

Higher than one. Triggering crystallization in mold flux slag.

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Mold flux is a family of formulated materials for industrial application in cast steel production, exhibiting the primary characteristic of melting at working temperature, into a liquid slag with controlled rheological properties. It is relevant for the present study the fact that this molten slag, when cooled down, undergoes a crystallization/devitrification reaction, which is phenomenological triggered by the basicity index, I.B., calculated as CaO/SiO_2 (wt./wt.), equal or higher than 1. Thermodynamics and kinetics of this reaction have been thoroughly studied in the past. Nevertheless, an effective explanation of the mechanism of its triggering remains mostly unexplained. Indeed, a value of $\text{IB} \geq 1.0$ corresponds to a molar ratio $\text{CaO}/\text{SiO}_2 \geq 1.07$, which is significantly less than 2.0, being that the ratio of the same components within the composition of the main crystallizing phase for this system. This consideration suggests that I.B. value is triggering some kinds of clustering phenomena in the liquid phase, which is then responsible for observed crystallization/devitrification reaction. This hypothesis is of particular interest since this system is a typical calcium fluor-alumino-silicate glass, material that covers a wide field of application from glass-ceramics, electronic, optoelectronic to dental applications. Spectroscopic studies have shown that calcium fluoro-alumino-silicate glasses cannot be considered as structurally and compositionally homogeneous at the nanometer scale, mainly due to cluster formation of Ca-F structures. Moreover, it has been shown that metal cations mix non-randomly in the alumino-silicate glass structures, producing a well-defined local order. Phenomena of medium-intermediate range order in cation distribution of calcium silicates and calcium alumino-silicates glasses are long time studying topic, counting a substantial number of investigation methods and published research papers. Then, supposing that this phenomenon of clustering is naturally relevant in mold flux related fluor-alumino-silicate glasses it's of particular interest to understand, as stated before, how specific values of I.B. can eventually trigger this and how this is related to primary crystallization reaction in this systems.

The present study tries to assess the occurrence of this phenomenon in well-defined formulations of commercial-like mold fluxes. Based on an extensive investigation with DTA, DSC and XRD measurements, a possible mechanistic explanation is also suggested.

KEYWORDS: MOLD FLUXESX, BASICITY, CRYSTALLIZATION, CUSPIDINE, DEVITRIFICATION

INTRODUCTION

Mold fluxes play an essential role in the continuous casting of steel. Their main functions are insulating steel from the atmosphere, avoid vertical heat loss and lubricate the steel strand in the mold [1].

Furthermore, this family of products is used to control the heat flow between steel and mold to reduce it for those steel grades that being crack sensitive require a milder cooling [2]. The liquid slag formed on top of the steel bath in the mold is pushed by the oscillatory movement of the same in the gap between the skin of the forming steel strand and the mold wall where it provides

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lubrication and near the mold wall solidifies.

The solid film in the gap is composed of crystalline and glassy phases. The first is the main responsible for mild cooling through a twofold mechanism. The formation of the crystalline phase causes a decrease in volume, which leads to the creation of air gaps and increases surface roughness, thus increasing thermal resistance [3,4] and reducing radiation transfer [4] by scattering it.

The amount of crystalline phase formed is dependent on mold flux composition [5] and empirically, it is considered to be related to the basicity, measured as the ratio in weight percent between CaO and SiO₂. The main crystalline phase formed is cuspidine, Ca₄Si₂O₇F₂, which is responsible for the effect on heat transfer.

The formation of cuspidine has been investigated in many works [5,6,7,8] but often model mold fluxes, which composition was simplified, were used instead of commercial ones.

This study aims to assess the crystallization and devitrification phenomena in mold fluxes and to start determining if the basicity index value corresponding to some kind of clustering in the liquid phase, which is then responsible for observed crystallization/devitrification reaction. Spectroscopic studies have shown that calcium fluoro-alumino-silicate glasses cannot be considered as structurally and compositionally homogeneous at the nanometer scale, mainly due to cluster formation of Ca-F

structures [9, 10]. Moreover, it has been shown that metal cations mix non-randomly in the alumino-silicate glass structures, casting a well-defined local order [11]. In mold fluxes, the presence/absence and size of clusters could be critical, as it varies the rheological and thermal properties of the materials substantially. Based on results obtained during this work, the microstructure of molten mold fluxes and mold flux glasses will be further studied by applying for a project on the NIMROD neutron diffraction line at ISIS synchrotron facility.

EXPERIMENTAL

A comprehensive collection of casting powders used for casting different steel grades was investigated during this work. The mold fluxes were chemically analyzed to obtain enough data for a reproducible and reliable interpretation. Carbon and Sulphur content was evaluated by using elemental analyzer G4 Icarus by Bruker.

Beads were prepared by mixing samples, calcined at 800°C, with a lithium tetraborate and lithium metaborate mixture in a platinum crucible and by using a Breitlander auto-fluxer. The beads were then analyzed using an S8 Tiger XRF spectrometer by Bruker to determine the complete chemical analysis of each casting powder. Table (1) reports the maximum and minimum value for each analyte in this study.

Tab.1 - Maximum and minimum values of components for the casting powders used in this study.

Maximum and minimum compositions										
Analyte	SiO ₂	CaO	CaF ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	Li ₂ O	B ₂ O ₃	MnO
Min	34.6	17.0	5.2	0.7	0.3	2.3	1.7	0.3	0.2	0.0
Max	42.2	35.0	23.2	11.9	6.5	16.7	17.4	0.8	1.0	7.3

A sample of each powder was examined by DSC-TGA, following a dynamic – isothermal – dynamic temperature path. The sample was heated up to a temperature of 1200°C. This temperature was kept for 10.00 minutes, and then the material was cooled down to room temperature. Both dynamic sections were performed with a temperature gradient of 10°C/min in air.

Another sample of each powder was placed in an alumina crucible and situated in an oven at T= 600°C. Decarburization time could vary and the process was

considered completed when the carbon content in powders was minor than 0.1 wt%.

Decarburized powders were put in platinum crucibles and melted at temperature 1200°C for 10 mins. The molten samples were quenched on copper plates, obtaining thin, glass discs.

The glass samples were analyzed by DSC. For these samples, the temperature was increased up to 1200°C with the same heating rate and atmosphere used during the previous DSC tests.

DSC analyses were carried out by using a Jupiter STA 449 F3 instrument by Netzsch and elaboration of data was achieved by using Proteus analysis software.

Another sample of the glasses, prepared as previously described, was placed in platinum crucibles and annealed at T=850°C for 4 hours. The result of this process was a crystalline material. The crystals were ground in a tungsten carbide ring mill, obtaining a homogeneous crystalline powder for XRD analyses.

XRD analyses were conducted using a D2 Phaser diffractometer by Bruker and interpretation of spectra was carried out using DIFFRAC.EVA software.

RESULTS AND DISCUSSION

SOLIDIFICATION

The study on solidification of casting powders was carried out by DSC analyses at a cooling rate of 10°C/min in air. The temperature and intensity of each crystallization peak during solidification were measured and related to parameters derived from the composition. The area of the crystallization peaks was considered to be a good approximation of the amount of crystalline phase formed during solidification.

One of the most critical parameters was the basicity index calculated as in equation (1).

$$I.B. = \frac{\%wt_{CaO}}{\%wt_{SiO_2}} \quad [1]$$

Whereas I.B. is the basicity index, %wt_{CaO} is the weight percent of CaO and %wt_{SiO₂} is the weight percent of SiO₂. As previously reported basicity index has been empirically used as a way to empirically define if the solid film in the gap would be more crystalline or more glassy with the

value of 1 being used as a threshold. Figures 1a and 1b show the DSC analyses of mold fluxes with a basicity index of 0.75 and 1.20, respectively.

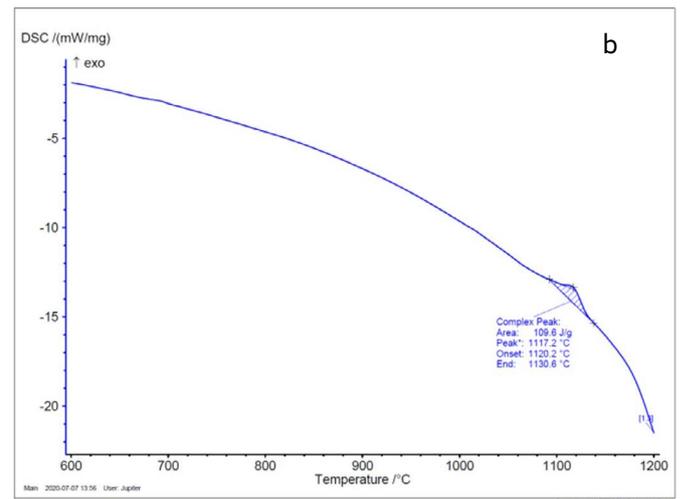
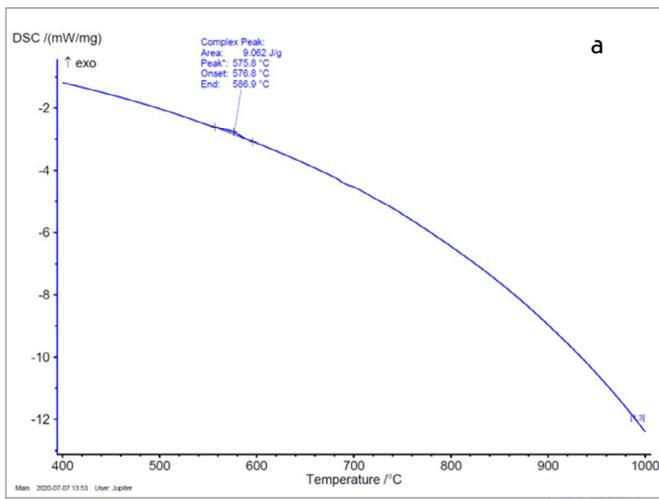


Fig.1 - DSC analyses of two mold fluxes with low (a) and high (b) basicity.

The data collected during this study show that basicity is indeed a way to correlate to crystallization peak intensity.

The graph in figure 2 shows that, when basicity increases over 1.07, the area of the peak sharply increases.

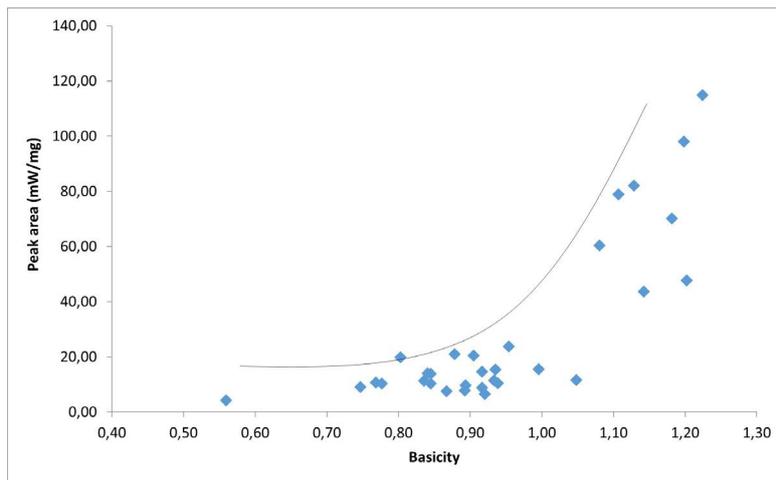


Fig.2 - DSC crystallization peak intensity vs. basicity.

The vector distance (d), calculated as for equation 2 in the casting powders, is another parameter that significantly influences crystallization. between the molar fraction of CaO, CaF₂ and SiO₂ in cuspidine and the molar ratio of these three components

[2]

$$d = \sqrt{(x_{CaO,cus} - x_{CaO})^2 + (x_{CaF_2,cus} - x_{CaF_2})^2 + (x_{SiO_2,cus} - x_{SiO_2})^2}$$

The graph in figure 3 shows that the intensity of crystallization peaks sharply increases after d decrease below 0.17. This indicates that the more the ratio between the three components is similar to the one of cuspidine, the more the crystallization is promoted during the solidification process. The concentration of SiO₂ is always in excess and CaO and CaF₂ taken individually, even when near to theoretical concentration, do not lead to an increase in peak intensity which happens only when the sum of both components molar fractions is above a certain threshold (0,55) which corresponds to a basicity index of 1.07.

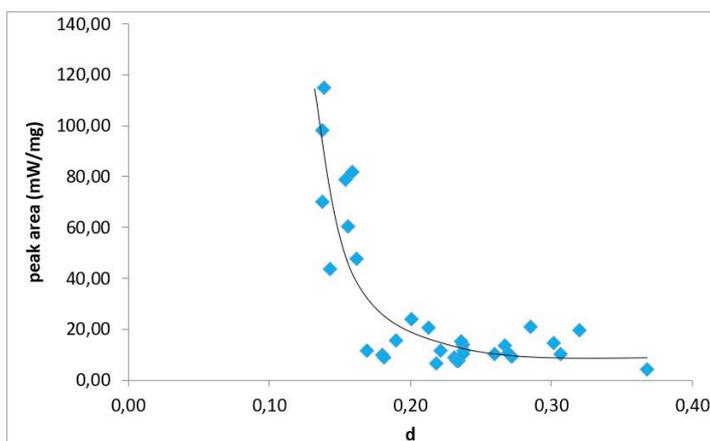


Fig.3 - DSC crystallization peak intensity vs. d.

Compositions and crystallization peak temperatures reported in the literature, such as alkaline elements and alumina content [6], are not consistent in this study. have no simple correlations. Those correlations usually

DEVITRIFICATION

The behavior of mold flux during devitrification of the glass obtained by quenching was studied by DCS and X-ray diffraction was conducted on devitrified samples to determine the crystalline phases present. The predominant crystalline phase was cuspidine and in all samples intensity of the devitrification peak was higher than the area of the

crystallization peak during solidification. This difference was one degree of magnitude higher whenever the content of magnesium oxide was more than 5%_{wt} and XRD of devitrified samples showed that, on these occasions, the main phases were mixed Ca-Mg fluorosilicates and silicates instead of cuspidine. Pictures 4a and 4b show the X-ray diffraction patterns for both cases.

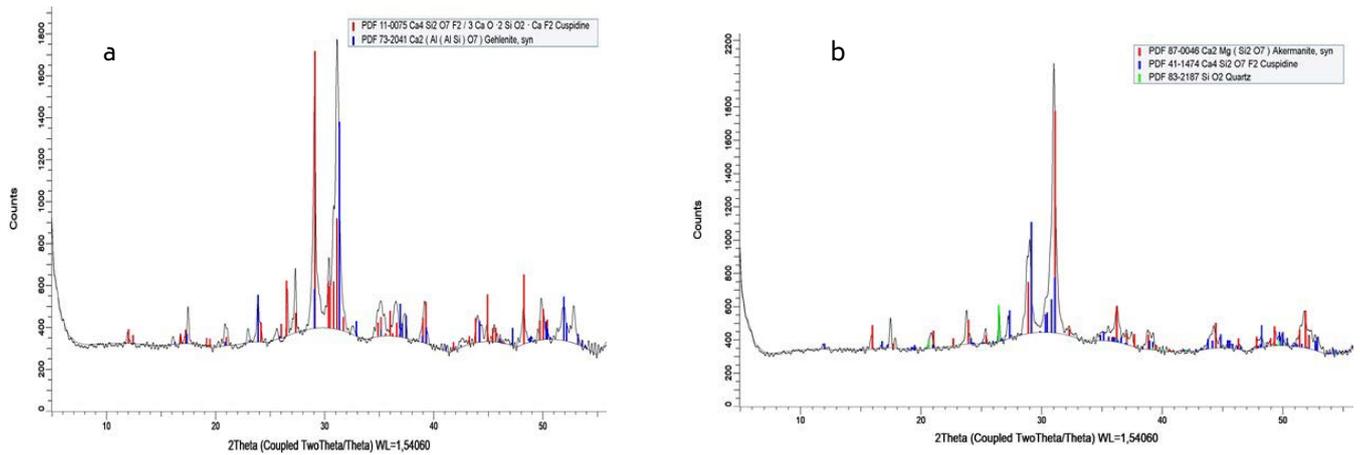


Fig.4 - XRD patterns for a devitrified mold flux having a low (a) and high (b) content of MgO.

No connection occurs between the devitrification peak intensity and the basicity index. Instead, a linear correlation is present if the devitrification peak area is

plotted against the modified NBO/T proposed by Li et al. [12] (see figure 5).

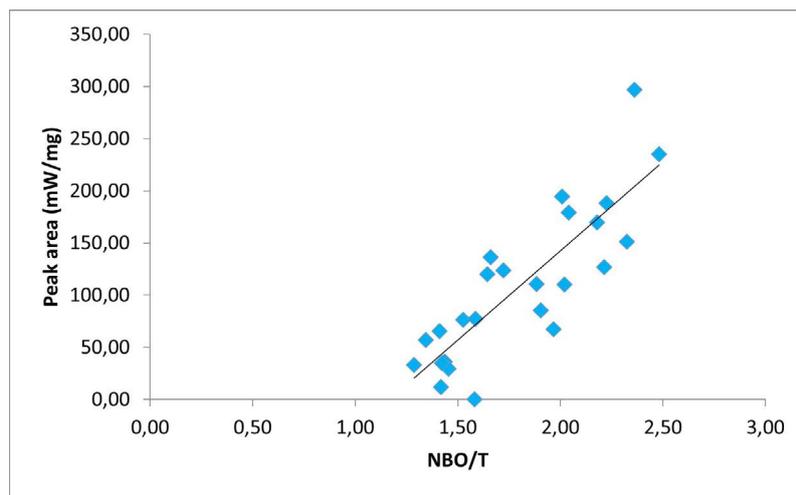


Fig.5 - DSC crystallization peak intensity vs. modified NBO/T.

As illustrated in the graph in figure 6, an even better correlation has been found by exponentially relating the sum of CaO, CaF₂ and MgO molar fractions to the peak

area. These three components seem to have a fundamental function during the devitrification process, particularly regarding the amount of crystalline phase formed.

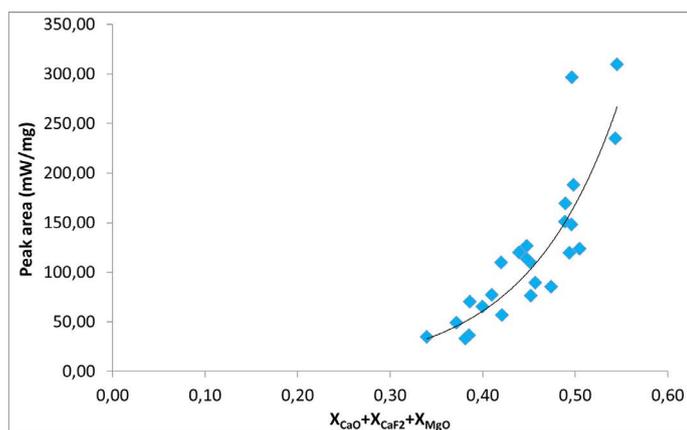


Fig.6 - DSC crystallization peak intensity vs. the sum of molar fractions of CaO, CaF₂ and MgO.

Contrary to what happens for the crystallization with increased content of alkaline metal oxides, as shown peak during solidification, during devitrification, the in the graph in picture 7. temperature of the devitrification peak decreases linearly

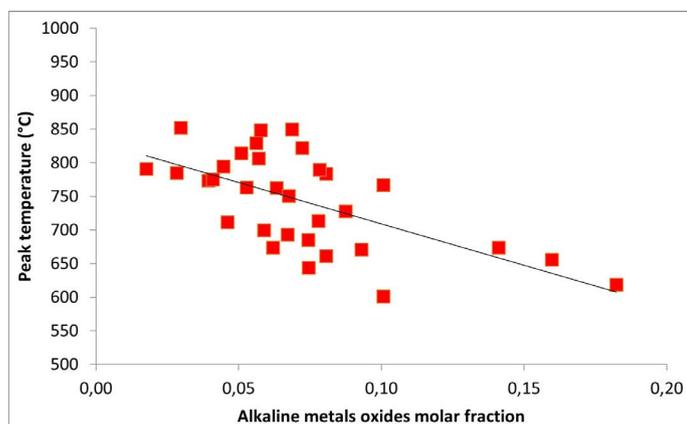


Fig.7 - DSC devitrification peak temperature vs. the sum of molar fractions of alkaline metals oxides.

During the DSC devitrification analyses, the glass transition temperature was determined. A linear dependence occurs between this parameter and alkaline metals oxides content, as reported in the graph in picture 8. This correlation indicates that an increase of Li₂O, Na₂O and K₂O has little effect on the amount of crystalline phase formed, however at the same time leads to increased mobility of species in the lattice, which lowers the temperature necessary for transitioning from glass to crystalline structure.

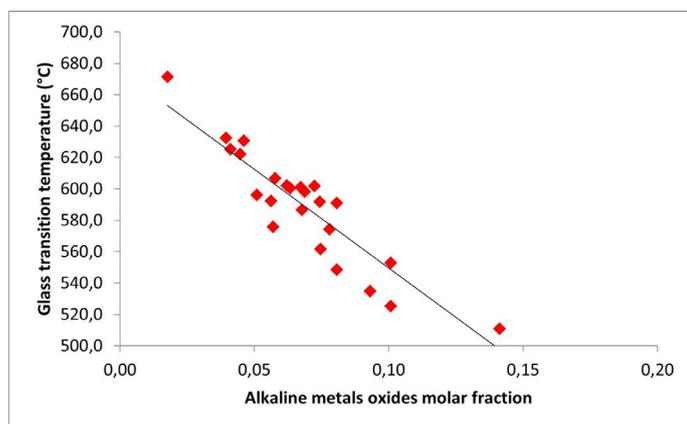


Fig.8 - DSC glass transition temperature vs. the sum of molar fractions of alkaline metals oxides.

The results obtained during the solidification and devitrification studies suggest that the two processes have a different mechanism.

Chiefly the solidification process is controlled by the possibility to form cuspidine showing that the more the structure of the mold flux is similar to that of cuspidine, the more it will crystallize during solidification.

Furthermore, this process is not linear and crystallization sharply increases when the basicity index is higher than 1.07 and MgO content has little influence on it. When considering the nature of clusters formed in molten slags, this study seems to confirm the presence of the hybrid species Ca-O-F, as reported in the literature [9].

During devitrification, instead, the content of MgO has a significant influence, especially when its concentration is above 5%_{wt.}, leading to the hypothesis that the clusters in the glass may also involve this component in their structure when. Furthermore, during devitrification, alkali content influences the process by increasing species mobility and lowering both glass transition temperature and peak temperature.

CONCLUSIONS

The solidification and devitrification processes of industrial mold fluxes have been studied. The data collected relatively to two phenomena indicate the presence of clustering of a different nature. For the solidification process, the content of both CaO and CaF₂ is essential to determine the amount of crystalline phase formed with a sharp increase of crystallization for basicity values over 1.07. Meanwhile, for the devitrification process, MgO also has a significant influence.

The distance from the theoretical composition of cuspidine seems to be a relevant factor whether the clustering that triggers the crystallization during the solidification is present or not confirming the hypothesis that calcium, oxygen and fluorine compose this clustering, giving birth to a short-range order that leads to cuspidine formation. A value of d lower or equal to 0.17 is the turning point for this phenomenon.

When considering the devitrification, instead, the nature of clusters seems to be related to the presence of chain breakers components. In particular, alkaline earth elements have a significant influence on the final structure of the system after the heating of the glass. Furthermore, it has been established that for the devitrification, the

amount of alkali contained in the mold flux has a strong influence on the temperature at which the process can start, suggesting that, while they have a lower impact on the composition of the clusters and thus of the final crystalline phases, they influence the mobility of chemical species in the whole system.

The data obtained in this study have been fundamental to determine which products to analyze and which temperatures to apply in the future research "In situ Ca-F cluster formation during crystallization of mold fluxes", proposal reference number 2010304, to be conducted on the NIMROD line at ISIS to determine the nature of clustering in both molten slag and glasses.

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