MELTING PROCESS OF MOLD FLUXES: IN SITU INVESTIGATION

Riccardo Carli & Carlo Righi
Prosimet SpA, Italy

Monica Dapiaggi
Università degli Studi di Milano, Italy

ABSTRACT

In modern steel continuous casting technology, mold fluxes hold a fundamental position in complex tribological system mold-solidifying-strand-shell and have a leading role in controlling heat extraction between strand and mold wall.

Aim of this study is to try to ascertain the nature of mechanism occurring in what we call "induction period", during which a mold flux, being in a solid powder state melts, forming a liquid slag which is actual lubricating agent of this tribological system.

Therefore, since this process greatly contributes to define technological performance of these products, deep investigation has been carried out on melting behavior of mold fluxes by means "in situ" experiments performed by Hot Stage Microscope, DTA and high temperature XRD techniques.

Peculiarity of this analysis allowed us to follow actual "in situ" evolution of all relevant phases without any quenching after heat treatment.

Moreover, especially by means of hot stage XRD measurements, phases patterns of minerals constituting the flux have been "in situ" monitored during melting process for the first time ever.

Formation of mineralogical phases like cuspidine, combeite and gehlenite probably originated in solid state reactions during melting process has been characterized.

INTRODUCTION

In modern steel continuous casting technologies mold fluxes are well-known to assure the lubrication required by systems of mold/solidifying strand shell. Beside other technological functions, these materials in principle have to be considered high temperature lubricants to which fundamental rules of hydrodynamic lubrication theory apply [1]. Actually, lubrication is provided by a liquid slag produced by melting of a mold flux in contact with liquid steel during working conditions. Therefore, as received mold flux takes a period of time, depending on its melting rate, to transform itself into that lubricant whose physical-chemical and rheological properties match thermo-mechanical characteristics of the system. How to extend this period of time or induction period, i.e., how to decrease melting rate of these materials has been one of most important achievement in history of technological field of mold flux manufacturing [2] and nowadays a very common practice, whose fundamentals have been described in a large number of research works [3]. On the other hand, how to shorten mold flux induction period to virtually obtain 'ready made' liquid lubricant, still follows a quite empirical approach. Indeed, one can formulate fast melting material using larger amount of fluxing components such as Na_2CO_3 or increasing content of low temperature melting glasses such as cullet, blast furnace slag and fly ash. Despite some remarkable results obtained in formulation of mold fluxes for high speed casting, a better understanding of mechanism of mold flux melting process is definitely essential to further improvements and unforeseeable developments.

Understanding melting process of mould flux substantially consists of studying complex net of components melting and solid state reactions which occur when a mold flux is heated till melting. Some research woks have been carried out analyzing mineralogical phases transformation and evolution by XRD, on heat-treated and subsequently quenched samples of different commercial mold flux, pointing out formation of many different new mineralogical phases even at relatively low temperatures [4, 5, 6, 7]. However, large differences in chemical compositions of mold fluxes samples, different samples preparations and analytical procedures result in a substantially qualitative description of the process.

In order to evaluate the real behaviour of a mold flux when heat treated, an *in-situ* technique would provide a better understanding of what actually happens during melting process. In particular, high temperature XRD may supply a greater insight into the different mineralogical phases transforming and evolving at various temperatures, providing a quantitative analysis of sample crystalline components through a Rietveld refinement [8]. Moreover, many high temperature phases are not quenchable, i.e., if the sample is quickly frozen from high temperature to room temperature, some of the phases present at high temperature may not be present at room temperature. This gives to *in-situ* high temperature powder diffraction an enormous advantage with respect to other techniques.

Here *in-situ* high temperature powder diffraction is combined by more traditional analyses, such as Differential Thermal Analysis (DTA) and Hot Stage Microscope (HSM) in a multidisciplinary approach.

METHODOLOGY

Parent material was synthesized using standard raw materials grinded and sieved through ASTM 170 mesh sieve, dried 24 hrs at 120°C, mixed in proper amount with lab mixer for 2 hrs. Parent material sample was kept under dry atmosphere in suitable dissicator. Samples used for this study were prepared adding different amount of Na_2CO_3 to the parent material, following same procedure and obtaining three different mixes of 'prototype' mold flux with same mineralogical and chemical structure but icreasing content of fluxing component. For details see Table 1.

Table 1: Characteristics of sample materials MIX1-3

	MIX1	**MIX2**	**MIX3**
SiO_2	40	37	35
CaO	42	39	37
Al_2O_3	7	6.5	6
Na_2O	2	6	9
F	9	8	7.5
Fe_2O_3	< 0.5	< 0.5	< 0.5
MgO	< 0.5	< 0.5	< 0.5
IB	1.05	1.05	1.06

From data reported in Table 1, it's important to retain that for all samples basicity as CaO/SiO_2 is of constant value of ~ 1 %wt./ %wt. in order to minimize eventual evolution of gaseous fluoride [9]. MgO and Fe_2O_3 phases are present at impurities level, while calcite $CaCO_3$ phase is present as adventitious component of commercial natural wollastonite within range 2-5 % wt. Then, major phases composing these samples are $CaSiO_3$, wollastonite, CaF_2, fluorite, Al_2O_3, corundum, SiO_2, quartz, $CaCO_3$, calcite and Na_2CO_3, natrite. Moreover, absence of low temperature melting glassy phases and Carbon free in any form allow to consider kinetic of melting to depend on componets proportion, being other factors as granulometric distribution and homogeneity of mixing reasonably been assumed constant by virtue of above described sample preparation procedure.

It's important to stress that MIX1-3 are a set of well-defined *prototype* mold fluxes showing physical-chemical and rheological properties of associated liquid slag, comparable to commercial products, yet having more homogeneous and reproducible melting behavior. In particular, this initial study focus on sole effect of Na_2CO_3 fluxing component content.

As prepared samples were grinded again in an agate mortar in order to obtain the particle size suitable for powder diffraction and then loaded on a high-density alumina sample-holder. The measurements were performed on a Philips 'Xpert diffractometer, with a θ-θ Bragg-Brentano geometry, equipped with a high temperature chamber (AHT-PAP1600) that can reach a maximum temperature of 1600°C. The chamber is heated by two $MoSi_2$ resistances, while two fiber alumina blocks assure temperature homogeneity. The sample can be spinned, for a better temperature homogeneity and higher counting statistics. The sample holder is placed over a cold finger and a motorized stepper motor keeps the sample surface at the goniometer axis level, compensating for all thermal expansion, and avoiding any sample shift aberration [10].

First run consisted in heating MIX1-3 samples with a heating rate of 25°C/min up to 1500°C, with a data collection from 600°C every 100ºC. In this way, it was possible to gain preliminary information on evolution of different phases reacting and forming with temperature.

Data collection was performed between 10 and 45° 2θ, with a step size of 0.03° 2θ and a counting time of 0.8 sec, our best compromise between fast data collection (to detect fast changes as a function of temperature) and a reasonably accurate diffraction pattern. The optics encompass an incident slit of ½, an antiscatter slit of ½, and a receiving slit of 0.6mm, in order to maximize peak intensity in spite of resolution. Every pattern collection lasts 15. minutes, a realistic time given the kinetics of the reaction.

Particularly for MIX3, another data collection was performed, in order to better evaluate the phase composition. A better quality data set was necessary for accurate Rietveld analysis, therefore data collection was carried out between 5 and 90° 2θ, with a step of 0.02° 2θ and a counting time of 5 sec/step. The weight percent of major phases in MIX3 has been determined through a Rietveld refinement procedure of the XRD pattern collected at during melting process. The refinement was performed using the program GSAS + EXPGUI [11, 12].

Melting process of MIX1-3 as prepared samples was also studied with Differential Thermal Analysis and Hot Stage Microscope measurements.

DTA experiments were carried out by means of L62 DTA instrument, equipped with the controller L70/215C and data acquisition card L70/2001 from Linseis GmbH. The apparatus was modified by installing a Pt/Rh sample holder for better quantitative evaluation of heat changes. Data elaboration was provided by software WIN-HDSC by Linseis. DTA was performed with a heating rate of 10°C/min up to 1450°C, using about 70 mg of the glass sample and about 70 mg of Al_2O_3 nr. 102 Nabalox at 99.5 % purity from Nabaltec Gmbh as a standard material.

HSM measurements performed by MISURA from Expert System srl following DIN51730 procedure. Data elaboration was provided by image treating software MISURA 3.32 from Expert System srl. HSM was performed with a heating rate of 10°C/min up to 1450°C, using about 70 mg of the MIX1-3 sample.

RESULTS AND DISCUSSION

HSM and DTA Measurements

Studying melting process of MIX1-3 through HSM allows measurement of characteristic melting temperatures, T_m, of each sample. As largely expected, well-defined decreasing trend of measured T_m was observed from MIX1 to MIX3, see Figure 1.

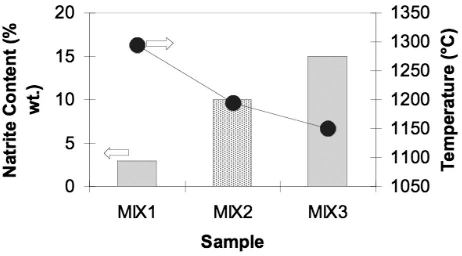

Figure 1: HSM measured Tm for MIX1-3 correlated to their Na_2CO_3, natrite, contents

From phenomenological point of view, this observation is very consistent with empirical criterion of decreasing T_m by increasing content of Na_2CO_3 fluxing component.

DTA analysis clearly confirmed this trend of measured T_m from MIX1 to MIX3. Further examination of DTA traces of melting process of MIX1-3 evidenced a clear shift to lower temperature of endothermic peak associated with Na_2CO_3 thermal decomposition with respect to decomposition of pure Na_2CO_3, as depicted in Figure 2.

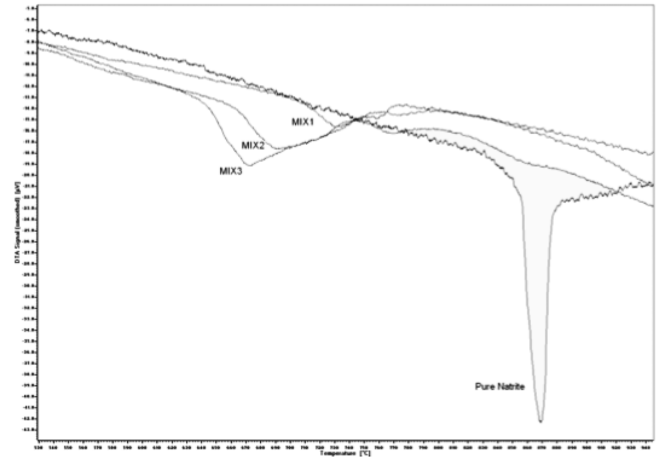

Figure 2: DTA analysis of Na_2CO_3 thermal decomposition for MIX1-3 samples compared with pure Na_2CO_3

This phenomenon of 'enhanced' carbonates decomposition, already described for mold flux [13, 14], refers to occurrence of a solid-state reaction involving Na_2CO_3, which is somehow correlated to observed trend of measured T_m from MIX1 to MIX3.

Under this perspective, the effect of increasing content of Na_2CO_3 appears more clearly comprehensible, being connected with classical solid state reactions and nucleation mechanism. In particular, it is well-known that exploiting decomposition reaction to supply reacting atomic-proportionate species, extremely increases number of nuclei per unit volume sig13nificantly fastening reaction rate [15]. Then, addition of Na_2CO_3 in MIX1-3 samples results in a strong rise of rate of this not-diffusion-limited solid sate reaction which finally results in a decrease of measured T_m.

Solid State Reaction

Melting process of MIX1-3 samples was investigated by high temperature XRD following above-described procedure. During first series of experiments, evolution of most abundant phase present in MIX1-3 samples was thoroughly analyzed. Thus, relative concentration of wollastonite was measured in relation with temperature for all samples, giving reaction curves reported in Figure 3.

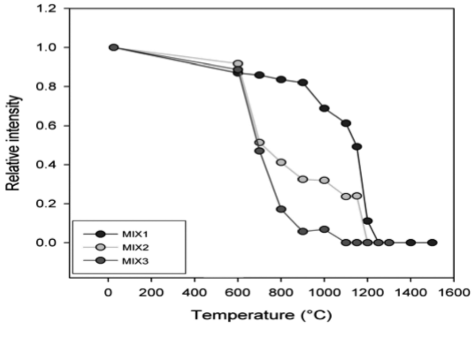

Figure 3: Transformation of wollastonite phase as a function of temperature for MIX1-3 samples

Based on data reported in Figure 3, it's possible to infer that presence of Na_2CO_3 induces conversion of wollastonite which can be almost completely transformed at 900°C with suitable amount of this fluxing component as in case of MIX3.

Very recently, a similar finding concerning last occurrence of wollastonite phase in commercial mold flux samples annealed at 870°C, quenched and analyzed by XRD has been reported [4]. Explanation proposed for this phenomenon was related to lower content of wollastonite phase in those particular commercial mold flux samples. In the present case, this observation can be clearly related with quantitative proportion of natrite and wollastonite phase reactants, attaining value of Na_2CO_3/ $CaSiO_3 \cong 0.3$ mole/mole in MIX3.

These points seem basically consistent with above stated preliminary conclusion, concerning occurrence of a solid state reaction driving melting process of MIX1-3 samples and role of Na_2CO_3 as decomposing reactant. In particular, it has been pointed out that this solid sate reaction evolves under composition control, being strongly affected by Na_2CO_3 content.

Phases Evolving in MIX3

In order to get more unambiguous knowledge of nature of solid sate reaction whose occurrence was sorting out from experimental results, in depth investigation of melting process of MIX3 sample was carried out in a second series of tests as above described.

Accurate Rietveld refinement procedure of the XRD patterns collected during these measurements allowed determination of relative phases composition in MIX3 during heating.

It was possible to verify that natrite and calcite decompose completely between 600 and 700°C, while corundum started reacting for low extent between 700 and 900°C. Quartz seemed not involved in any reactions below 800°C. Moreover, wollastonite transformation trend was confirmed and measured wollastonite conversion at 900°C showed to be approx 80 % of initial content. Similarly, fluorite underwent relevant transformation and its conversion at 900°C reached about 60%, see Figure 4.

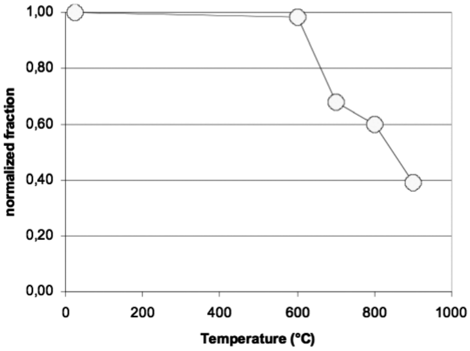

Figure 4: Transformation of fluorite in MIX3 as function of temperature

Correspondingly, important formation of cuspidine $Ca_4Si_2O_7F_2$ and combeite Ca4Na4-Si_6O_{18} phases was observed along with minor amounts of ghelenite $Ca_2Al_2SiO_7$, larnite Ca_2SiO_4 and rankinite $Ca_3Si_2O_7$, see Figure 5.

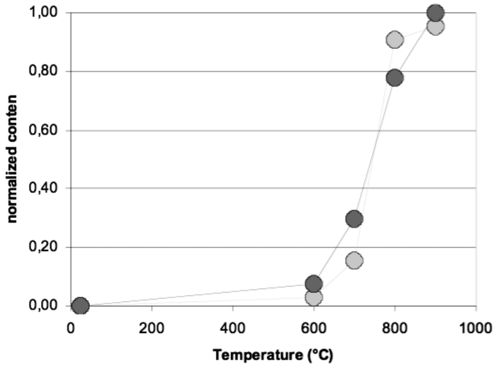

Figure 5: Transformation of fluorite in MIX3 as function of temperature

Cuspidine and combeite are most abundant phases in MIX3 after heating up to 900°C. Evolution of these phase at higher temperature in similar system has been discussed elsewhere [16].

Although, these findings are very consistent with data already reported in literature [4, 5, 6, 7], the present experimental observations clearly suggest that wollastonite is mainly transformed into cuspidine and combeite phases through a solid state reaction strongly enhanced by Na_2CO_3 content.

Melting

It has been shown that increasing amount of Na_2CO_3 fluxing component in MIX1-3, results in a strong rise of rate of not-diffusion-limited solid sate reaction, converting wollastonite mainly into cuspidine and combeite phases at 900°C. Wollastonite conversion at 900°C showed to be approx 80% of initial content, when proportion phase reactants attained value of Na_2CO_3/ $CaSiO_3 \cong 0.3$ mole/mole, as in MIX3. This reaction came with parallel decrease of measured T_m, as shown by HSM and DTA measurements for MIX1-3 samples.
Even though, more studying is required for better understanding of reaction mechanism, nature and role of other reactants as fluorite and effects on melting process, a tentative interpretation can be given on the basis of data on $CaO\text{-}SiO_2\text{-}CaF_2$ system, recently publish as a result of a very rigorous research work [17]. In particular, it has been found out that for this system liquidus lines of cuspidine vary in the temperature range from 1114°C to 1407°C, being latter one the melting temperature of pure cuspidine. Therefore, it’s possible that in the present prototype’ mold fluxes, cuspidine formed by solid state reaction drives materials to melting on its liquidus line, through lowest eutectic point which can be gained. From this point of view, residual amount of wollastonite, fluorite and minor phases as larnite may play an important role in defining lowest eutectic point which can be gained by the system.

CONCLUSIONS

In the present study of melting process of mold flux, it has been shown that increasing amount of Na_2CO_3 fluxing component, results in a strong rise of rate of not-diffusion-limited solid sate reaction, converting wollastonite mainly into cuspidine and combeite phases at 900°C. Wollastonite conversion at 900°C showed to be approx 80% of initial content, when proportion phase reactants attained value of Na_2CO_3/ $CaSiO_3 \cong 0.3$ mole/mole.

This reaction came with parallel decrease of measured T_m, as shown by HSM and DTA measurements. Correlation between these observation is tentatively proposed on the basis of data on CaO-SiO_2-CaF_2 system, where liquidus lines of cuspidine vary in the temperature range from 1114°C to 1407°C, suggesting that cuspidine formed by solid state reaction drives materials to melting on its liquidus line, through lowest eutectic point which can be gained.

REFERENCES

Del Moro, A., Carli, R. & Righi, C. (2006). Proceeding of Convegno del 60° AIM, p. 73. [1]

Carli, R., Del Moro, A. & Righi, C. (2008). La Metallurgia Italiana, pp. 13-18. [2]

Mills, K. C. (2003). *Mold Powders for Continuous Casting*. Chapter 8, in Making, Shaping and Treating of Steel, 11th Edition, A.Cramb Ed., 58.1-8.41. [3]

Marschall, I., Koelbl, N. & Harmuth, H. (2008). Proceeding of 6th European Conference on Continuous Casting. [4]

Cruz, A., Chavez, F., Romero, A., Palacio, E. & Arredondo, V. (2007). J. Mat. Process. Tech., 182, pp. 358-362. [5]

Grievson, P., Bagha, S., Machingawuta, N., Liddel, K. & Mills, K. C. (1988). *Ironmaking and Steelmaking.* 15(4), pp. 18-186. [6]

Hiromoto, T., Sato, R. & Shima, T. (1979). AIME Steelmaking Proc., 62, pp. 40-47. [7]

Young, R. A. *The Rietveld Method*. IUCr Monographs on Crystallography, Oxford Science Publication. [8]

Shilov, A. & Holappa, L. (2006). Steel Research Intl., 77, pp. 803-808. [9]

Dapiaggi, M., Artioli, G. & Petras, L. (2002). Rigaku Journal, 19, pp. 35-41. [10]

Larson, A. C. & Von Dreele, R. B. (1994). Los Alamos National Laboratory Report LAUR 86-748. [11]

Toby, B. H. (2001). J. Appl. Cryst., 34, pp. 210-213. [12]

Kim, J. W. , Lee, Y. D. & Lee, H. G. (2001). ISIJ Intl., 41(2), pp. 116-123. [13]

Schwerdtfeger, K., Sardemann, J. & Grethe, H. J. (1994). *Stahl und Eisen.* 114(2), pp. 57-63. [14]

Ropp, R. C. (2004). Studies in Inorg.Chem., 21, pp. 113-2189. [15]

Dappiaggi, M., Artioli, G., Righi, C. & Carli, R. (2007). J. NonCrys. Solids, 353, pp. 2852-2860. [16]

Watanabe, T., Fukuyama, H. & Nagata, K. (2002). ISIJ Intl., 42(5), pp. 489-497. [17]