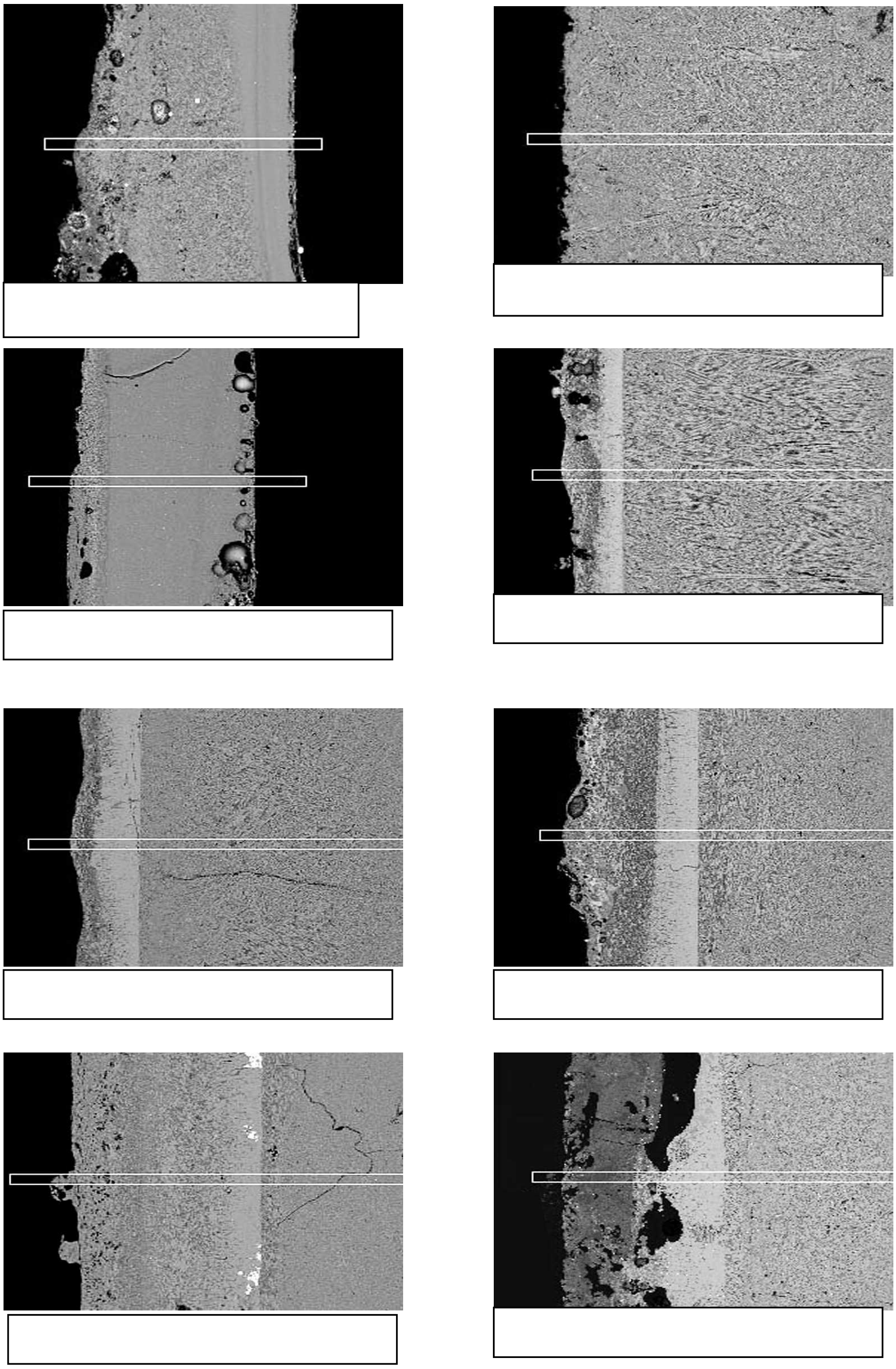


Figure 3. Flux layers schematically: 1) a layer remaining on the mould wall; 2) a layer with the sampled layer, which has been there during the steady state casting, can contain holes; 3) an extra layer, which has not been there during casting but has formed during the tailout. Dotted line shows principally the behaviour of the content of the elements.

Cast 81502; 2 heats **Cast 71056; 5 heats**



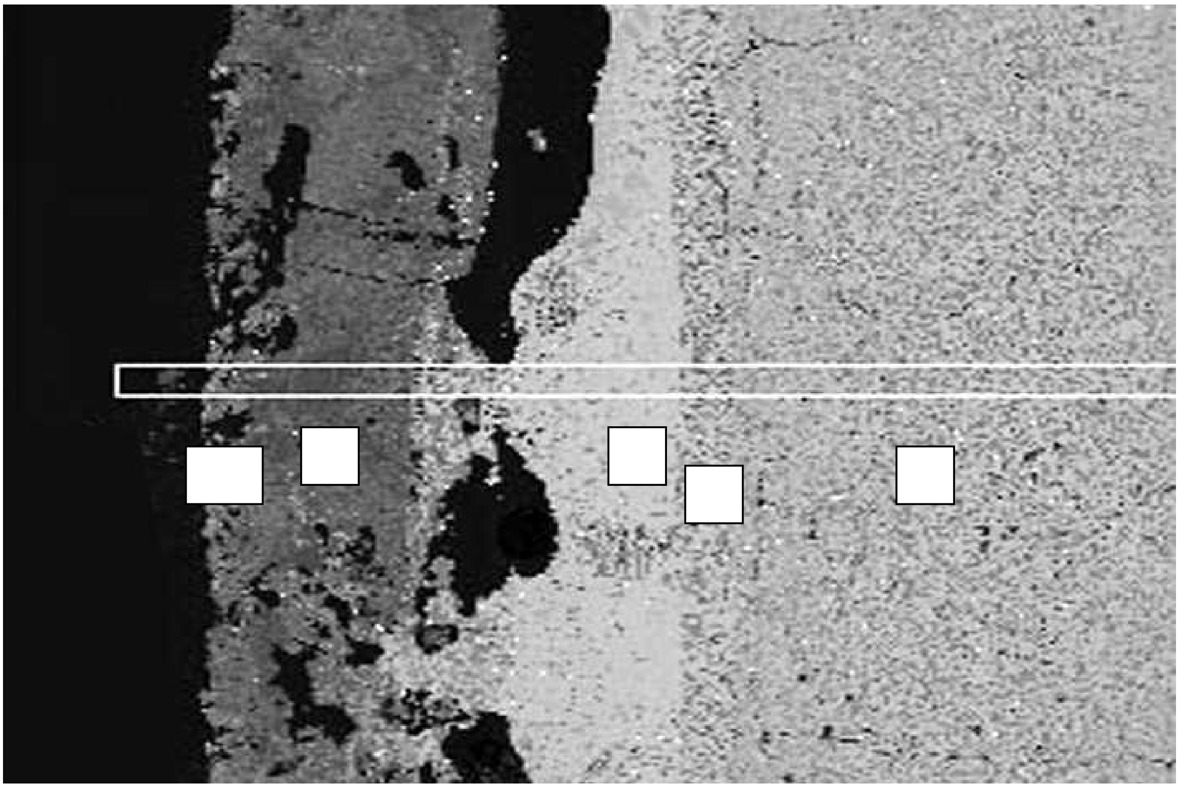
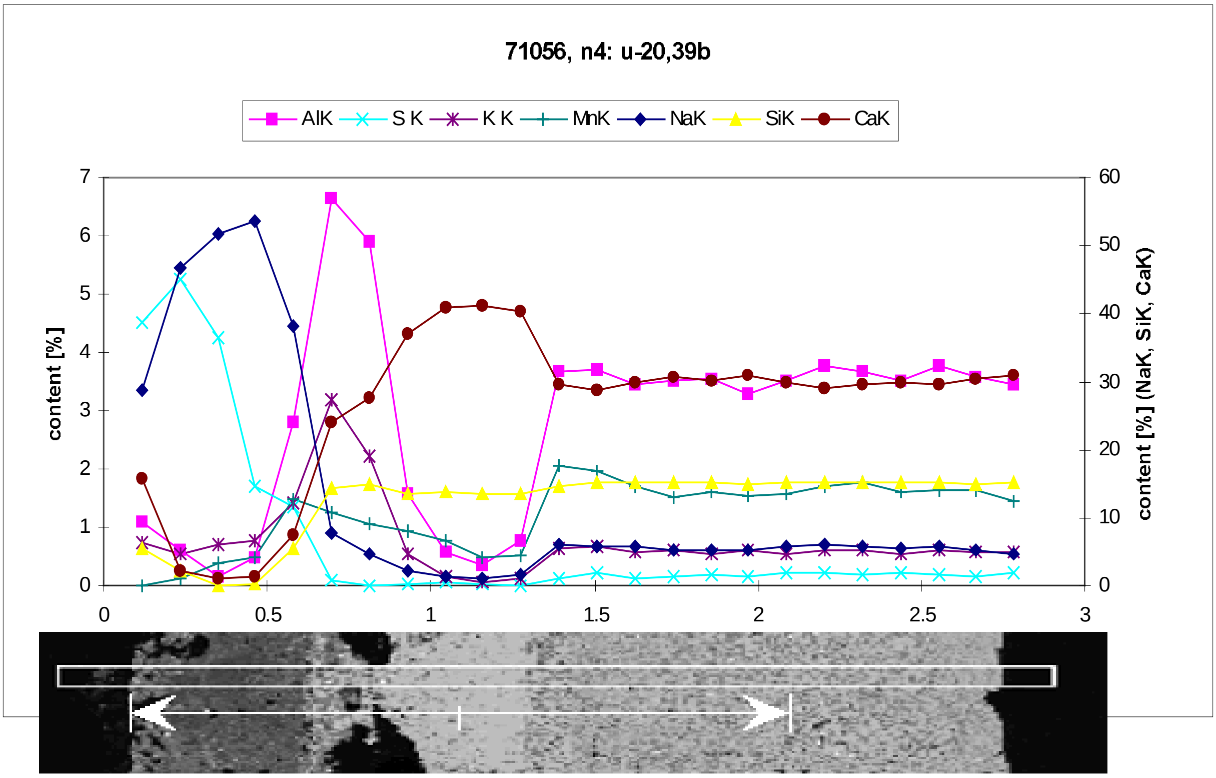
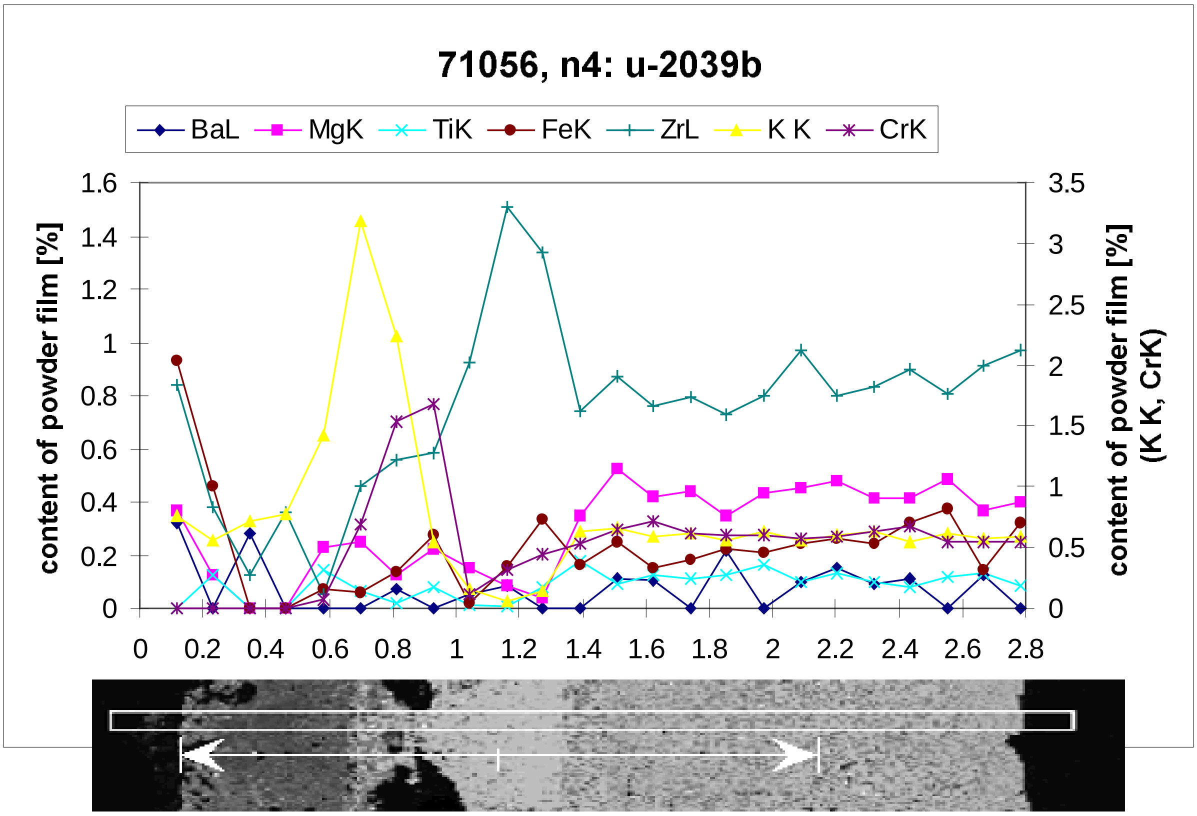


Figure 5. Layers: 1 is solidified during the tailout ; 2 is thin layer with coarser structure, but otherwise similar with 1; 3 is a layer with high calcium content; 4 is Na,F-rich; in area 4b is among Na,F-rich phase some additional, isolated phases.


71056, n4: u-20,39b
AlK
S K
K K
MnK
NaK
SiK
CaK
content [%]
content [%] (NaK, SiK, CaK)
0
0.5
1
1.5
2
2.5
3


71056, n4: u-2039b
BaL
MgK
TiK
FeK
ZrL
K K
CrK
content of powder film [%]
content of powder film [%] (K K, CrK)

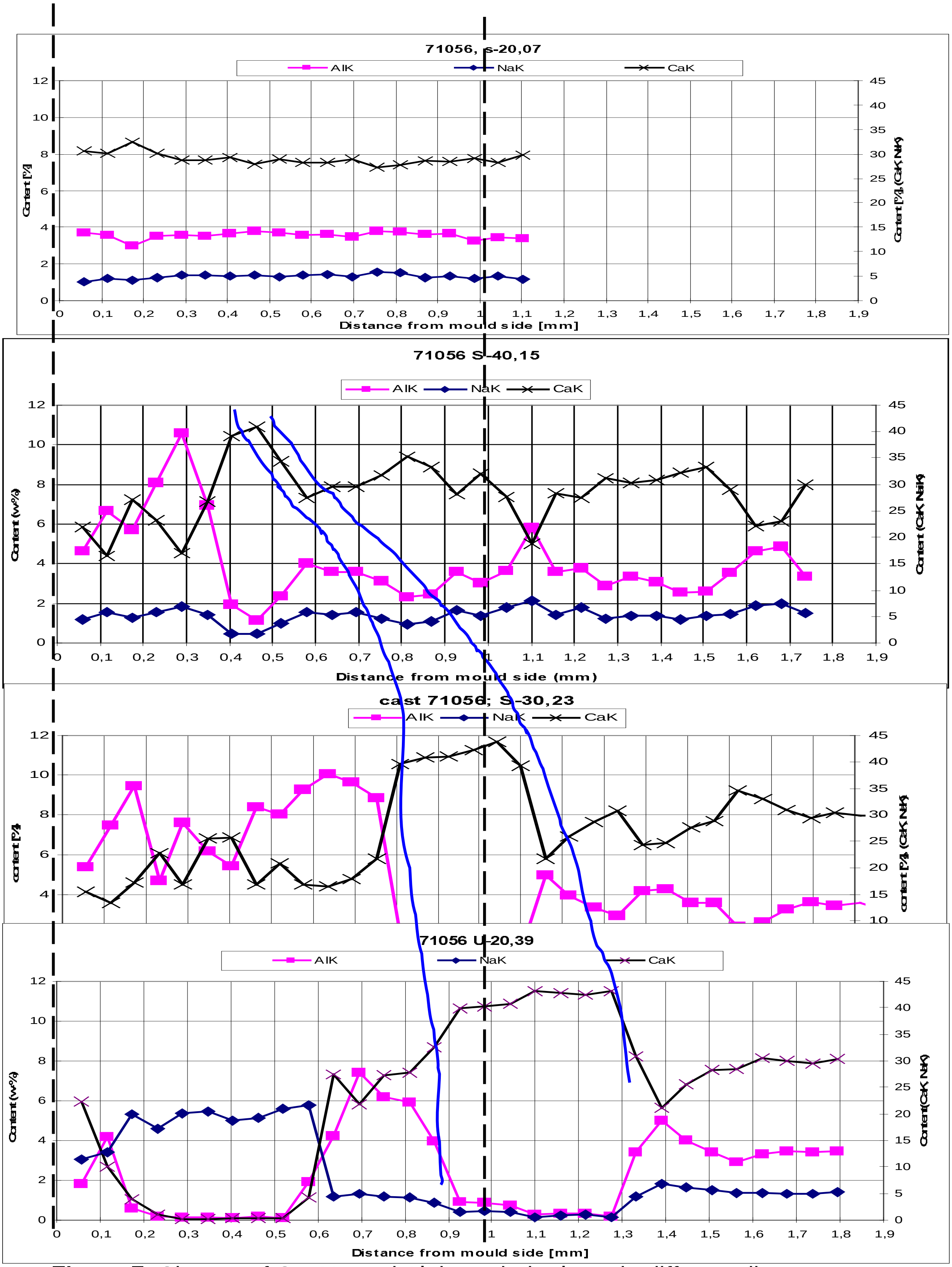


Figure 7. Change of Ca, Na and Al through the layer in different distances downward from meniscus. Additional lines are showing the development of "high Ca" layer. Distances from meniscus of the graphs are 7, 15, 23 and 39 cm. Dotted lines are 0 and 1 mm distances from the surface.

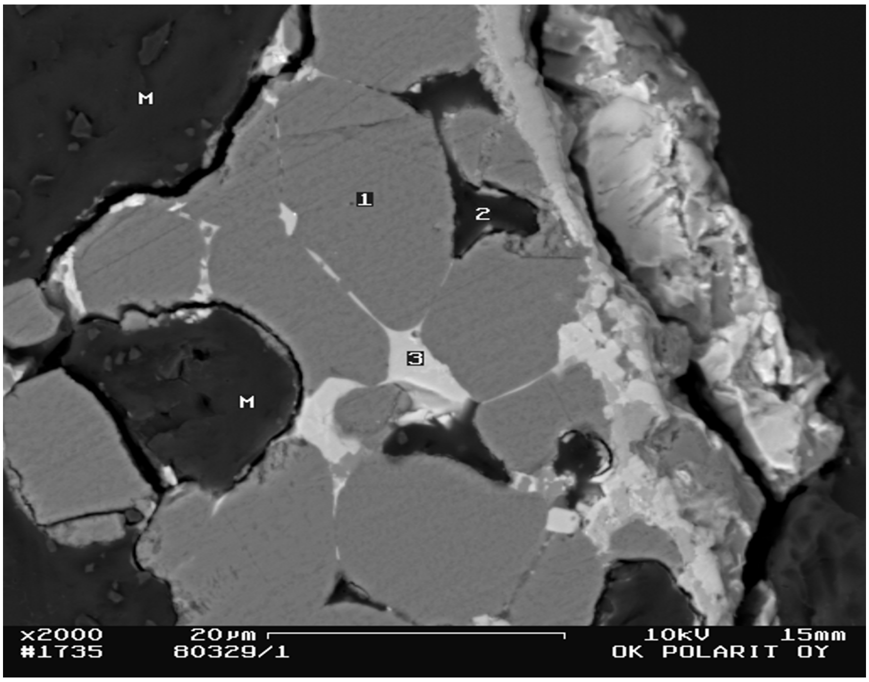


Figure 8. The slag layer ("white layer") of the sample No. 80329/1 on mould side (1=Na 52 %, F=48 %).

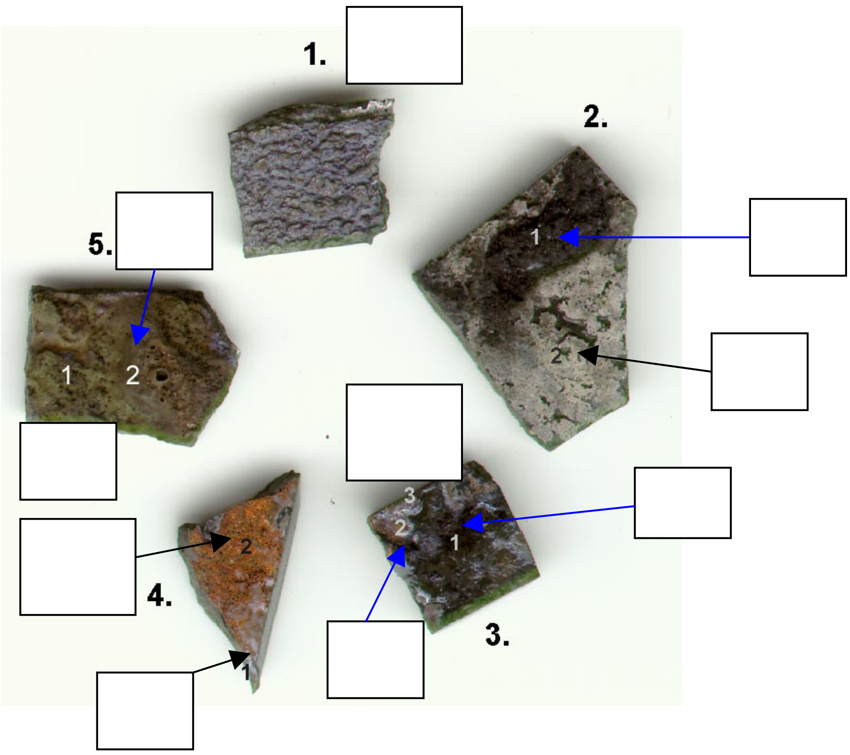


Figure 9. Different regions of powder slag layer ”in contact with mould”. (pieces was originally as a one bigger piece). Main elements in surface regions are shown in boxes. Typically compared with the powder composition: Ca clearly lower in all regions, Si lower, Al mostly lower, Na higher, Mn in some areas very high.

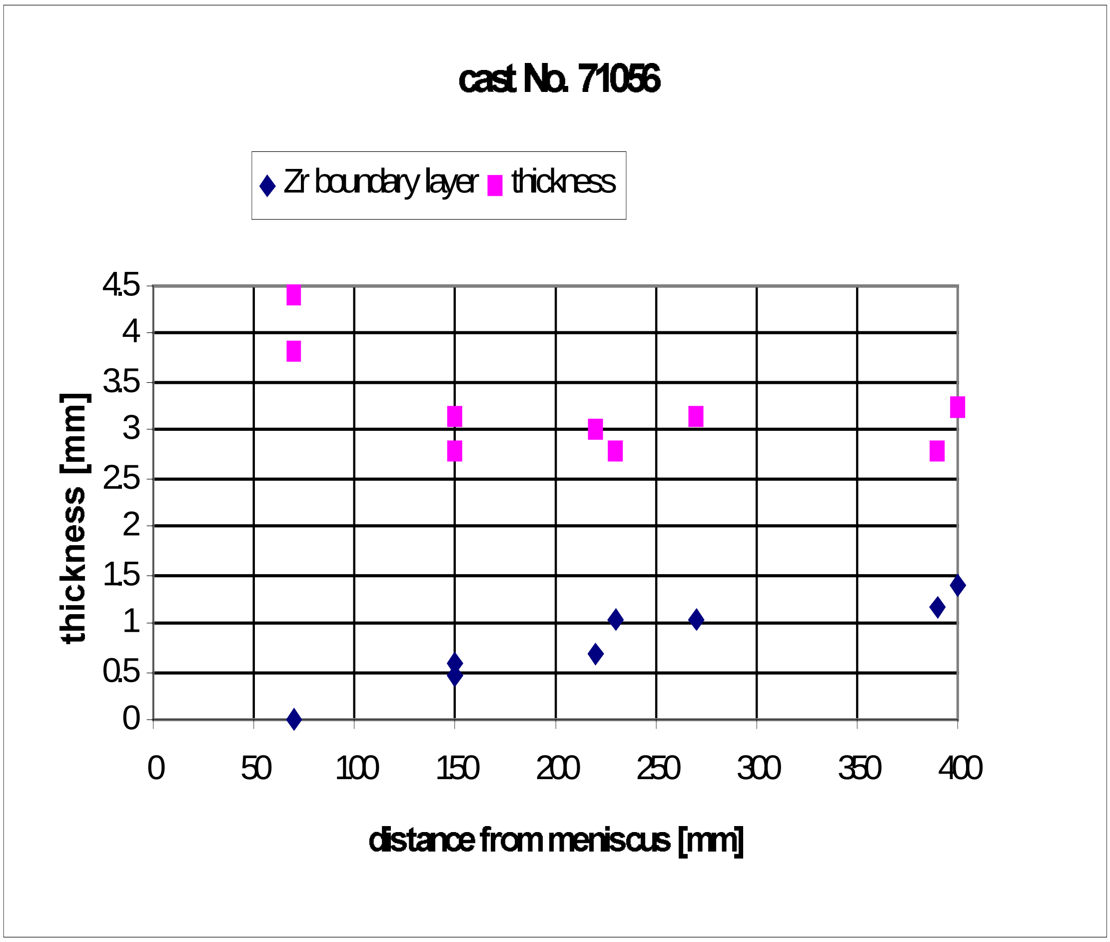


Figure 10. A result of tracer test with ZrO. Total thickness and "Zr low" thickness versus distance from meniscus.

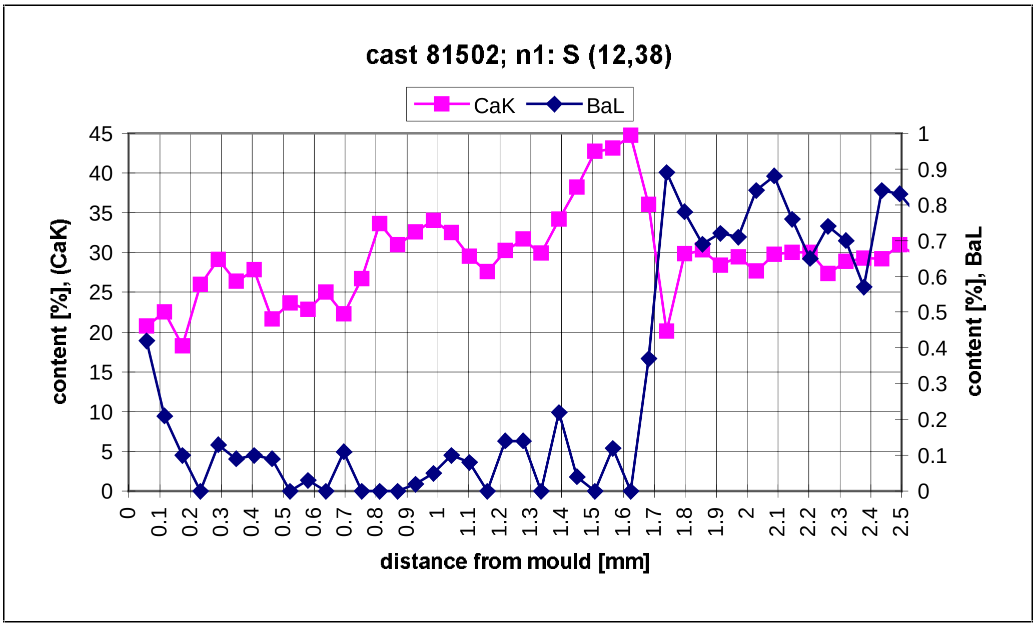


Figure 11. Contents of some elements in the flux film from cast No. 81502.
Thin "lubricating?" layer is between 1,7-1,8 mm, where Ba (added under last 15 minutes) goes to zero.