Review Article

Physical properties characterization of a peritectic mold flux formed from the addition of calcitic marble residue in the commercial one

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Abstract
Mold fluxes play an important role in the lubrication and heat transfer control between the mold wall and steel shell during the continuous casting process. To ensure control of the heat transfer, it is necessary to evaluate the crystallinity of mold flux. The casting of peritectic steel commonly uses the mold flux that forms crystalline phases. These phases, in particular the cuspidine (Ca₄Si₂O₇F₂), increase resistance to radiation heat transfer, leading the steel to cool slowly and to ensure the production of defect-free products. The purpose of this paper is to create alternative peritectic fluxes obtaining gain due to the use of a cheaper raw material, avoiding the disposition of residues in the environment. Thus, using FactSage® software, new mold fluxes were simulated from a commercial peritectic flux with additions of calcitic marble residue, SiO₂ and CaF₂. From the thermodynamics simulations, three new fluxes were chosen and experimentally developed. In those fluxes, the physical properties such as melting point, break temperature, phases and microstructure were analyzed and compared with the commercial peritectic flux. The measurements using Differential Thermal Analysis (DTA) showed that there was no significant change in the melting point and break temperature. Cuspidine, crystalline phases and dolomite were established in all new samples. By using the thin-film technique, it was possible to observe that the microstructures of the new fluxes obtained were similar to with the commercial one. The presence of acicular grains was the main difference in the sample with highest residue concentration.

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1. **Introduction**

The mold fluxes used in the continuous casting process are synthetic slags formed basically by CaO-SiO$_2$-Al$_2$O$_3$-Na$_2$O-CaF$_2$. When they come into contact with melted steel, a liquid phase is generated with specific characteristics for each casting solidification condition [1,2]. The mold flux infiltrates into the gap between the steel shell and the copper wall of the water-cooled mold [3], forming a solid slag film of 1–2 mm thick followed by a thin liquid layer of 0.1–0.3 mm thick against the shell [4–6]. These layers are responsible for two main functions: (i) lubrication; and (ii) horizontal heat transfer between the solidified shell and the mold [3,6,7]. The liquid layer is responsible for the lubrication and the crystallinity of solid flux layer has strong influence on the heat transfer.

To obtain a final product with a surface that is free from defects, the control of the horizontal heat transfer is a critical issue [2,3,5,6,8] alone with no operation problems [3]. Some defects are correlated with the mold flux crystallinity, which is responsible for the increase of the resistance to heat transfer between the steel shell and the mold. To the casting of peritectic steel, high heat rate losses can produce longitudinal cracks. To prevent this condition it is necessary to use a mold flux which exhibits high resistance to heat transfer. In this case, it is used the peritectic flux, and its main characteristic is the predominance of crystalline phases [3,5,8].

One of the ways to analyze the crystallinity of the different types of mold fluxes is to use the modified Stollberg method [5]. It is already well documented that cuspidine (Ca$_4$Si$_2$O$_7$F$_2$) is the main crystalline phase responsible for heat transfer control in continuous casting for fluorine-containing peritectic fluxes [9,10], and its presence can be identified by the technique of X-ray diffraction. To observe the microstructures formed, the thin-film method has recently been proposed for the study of mold fluxes [11]. This technique allows the observation of the microstructural difference between different types of mold fluxes. Through the microstructural analysis, it is possible to evaluate the grain size. The grain size affects the heat transfer by radiation of mold flux because larger the grain, greater the thermal resistance of radiation heat transfer [12]. Thus, as this parameter may be important in peritectic fluxes, this paper aimed to use the thin-film method for the evaluation of the microstructures of commercial peritectic mold flux and two other types with addition of calcitic marble residue, composed of CaO and MgO. In addition, the melting and break temperature were analyzed as well as the phases formed, aiming, mainly, at the cuspidine. In this study the proposal is to create alternative peritectic fluxes obtaining gain due to the use of a cheaper raw material and avoiding disposition of residues in the environment.

2. **Method**

In this work, there were used as raw material one commercial mold flux and one common calcitic marble waste. Besides of them, there were also added high purity fluorite and silica to adjust. Table 1 shows the chemical composition of these materials. From the chemical composition, mixtures were simulated using the FactSage® software that could be elaborated using commercial mold flux with the addition of marble waste and the correctives. During the simulations and mass balance it was possible to predict the presumable phases that could be formed in each mixture. The thermodynamic simulation showed that, as the calcitic marble residue is added, it occurs the suppression of the formation of cuspidine (Ca$_4$Si$_2$O$_7$F$_2$), which is the most important phase that must form in peritectic fluxes. The cuspidine disappears completely, according to the simulation, when 8% of residue was reached. Thus, to accomplish this paper, it was decided to formulate three types of fluxes with a mixture of calcitic marble, the first one with 2% of residue where cuspidine is still expected, the second with 10% where total suppression of

| **Table 1** - Chemical composition in % by mass of raw materials used. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Components                  | Commercial peritectic mold flux | Calcitic marble waste       | High purity silica          | High purity Fluorite        |
| CaO                         | 35.1                        | 46.7                        | –                           | –                           |
| SiO$_2$                     | 23.8                        | 0.5                         | 100                         | –                           |
| Al$_2$O$_3$                 | 3.5                         | 0                           | –                           | –                           |
| Fe$_2$O$_3$                 | 0.6                         | 0                           | –                           | –                           |
| TiO$_2$                     | 0.1                         | 0                           | –                           | –                           |
| MgO                         | 1.4                         | 10.4                        | –                           | –                           |
| Na$_2$O                     | 3.2                         | 0                           | –                           | –                           |
| K$_2$O                     | 0.1                         | 0                           | –                           | –                           |
| MnO                         | 0.1                         | 0                           | –                           | –                           |
| P$_2$O$_5$                  | 0.6                         | 0                           | –                           | –                           |
| CaF$_2$                     | 15.8                        | 0                           | 100                         | –                           |
| PPC*                        | 15.1                        | 42.3                        | –                           | –                           |

* Loss by calcination.


cuspide is predicted, and a third formulated containing in addition to the 10% residue 4% fluorite and 6% silica where the objective was to favor the return of the cuspide phase. Chemical compositions of the commercial peritectic mold flux and also the different mixtures obtained are shown in Table 2.

| Table 2 – Chemical composition of commercial flux (100F) and of the samples containing commercial flux and marble residue (98F and 90F). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | SiO₂            | Al₂O₃           | Fe₂O₃           | TiO₂            | CaO             | MgO             | Na₂O            | K₂O             | MnO             | P₂O₅            | CaF₂            |
| 100F            | 28.2            | 4.2             | 0.7             | 0.1             | 41.7            | 1.7             | 3.8             | 0.1             | 0.1             | 0.7             | 18.7            |
| 98F             | 27.7            | 4.1             | 0.7             | 0.1             | 42.5            | 2.0             | 3.8             | 0.1             | 0.1             | 0.7             | 18.3            |
| 90F             | 25.5            | 3.8             | 0.6             | 0.1             | 45.6            | 3.3             | 3.5             | 0.1             | 0.1             | 0.6             | 16.8            |
| 80FC            | 28.9            | 3.4             | 0.5             | 0.1             | 41.0            | 3.0             | 3.1             | 0.1             | 0.1             | 0.6             | 19.2            |

Fig. 1 – Sample with transversal cut embedded in acrylic resin (a) and thin-film ready to be analyzed (b).

2.1. Crystallinity – modified Stollberg test

In order to determine the crystallinity of the samples, we opted for the modified Stollberg test [6]. First the samples were decarburized at 650 °C for 16 h in the air. Then, 30 g of these samples were placed in an alumina crucible and heated to a temperature of 1300 °C for 20 min to ensure the fluxes were completely melted [3]. The melting was done in a vertical furnace, and the period of time at high temperature was kept in order to minimize the evaporation of volatile components such as fluorides and alkalis from the mold flux liquid slag [13]. After the melting, the samples were placed in a stainless-steel crucible and heated for 20 min at a temperature of 610 °C to induce the crystallization of the material [7]. For cooling, a quench in water was performed in which half of the crucible was immersed in this fluid.

2.2. Microstructural characterization

In order to observe the microstructure formed after the modified Stollberg test, the thin-film technique was used. This type of characterization is commonly used by geologist and rocks specialists [14,15] and it has shown some interesting results when applied to fluxes characterization after the Stollberg test [8]. To apply this technique, first the samples must be embedded in acrylic resin as shown in Fig. 1a. In order to obtain a smooth finish surface, they were sanded and polished with diamond particles. Then the polished surface of each sample was glued onto glass blade. After that, thin samples were obtained by transversely cut with about ~1.5 mm of thickness and prepared according to the technical standards of ABNT/NBR 15845-1 [16]. Thus, another surface of the samples was submitted to the same process. When the sample reached a thickness around 0.03 mm a thin-film was obtained as shown in Fig. 1b. The thin-films were analyzed in the transmitted-light microscope with the help of a 530 µm equalizer.

All samples obtained were analyzed by the X-ray diffraction method to determine the crystalline phases that were formed after the modified Stollberg test. The samples were analyzed by X-ray with an angle of 20° ranging from 20 to 100°, step of 0.02° with reading time of 1 s and rotation of 10 rpm.

2.3. Melting and break temperature

The laboratory studies carried out in the present work included measurements of the melting point and break temperature of the samples. These analyses were performed using a Differential Thermal Analysis – DTA. The samples were heated up to 1400 °C and cooled to room temperature at rate of 10 °C/min. This process was repeated three times for each sample to ensure an accurate temperature measurement of the phases transformations which were obtained at the last cycle. The melting temperature was determined through the first exothermic peak during heating and the break temperature through the first exothermic peak during cooling [13]. A comparison was performed between the melting point and break temperatures obtained from the DSC with Eq. (1) proposed by Mills et al. [7] and by Sridhar et al. [17] in Eq. (2).

\[
T_{\text{liq}} (^{\circ}C) = 1191 + 11.4\% \text{SiO}_2 - 11.0\% \text{CaO} + 4.2\% \text{Al}_2\text{O}_3 + 5.7\% \text{MgO} - 10.1\% \text{Na}_2\text{O} - 15.8\% \text{K}_2\text{O} + 11.9\% \text{F} + 8.3\% \text{Fe}_2\text{O}_3 + 11.6\% \text{MnO}
\]
(1)

\[
T_{\text{br}} (^{\circ}C) = 1120 - 8.43\% \text{Al}_2\text{O}_3 - 3.3\% \text{SiO}_2 + 8.65\% \text{CaO} - 13.86\% \text{MgO} - 18.4\% \text{Fe}_2\text{O}_3 - 3.2\% \text{MnO} - 2.2\% \text{K}_2\text{O} - 3.2\% \text{Na}_2\text{O} - 6.47\% \text{F}
\]
(2)
where \(T_{\text{eq}}\) is the liquid temperature and \(T_{\text{bp}}\) is the break temperature and mass content of the elements are expressed in wt%.

### 3. Results and discussion

Analyzing the microstructures obtained by the transmitted-light microscopy presented in Figs. 2–5, it is possible to realize that all samples have presented crystalline layers, making them suitable for the use in continuous casting of peritectic steels plates. However, it is important to evaluate the microstructure of the samples and the presence of the crystalline phase cuspidine, since this phase has great importance in the solidification process of the peritectic steels. When analyzing the results obtained by X-ray diffraction, shown in Fig. 5, the formation of crystalline phases was confirmed, complementing the crystallinity analysis made by the modified by the modified Stollberg and thin-film test. Through the peaks, it can be observed that crystalline phases were formed on the basis of calcium, silicon, fluorine, sodium, aluminum and magnesium, which was expected because they are the most concentrated elements in the commercial mold flux and in the samples that were made.

The results obtained through X-ray diffraction in the transversal section of the samples have shown the presence of the cuspidine \((\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2)\) in all samples. The simulation using FactSage® showed that 90F would not this phase, but some smaller and suppressed peaks were manifested when analyzed by an experimental test. The nepheline and gehlenite were other phases that were present in all samples. These phases normally appear in mold fluxes containing \(\text{Al}_2\text{O}_3\) and \(\text{Na}_2\text{O}\), and interfere with the formation of cuspidine [18]. The dolomite did not appear in the commercial peritectic mold flux (100F). The dolomite is a phase that inhibits the crystalline phases formation, especially cuspidine [19], this aspect to a peritectic flux is harmful, as already explained, cuspidine is a phase that promotes the smoother heat exchange between mold and plate, avoiding the formation of surface defects, especially longitudinal cracks. However, when the calcitic marble residue is added, consequently increasing the concentration of \(\text{MgO}\), none of the samples have total suppression of cuspidine. Another phase that was found was the akermanite, only in the commercial peritectic flux. The akermanite is a phase that exists in free fluorite flux, and it can replace the cuspidine, affecting basicity and the crystallization of the flux [20]. Wollastonite and calcite were other phases that occurred in all samples. Finally, it was identified the peak of fluorite for the samples 100F, 98F, 80FC expected, since they are the samples with the highest concentration of fluorine.

With the addition of 10% of calcitic marble residue, any peak of fluorite was found due to the reduction of the
fluorine concentration. When the flux is free of fluorine, the operation in the continuous casting plant is better, because some problems with corrosion due to the formation of HF is inhibited. Also, the health is increased and safety hazards are avoided.

The microstructures presented in Fig. 2 show the grain growth from the base toward the top. However, in Fig. 3, when 2% of calcitic marble residue was added, the microstructure remains equiaxial and with an evolution very similar to the 100F, and the grains size are significantly altered. Larger grains favor the heat exchange due to the decrease of the boundaries between different crystalline orientations [12]. This microstructural change directly affects one of the main functions of peritectic mold flux, which is the horizontal heat transfer control. For this type of flux, it is essential that it presents a good thermal resistance, causing the reduction of the heat transfer rate [21]. It was observed that smaller grains present a lower thermal resistance [12]. Based on this paper, it is possible to believe that a microstructural change, equiaxial to acicular, would have a negative impact on the casting of peritectic steels, because it would reduce their thermal resistance.

With 10% of residue, as shown in Fig. 4, it is noticed that the grains become thinner and a significant fraction of acicular grains appear.

The crystallinity of the mold fluxes was analyzed through the thin-film technique, and it was also noticed the formation of acicular grains [11]. Among the analyzed samples, only the sample 90F presented acicular grains in its microstructure. It was also found that the acicular microstructure had a higher concentration of MgO and a reduction in the concentration of F. The MgO resulted in this microstructural change, consequently, impacting in the performance of the commercial mold flux.

Fig. 6 shows the DSC results, which shows the melting and break temperatures of the mold flux. Table 3 presents the results of the melting and break temperatures of the samples through the mathematical method presented in Eqs. (1) and (2).

When analyzing the results of the DSC, we noticed that there were slight variations between each sample. As calcitic marble residue was added to the commercial peritectic mold flux, there was an increase in the CaO content in 98F and 90F, causing a slight increase in the break temperature [17]. When comparing the results obtained from the break temperature by the DSC and the results obtained by mathematical method, Table 3, it is noticed that the results are very similar, with variations below 20 °C.

The melting temperatures of the samples did not follow the same break temperature linearity. Nevertheless, the results agree with those expected, with the melting temperature of each sample is near 1300 °C, temperature at which the melting of mold flux occurs [1]. However, when comparing with the results obtained in Table 3, a great discrepancy

Fig. 3 – Microstructure and X-ray diffraction obtained for the sample 98F after the Stollberg test: (a) top, (b) middle, (c) bottom and (d) transverse X-ray diffraction.
between them is noted. Fig. 7 summarizes the comparison of the results by mathematical calculation with the results via DSC. Overall, the DSC curve of sample 98F – Fig. 6b – was very similar to the curve presented by the commercial peritecticmold flux – Fig. 6a. Meanwhile, in the curve of sample 90F – Fig. 6c – occurred a distance from the others. 

Due to the discrepancy result obtained for the melting temperature between the mathematical method and those obtained by DSC experimental analysis, a new equation was proposed, Eq. (3), in order to make the mathematical results closer to the experimental ones. In this case, an empirical method was used, in which the best possible mathematical polynomial fit was obtained, which adjusted the proposed mixtures. Fig. 8 shows the comparison between the results obtained by the new equation and the results obtained through DSC for the melting temperature.

\[
T_{\text{liq}} \ (\degree \text{C}) = 1191 + 15.2\% \text{SiO}_2 - 11.0\% \text{CaO} + 4.2\% \text{Al}_2\text{O}_3 \\
+ 13.6\% \text{MgO} - 3.1\% \text{Na}_2\text{O} - 15.8\% \text{K}_2\text{O} + 11.9\% \text{F} \\
+ 8.3\% \text{Fe}_2\text{O}_3 + 11.6\% \text{MnO} 
\] (3)
Fig. 5 – Microstructure and X-ray diffraction obtained for the sample 80FC after the Stollberg test: (a) top, (b) middle, (c) bottom and (d) transverse X-ray diffraction.

Fig. 6 – Example of the measurement of the melting and break temperature obtained by DSC – sample 98F.

Table 3 – Melting (Liquidus) and break temperature (°C) obtained by Eqs. (1) and (2) respectively, and comparing with the results obtained by DSC (Differential Scanning Calorimetry) in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>100F</th>
<th>98F</th>
<th>90F</th>
<th>80FC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting (Liquidus) temperature</td>
<td>1053.2 (1306.6)</td>
<td>1042.1 (1318)</td>
<td>998.2 (1298.5)</td>
<td>1087.9 (1313.5)</td>
</tr>
<tr>
<td>Break temperature</td>
<td>1260.7 (1276.5)</td>
<td>1265.9 (1283.6)</td>
<td>1286.1 (1289.7)</td>
<td>1227.2 (1270.5)</td>
</tr>
</tbody>
</table>
4. Conclusion

- It is possible to add the calcitic marble residue into peritectic mold flux while maintaining its crystallinity, formed phases and break and melting temperature. The 98°F showed better results.
- The appearance of the acicular microstructure in the flux containing higher concentration of calcitic marble residue may have been caused by the increase of the concentration of MgO in the flux.
- The microstructural changes from equiaxial to acicular can significantly impair the thermal resistance of the mold flux, making it unfeasible to use 10% of the calcitic marble residue in the flux.
- The only phases that were not shown in all samples were dolomite and fluorite. The dolomite was present only in the samples containing higher MgO content, 98°F and 90°F, and the fluorite disappeared in the sample containing 10% of marble residue, 90°F, due to the reduction of the fluorine concentration.
- The break temperature increased slightly as the CaO concentration was increased with the addition of the marble residue. The result obtained by the DSC was very similar to the result obtained by the mathematical method. The melting temperature analyzed by the DSC was consistent with the literature, showing that the fluxing melting temperature usually occurs at 1300 °C. However, when comparing it with the results obtained through the mathematical method, it can be inferred that they were not close. Because of that, a new equation was proposed.

Conflicts of interest

The authors declare no conflicts of interest.

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