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DEVELOPMENT OF FLUORINE FREE MOULD POWDER FOR USING IN CONTINUOUS CASTING OF BILLETS – PRELIMINARY INDUSTRIAL TEST[1]

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Abstract
The development of fluorine-free mould powders is object of several researches and has attracted the interest of industry in recent years. The challenge is to provide F-free mould powders able to reproduce technological parameters of fluorine-bearing mould powders. For this purpose, a research and development cooperation project between university and industry aiming to the development of fluorine-free mould powders for billet casting has been established. In the present work, preliminary industrial tests results obtained from the application of the fluorine-free mould powder Accutherm ST-SP/512SV-DS-1 are reported. The preliminary industrial trials, performed in a Brazilian steelworks, were accomplished aiming to analyse its behaviour during continuous casting operation regarding some operational aspects and to provide information about its influence on the superficial quality of the steel.
Keywords: F-free mould powders; Continuous casting.

DESENVOLVIMENTO DE PÓS FLUXANTES SEM FLÚOR USADO NO LINGOTAMENTO CONTÍNUO DE TARUGOS – TESTE INDUSTRIAL PRELIMINAR

Resumo
O desenvolvimento de pós fluxantes isentos de flúor tem sido objeto de diversas pesquisas e tem despertado o interesse da indústria. O desafio é fornecer receitas de pós fluxantes sem F capazes de reproduzir as características e o comportamento de pós fluxantes com flúor. Com este propósito, um projeto de investigação e cooperação entre a universidade e a indústria visando o desenvolvimento de pós fluxantes sem flúor para o lingotamento contínuo de tarugos foi estabelecido. No presente trabalho são relatados os resultados de testes industriais iniciais obtidos com a aplicação do pó fluxante sem flúor Accutherm ST-SP/512SV-DS-1. Os ensaios industriais preliminares, efetuados em uma usina siderúrgica brasileira, foram realizados com o objetivo de analisar seu comportamento na operação de lingotamento contínuo em relação a alguns aspectos operacionais e de fornecer indícios sobre sua influência na qualidade superficial do aço.
Palavras-chave: Pós fluxantes sem flúor; Lingotamento contínuo.

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1 INTRODUCTION

Mould powders are synthetic slags used in continuous casting process with the aim to promote (i) lubrication the strand through the mould (ii) uniform heat transfer across the infiltrated slag layer formed between steel shell and mould, (iii) protection of the molten against oxidation, (iv) absorption of non-metallic inclusions and (v) thermal insulation of molten steel. In addition, it is also clarified that mould powders play an important role on affecting surface quality of steel.[1] All these functions are essential to the good work of casting process, in which the two first ones are the most relevant functions.[2]

The chemical composition of mould powders includes a great variety of components – oxides, fluoride and carbonates – and their composition varies according to steel grade and operational parameters.[3] The main components present in the mould powders are CaO-SiO_2-Al_2O_3-Na_2O-CaF_2. Fluorine is an important constituent of the mould powders that aids in reducing the melting point of slag as well as increasing its fluidity by lowering the viscosity. However, fluorine containing mould powders liberates gaseous fluorides to the atmosphere resulting from evaporation and chemical reactions in the mould powder. This alters the composition and subsequently the thermo-physical properties of the flux. Moreover, the volatile fluorides liberated cause environmental degradation, corrosion of equipment, acidification of the cooling water and are a potential health and safety hazard.[4,5]

Within this context, the elimination of fluorine from the mould powder composition becomes essential. Actually, fluoride-free fluxes are developed for slab and billet casting. Different oxides as B_2O_3, Li_2O and Na_2O, are used in order to substitute CaF_2. Thus any substitutes of F would have to replicate these physical properties.[6]

In recent work, in the initial stage of the development of F-free mould powders, five new fluorine-free recipes were elaborated following a standard procedure. The recipes were submitted to laboratory tests performed in Stollberg do Brasil to evaluate mould powders behavior. The following technological parameters were considered and tested: melting characteristics, viscosity, melting rate and %cristallinity. The methodology applied is described in a previous work.[7] The properties of the mould powder Accutherm ST-SP/512SV-DS, produced by Stollberg Group and used at steelworks for billet casting, are used as standard in the present work.

From the results, the recipe whose characteristics were similar to the standard mould powder was selected for further development – Accutherm ST-SP/512SV-DS-1.

In the present work, the preliminary industrial tests results obtained from the application of the fluorine-free mould powder Accutherm ST-SP/512SV-DS-1 are reported. The preliminary industrial trials, performed in a steelworks, were accomplished aiming to analyse its behaviour during continuous casting operation regarding some operational aspects and to provide information about its influence on the steel superficial quality.

2 EXPERIMENTAL DEVELOPMENTS

Industrial tests with the Accutherm ST-SP/512SV-DS-1 were performed in three heats using two different steel grades. The first heat was performed with the

steel grade A, and the second and third heats were performed with the steel grade B. Each heat has about one hour of duration and was applied in one strand. Technological parameters were monitored during continuous casting with the objective to evaluate the performance of fluorine-free mould powder. The chemical composition of the mould powders used during the industrial tests is showed in Table 1.

Table 1– Chemical composition of mould powders used in industrial test (wt.%)

Mould powder		Accutherm ST-SP/512SV-DS	Accutherm ST-SP/512SV-DS-1
Basicity (V-ratio)		0.70	0.70
SiO_2	%	35.70	38.00
CaO	%	24.98	26.50
MgO	%	2.95	2.64
Al_2O_3	%	12.07	7.82
TiO_2	%	0.47	0.29
Fe_2O_3	%	2.61	2.22
MnO_2	%	0.09	0.12
Na_2O	%	4.11	7.28
K_2O	%	1.60	1.03
F	%	4.20	0.00
C_{free}	%	6.02	6.05
CO_2	%	3.83	4.43
C_{total}	%	7.07	7.23
$T_{melting}$	°C	1188	1166
$T_{flowing}$	°C	1199	1172

Viscosity measurements were performed through a rotation viscometer in the Institute of Iron and Steel Technology of TU Bergakademie Freiberg Germany.
The viscosity results calculated through IRSID model according to specification of Stollberg do Brasil are reported in Table 2.

Table 2 – Viscosity of both mould powders with and without F, respectively, calculated through

	Accutherm ST-SP/512SV-DS	Accutherm ST-SP/512SV-DS-1
Viscosity (1300 °C, IRSID) Pa.s	1.99	2.08

The compositions of the steels used in the tests are at Table 3. Parameters used during the tests can be seen at Table 4.

The superficial quality of the billets was reported considering the amount of steel scrap formed during rolling process.

The submerged entry nozzle (SEN) external diameter measurements for the steel grade B to both Accutherm ST-SP/512SV-DS and Accutherm ST-SP/512SV-DS-1 were accomplished. The measures were taken at the end of the industrial trials and the results are showed in the following topic.

Table 3 - Chemical composition of the steels used during the industrial test

Component		Steel grade A	Steel grade B
C	%	0.390	0.146
Si	%	0.240	0.228
Mn	%	0.780	1.143
P	%	0.021	0.019
S	%	0.023	0.023
Cr	%	0.930	0.942
Mo	%	0.170	0.047
Ni	%	0.080	0.103
As	%	0.000	0.001
Cu	%	0.170	0.132
Nb	%	0.003	0.003
W	%	0.010	0.004
Pb	%	0.001	0.0012
Sn	%	0.011	0.012
Ti	%	0.002	0.0021
V	%	0.003	0.002
Ti/V	%	0.670	0.000
Zn	%	0.000	0.002
N	%	0.0093	0.000
Sb	%	0.000	0.001
Al_{sol}	%	0.010	0.000
Co	%	0.010	0.006
Zr	%	0.000	0.417

Table 4 – Operational parameters range

Parameters	Steel grade A	Steel grade B
Casting Speed (m/min)	1.870	1.929 – 2.030
Mould Oscillation (cpm)	192	201 - 203
Billet section (mm)	155x155	155x155
Water Flow in the Mould (L/min)	1860	1850
Liquidus Temperature (°C)	1486	1512
Superheat (°C)	45	53

3 RESULTS AND DISCUSSION

The operational parameters evaluated during industrial tests concerning the performance of both mould powders Accutherm ST-SP/512SV-DS-1 and Accutherm ST-SP/512SV-DS for steel grades A and B are reported in Tables 5 and 6, respectively. The results regarding steel B include measures of the two heats performed with this steel grade.

Table 5 – Parameters monitored during test with steel A

Mould Powder	ΔT(°C) (mould)	Slag Pool Thickness* (mm)	Slag Pool Thickness + powder (mm)	Billet Temperature (°C)
Accutherm ST-SP/512SV-DS-1	7.2 – 7.3	11 - 17	35 - 55	1124
Accutherm ST-SP/512SV-DS	6.7 – 6.8	10 - 12	35 - 40	1124

Table 6 - Parameters monitored during test with steel B

Mould Powder	ΔT(°C) (mould)	Slag Pool Thickness* (mm)	Slag Pool Thickness + powder (mm)	Billet Temperature (°C)
Accutherm ST-SP/512SV-DS-1	7.1 – 7.4	6 - 10	45 - 50	1205
Accutherm ST-SP/512SV-DS	6.8 – 7.0	5 - 6	25 - 40	1158 - 1271

** Slag pool thickness range reference used as at the steelworks: 5 – 12mm.*

The billet temperature is taken exactly before straightener by a pyrometer. The temperature difference (ΔT) in the mould is the difference temperature value between the water cooling inlet (base of the mould) and the water cooling outlet (top of the mould). This parameter provides an estimate on the horizontal heat transfer between the steel shell and the mould copper-wall. The horizontal heat transfer is important since it is the controlling factor in longitudinal cracking, but it is also involved in the formation of the strand depression.[8] The maximum difference ΔT between commercial and fluorine-free mould powder was 0.6°C. The results indicate a slightly higher heat extraction with the fluorine-free mould powder tested with both steel grades.

The slag pool thickness is an important parameter since its depth is related to mould powder consumption and the supply of liquid slag into the mould/shell of gap acting as a reservoir.[9] The depth of the molten pool affects both the amount of liquid slag infiltrating into mould/strand channel and the number of inclusions transferred from the steel to the molten slag.[2] The thickness measurements were performed by the three-wire method.[9] For steel grade A, the measurements taken with the F-free mould powder showed depth range from 11 to 17 mm and had a maximum difference of 7 mm on the liquid flux depth compared to standard mould powder. For the steel grade B, the depth range was from 5 to 10 mm and the difference was 4 mm. Mills[2] suggest a depth of >10 mm to ensure a good slag infiltration and lubrication of the steel shell. Several other researchers have recommended a flux pool thickness in the 10 to 15 mm range as an optimum value.[9] Bommaraju, mentioned by Pinheiro,[9] recommended a minimum thickness of 6 to 12 mm.

The melting rate has a significant effect on powder performance since it determines the ability of the molten slag to maintain a stable liquid poll depth (10). The melting behaviour of Accutherm ST-SP/512SV-DS-1 was monitored during tests. It was observed that the melting rate of F-free mould powder was similar to commercial one.

The powder consumption was measured in industrial test by amount of the mould powder used during the two heats with the steel B. The powder consumption of Accutherm ST-SP/512SV-DS-1 was 0.24 kg mould powder/t of steel. The average of powder consumption of the commercial mould powder used in steelworks is 0.30 kg/t.

Viscosity measurements performed through a rotation viscometer were done with three samples of the Accutherm ST-SP/512SV-DS-1 and the results obtained are showed in Figure 1. The measurements were performed in the Institute of Iron and Steel Technology of the TU Bergakademie Freiberg, Germany.

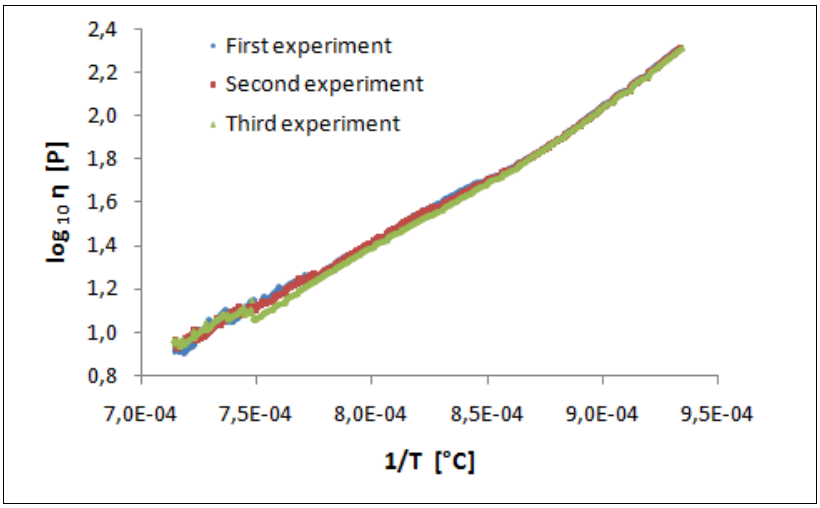

Figure 1 – Viscosity measurements through rotation viscometer for Accutherm ST-SP/512SV-DS-1.

The average value of the viscosity for the Accutherm ST-SP/512SV-DS1 at 1300°C was 16.78 P. This value is similar to the viscosity of commercial product (19.9 P). Moreover, no break temperature was observed. The break temperature represents the point at which the solids are first precipitated in the melt and is important since it helps to control the horizontal heat transfer and lubrication between the steel shell and the mould (11). These measurements of viscosity were applied on the samples extracted from the product used in the industrial trials. Such values are close to that calculated by IRSID method.

For all trials with both steel grades, the visual appearance of billets with F-free mould powder was apparently similar to the standard mould powder. The superficial quality of the billets was reported considering the amount of scrap formed during rolling process. Data related to the steel surface quality are showed in Tables 7, 8 and 9 (tests performed with steel grade A and B, respectively).

Table 7 – %scrap formed during rolling process (steel grade A)

Mould powder	Steel weight processed (kg)	Steel scrap (wt.%)
Accutherm ST-SP/512SV-DS	37980	0.05
Accutherm ST-SP/512SV-DS-1	18990	2.00

Table 8 – %scrap formed during rolling process for the first heat (steel grade B)

Mould powder	Steel weight processed (kg)	Steel scrap (wt.%)
Accutherm ST-SP/512SV-DS	40091	0.46
Accutherm ST-SP/512SV-DS-1	19845	0.00

Table 9 – %scrap formed during rolling process for the second heat (steel grade B)

Mould powder	Steel weight processed (kg)	Steel scrap (wt.%)
Accutherm ST-SP/512SV-DS	37331	0.00
Accutherm ST-SP/512SV-DS-1	19745	0.71

For the preliminary test using the steel grade A, the %scrap of the fluorine-free mould powder was about 2% against 0.05% from the Accutherm ST-SP/512SV-DS. The results concerning steel grade B, divided in two heats, showed 0% of scrap for the steel produced in the first heat and 0.71% of scrap originated from second heat. For this steel grade and for the particular rolling gage, the amount of scrap produced is not critical. However, it is too early to asseverate about the positive or negative influence of the fluorine-free mould powder on the superficial cracks of rolled bars.

The SEN erosion rate is proportional to fluidity of molten slag that, in turn is related to the viscosity of the mould slag. The SEN erosion rate is higher with the use of low viscosity mould powders, which has made the life of submerged nozzle shorter (2, 12, 13). The SEN external diameter was measured at the end of the trials for the steel grade B both Accutherm ST-SP/512SV-DS and Accutherm ST-SP/512SV-DS-1. The results are at Table 10. There was a decrease on the SEN erosion for the F-fluorine mould powder Accutherm ST-SP/512SV-DS-1. This result is not definitive about an effective erosion decrease, but provides an indication concerning the SEN wearing reduction.

Table 10 – Measurements of SEN external diameter

Mould powder	SEN diameter (mm)
Accutherm ST-SP/512SV-DS	58
Accutherm ST-SP/512SV-DS-1	65

When evaluating these preliminary industrial tests results some carefulness is required because they reflect the data obtained with three heats and two different steel grades – in other words, concerning steel surface quality, they are not conclusive about the utilization of these mould powders in large scale by the steelmaking industry. These tests have to be seen as an initial analysis of their operational capacity and behaviour during continuous casting – a large industrial tests sequence must take place aiming at possible adjustments, if necessary, to confirm its performance and benefits compared with traditional fluorine-bearing mould powders.

4 CONCLUSIONS

From the results provided by preliminary industrial trials the initial behaviour of the fluorine-free mould powder concerning to operational and technological parameters could be evaluated.

The performance of Accutherm ST-SP/512SV-DS-1 regarding to technological parameters was comparable to commercial mould powder. The viscosity of the F-free mould powder measures by viscometer was similar to standard mould powder. The trials performed with fluoride-free mould powder showed reduction of erosion of the SEN. The superficial quality of billets was related to scrap formation during rolling process. The percentage of scrap to both steel grades was not critical. However, is not possible to asseverate about the positive or negative influence of the F-free mould powder on the superficial cracks of the rolled bars.

Among the operational aspects that were observed regarding the performance of Accutherm ST-SP/512SV-DS-1 throughout the initial tests – powder consumption, melting rate, among others – a positive perspective towards continuity of development and improvement of this fluorine-free mould powder can be seen.

Further industrial tests should be completed to confirm its performance and benefits compared with traditional fluorine-bearing mould powders.

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