FLUORINE-FREE MOULD POWDERS FOR BILLET CASTING – TECHNOLOGICAL PARAMETERS [1]

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Abstract
There is a clear trend in industry to eliminate fluorine from slags which are used during production of steel. Regarding continuous casting process, 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. The aim of the present work is to determine technological parameters related to new fluorine-free recipes: melting characteristics (heating microscope), viscosity, melting rate and %crystallinity. Several laboratory tests have been performed by Stollberg Group to determine the recipe that reproduces the properties of the mould powder Accutherm ST-SP/512SV-DS – produced by Stollberg Group and used at steelworks plants to billet casting – regarding the aforementioned technological parameters.
Keywords: Continuous casting; Mould powder; Fluorine; Fluorspar.

PÓS FLUXANTES SEM FLÚOR PARA O LINGOTAMENTO DE TARUGOS – PARÂMETROS TECNOLÓGICOS

Resumo
Há uma clara tendência na indústria para eliminar o flúor de escórias utilizadas durante a produção de aço. No processo de lingotamento contínuo, flúor em pós fluxantes é indesejável do ponto de vista ambiental e de segurança no trabalho devido às seguintes razões: (i) volatiliza facilmente de escórias, produzindo substâncias gasosas prejudiciais à saúde (tal como ácido fluorídrico); (ii) gera problemas de disposição e utilização de resíduos sólidos e (iii) causa corrosão na máquina de lingotamento contínuo. O objetivo do presente trabalho é determinar parâmetros tecnológicos de novas receitas sem flúor: temperaturas características (microscópio de aquecimento), viscosidade, taxa de fusão e fração de fase cristalina. Vários testes laboratoriais têm sido executados pelo Grupo Stollberg para determinar a receita que reproduz as propriedades do pó fluxante Accutherm ST-SP/512SV-DS – produzido pelo Grupo Stollberg e utilizado no lingotamento contínuo de tarugos – considerando os parâmetros tecnológicos supracitados.
Palavras-chave: Lingotamento contínuo; Pó fluxante; Flúor; Fluorita.

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1 INTRODUCTION

Mould powders are synthetic slags used to cover the liquid pool surface during the continuous casting of steel, designed for specific steel grades and steel plant conditions. Their chemical composition varies greatly depending on the required properties. Typically, mould powders contain the following major constituents: CaO-SiO_2-Al_2O_3-Na_2O-CaF_2. Some of the raw materials used in industrial mould powders production are wollastonite, bauxite, fly ash, *etc*. Moreover, fluorspar (CaF_2) and sodium carbonate (Na_2CO_3) are normally used to decrease viscosity and *liquidus* temperature.

The functions of the mould powders are the following: (i) protect the steel meniscus from oxidation, (ii) provide thermal insulation, (iii) absorb inclusions into the mould slag, and (iv) lubricate the strand and provide uniform heat transfer across the infiltrated slag layer between the steel strand and the mould.(1,2)

The choice of the casting powder for billet casting is very important in the achievement of a successful casting practice. Since the powder consumption demands for billet casting are not stringent, steelmakers frequently use high viscosity mould powders to overcome problems with slag entrapment and SEN (Submerged Entry Nozzle) erosion.(3)

Fluorine in mould powders composition is undesirable from the health and environmental points of view due to the following reasons:(4)

(i) evolves easily from slags, producing health-injurious gaseous substances, such as hydrofluoric acid;

(ii) creates problems for storage and utilisation of solid waste;

(iii) causes machinery corrosion.

Regarding machinery corrosion, the hydrofluoric acid – which is generated during continuous casting process from mould powder – increases dramatically the corrosion rate, especially below the mould, where there is a high amount of water accelerating the corrosion process.(5)

A work has been done, in a research and development cooperation project between university and industry, to develop fluorine-free mould powders for billet casting. Some preliminary results were presented in a previous work.(6)

1.1 Objective

The aim of the present work is to determine technological parameters of new fluorine-free recipes: melting characteristics (heating microscope), viscosity, melting rate and %crystallinity.

2 METHODOLOGY

Properties of the mould powder Accutherm ST-SP/512SV-DS, produced by Stollberg Group and used at steelworks plants for billet casting, are used as standard in the present work.

Five new laboratory fluorine-free recipes (RA, RB, RC, RD, and RE) were elaborated following a standard procedure. Then, laboratory tests were employed to evaluate mould powders behaviour. In the following, more details about the performed tests will be given.

2.1 Raw Materials

Different Brazilian raw materials with fluxing ability were selected to produce fluorine-free mould powders recipes. Each raw material was analysed through X-ray fluorescence spectrometry in order to determine chemical composition.

2.2 Melting Characteristics

For the evaluation of melting characteristics it was used a heating microscope. A temperature regulator increases the temperature of the furnace with a linear heating rate of 10℃/minute. After measurement, the characteristic temperatures of the sample material, such as melting and flowing points, can be analysed. The working method refers to the German standard DIN 51730.(7) Regarding repeatability limit (same operator, same apparatus) results shall be considered acceptable if the characteristic temperatures do not differ by more than 30℃. Regarding reproducibility limit (different operators, different apparatus) the results shall be considered acceptable if the characteristic temperatures do not differ by more than 50℃.

2.3 Viscosity

Initially, the chemical compositions of the recipes RA, RB, RC, RD, and RE were determined through IRSID model, considering the same viscosity values for all of them (~ 2 Pa.s).

To evaluate fluidity of the fluorine-free mould powders the test named Ramp Test was performed. That is a test where 0.5 g of a mould powder sample is put inside an Al_2O_3 boat with a fixed slope. The inclined vessel with the sample on its higher part is heated in a furnace during certain periods (3, 4 and 5 minutes) at 1280℃ (temperature must be higher than melting tem perature). The slag ribbon length (molten mould powder) on the vessel is measured through a software from digital images. In this way, different slag ribbons can be compared.

Viscosity measurements were performed through a high-temperature equipment and a rotation viscometer. After preparation of the specimen (decarburisation, fusion and crushing) and preparation of the measuring device, the measuring procedure is executed. It is computerized and runs automatically. A computer calculates and prints the graph "viscosity [Pa·s] *versus* temperature [℃]".

2.4 Melting Rate

Different methods have been developed for obtaining melting rates. In combustion boat tests, a known mass of powder is poured into an opensided porcelain combustion boat and then placed in a furnace at a known temperature; the time for the sample to melt provides an inverse ratio of the melting rate.(1)

In the present work, results from the test named Boat Test are showed. In the Boat Test 1 g of the sample material is put inside an Al_2O_3 boat and left in a temperature higher than the melting temperature for 1, 2, 3… minutes up to complete fusion. Afterwards, the boats are examined for comparative purposes.

2.4 Crystallinity Analysis

In crystallinity analysis, decarburized sample is placed in a platinum crucible and heated at 1300℃ for 20 minutes. The molten flu x is then poured into a platinum mould at the desired temperature (900℃ and 950℃ i n the present work) and maintained at the particular temperature for a period of 20 minutes for annealing. The samples are cut, examined with a low power microscope and photographed. With the help of a software %crystallinity is determined.

In the present work, aim of the crystallinity analysis is to compare %crystallinity of fluorine-free recipes with the standard mould powder.

3 RESULTS AND DISCUSSION

From mould powder Accutherm ST-SP/512SV-DS ("RS" in the present work) were elaborated five new recipes without fluorine – RA, RB, RC, RD and RE – using Brazilian raw materials, see Table 1. Fluorine-free recipes were adjusted until viscosity values close to RS through IRSID model (1300℃) were found.

3.1 Melting Characteristics

Regarding melting characteristics, each value at Table 1 is the mean from two measurements. All the recipes are similar to RS except RD (considering the repeatability limit of 30℃).

As these measurements are carried out on powders on 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 channels.(1) Worth to say, very little data is available in the literature on the effect of chemical composition on the melting range of mould powders.(8)

3.2 Viscosity

Mould powder main function is the creation of a lubricant film at mould/strand interface. It is essential that the mould be lubricated throughout. Failure to do so could lead to a variety of problems, including sticker breakouts.(1)

At Figure 1 it can be seen Ramp Test results for 5 minutes at 1280℃. According to these results, all fluorine-free recipes present adequate fluidity except RB and RC.

The recipes of the present work have different phases and different proportion of phases; each raw material has its own melting behaviour. In Ramp Test, initially the sample is solid. The sample must melt to create the slag ribbon, *i.e.* the melting behaviour of the mixture probably influences the results.

For the situation at rotation viscometer, the entire sample is initially liquid. The viscosity results at 1300℃ obtained through the ro tation viscometer can be seen at Table 1. The most discrepant value is RA; the reason for this high viscosity value is unknown (see also Figure 2).

In terms of chemical composition, silica and alumina are the major constituents that determine mould slag viscosity. In addition to these oxides, other components of mould slags – the so called *network modifiers* – such as CaF_2, Na_2O, K_2O, CaO, MgO lower the viscosity.(9)

Table 1 – Technological parameters of the recipes analysed in the present work

Mould powder		**RS**	**RA**	**RB**	**RC**	**RD**	**RE**
Basicity (V-ratio)		0.70	0.70	0.70	0.70	0.70	0.70
SiO_2	%	35.70	36.83	36.90	38.31	36.97	38.17
CaO	%	24.98	25.69	25.93	26.63	25.84	26.60
MgO	%	2.95	3.23	3.04	3.15	3.26	3.04
Al_2O_3	%	12.07	8.97	8.59	7.57	8.77	8.16
TiO_2	%	0.47	0.36	0.29	0.24	0.45	0.30
Fe_2O_3	%	2.61	2.24	2.69	2.38	2.25	2.30
MnO_2	%	0.09	0.15	0.16	0.18	0.13	0.17
Na_2O	%	4.11	7.53	7.18	6.02	5.92	7.10
K_2O	%	1.60	0.93	0.61	0.47	0.56	0.99
F	%	4.20	0	0	0	0	0
B_2O_3	%	0	0	0	0	3.69	0
Li_2O	%	0	0	0.29	0.33	0	0
C_{free}	%	6.02	5.93	6.03	5.87	6.02	6.02
CO_2	%	3.83	4.79	4.93	6.05	3.84	4.43
C_{total}	%	7.07	7.24	7.38	7.52	7.07	7.23
$T_{melting}$	℃	1188	1167	1162	1191	1148	1166
$T_{flowing}$	℃	1199	1175	1171	1198	1156	1172
Viscosity (1300 ℃, IRSID)	Pa.s	1.95	2.10	1.95	2.15	2.04	2.11
Viscosity (1300℃, viscometer)	Pa.s	1.84	3.03	1.12	1.20	1.09	1.25

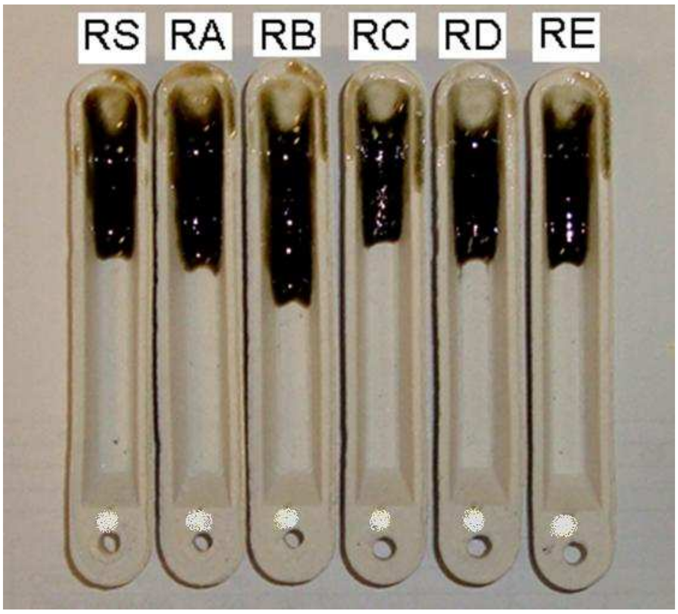

Figure 1 – Ramp Test results (5 minutes at 1280℃ in a furn ace).

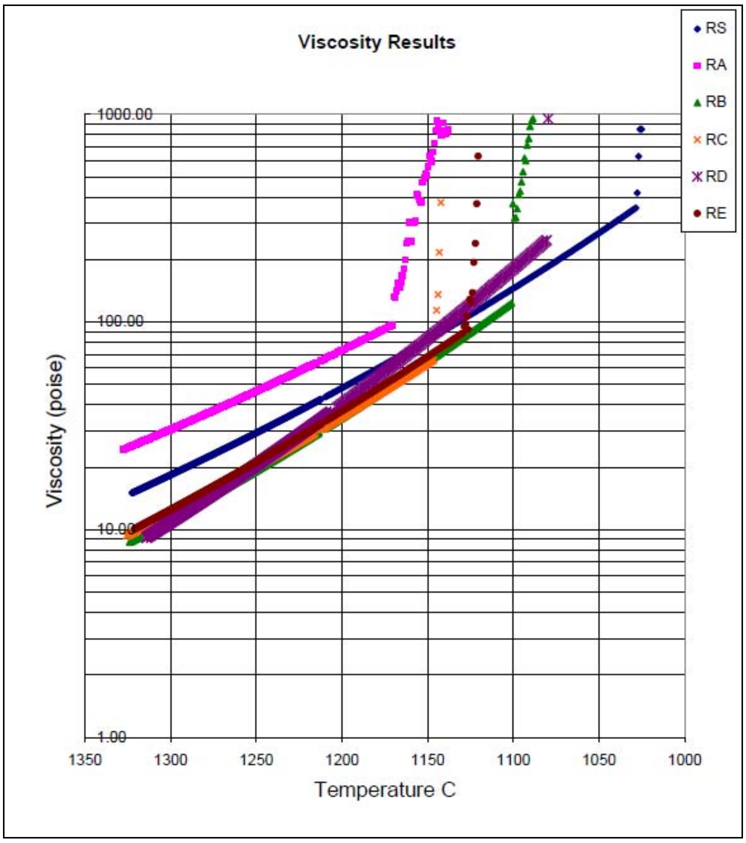

Figure 2 – Viscosity measurements results obtained from rotation viscometer, recipes RS-RE.

3.3 Melting Rate

Below, at Figure 3, Boat Test results (five minutes at 1280℃ in a furnace) can be seen. Considering melting rate, recipes RD and RE are comparatively closer to RS than the others recipes. This inspection is made visually.

That the mould powder should melt at a rate that is compatible with the demand for liquid slag it is obviously important. According to Mills(1) the melting rate is controlled by several factors, such as:

- vertical heat flux, which is affected by various casting parameters such as casting speed, superheat, turbulence, *etc.*;
- free carbon content of the mould powder;
- type and particle size of carbon;
- carbonate content of the mould powder.

Carbon particles separate the mineral particles and slow down the agglomeration of the molten slag globules. Thus, the more carbon is present, the more time is required to agglomerate and the slower the melting rate is. For a given carbon content, the finer the carbon particles, the greater the separation of the partially molten particles, and hence the slower the melting rate.(1)

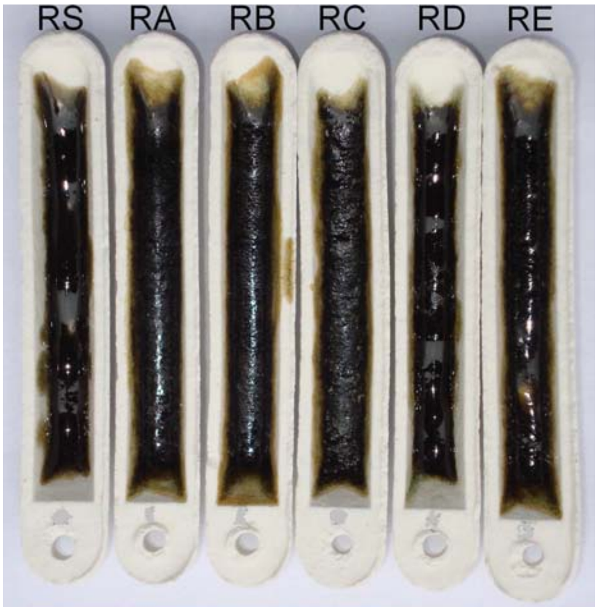

Figure 3 – Boat Test results (five minutes at 1280℃ in a fu rnace).

Riboud and Larrecq have determined the melting rate of several mould powders and confirmed that the free carbon content of the mould powder has a profound influence on the rate of fusion. Moreover, their results also showed that mould powders with similar overall chemical composition could have different rates of fusion; this fact led to the conclusion that the mineralogical nature of the mould powder constituents influences the melting rate.(10)

In the present work, different raw materials (different mineralogical natures) were used for the production of the recipes. This fact probably influenced melting rate (carbon type was the same for all recipes).

3.4 Crystallinity Analysis

At Figures 4 and 5 it can be seen crystallinity analysis results for the recipes of the present work, for annealing at 900℃ and 950℃ duri ng 20 minutes (after heating at 1300℃ for 20 minutes).

Original value of the image magnification which was got through the optical microscope is 20X. A crystalline layer can be seen at the bottom of the figures (slag/mould interface). The pockets of crystals throughout the bead were also included in the %crystallinity determination. The samples were not etched to avoid interference with the visual observation of glass versus crystal.

The margin of error in percentage of crystallinity is around 5% (determined through previous tests). Thus, it can be seen that the %crystallinity for all the fluorine-free recipes are close to RS.

From literature(11) it is well known that silica-rich slags can be cooled easily to form glasses in the temperature range where they should crystallize under equilibrium conditions. On the other hand, basic slags rich in CaO are extremely difficult to quench as glasses. Most mould powders lie between these two extremes. The recipes of the present work are silica-rich slags, *i.e.*, vitreous phase is formed easily even at low cooling rates.

Li, Thackray and Mills(12) discussed a test to predict %crystallinity found in slag films formed between the steel strand and the mould. According to them, it should be noted that the slag film may be present in the mould/strand gap for a considerable time; thus, some of the crystallization developed in the slag film may develop as a consequence of annealing in a temperature gradient: the hot face of the slag film (against steel shell) will be between the steel liquidus and 1150℃, but there has been some dispute concerning the temperature of the slag film on the mould side ranging from 300℃ lower down to the mould to above 600℃ although the temperature in the hot face of a copper plate slab mould is estimated between 260℃ and 110℃. They recommended a holding time of 20 minutes at 610℃ in stainless steel crucible (after decarburisation and heating at 1300℃ for 20 minutes) to match with the %crystallinity found in slag films taken from the mould.

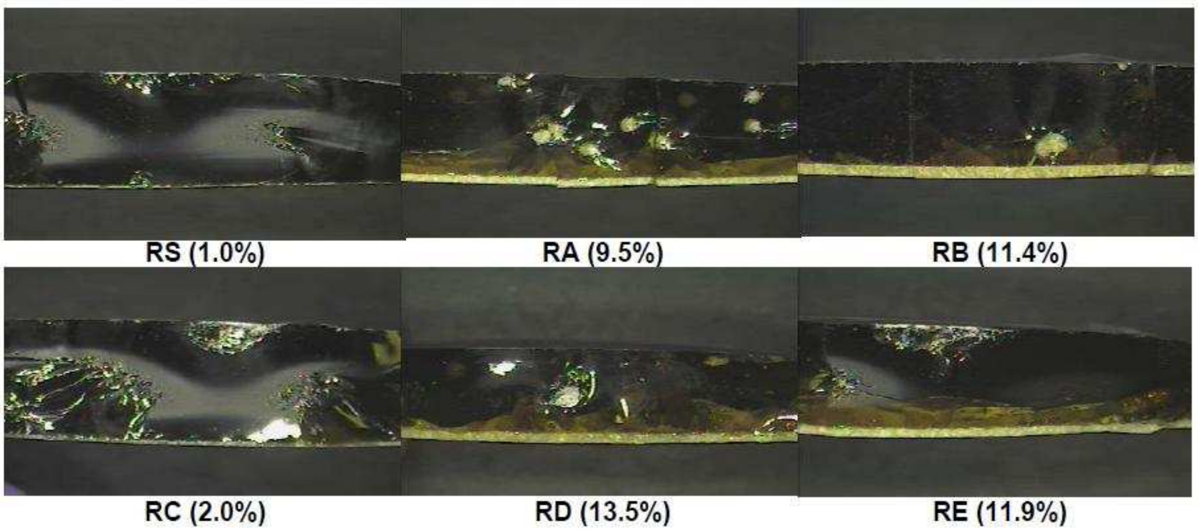

Figure 4 – Crystallinity analysis results at 900℃.

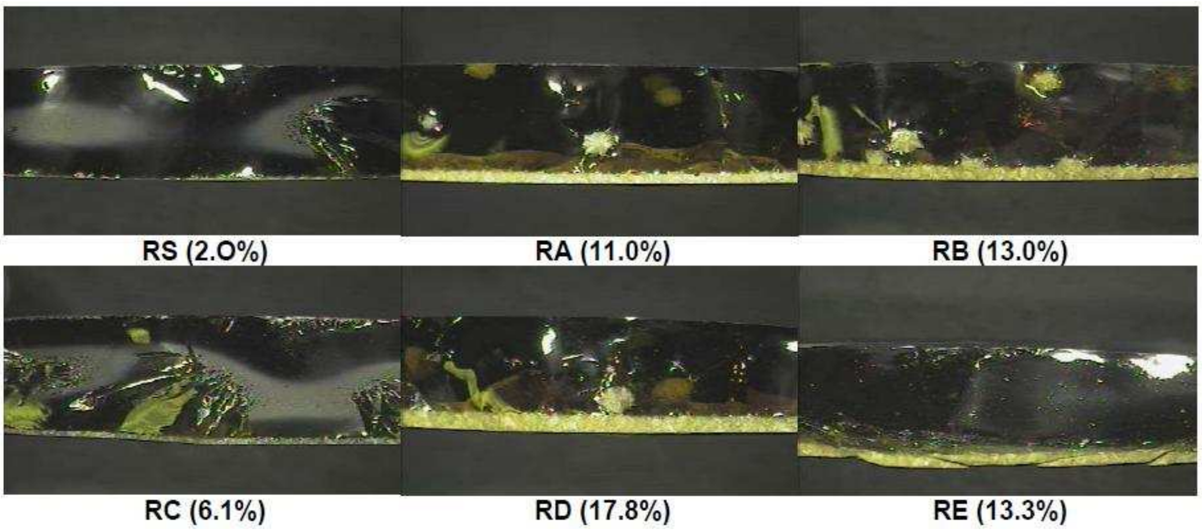

Figure 5 – Crystallinity analysis results at 950℃.

In the present work the annealing temperatures were higher (900℃ and 950℃) since all the recipes present low tendency to crystallize (the lower the annealing temperature, the lower the %crystallinity). The experimental procedure was also applied at 610℃, and the determined percentage of crystallinity is 0% for all the recipes at this annealing temperature (see Figure 6). The crystallinity analysis is a test which is still under development; in the present work it is used for comparative purposes. Trying to determine how the measured crystallinity is relative to continuous casting process is one of the goals.

Regarding continuous casting process, in the gap between mould and strand the global friction force is not only given by viscosity and thickness of the liquid slag layer, but also by the nature and proportion of the different mineralogical phases which can exist in the mould powders after solidification.(13)

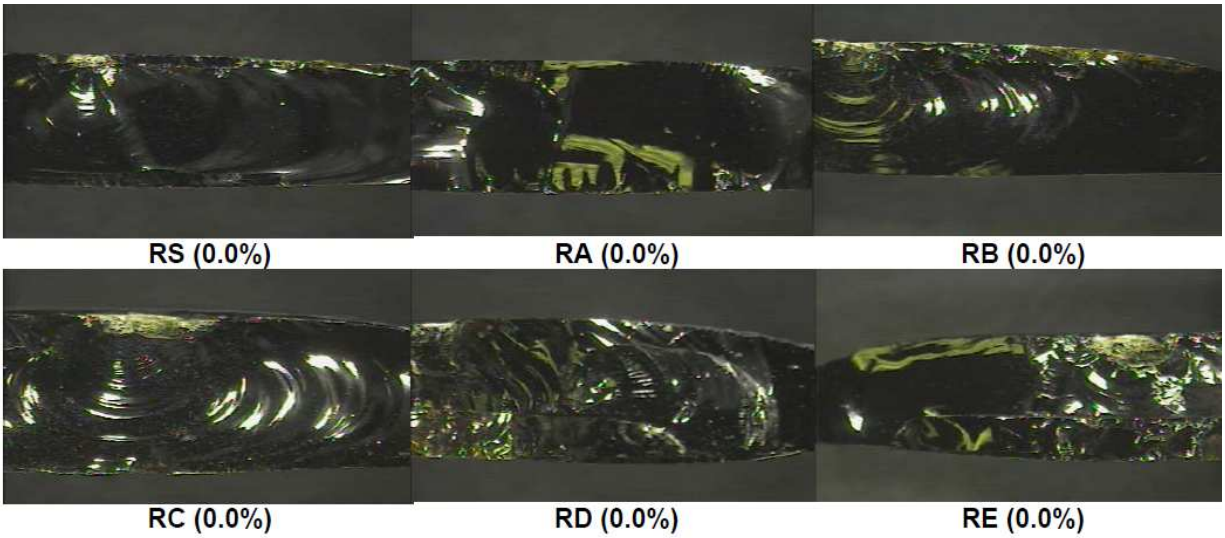

Figure 6 - Crystallinity analysis results at 610℃.

4 CONCLUSIONS

The following technological parameters: melting characteristics, viscosity, melting rate and %crystallinity can all be related to mould powders performance at continuous casting equipment.

Regarding these parameters, from the recipes which were studied in the present work the recipe closer to the mould powder Accutherm ST-SP/512SV-DS, taken as reference and currently used at steeworks plants for billet casting, is RE.

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