Application of Cathodoluminescence in Analyzing Mold Flux Films

Elizabeth Nolte[1], Jeffrey D. Smith[1], Michael Frazee[2], Neil Sutcliffe[2], Ronald J. O'Malley[1]

[1]Missouri University of Science and Technology
238 McNutt Hall, 1400 N. Bishop Ave., Rolla, MO, 65401, USA

[2]Nucor Steel Gallatin
4831 US Highway 42 West, Ghent, KY, 41045, USA

Keywords: Mold Flux, Continuous Casting, Cathodoluminescence

Abstract

Mold fluxes are used in continuous casting of steel to control heat transfer from the steel shell to the copper mold based on their structure and properties. Structures observed in mold flux film samples extracted from conventional and thin slab continuous casters at the end of a cast were examined using cathodoluminescence (CL) imaging in conjunction with XRD and SEM/EDS analysis. Glassy and crystalline structures in the flux films varied greatly depending on sampling location in the mold, distance from the mold wall and the mold flux being examined. Temperature data collected from thermocouple arrays in a thin slab funnel mold indicated saw-tooth temperature fluctuations in the lower area of the funnel region, presumably due to cyclic fracture and regrowth of the mold flux crystalline layer in that region of the mold. The temperature observations correlate well with the structures observed in the flux film samples from the region. CL microscopy clearly distinguishes glassy regions from regions with devitrified and dendritic crystal growth, as well as continuous and fractured crystallite layers and cuspidine and nepheline phases that are present. The technique also highlights small variations in Mn oxide content in the glassy region of the flux that results from exchange reactions with the steel, making flow lines in the previously liquid portion of the flux film clearly visible. The benefits of applying cathodoluminescence imaging to the analysis of mold flux films in continuous casting are discussed.

Introduction

Mold flux is critical for regulating mold heat flow and controlling slab surface quality in the continuous casting process [1,2,3]. The crystalline structure that forms in the mold flux film in the mold gap region of the continuous caster plays a significant role in the performance of a mold powder for a given steel grade and caster (Figure 1). Mold powders are often selected based on their viscosity and primary crystallization temperature even though the crystallite phases and morphologies that are observed in the mold gap generally do not form by the primary crystallization path [4]. The crystalline layers that are observed in the mold gap have been found to form by devitrification of the super-cooled glass layer that remains in contact with the caster mold well beyond the residence time of the steel shell [4,5]. The phases and structures formed by devitrification have a strong influence on the mold thermal behavior through their influence on the crystalline layer's resistance to shear and fracture in the mold gap. Crystalline film fracture and reformation appears to be a primary cause of periodic temperature and heat transfer fluctuations in the mold [4]. Techniques such as: DSC [6-8], DTA [9-11], SHTT [6,12-14], and DHTT [14], can be used to characterize mold flux. However, these techniques rely on simulating only a small portion of the mold environment. Cathodoluminescence (CL) analysis has been a standard technique for geological materials for 30 years, but in the last 20 years has been developed as an effective method to observe refractory corrosion. [15] This paper will discuss the application of cathodoluminescence analysis to the investigation of crystallization behavior for industrial flux films, in conjunction with XRD and SEM.

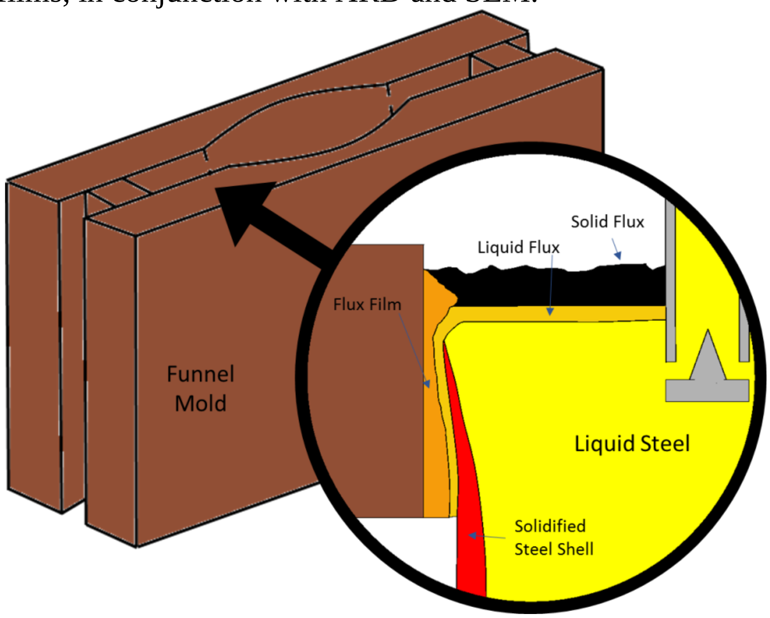


Figure 1: Schematic of the funnel mold and the cross section of the mold.

Experimental Procedure

Flux film samples were extracted from the funnel mold of a thin slab caster at the end of a cast. The flux composition, as reported by the supplier, is recorded in Table I.

Table I. Composition of mold flux in wt% (R=Na, K, Li).

Basicity	MgO	Al_2O_3	ΣR_2O	F
0.8	2.6	5.9	16.5	8.6

Specimens were analyzed using powder x-ray diffraction (XRD) on a PANalytical X'Pert Pro Multi-Purpose Diffractometer with a Cu Kα x-ray source. Specimens were mounted in epoxy and polished to a 0.1μm finish. Crystallite structures were analyzed using cathodoluminescence (CL) microscopy (model 8200 MK II) and SEM/EDS using an ASPEX-PICA 1020.

Results & Discussion

Many of the flux film samples exhibited a crystalline layer on the mold wall side of the film as reported elsewhere [5,24,25]. Samples obtained from lower in the funnel also exhibited fractures in the crystallite film, and areas that were almost fully glassy. Figure 2 shows the variation in the flux film appearance as the sample location progressed lower into the funnel.

Figures 2 (a) and (b) are primarily crystalline with very little glass infiltration except along a large crack in (b). Figures 2 (c) and (d) are glassy and show longitudinal striations across the face. This structure is believed to result from crystalline layer fracturing and re-filling with glass. This behavior is consistent with thermal data collected from an instrumented funnel mold, where temperature was monitored at several locations both within and outside of the funnel region. Large saw tooth shaped fluctuations in temperature (± 45°C) were evident within the high-stress funnel region (Figure 3a). The rapid temperature decrease is associated with crystal fracture and removal, while the rapid temperature increase is associated with glass infiltration in the fractured region. The slow drop in temperature is associated with aging and crystallization of the glass. Outside of the funnel region, smaller (± 10°C) temperature fluctuations were evident (Figure 3b).

CL imaging proved to be a valuable method for identifying crystalline phases and structure in polished flux film samples. Figure 4 shows a cross section of a flux film from lower in the funnel area. The yellow and bright orange regions are crystalline and the light orange regions are glassy. The crystalline layer on the mold side of the flux film is fractured. The flow lines in the glassy region suggest that glass flowed and infiltrated the fracture region. The structures in the CL image support the theory of crystalline fracture and backfilling with glassy material by the mechanism proposed in Figure 5.

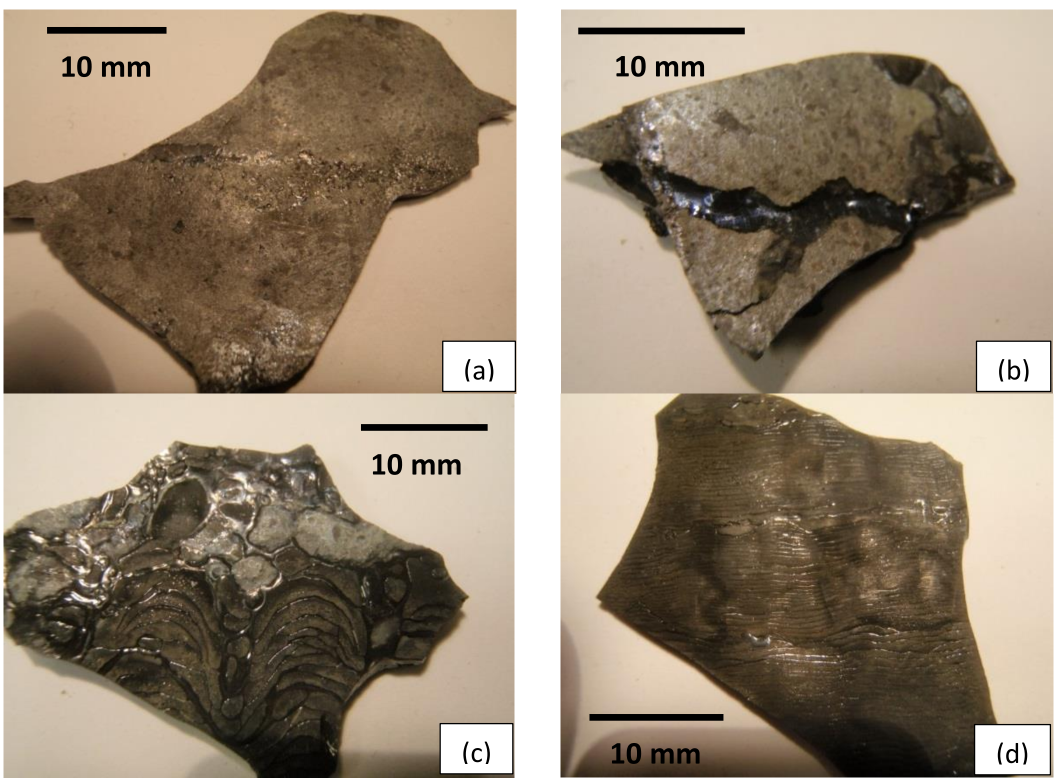
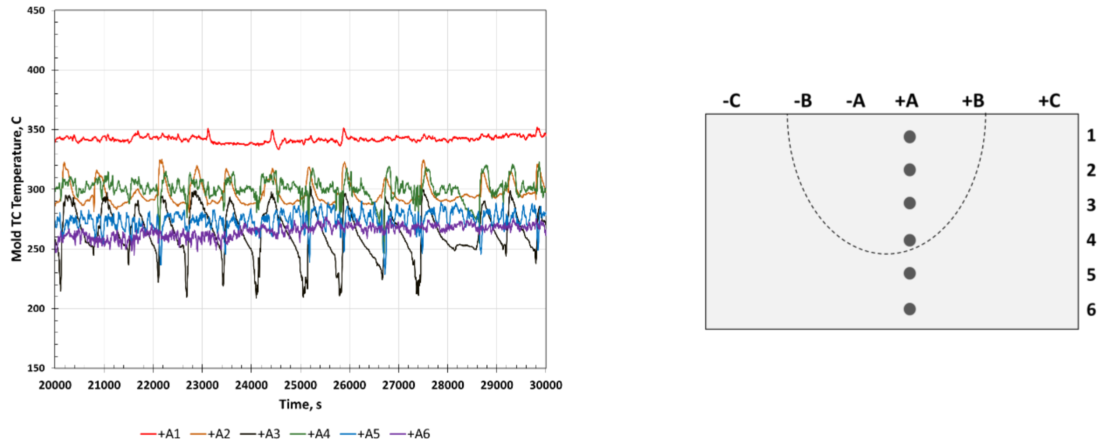
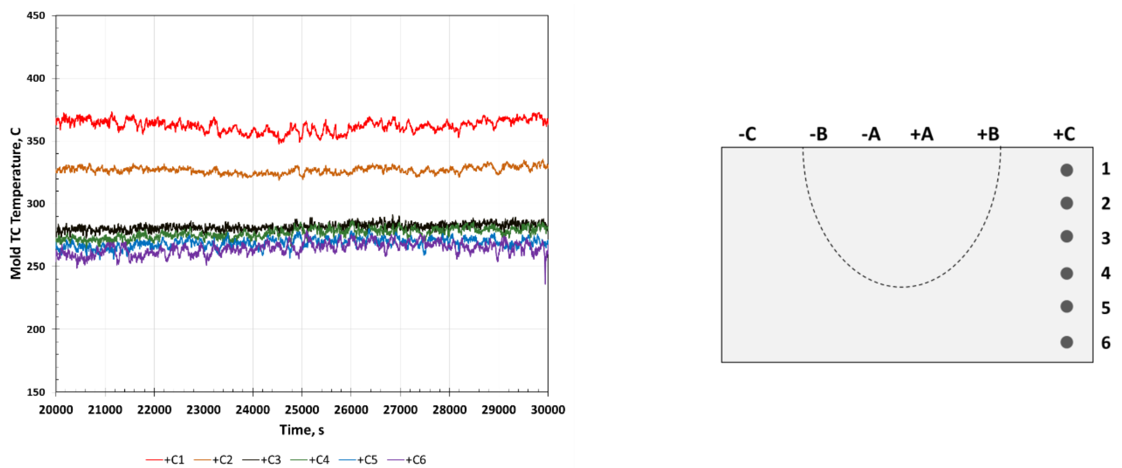


Figure 2: Flux film samples from upper funnel area (a) to lower funnel area (d) - Mold side.

The variation in shades in the darker orange region opposite the mold highlights the flow lines in the glassy region of the flux film that was fluid during casting. The color variations are directly related to variations in manganese oxide content in the flux that was picked up during casting from interaction of the mold flux with the molten steel. Figure 6 documents this pickup. These variations in manganese oxide level were also documented using SEM/EDS analysis.



(a)



(b)

Figure 3: Inside the funnel area (a) exhibits saw tooth behavior, where temperature fluctuates on a semi-regular basis with respect to time. Outside the funnel area (b), temperature fluctuations are mild (± 10°C). Corresponding diagrams indicate thermocouple locations in the funnel mold.

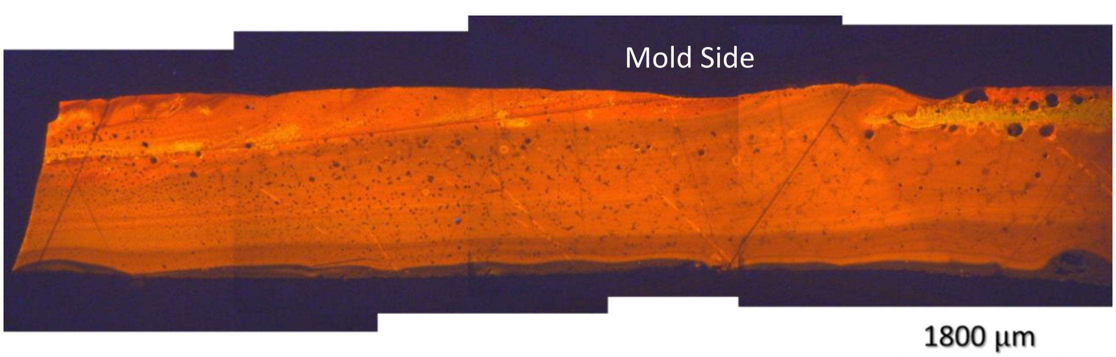


Figure 4: CL image of flux film sample – lower funnel region.

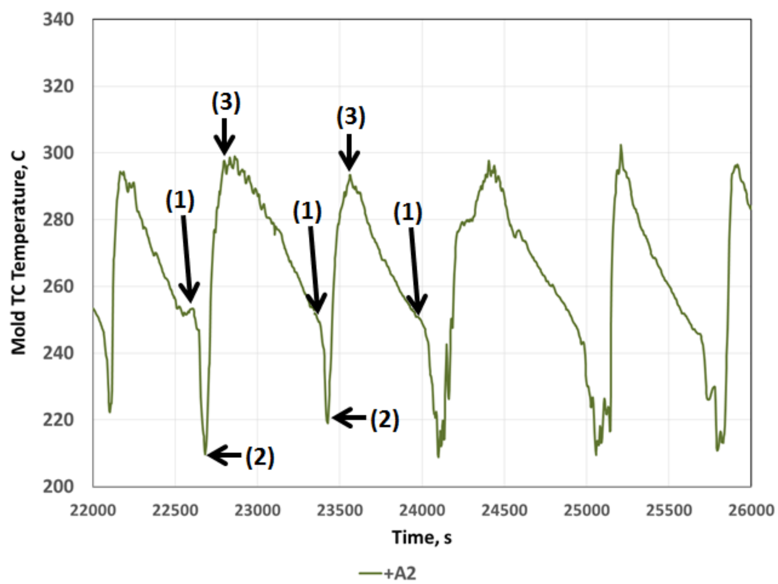


Figure 5: Proposed origin of saw tooth temperature fluctuations: (1) fracture of flux crystalline film, (1→2) withdraw of flux crystalline film, (2) air gap, (2→3) inflow of glass, (3) complete glass infiltration, (3→1) aging and crystallization of glass.

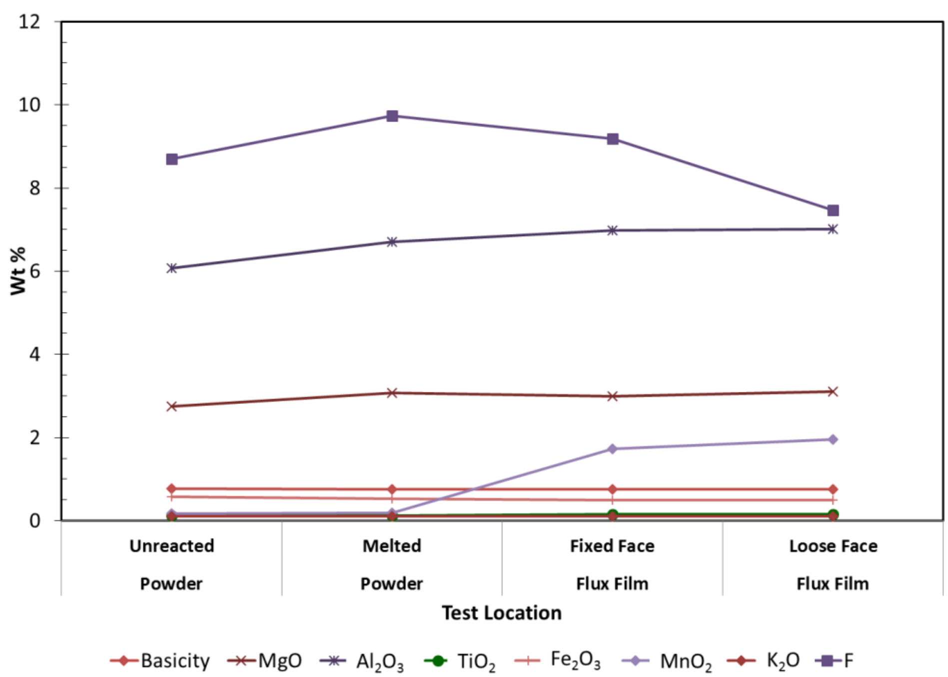
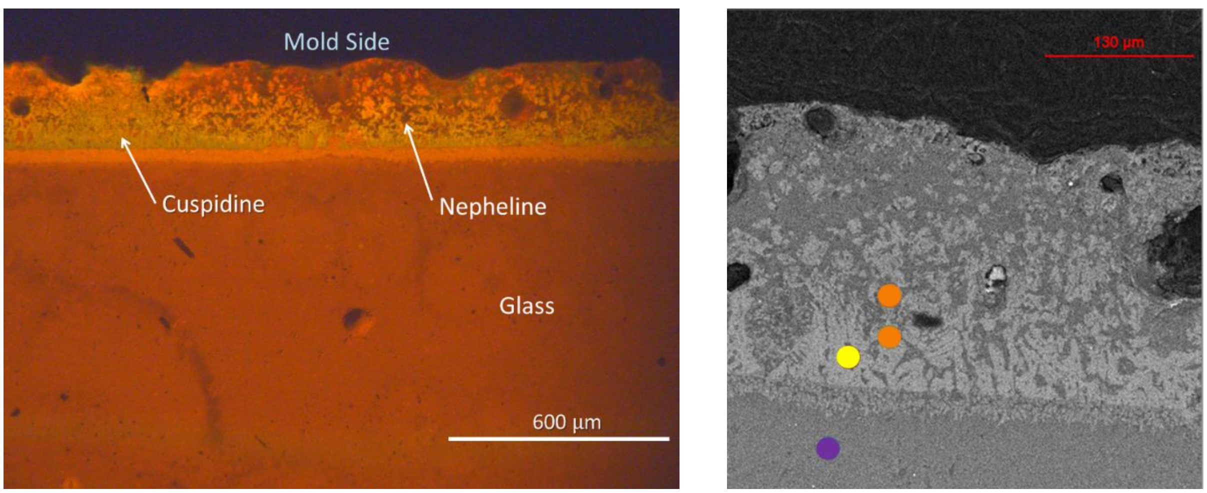


Figure 6: Flux film chemical analysis indicating manganese oxide pickup in mold flux.

XRD analysis of the flux films shows both the cuspidine and the nepheline phases are present in the flux film. The presence of nepheline in the crystalline layer suggests that this layer formed by devitrification of a super-cooled glass and not by primary crystallization [1, 9]. Devitrification follows a cooling path achieved by cooling faster than the critical cooling rate, avoiding crystallization, and isothermally holding at a temperature. In flux films, nepheline can only be formed through devitrification [9]. Its presence suggests that a super-cooled glass layer that remains in contact with the caster mold well beyond the residence time of the steel shell [1]. The distribution of cuspidine and nepheline in the crystalline layer can be seen more clearly in the CL image in Figure 7 (a), cuspidine being yellow and nepheline being brown. These phases were also confirmed by SEM EDS analysis, Figure 7 (b).

CL images best show the morphology and crystallites present. The cuspidine (yellow-orange) appears to co-crystallize with nepheline (dark orange) along the mold face. The crystal structures in the flux film change based on distance from the mold wall. Along the mold wall both cuspidine and nepheline have crystallized as small equiaxed crystals. As the temperature increases with distance away from the mold wall, the nepheline crystals do not appear to form as readily and the cuspidine crystal concentration increases. This forms a dense crystalline layer approximately 200µm from the mold wall. EDS confirmed the compositions of the crystals. In Figure 6 (b) the orange region indicates nepheline, yellow is cuspidine and purple is the bulk glass where the Ca to Si ratio is approximately 1:1.

Although the nepheline and cuspidine phases can both be distinguished in the SEM image, it is much easier to visualize the crystallization of cuspidine and nepheline using CL analysis. In addition, small variations in manganese oxide content in the glass can be easily observed.



(a) (b)

Figure 7: CL image (a) and SEM image (b) of the crystal growth along the mold wall. In (b) orange is nepheline, yellow is cuspidine, and purple indicates the bulk glassy region.

Conclusions

Flux films have widely varying structures based on distance from the mold wall and position in the mold. Information on these structures can be obtained by carefully extracting flux films at the end of a cast sequence and analyzing their microstructure. Cathodoluminescence imaging allows different structures to be observed more readily than by SEM analysis. This technique makes variations in the content of transition metal oxides in the flux film readily visible. Flux film structures can also vary significantly within a funnel mold. Flux film samples from high stress regions in the funnel area are observed to have fracture and glass re-infiltration marks that match the saw tooth temperature behavior in these regions. The following specific conclusions are made based on these experiments:

1. Large fluctuations in temperature on the mold side of the flux film are observed in the funnel region. In addition, glassy striations are observed on the mold face side of the flux film suggesting that the flux film repeatedly fractures, dropping the mold temperature sharply on initial withdrawal of the crystalline layer and then increasing temperature sharply when new glass infiltrates the fractured region. Following infiltration, the mold temperature then drops slowly as the re-infiltrated glass ages and crystallizes. This mechanism explains the observed periodic saw tooth mold temperature behavior.
2. Cathodoluminescence is a useful tool for studying flux films. It provides high resolution at low magnification, so phases can be easily distinguished optically and other small details can be observed that may have been missed using other techniques. It provides better visualization the distribution and type of crystal structures than SEM analysis and can also be used to observe small variation in composition in the bulk glass regions. Therefore, use of CL in analyzing flux films is recommended.

References

1. K.C. Mills, "Mold Fluxes for Continuous Casting and Their effect on Product Quality", McLean Symposium, Proc., ISS, Toronto, Canada, 1998, pp. 195-201.

2. K. Ichikawa, A. Morita, Y. Kawabe, "Behavior of Powder Slag Film and Influence of Powder Slag Film on Mold Heat Transfer Rate", Shinagawa Technical Report, Vol. 36, pp. 99-107, 1993.

3. K. Watanabe, M. Suzuki, K. Murakami, H. Kondo, A. Miyamoto, and T. Shiomi, "The Effect of Mold Powder Crystallization on Heat Transfer in Continuous Casting Mold", NKK Technical Review, No. 77, 1997, pp. 20-26.

4. R.J. O'Malley , "Observations of Various Steady State and Dynamic Thermal Behaviors in a Continuous Casting Mold", Proc. 82nd Steelmaking Conf., ISS, Chicago, IL, March 21-24, 1999.

5. Y. Meng and B.G. Thomas, ''Simulation of Microstructure and Behavior of Interfacial Mold Slag Layer in Continuous Casting of Steel'', ISIJ Int., 46, 2006, pp. 660-669.

6. Y. G. Maldonado et al., "Estimation of Time-Temperature-Transformation Diagrams of Mold Powder Slags from Thermo-analysis of Non-isothermal Crystallizsation," *Met. And Mat. Trans. B*, (2014).

7. M.-D. Seo, C.-B. Shi, J.-W. Cho, and S.-H. Kim, "Crystallization Behaviors of CaO-SiO 2 -Al 2 O 3 -Na 2 O-CaF 2 - (Li 2 O-B 2 O 3) Mold Fluxes," (n.d.).

8. M.-D. Seo, C.-B. Shi, H. Wang, J.-W. Cho, and S.-H. Kim, "Non-isothermal melt crystallization of cuspidine in CaO–SiO 2 –CaF 2 based glasses," *J. Non. Cryst. Solids*, **412** 58–65 (2015).

9. Y.G. Maldonado, F.A. Acosta, A.H. Castillejos, and B.G. Thomas, "Kinetic Study of the Devitrification of Mold Powder Slags," *AISTech*, 11 (2012).

10. R. Carli and C. Righi, "Mould flux crystallization : A kinetic study," *VII Int. Conf. Molten Slags Fluxes Salts*, [Mm] 821–826 (2004).

11. Z. Wang et al., "Crystallization Kinetics and Structure of Mold Fluxes with SiO_2 Being Substituted for Casting of Titanium Stabilized Stainless Steel," *Met. And Mat. Trans. B,* 44 606-612 (2013).
12. J. Li et al., "A Kinetic Study of the Effect of Na_2O on the Crystallization Behavior of Mold Fluxes for Casting Medium Carbon Steel," *ISIJ Int.*, 52 [12] 2220-2225 (2012).
13. B. Jiang et al., "A Kinetic Study of the Effect of ZrO_2 and CaO/Al_2O_3 Ratios on the Crystallization Behavior of a CaO- Al_2O_3-Based Slag System," *Met. And Mat. Trans. B,* 45 1057-1067 (2014).
14. Y. Kashiwaya, C.E. Cicutti, A.W. Cramb, and K. Ishii, "Development of Double and Single Hot Thermocouple Technique for in Situ Observation and Measurement of Mold Slag Crystallization.," *ISIJ Int.*, **38** [4] 348–356 (1998).
15. M. Karakus and R. E. Moore, "Cathodoluminescence (CL) Microscopy Application to Refractories and Slags", Journal of Minerals & Materials Characterization & Engineering, Vol. 1, No. 1, 2002, pp. 11-29.
16. R.B. Tuttle, K.D. Peaslee and J.D. Smith, "Interaction of Molten Ultra Low Carbon Steel with Carbide and Nitride Refractory Materials", Refractories Applications Transactions, **3** [1] 101-108 (2007).
17. L. Trueba, K.D. Peaslee, J.D. Smith and M. Karakus, "Effect of Nozzle Base Material on the Rate of Clogging during the Continuous Casting of Aluminium-killed Steels," Steel Research International, **77** [1] 37-47 (2006).
18. S. Ramachandran, K.D. Peaslee and J.D. Smith, "Thermochemistry of Steel-Refractory Interactions in Continuous Casting Nozzles," ISS Transactions, September 2003, 55-63 (2003).
19. M. Karakus, J.D. Smith and K.D. Peaslee, "Study of Non-Metallic Inclusions in Continuously Cast Steel Using Cathodoluminescence Microscopy," 38th Annual Meeting of the St. Louis Section of the American Ceramic Society, Chesterfield, MO, 201-212 (2002).
20. M. Karakus, J.D. Smith and R.E. Moore, "Cathodoluminescence Mineralogy of used MgO-C Bricks in Basic Oxygen Furnaces," Veitsch-Radex Rundschau, **1** 24-32 (2000).
21. J.D. Smith, K.D. Peaslee, M. Karakus and L. Trueba, "Study of Continuous Casting Nozzle Clogging Using Cathodoluminescence Microscopy," Advances in Refractories for the Metallurgical Industries III, eds. C. Allaire and M. Riguad, 187-200 (1999).
22. J.D. Smith, K.D. Peaslee, M. Karakus and H. Ruiz, "Post Mortem Analysis of Foundry EAF Refractories," 53rd Technical and Operating Conference, Steel Founders' Society of America, Chicago, IL, (1999).
23. M. Karakus, J.D. Smith, and R.E. Moore, "Mineralogy of the Carbon Containing Steelmaking Refractories," UNITECR '97, New Orleans, LA, **2**745-754 (1997).
24. R.J. O'Malley and J. Neal, ''An Examination of Mold Flux Film Structures and Mold gap Behavior Using Mold Thermal Monitoring and Petrographic Analysis at Armco´s Mansfield Operations'', METEC Congress 99, Dusseldorf, Vol. 1, 1999, pp.188-195.
25. W. Yan, W. Q. Chen, C. Lippold, H. G. Zheng, "Structure and performance characteristics of mold flux films for continuous casting of special alloy steels", La Metallurgia Italiana - n. 11-12/2013, pp. 35-42.
26. Y. Kashiwaya, C. Cicutti, A. Cramb, "Crystallization Behavior of Mold Slags", ISS Steelmaking Conference Proc., Vol. 81, pp. 185-191, 1998.
27. Grieveson, P., Bagha, S., Machingawuta, N., Liddell, K. and Mills, K.C. 1988: 'Physical properties of casting powders: Part 2 Mineralogical constitution of slags formed by powders', Ironmaking and Steelmaking Vol.15 No.4, pp. 181-186.