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F-free mould powders for low carbon steel slab casting – technological parameters and industrial trials

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The choice of the mould powder for slab casting is a difficult task because mould powders have many important functions during the continuous casting of steel. CaF_2 is a key ingredient in conventional mould slags since it reduces the viscosity, the *liquidus* temperature and the break temperature. Fluorine in mould powders is undesirable from the environmental and health points of view due to the following reasons: (i) evolves easily from slags, producing health-injurious gaseous substances, such as hydrofluoric acid; (ii) creates problems for storage and utilisation of solid waste and (iii) causes machinery corrosion. Aim of the present work is to describe the development of a new F-free mould powder for low carbon steel slab casting replacing CaF_2 with B_2O_3 . Laboratory tests and industrial trials were performed considering the technological parameters viscosity, break temperature and crystallisation tendency. From laboratory tests it was concluded that important technological parameters are similar when comparing the F-bearing mould powder (reference) and the new F-free B-bearing mould powder for low carbon steel slab casting: viscosity at 1300°C, break temperature, and crystallisation tendency. It was observed during industrial trials that a significant decrease of the submerged entry nozzle erosion was observed. The results were similar when comparing the F-bearing and the F-free performance: slag pool thickness measurements, melting behaviour, Al_2O_3 absorption, mould powder consumption and slabs superficial quality.

Keywords: Metallurgical slags, Slab casting, Fluorine-free slags, Mould powders, Mould slags

Introduction

The choice of the mould powder for slab casting is a difficult task because mould powders have many important functions during the continuous casting of steel.¹⁻⁴ CaF_2 is a key ingredient in conventional mould slags since it reduces the viscosity, the *liquidus* temperature and the break temperature; all of which lead to an improvement in the lubrication supplied to the steel shell. The CaF_2 also forms cuspidine in the solid slag film which reduces the heat transfer between shell and mould.⁵⁻⁷ However, the use of fluorine in siliceous melts can lead to the formation of volatile, water-soluble fluorine compounds, in this respect primarily SiF_4 . In continuous casting machines fluorine can accumulate in the

secondary cooling water, accompanied by a reduction of the pH-value. In such a medium, plant and equipment components are susceptible to wear. Fluorine in mould powders is undesirable from the environmental and health points of view due to the following reasons: (i) evolves easily from slags, producing health-injurious gaseous substances, such as hydrofluoric acid; (ii) creates problems for storage and utilisation of solid waste and (iii) causes machinery corrosion. Regarding machinery corrosion the hydrofluoric acid increases dramatically the corrosion rate especially below the mould where there is a high amount of water accelerating the process.⁸⁻¹⁰

In a recent work, CaF_2 was replaced with Na_2O for developing a new fluorine-free mould powder for billet casting.¹¹ As the powder consumption demands for billet casting are not stringent steelmakers frequently use high viscosity low basicity (V-ratio 0.7) mould powders to overcome problems such as slag entrapment and submerged entry nozzle (SEN) erosion.

Aim of the present work is to describe the development of a new F-free mould powder for low carbon steel slab casting replacing CaF_2 with B_2O_3 . Laboratory tests and industrial trials were performed considering the

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technological parameters viscosity, break temperature and crystallisation tendency. The performance of the new F-free mould powder was compared with the performance of the traditional commercial F-bearing.

Laboratory tests

The new fluorine-free mould powder – herein referred to as ‘F-free’ – was produced as granulated mould powder to replace the commercial one – herein referred to as ‘F-bearing’ – , which is used at steelworks for low carbon steel slab casting.

Chemical composition

The elemental compositions of the F-bearing and F-free mould powders determined through X-ray fluorescence are shown in Table 1. From the original composition (‘F-bearing’) it can be seen that (i) F was removed, (ii) B₂O₃ was added to, (iii) V-ratio remained the same and (iv) Na₂O content was increased.

Melting characteristics

For obtaining the characteristic temperatures a heating microscope was used increasing the temperature from room temperature. The working method refers to the German standard DIN 51730.¹² The results are in Table 1; each value is the average of two measurements. The F-free has characteristic temperatures ca. 120°C lower than the F-bearing.

When B₂O₃ is added to mould powders, it has been reported that B₂O₃ causes dramatic reduction of the melting temperature determined by the heating microscope.¹³ As these measurements are carried out on powders during the heating cycle, they apply to the conditions in the upper mould i.e. the formation of the liquid slag pool but not to formation of the slag films in the mould/strand interface.¹⁴

Viscosity

Viscosity measurements were performed using a rotation viscometer for a sample extracted from the lot which was sent to the steelworks. The measurements were made

Table 1 Elemental compositions and technological parameters for the F-bearing and F-free mould powders

Mould powder		F-bearing	F-free
Basicity (V-ratio)		0.93	0.93
SiO ₂	wt-%	37.8	33.6
CaO	wt-%	35.1	31.1
MgO	wt-%	5.2	5.8
Al ₂ O ₃	wt-%	2.9	1.8
Na ₂ O	wt-%	4.6	7.9
F	wt-%	7.0	0.0
B ₂ O ₃	wt-%	0.0	5.6
C _{free}	wt-%	1.9	2.5
CO ₂	wt-%	4.8	8.5
T _{melting}	°C	1191	1069
T _{flowing}	°C	1202	1084
Viscosity at 1300°C (rotation viscometer)	Pa s	0.34	0.33
Break temperature (rotation viscometer)	°C	1083	1078

using a standardised rotation viscometer for high temperatures according to international standards. To measure viscosity of liquid slag a high temperature measuring device of the company BÄHR with rotation viscometer type VIS 403 was applied.

Regarding sample preparation, it is decarburised at 600°C in an oven at ambient air to burn off carbon (minimum duration 8 h) and then put into the platinum vessel. The vessel is put into a pre-heated oven at 1350°C for 40 min for pre-melting. The content of the vessel is cast into a stainless steel bowl. After solidification the sample is crushed into pieces of 2–5 mm in size.

After sample preparation and the preparation of the measuring device, the procedure is executed automatically. A computer calculates and prints the graphic ‘viscosity [Pa s] versus temperature [°C]’. The material is heated at 10°C min⁻¹. From the completely liquid slag at 1430°C a cooling rate of 10°C min⁻¹ was applied, measuring the viscosity at a rotation speed of 200 rpm. Measuring crucible and bob (rotor) consist of platinum. Calibration of the equipment is performed by measuring the shearing force of a reference slag.

Viscosity value for the F-free slag at 1300°C is 0.33 Pa s, which is similar to the specification for the F-bearing (0.34 Pa s at 1300°C). The break temperatures for the F-free and for the F-bearing are also similar. The break temperature is the point where there is a sudden increase of the viscosity due to crystals precipitation during cooling.

Crystallinity analysis

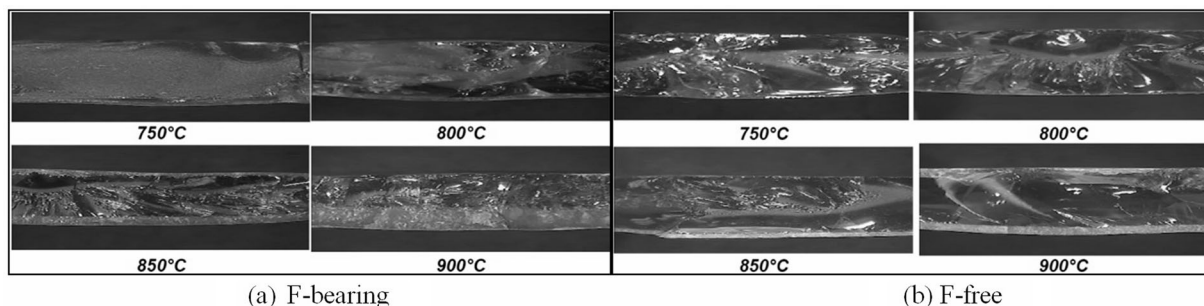
Decarburised sample was placed in a platinum crucible and heated at 1300°C for 20 min. The mould slag was then poured into a platinum mould at particular temperatures and maintained at these temperatures for 20 min for annealing. The samples were cut, examined with an optical microscope (20×) and photographed. The amount of crystals can in this way to be analysed (see Fig. 1).

A yellow crystalline layer can be observed at the bottom of the figures (at the slag/mould interface). At higher temperatures the area occupied by crystals is bigger because devitrification is easier. The samples were not etched. Thus, crystallinity fractions for both recipes – F-bearing and F-free – are close to each other, although for the F-bearing mould powder devitrification is easier (it can be clearly seen at 900°C in Fig. 1).

For industrial F-bearing mould powders for slab casting typically the main crystalline phase that is found when solid slag films are collected from the mould at the end of casting sequences is cuspidine (3CaO·2SiO₂·CaF₂). The films have a crystalline structure that either formed during cooling or via devitrification, i.e. crystallisation from the glassy state.^{1,5}

In a recent work¹⁵ slags in the CaO–SiO₂–Al₂O₃–MgO–Na₂O–TiO₂–B₂O₃ were studied, regarding their crystallisation behaviour. Considering three compositions which were studied through the single hot thermocouple technique (SHTT), DTA and XRD:

- (i) V-ratio 1, 7% Al₂O₃, 2% MgO, 10% Na₂O, 5% TiO₂, B₂O₃ 0%
- (ii) V-ratio 1, 7% Al₂O₃, 2% MgO, 10% Na₂O, 5% TiO₂, B₂O₃ 5%
- (iii) V-ratio 1, 7% Al₂O₃, 2% MgO, 10% Na₂O, 5% TiO₂, B₂O₃ 10%



1 Crystallinity analysis results

It was concluded that B_2O_3 can significantly increase the incubation time for crystallisation, which means that B_2O_3 could decrease crystallisation ability of slags. The slag with 0% B_2O_3 has a minimum incubation time less than 1 second at nose temperature, while for the slag with 10% B_2O_3 no crystal was detected within 1000 s. Details for the SHTT apparatus which was used for building the TTT diagrams which led to this conclusion can be found elsewhere.⁴ Besides, it was found that for the three aforementioned compositions (i)–(iii) *liquidus* temperature decreases with increase of B_2O_3 content from 0 to 10%. Regarding the phases which were detected through an X-ray diffraction study three crystalline phases were detected: wollastonite, gehlenite and perovskite. It was observed that with increase of B_2O_3 the amount of gehlenite increases.¹⁵

Considering the mould powders under study in the present work, the nature of the crystalline phases was not determined.

Industrial tests

At a Brazilian steelworks industrial tests were performed during continuous casting of slabs. The composition of the steel used during the industrial trials is shown in Table 2. The tests were performed in 13 heats for one sequential (2999 tons of steel). The average casting speed was around 1.15 m min^{-1} (maximum 1.5 m min^{-1}). The slab section was $1300 \times 250 \text{ mm}$.

Slag pool thickness and melting performance

The slag pool thickness is related to mould powder consumption. Failure to maintain it can lead to lack of lubrication and ultimately to surface defects or sticker breakouts. The depth of the slag pool influences on the amount of liquid slag infiltrating into the mould/strand gap and the number of inclusions transferred from the steel to the slag.¹⁶

For doing slag pool thickness measurements steel wire and copper wire are simultaneously immersed in the mould according to Fig. 2. The temperature for the liquid slag in contact with the steel is ca. 1350°C , enough to melt the copper wire. However, this temperature is not enough

Table 2 Composition of the steel used for industrial tests [wt-%]

C	Mn	Si	P	S
0.05–0.08	0.25–0.40	0.020 max.	0.020 max.	0.025 max.

to melt the steel wire. So, the difference between the lengths of the wires after the immersion represents the slag pool thickness (L1–L2). The total length of the steel wire represents the total layer (powder in natura, sintered and liquid), assuming that the wire will be melted by getting into contact with the liquid steel.

To fix the wires a standard measurer was developed. It consists of a retractable aluminium rod that allows the fixation of the wires in its extremity, guaranteeing herewith the safety of the operator during the measurements. The immersion time is ca. 5 seconds (it depends on the thickness of the used wires).

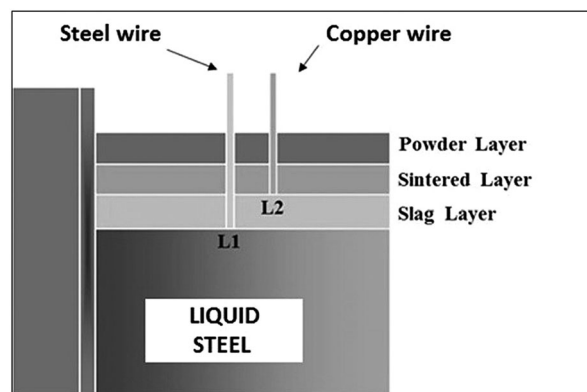
The slag pool thickness measurements results are the following: for the F-bearing 15–20 mm, and for the F-free 15–20 mm. It means that for this parameter the F-free product is adequate.

It was visually observed that the melting performance of the F-free mould powder is similar to the F-bearing one. The melting behaviour depends on chemical and physical properties, like free carbon, CO_2 content, bulk density, and choice of the raw materials. The melting rate has a significant effect on powder performance since it determines the ability of the molten slag to maintain a stable liquid pool depth.

Inclusions absorption

Al_2O_3 content in mould slag increases with time, and it remains constant 20 min after the beginning of the casting. Al_2O_3 dissolution in slag is increased using mould powders that present high basicity, low content of Al_2O_3 and high contents of F, Li_2O or Na_2O .¹⁷

During casting using the F-free mould powder, 12 mould slag samples were collected and submitted to X-



2 Slag pool thickness measurements

Table 3 X-ray fluorescence results for Al₂O₃ content of mould slag samples for the F-free mould powder [wt-%]

Heat											
1	2	3	4	5	6	7	8	9	10	11	12
6.5	5.7	5.9	6.7	6.5	6.4	5.4	5.4	5.5	5.8	6.1	6.1

ray fluorescence analysis using an apparatus Philips Axios 4KW. One sample was collected per heat. These samples were withdrawn 10 min before the ending of the heats, starting from 2nd heat. Table 3 shows the result.

In order to do a comparison for Al₂O₃ increase it is necessary to correct the original composition for the losses that happen during heating. The factor f should be calculated¹⁸:

$$f = \left[1 - \frac{\%C_{\text{free}}}{100} - \left(\frac{44}{12} \times \left\{ \frac{\%C_{\text{total}} - \%C_{\text{free}}}{100} \right\} \right) \right] \quad (1)$$

where f is the fraction of the mould powder converted into slag; %C_{free} and %C_{total} are free carbon and total carbon, respectively.

With the aforementioned factor f the corrected alumina content is %Al₂O₃ = 2.0; for the original composition of the mould powder, it can be seen that %Al₂O₃ = 1.8 according to Table 1.

Alumina absorption for the F-bearing mould powder (the reference material) is ca. 3%. It can be observed in Table 3 that for the F-free mould powder the Al₂O₃ content increase is similar.

SEN erosion rate

SEN diameter measurements were got after the tests. A significant decrease of the SEN erosion was observed. According to Table 4 two shafts were compared: for the F-bearing and for the F-free. SEN erosion rate with the F-free mould powder was lower.

Mould powder consumption

For the industrial tests mould powder consumption was calculated in terms of the amount of mould powder per ton of casted steel (kg ton⁻¹). The tests were performed in 13 heats for one sequential (2999 tons of steel). The result is: for the F-bearing 0.40 kg ton⁻¹, and for the F-free 0.37 kg ton⁻¹.

The slabs produced during the industrial trials with the F-free mould powder presented good surface quality, which is similar to the quality related to the F-bearing mould powder.

The consumption of mould powder is an important variable in the continuous casting process. The main factors that influence the powder consumption are: casting

Table 4 SEN erosion rate measurements for mould powders F-bearing and F-free

	Shaft	
	F-bearing	F-free
Total wear (mm)	103.1	87.5
Medium wear rate (mm min ⁻¹)	0.092	0.078
Tube potential/medium set point (min)	793.0	934.0

speed, viscosity, amplitude, oscillation frequency and solidification temperature.¹⁹

Conclusions

- (i) From laboratory tests it was concluded that important technological parameters are similar when comparing the F-bearing mould powder (reference) and the new F-free mould powder for low carbon steel slab casting: viscosity at 1300°C, break temperature, and crystallisation tendency.
- (ii) From industrial trials for a particular low carbon steel during slab casting a significant decrease of the SEN erosion was observed. Regarding the following evaluations the results were similar when comparing the F-bearing and the F-free performance: slag pool thickness measurements, melting behaviour, Al₂O₃ absorption, slabs superficial quality and mould powder consumption.

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