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Chapter 7

Mould Fluxes in the Steel Continuous Casting Process

Elena Brandaleze, Gustavo Di Gresia, Leandro Santini, Alejandro Martín and Edgardo Benavidez

Additional information is available at the end of the chapter

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1. Introduction

During the last decades, the continuous casting process has made enormous advances and more than 90% of the world steel production is now continuously cast [1]. In this process, the liquid steel is poured into a water-cooled copper mould through a submerged entry nozzle (SEN), see Figure 1 [2]. At this stage the solidification process begins. In this way semi-finished products with specific characteristics such as slabs and billets are obtained. During this process the mould fluxes perform several critical functions to obtain products with the quality required.

The mould fluxes are synthetic slags constituted by a complex mix of oxides, minerals and carbonaceous materials. The main oxides are silica (SiO$_2$), calcium oxide (CaO), sodium oxide (Na$_2$O), aluminum oxide (Al$_2$O$_3$) and magnesium oxide (MgO). The (CaO/SiO$_2$) ratios are 0.7 to 1.3 with fluorite (F,Ca) and carbonaceous materials additions in their compositions. The compounds content ranges and their effects on mould fluxes behaviour at process conditions are summarized in Table 1.

These fluxes can be added through the top of the mould on the liquid steel, manually or automatically, the second way being the one that offers greater stability and constancy of the required properties.

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Figure 1. Schematic drawing of the continuous casting process [2].

Table 1. Typical composition of mould fluxes (wt %).

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Range (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass formers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
<td>17 – 56 %</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>0 – 13 %</td>
</tr>
<tr>
<td>B₂O₃</td>
<td></td>
<td>0 – 19 %</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td>0 – 6 %</td>
</tr>
<tr>
<td>Basic oxides or modifiers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>22 – 45 %</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>0 – 10 %</td>
</tr>
<tr>
<td>BaO</td>
<td></td>
<td>0 – 10 %</td>
</tr>
<tr>
<td>SrO</td>
<td></td>
<td>0 – 5 %</td>
</tr>
<tr>
<td>Alkalis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td>0 – 25 %</td>
</tr>
<tr>
<td>Li₂O</td>
<td></td>
<td>0 – 5 %</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0 – 2 %</td>
</tr>
<tr>
<td>Fluidizing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>2 – 15 %</td>
</tr>
<tr>
<td>MnO</td>
<td></td>
<td>0 – 5 %</td>
</tr>
<tr>
<td>Melting control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>2 – 20 %</td>
</tr>
</tbody>
</table>
2. Mould fluxes functions

The continuous casting process is a very complex one which involves many variables: casting speed, mould oscillation characteristics, steel grade, mould dimensions and metal flow. All these variables need to be optimized but this is very difficult because it is not possible to see what is occurring inside the mould. In general, it is important to collect information on: analysis of plant data, simulations of different phenomena and measurements of different specific physical properties of the fluxes.

The additions of mould fluxes on the free liquid steel surface form different layers that are described in Figure 2. Each layer in isolation or combined with another one, provides the required functions of the powder.

![Figure 2. Different layers formed by the mould flux on the liquid steel.](http://dx.doi.org/10.5772/50874)

The functions of the mould fluxes can be divided into two types, depending on the specific contact zone:

i) **Zone of contact with the liquid steel**

2.1. **Thermal insulation**

In this case, the objective is avoiding heat loss that could cause the premature solidification of the liquid steel in the meniscus zone. The properties of the mould fluxes that control these functions are:

- The mould flux density
- The thickness of the flux layer
- The carbon content
- The particle size distribution in the material

A bad thermal insulation in the meniscus promotes operation problems such as breakouts and could also cause surface defects in the products, such as cracks and oscillation deep marks.
2.2. Prevention of reoxidation

The liquid slag constitutes a barrier to avoid steel reoxidation by contact with air and the entrapment of other gases, such as nitrogen.

The steel reoxidation in the surface promotes oxide generation that could be incorporated as inclusions into the liquid steel (i.e. $\text{Al}_2\text{O}_3$) or into slag, changing its physical properties.

2.3. Inclusions entrapment

Mould fluxes are also designed to have the capacity to absorb or entrap inclusions in the interface of liquid slag–metal. In this way, it is possible to improve the cleanliness of the steel within certain operation parameters and depending on the process conditions. One of the important conditions is the depth of the liquid pool of slag [1].

The control of alumina ($\text{Al}_2\text{O}_3$) pickup in the liquid slag, during a certain period of time gives information of the slag absorption capacity. This oxide is produced by the reaction between the metal and the slag (Eq. 1):

$$4 \text{Al} + 3 \text{SiO}_2 \stackrel{\text{slag}}{=} 2 \text{Al}_2\text{O}_3 + 3 \text{SiO}_2$$

The large particles can cross the slag/metal interface easily but the smaller inclusions need more time to do it. Absorption of inclusions can be enhanced using fluxes with high $(\text{CaO}/\text{SiO}_2)$ ratios, high $\text{Na}_2\text{O}$, $\text{Li}_2\text{O}$ and $\text{CaF}_2$ contents or low $\text{Al}_2\text{O}_3$, $\text{TiO}_2$ contents.

ii) Zone of contact with solidified steel

2.4. Lubrication between the solidified steel shell and the mould

Good lubrication is the most important function of the mould fluxes. The lubrication capacity of the liquid slag is related to the viscosity and the solidification temperature. For this reason, it is important to establish the viscosity values at operation temperatures by experimental tests or applying theoretical models. The lubrication is indirectly influenced by process conditions such as casting speed, superheat temperature and submerged nozzle (SEN) design. When the liquid slag layer is interrupted for any reason, sticker breakouts or cracks could occur. Surface cracks in slabs are also promoted by bad lubrication.

2.5. Heat transfer control

Heat transfer in the mould can be divided into horizontal and vertical heat transfer. The horizontal heat transfer has the more significant effect on the surface quality of the product. Nevertheless, the control of vertical heat flux permits to overcome problems such as pinholes and deep oscillation marks [1].

The heat transfer in the continuous casting mould is largely controlled by the film generated in the gap between the steel shell and the mould, due to the solid and liquid proportion characteristics of the slag. These characteristics are associated with the high or low crystallization tendency of the mould flux, because in this way a greater or lesser heat extraction can be controlled. For this reason, the mould flux has to be specifically selected for each steel grade.
Figure 16. Melting behaviour of the samples PC, A, B, C and D. Similar studies have been performed on mould fluxes applied in the processing of long products. In this application, mould fluxes are characterized by higher viscosities (2 to 3 Poise).

The heat extraction in the mould can be controlled by the crystalline proportion generated in the film of mould flux during the cooling stage. For this reason it is relevant to know the temperature at which the crystallization process begins (break temperature, $T_{br}$). Also, it is necessary to increase the knowledge of the crystallization mechanisms and tendency of mould fluxes at interest conditions.

The break temperature of the samples revealed that sample B (with 6% $\text{B}_2\text{O}_3$ and 4% $\text{Li}_2\text{O}$) presents a $T_{br} = 1071°C$ and sample D (with 6% $\text{B}_2\text{O}_3$) a $T_{br} = 1066°C$. Both present a good agreement with PC sample in which $T_{br} = 1064°C$.

In the case of mould fluxes that are applied to long products casting, it is difficult to identify a clear change to verify the beginning of crystallization process because they are characterized by a high viscosity and a vitreous slag generation (or a supercooled liquid).

To evaluate the crystallization mechanisms of the samples, they were melted at 1300°C and then cooled drastically. These samples were identified as quenched (AQ). Then some of them were heat treated at different temperatures between 600°C and 870°C. All the samples were prepared for the microscopy study by light and electron scanning microscopy. Also, parts of the samples were ground to be analyzed by X-Ray Diffraction (XRD) and DTA.

The XRD results in PC at different temperatures show the evolution of the structure from a vitreous state to a crystalline one. The AQ sample is completely glassy. Nevertheless, sample B presents a crystalline structure at 870°C.
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The heat extraction in the mould can be controlled by the crystalline proportion generated in the film of mould flux during the cooling stage. For this reason it is relevant to know the temperature at which the crystallization process begins (break temperature, $T_{br}$). Also, it is necessary to increase the knowledge of the crystallization mechanisms and tendency of mould fluxes at interest conditions.

The break temperature of the samples revealed that sample B (with 6% $\text{B}_2\text{O}_3$ and 4% $\text{Li}_2\text{O}$) presents a $T_{br}=1071^\circ\text{C}$ and sample D (with 6% $\text{B}_2\text{O}_3$) a $T_{br}=1066^\circ\text{C}$. Both present a good agreement with PC sample in which $T_{br}=1064^\circ\text{C}$.

In the case of mould fluxes that are applied to long products casting, it is difficult to identify a clear change to verify the beginning of crystallization process because they are characterized by a high viscosity and a vitreous slag generation (or a supercooled liquid).

To evaluate the crystallization mechanisms of the samples, they were melted at 1300°C and then cooled drastically. These samples were identified as quenched (AQ). Then some of them were heat treated at different temperatures between 600°C and 870°C. All the samples were prepared for the microscopy study by light and electron scanning microscopy. Also, parts of the samples were ground to be analyzed by X-Ray Diffraction (XRD) and DTA.

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The XRD results in PC at different temperatures show the evolution of the structure from a vitreous state to a crystalline one. The AQ sample is completely glassy. Nevertheless, some samples show a partial crystallization.
Figure 16. Melting behaviour of the samples PC, A, B, C and D. Similar studies have been performed on mould fluxes applied in the processing of long products. In this application, mould fluxes are characterized by higher viscosities (2 to 3 Poise).

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The break temperature of the samples revealed that sample B (with 6% $B_2O_3$ and 4% $Li_2O$) presents a $T_{br} = 1071°C$ and sample D (with 6% $B_2O_3$) a $T_{br} = 1066°C$. Both present a good agreement with PC sample in which $T_{br} = 1064°C$.

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The XRD results in PC at different temperatures show the evolution of the structure from a vitreous state to a crystalline one. The AQ sample is completely glassy. Nevertheless, samples A, B and C presented the growth of crystals after heat treatment. Sample D remained a vitreous material.
Melting behaviour of the samples PC, A, B, C and D. Similar studies have been performed on mould fluxes applied in the processing of long products. In this application, mould fluxes are characterized by higher viscosities (2 to 3 Poise).

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The XRD results in PC at different temperatures show the evolution of the structure from a vitreous state to a crystalline one. The AQ sample is completely glassy. Nevertheless, sam-
ples treated at from 600°C produce a pronounced crystallization. In Figure 17a it is possible to observe the evolution of the crystal phases between 600°C and 850°C. By DTA, it was possible to identify the crystallization peaks of cuspidine (3 CaO.2SiO$_2$.CaF$_2$) present at all temperatures from 610°C, nepheline (Al$_4$Ca$0.6$Na$_0.8$Si$_4$O$_{16}$) at 729°C and villiaumite (NaF) at 854°C (Figure 17b).

Samples B and D, with (6% B$_2$O$_3$ and 4% Li$_2$O) and (6% B$_2$O$_3$) respectively, present different temperatures of crystallization. Sample B starts the crystallization at 610°C and sample D at 670°C. In Figure 18a, it is possible to observe the crystallization peaks of samples B and D and also the evolution of the crystallization peaks determined by DTA curves. It is found that the main phase in both cases is combeite (Na$_2$Ca$_2$Si$_3$O$_9$). In sample D the combeite crystallization peak is at 670°C and in sample B is at 610°C. The lower temperature in the crystallization peak of sample B could be due to the presence of Li$_2$O.

Figure 17. Crystallization evolution with temperature of sample PC: (a) XRD and (b) DTA.

Figure 18. Crystallization evolution with temperature of samples B and D: (a) XRD, (b) DTA.
Microscopy observations of all the samples permit to corroborate the information obtained by X ray diffraction and DTA curves. The crystallization mechanism begins at the surface of the samples where columnar crystals are developed. In samples PC and A crystals are constituted by cuspidine phase and in samples B and D by combeite phase. At higher temperatures (> 800°C), nuclei of irregular crystals appear in the inner part of the sample PC (Figure 19).

Figure 19. Morphology of sample PC at 850°C.

Figure 20. Liquid immiscibility phenomena observed at 610°C in sample B.

Figure 21. Liquid immiscibility phenomena observed at 680°C in sample D.
Samples B and D, present a liquid immiscibility phenomena (supercooled liquid effect), previous to the onset of the crystallization process (Figures 20, 21).

Figure 22. Morphology of sample B at 870°C.

In spite of liquid immiscibility and phase differences observed, the crystallization mechanism in the sample B at 870°C (Figure 22) is quite similar to sample PC. The presence of immiscible liquids phenomenon can be controlled by the degree of supercooling promoting a more homogeneous crystal nucleation.

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