Research Article

Use of Borom and Lithium Oxides as a Replacement of Fluoride Compounds in Mold Powders

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Abstract: The demands on the care of the environment, has impulsed the researchers to develop new mold powders without fluor content in their composition. Nevertheless, the new products need cover the important process requirements and avoid metallurgical problems. The main reason of the substitution of fluoride compounds is associated with emissions of fluorinated gases that cause health problems in operators. Also, provoke environment contamination and cooling water that could cause serious damage or corrosion on the equipment in the industrial plants. In the steel continuous casting process, the presence of a lubricant layer between the oscillating mold and the steel shell formed (during the first stage of solidification) is essential to ensure the good quality of the product. This layer should permit the transfer of heat from the liquid steel to the cooling water in the mold and ensure good physical properties in order to achieve the required lubrication. The use of mold powder, which forms a liquid slag film in the space between the steel shell and the mold, is now standard practice in the continuous casting process. That is why the design of these products acquires a significant importance. This paper presents a comparative characterization of a commercial mold powder and a synthetic slag without fluor compounds, designed in the laboratory. The oxides used in order to replace fluorine are B_2O_3 and Li_2O. The results include physical properties such as viscosity at different process temperatures. These values obtained, by theoretical calculus using Riboud model, were compared with results estimated applying the software Fact Sage. In order to predict heat transfer behavior of both slags, the crystallization tendency was studied by experimental tests. The crystalline and glassy phases identification, were carried out by light and scanning electron microscopy (SEM/EDS) and checked by X ray diffraction (XRD). A thermodynamic simulation of the systems using Fact Sage corroborated the information obtained.
Keywords: mold powders, viscosity, crystallization tendency, environment, continuous casting

INTRODUCTION

In the steel continuous casting process, the main factors to control during the operation includes, to provide the adequate lubrication and the heat transfer at the mold/metal interface, the absorption of non-metallic inclusions and to avoid steel reoxidation and freezing. In this sense, the mold powders play and important role. The physicochemical properties and crystallization behaviour of these synthetic slags, at process conditions, are associated with their chemical composition. A complex oxides system, fluorine compounds and carbonaceous materials constitute the mold powders. The chemical composition integrates different oxides: SiO_2, CaO, MgO, Al_2O_3, Na_2O, K_2O, FeO, TiO_2, among others. The CaF_2 (added in the range of 4 to 10%) controls principally the viscosity, fluidity and the precipitation of cuspidine ($3\ CaO.2SiO_2.CaF_2$) in the film at the mold strand gap. The crystalline phases affect the heat transfer. The carbonaceous materials determine the melting behaviour [1-3]. The

specific formula of the mold powder is different for each casting condition grade of steel produced. Van Ende et al. in [4], mention that a successful mold powder for one plant often may not provide the same performance in another plant due to the differences in mold dimensions, steel grades and variability in casting conditions between the plants.

These authors also present an overviewed of the thermodynamic database for the oxyfluoride system. It is important to remember that, the mold powder is placed over the liquid steel and forms a liquid pool of flux by contact with the molten metal. The second layer (over the liquid pool), is constituted by a sintered powder and finally at the top; a black granular mold powder is always present. Each of these layers has different functions:
- The granular layer, provides insulation of the steel to avoid heat loss by radiation. Also the carbon

combustion product reductor gas, prevents steel reoxidation.

▪ The sintered layer ensures the thermal insulation.
▪ The liquid layer provides lubrication between the water-cooled mold and solidified steel surface (shell). This layer, also helps to reduce the wear on the mold plate and diminished the risks of breakout during casting process.

The fluorine content, common in commercial mold fluxes, is harmful because their emissions at the working temperature produces environmental pollution and alter the cooling water of the mold [5, 6]. For this reason, in the last years numerous studies on different possibilities of fluorine compounds substitution were carried out. Persson et al. in [7] provides information of a systematic study on the fluoride emission from slags and fluxes at relevant temperatures to steelmaking and casting processes. Fluorides are lost in the vapor phase during the casting operation due to the high vapor pressure of fluoride compounds. Especially SiF_4 gas, as a product of the reaction between CaF_2 and SiO_2, in the slag. In addition, the humidity presence in the environment could react with the CaF_2, resulting in the formation of FH. Fluorine is very toxic and reactive. Many of its compounds can cause severe damage. It is important to avoid the risk of the vapors generation during operation in order to prevent that these vapors take contact with the operator's skin and eyes, causing serious health problems. Also to avoid the equipment corrosion [8, 9]. Fluoride emissions from the slag melt could alter the slag chemistry, causing changes in the critical behavior of viscosity and the crystallization [7].

In this study, one synthetic slag was designed and prepared in the laboratory (without CaF_2) using B_2O_3 and Li_2O oxides, as fluorite substitutes. In order to compare the behaviour, other commercial mold flux that contains fluorite, used in the casting process of medium carbon steel, was considered. The viscosity of both slags (at different temperatures) were obtained by the Riboud theoretical model and the software Fact Sage. It is relevant to know, that the initial solidification of steel, is strongly influenced by the crystallization process of mold flux. The interfacial thermal resistance between the mold and the crystalline layer of mold flux controls the total heat transfer during the steel solidification at the meniscus [9, 10]. This crystallization process ensures a stable and controlled steel solidification leading to obtain the material with the desired quality [11, 12]. For this reason, the crystallization tendency and crystalline phases present in the samples (considering the characteristics and chemical composition) were studied applying light microscopy and scanning electron microscopy (SEM) with EDS. In order to corroborate the presence of the phases identified, a thermodynamic simulation of both systems was carried out, applying the software Fact Sage.

EXPERIMENTAL PROCEDURE

In this paper, a study on two slags is presented. One consists in a complex oxide mix designed and prepared in the laboratory with additions of B_2O_3 and Li_2O (6B4Li) in order to substitute CaF_2 in the chemical composition. The other slag consist in a commercial mold powder (PC) with 10 % of CaF_2. The chemical compositions of both slags and the binary basicity index (BI) are detailed in Table 1.

The sample (6B4Li) was prepared according to a formulation based on a mass balance, using a model developed in the laboratory**.** The raw materials were introduced in a ball mill where it was dry blended for 1 hour at 65 rpm in order to grind and homogenize the mixture. The basicity index of the slag 6B4Li designed is close to the value of the PC slag. The content of B_2O_3 and Li_2O were considered in order to achieve similar physical properties respect to PC slag.

Table 1. Chemical composition of the slags (wt.%).

Slag	SiO_2	CaO	MgO	Al_2O_3	Na_2O	F	B_2O_3	Li_2O	Others	BI
PC	36.2	30.8	2.1	5.1	12.7	10.4	-	-	2.6	0.85
6B4Li	33.2	28.6	1.4	4.7	18.6	-	5.8	3.9	3.9	0.86

*Others column include the oxides: K_2O, Fe_2O_3, Ti_2O y P_2O_5

The basicity index of the mold fluxes is relevant to predict the heat transfer behavior in the mold during casting process through the promotion of crystallization in the molten slag film. The values of both samples (see, Table 1) were within the optimum range for this type of fluxes. It is important to remember that heat transfer in the mold takes place through two mechanisms: conduction and radiation. When a crystalline fraction in the film is present, the conduction component in the heat extraction process increases. It means that a lower cooling rate in the mold is present. If BI is less than 1, the crystalline proportion is very low in the film between the mould and the steel shell, so the powder has the appropiate ability to lubricate and achieves the cooling rate required for medium carbon steels [13-14].

Viscosity

This physical property was calculated using the Riboud model [15]. This model is based on the chemical composition of the slags. The Riboud model is widely used for mold fluxes viscosity predictions in the industry. It is applicable for the slags of following chemical composition: SiO_2 (28-48%), CaO (13-52%),

Al_2O_3 (0-17%), CaF_2 (0-21%), Na_2O (0-27%). This model allows to evaluate the mold flux viscosity according to the following equation (Eq.1):

$$\eta = A.T.\exp\left(\frac{B}{T}\right) \quad \text{-------------------------(1)}$$

Where: T is temperature in Kelvin degrees, Xi is the molar fraction of the *i*-compound, A and B are parameters that are calculated by the following expressions:

$$A = \exp\left[-19.81 + 1.73\left(X_{CaO} + X_{MnO} + X_{MgO} + X_{FeO}\right) + 5.82\left(X_{CaF_2}\right) + 7.02\left(X_{Na_2O} + X_{K_2O}\right) - 35.76\left(X_{Al_2O_3}\right)\right] \quad (2)$$

$$B = 31140 - 23896\left(X_{CaO} + X_{MnO} + X_{MgO} + X_{FeO}\right) - 46356\left(X_{CaF_2}\right) - 39159\left(X_{Na_2O} + X_{K_2O}\right) + 68833\left(X_{Al_2O_3}\right) \quad (3)$$

In order to corroborate the viscosity of the slags (PC and 6B4Li systems) a Fact Sage simulation (using the glass option of the viscosity module of the software) at temperatures between 1300°C and 1500°C was carried out. The module uses to calculate the thermodynamic base Ftoxid [16].

Crystallization

Besides the heat extraction, the viscosity is also a physical property that depends on the degree of crystallization of the mold flux. For this reason is relevant to consider a study on the crystallization tendency of both samples, in order to complete the characterization of the new slag with B_2O_3 and Li_2O oxides. In this case, it is desirable that the powder 6B4Li achieves a similar behaviour of viscosity and crystallization tendency, respect to the PC flux.

In order to evaluate the crystallization tendency, 10 g of mass of each powder were placed in a graphite crucible and melted at 1300 °C in air. When the temperature is homogenous in the sample, the molten flux was poured and quenched onto a stainless steel plate. By this technique [17], solid glass layers of approximately 25 mm^2 in section and 150 mm in length were obtained. These layers were cut and prepared for microscopy observation. The structural aspect was studied by light microscopy applying a microscope Olympus GX 51 with a Leco IA 32 image system and the scanning electron microscopy (SEM) FEI QUANTA 200F with EDS. The semiquantitative chemical composition of the crystalline and glasses phases were determined by EDS analisys in order to identify them. A thermodynamic simulation of both systems at 1300°C was carried out with the Equilibrium Module of the Fact Sage including different thermodynamic bases of the software [18]. The crystal phases were also checked by X ray diffraction using a diffractometer Philips X´Pert.

RESULTS AND DISCUSSIONS

The liquid pool of the mold slag is the result of flux melting. The liquid slag flows into the space between the steel shell and the copper mold walls. In the upper part of the mold, the slag is fully liquid and provides lubrication in the first seconds of the steel solidification. In the middle section of the mold, at lower temperatures, the slag layer is partially liquid because it contains crystals precipitated. However, the liquid slag acts as a lubricating agent. At the lower region of the mold, the slag is solidified and cause the generation of a gap of air, by contraction. For this reason, it is relevant to know the viscosity evolution at different temperatures. The viscosity values at temperatures between 1300°C and 1500°C determined for both slags allow comparing the behavior between them. This information is useful to predict the lubrication condition in the mold and the thickness of slag layer in the space between mold and steel shell.
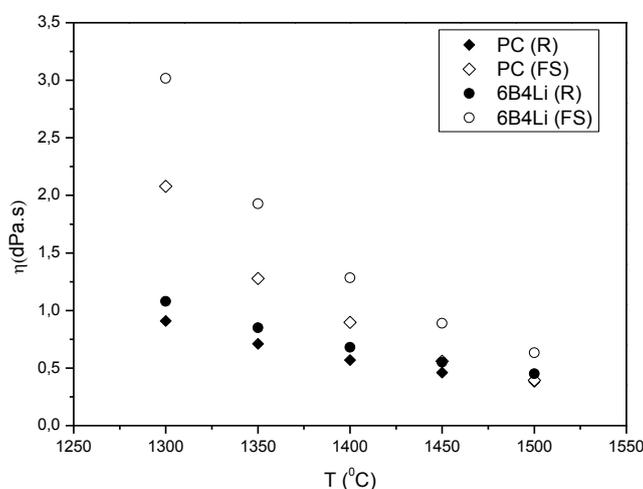
There are different theoretical models to determine the mentioned physical property; however, the Riboud model is one of the most widely used for estimating viscosity for industrial mold fluxes (that are in the range of the chemical composition in which the model is applicable). The viscosity depends on the chemical composition of the mold flux and the temperature. It is important the understanding of the effect of each different oxides present in the chemical composition, as well as the impact of the structural characteristics of the flux film during the operation. Different researches described in [18, 19] have shown that:

- SiO_2 is consider as acidic oxide and a network former.
- Al_2O_3 and B_2O_3 additions could cause an increase in viscosity. This effect is present in the case that these oxides act as silicate network formers, because they are amphoteric oxides. At particular contents, the function is as modifiers of the network.
- CaO, MgO, FeO, MnO and others oxides are considered alkaline oxides and modifiers of the network. Li_2O, Na_2O, K_2O and CaF_2 causes a decrease in viscosity, since they break the Si-O-Si bonds.

In the slags studied in this paper, the chemical composition in the principal oxides (network formers and modifiers) are near. In addition, the basicity index (BI) are quite similar. The differences to take into account between PC and 6B4Li are that; PC contains 10.4% of F while 6B4Li have 5.8 % of B_2O_3 and 3.9 % of Li_2O. In PC slag, F and Na_2O contents are the principal compounds that controls the viscosity. However, in 6B4Li slag, Li_2O and Na_2O acts as viscosity controllers.

The comparison of the viscosity values obtained, at temperatures between 1300°C and 1500°C, by the Riboud model (for the PC and 6B4Li) presents a good approximation and a similar behavior at the temperature range considered. In addition, a comparative analysis of the viscosity values using the Quasichemical Model Fact Sage (FS, selecting the glass option at the same temperature range) in order to evaluate the influence of the structural aspects in relation with temperature, was carried out. Figure 1

It is possible to consider that the viscosity behavior present a good fit between the two slags (Δ% ~15 %) at the mentioned temperature range. It is relevant to comment that the Riboud model implies uncertainties in the magnitude because not includes in the calculation the structural impact. The error range of the model is Δ% ~ 30 % [20]. From the chemical composition point of view, it is possible to think that a little change of B_2O_3 content in the flux could achieve a one better approximation in the viscosity between both slags.

At lower temperatures, the viscosity differences between Fact Sage and Riboud model calculations, are considerable: Δη~65%. It is possible to think that the viscosity results obtained by FSage simulation show the crystal precipitation impact on the physical property during cooling. This phenomenon is present probably at the middle part of the mold.

However, at higher temperatures (when the slag is fully liquid in the upper part of the mold) the difference between viscosity values obtained by Fact Sage and Riboud model is lower for both slags (Δη~ 30%) . The Δη is in the order of Riboud model uncertainties.

Figu-1: Comparison between viscosity values obtained applying Fact Sage and Riboud model for PC and 6B4Li samples.

C.W. Bale et al, in [16], comments that the FToxid data base (for slags and glasses) has been fully optimized from 25°C up to liquidus temperatures, at all compositions and oxygen partial pressures. In addition, the simulation relates the structure of the slag. The structure is calculated by using the thermodynamic description of the model [19]. On this base, it is possible to think that the Fact Sage viscosity values represent the physical property condition in all the zones of the mold. Nevertheless, the Riboud model constitute a good and orientative tool to compare the behavior of the mold slags, but only is confiable to represent the conditions in the upper part of the mold, at higher temperatures.

The differences in the viscosity values obtained (see figure 1) between Fact Sage and Riboud model are also consistent with the results obtained by Kalisz et al. in [19].

CRYSTALLIZATION TENDENCY

K.C. Mills et al. in [20], sustains that the thermal resistance $R_{Cu/slag}$, increase with the crystalline fraction and thickness of the slag layer. This phenomenon is related with the air gap generated due to the roughness resultant of the crystalline phases precipitated in the film. In order to predict the thermal behavior in the mold, the crystallization tendency was studied on both samples, in a quenched condition.

The structural study by light microscopy of the samples (PC and 6B4Li) determines the presence of a similar structural characteristic between them. The crystalline layer (CS) in the surface and the glassy phase (GP) in the inner zone of both samples are shown, in Figure 2 and 3. The crystalline layer presents dendrite crystals (~110 μm of thickness in average) in both cases. The crystalline proportion of the samples is quite similar and low, the result is consistent with the values of the basicity index of the slags BI ~0.85/0.86 [13-14]. This result allow thinking in a similar ability of lubrication and heating extraction between both slags.
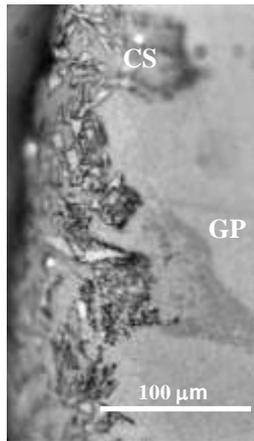
Fig-2. Layer of dendritic crystals developed on the surface of the sample PC, observed with Nital 2 attack.


Fig-3. Layer of dendritic crystals developed on the surface of the sample 6B4Li, observed with Nital 2 attack.

The dendrites crystals and glassy phases (matrix) of both samples were observed in more detail by scanning electron microscopy (SEM). It was possible to establish that the dendrite crystals, present a quite similar morphology in both samples. Figure 4 shows the crystalline layer present in the surface of PC sample, in which the dendrite crystals (D) and interdendritic phase (IP) are visualized. It is also clearly

observed the growing direction of the crystals, from the surface of the layer to the center. By EDS, the present phases were analyzed at high magnification in order to identify all the phases. In Figure 5, a zone of the 6B4Li surface crystal layer is presented. It is possible to distinguish the characteristics of the dendrite structure and the interdendritic phase aspect.
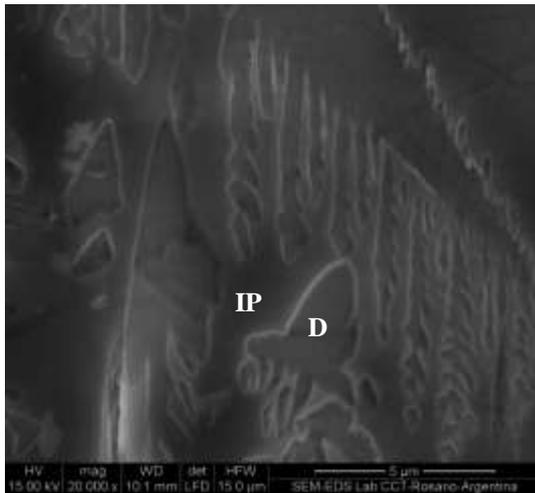
Fig-4. Crystalline layer in the PC sample in which dendrites (D) and interdendritic phase (IP) are observed.
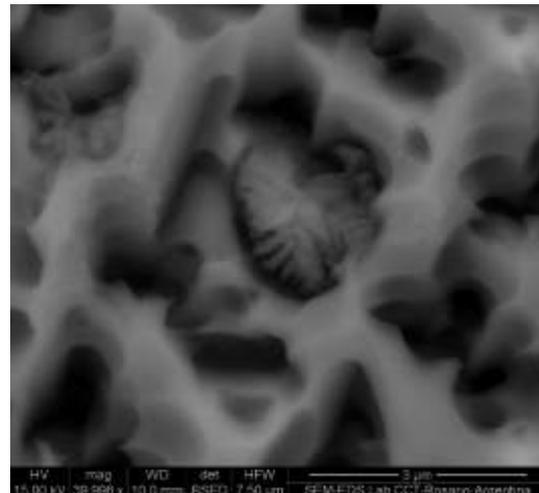
Fig- 5. Detail of the dendrite and interdendritic phase in the 6B4Li sample in the crystal layer.

The chemical composition of the crystalline layer (considering dendritic phase (D), interdendritic phase (IP) and glassy phase (G)) were determined by EDS (SEM) in both samples. Finally, the results were correlated with the thermodynamic simulation of both slag systems carried out at 1300ºC, using the Fact Sage

Equilibrium Module. The information is detailed for each sample.

Sample PC:
In Table 2, the semi quantitative chemical composition including the principal compounds of the phases present in the sample, are showed.

Table 2. Chemical composition of the dendrites (D), interdendritic phase (IP) of the crystalline layer and the glassy matrix (G) of the sample PC determined by EDS (wt%)

Zone	F_2Ca	Na_2O	MgO	Al_2O_3	SiO_2	CaO
D	2.36	3.59	6.82	5.64	26.93	54.66
IP	2.60	11.92	1.78	16.98	35.77	30.96
G	2.80	16.23	1.79	15.6	31.70	31.87

The solids predicted by the Fact Sage simulation are consistent with the EDS analysis results. In the case of the dendrites (D), the principal solid phases includes cuspidine ($Ca_4Si_2F_2O_7$) and nepheline ($NaAlSi_4$). Both crystalline phases, were also identified as the principal phases present by X ray diffraction method (XRD). In addition, the simulation has predicted the presence of a lower proportion of dicalcium silicate (Ca_2SiO_4).

Mills et al in [20], have confirmed that the cuspidine is the first phase formed and which precipitate on the mold side. The crystals grows in normal direction, respect to the shell side (in the surface of the slag layer). At lower temperatures precipitates the nepheline. The authors mentioned that lower proportion of solid phases such as: $(Na_2Ca_2)Si_3O_9$ and $Na_4CaSi_3O_9$, are possible to be present.

The thermodynamic simulation also predicts the presence of two liquid phases (L1 and L2) both rich in SiO_2, CaO, Na_2O and Al_2O_3. One of them (L2) fits very well with the interdendritic phase (IP) analyzed by EDS, see Table 2. In this liquid phase, the Fact Sage simulation also predicts the presence of NaF. The other liquid phase is (L1), interpreted as the glassy phase or matrix (G) present in the rest of the sample. These phases are also coincident with the information reported by Mills et al. in [20].

Sample 6B4Li:

The same methodology, respect to PC, was applied with this sample 6B4Li. The semi quantitative chemical composition of the dendrites (D), interdendritic phase (IF, present in the surface crystalline layer) and the glassy matrix (G) of the sample, were determined. In the Table 3, the results, are visualized. It is important to consider that elements such as B or Li are difficult to be determined by EDS analysis. For this reason, only the content of: Na_2O, MgO, Al_2O_3, SiO_2 and CaO are detailed.
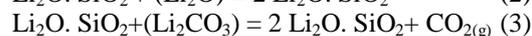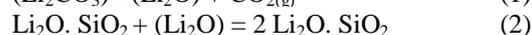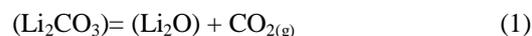
Table 3. Chemical composition of the dendrites (D), interdendritic phase (IP) and the glassy matrix (G) of the sample 6B4Li obtained by EDS (wt%).

Zone	Na_2O	MgO	Al_2O_3	SiO_2	CaO
D	20.02	2.06	14.87	35.70	27.35
IP	21.89	1.77	10.38	35.14	30.82
G	23.35	1.60	10.95	36.60	27.48

In this case the simulation of the slag system by Fact Sage at 1300ºC, predicts the formation of a solid phase without boron content ($Na_4CaSi_3O_9$) in a high proportion and others solid phases such as: $Ca_3B_2O_6$, $Ca_{11}B_2Si_4O_{22}$ in which boron is present. This is due to B_2O_3 promotes the formation of small anionic clusters B-O-B when the oxide content is between 5% and 9%, such as in the case of 6B4Li slag with 5.8 % of B_2O_3. It is possible to think that, the EDS results of the dendrites (D), are consistent with the phases predicted by Fact Sage in which the principal oxides are: CaO, SiO_2 and Na_2O. However, the analytical technique is limited, for the B_2O_3 determination. By X ray diffraction (XRD) it was possible to confirm that the crystal phases present in the sample were Combeite ($Na_4CaSi_3O_9$) and Damburite ($Ca_{11}B_2Si_4O_{22}$) which complete the information obtained by Fact Sage simulation and EDS results.

Fact Sage predicts the lithium principal presence, in two liquid phases: $(Li_2O)_2SiO_2$ and Li_2SiO_3. This information is in coincidence with [21], both liquids are products of the Li_2CO_3 decomposition in presence of SiO_2. Because the Li_2CO_3 is one of the raw material used during slag preparation. The authors also describe the Li_2CO_3 decomposition mechanisms during flux melting by the reactions (1 to 3):

$$(Li_2CO_3) = (Li_2O) + CO_{2(g)} \qquad (1)$$
$$Li_2O. SiO_2 + (Li_2O) = 2 Li_2O. SiO_2 \qquad (2)$$
$$Li_2O. SiO_2 + (Li_2CO_3) = 2 Li_2O. SiO_2 + CO_{2(g)} \; (3)$$

Although the system did not reach the equilibrium, on the base on the standard free energy changes considering the reactions in the system Li_2CO_3 – SiO_2 [21], it is possible to say that the liquid phase more stable at temperatures above 700 °C is $2Li_2O. SiO_2$ while at low temperatures, below 700 °C is the liquid phase $Li_2O. SiO_2$. For this reason, probably the matrix contains more proportion of the last phase, generated during the cooling conditions. The Fact Sage prediction in relation with the liquid phases with lithium, is difficult to corroborate by EDS analytical technique or X ray diffraction. Nevertheless, it is

relevant to mention that the chemical composition of the liquid phases (IP) and (G) determined by EDS in this sample, shows the presence of phases rich in SiO_2, CaO, Na_2O and Al_2O_3, with contents close to those of PC sample.

Several researchers [23-25], given the need for replacement of fluorine compounds (due to contaminating action) studied the possibility of selecting other compounds that produce no harmful emissions, including B_2O_3 and Li_2O, developing different types of mixtures analyzing its physical properties and in some cases their behavior in the process.

The results obtained in this paper, on the comparison between PC and 6B4Li slags, allows thinking in a concrete possibility of CaF_2 substitution by B_2O_3 and Li_2O addition in the mold fluxes. In this paper, the viscosity and crystallization tendency (of two system with and without CaF_2), was discussed. The viscosity of both slags are slightly different and the crystallization tendency results are quite similar (in coincidence with the close values of BI). The similar behavior allow us to predict that the 6B4Li slag could promote good industrial conditions for the continuous casting of medium carbon steels avoiding fluorine emissions.

CONCLUSIONS

On the base of the results obtained in this and previous papers, it is possible to consider that the CaF_2 substitution could be done by the addition of B_2O_3 and Li_2O, in order to prevent the environment contamination and damage on worker health. Also it is possible to think in a similar ability of lubrication and heating extraction between both slags for the medium carbon steel continuous casting process.

In relation with viscosity behavior, that is established by Riboud model and Fact Sage simulation (between the two slags, PC and 6B4Li), a slightly difference is verified. From the chemical composition point of view, it is possible to think that a little change of B_2O_3 content could achieve a one better approximation in the viscosity between both slags. Anyway, the 5.8% of B_2O_3 present in 6B4Li slag is in range between 5% and 9% of the oxide that promotes B-O-B bonds.

The Fact Sage viscosity values represent the physical property conditions in all the zones of the mold. Nevertheless, the Riboud model constitute a good and orientative tool to compare the behavior of the mold slags, but the information only is confiable to represent the conditions in the upper part of the mold (at higher temperatures).

The correlation of the semiquantitative chemical composition obtained by EDS (SEM), the thermodynamic simulation with Fact Sage and the X ray diffraction results, allows to identify the crystalline phases present in both samples. Also permits to predict the probable glassy phases present in the matrix.

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