Radiative Heat Transfer Behavior of Mold Fluxes for Casting Low and Medium Carbon Steels

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An investigation was carried out to study the radiative heat transfer behavior of two typical mold fluxes for casting low (Flux1) and medium (Flux2) carbon steels. By using an infrared radiation emitter, a radiative heat flux was applied to a copper mold covered with solid mold flux disk to simulate the heat transfer phenomena in continuous casting. The effective thermal conductivities were determined by measuring the temperature gradient in the copper mold system. It was found that the solid crystalline mold Flux2 for casting medium carbon steel has a better capability to transfer heat than that of solid crystalline Flux1, while their glassy fluxes behave similar capability. The DHTT (Double Hot Thermocouple Technique) was employed in this paper to study the heat transfer capability of the crystalline mold fluxes. DHTT measurements suggested that the thermal diffusivity of crystalline sample of Flux2 is higher than that of Flux1. The XRD and SEM results were indicated that the precipitated crystalline phase for Flux1 is only granular cuspidine, Ca4Si2O7F2, while those for Flux2 are consisted of dendritic cuspidine, Ca4Si2O7F2 and gehlenite, Ca2Al2SiO7.

KEY WORDS: radiative heat transfer; mold fluxes; effective thermal conductivities; DHTT.

1. Introduction

It is well known that mold flux at the meniscus in continuous casting of steel plays a very important role in terms of controlling heat transfer and lubrication. The mold flux film is usually composed of three layers depending upon the cooling rate, i.e., a solid glassy layer against the mold wall due to the large cooling rate, a crystallized layer and a liquid layer between the partially solidified shell and solidified flux.1)

Mold fluxes with various properties such as crystallization temperature and viscosity have different impacts on controlling heat transfer and lubrication. For example, longitudinal cracking is a serious problem and particularly prevalent in medium carbon (MC) steels. The problem arises as a result of the volumetric shrinkage during the δ-γ phase transformation giving rise to the thermal-stresses within the solidified shell that may introduce the longitudinal cracks.2) It has been a common practice to minimize the stress introduced longitudinal cracks by lowering the heat transfer rate across the mold flux and keeping the solid mold flux thick and uniform. A thick solid flux film can typically be obtained by using a flux with a high crystallization or break temperature. Therefore, the characteristic features of medium carbon steel flux compared with the low carbon steels mold flux, is high basicity and crystallization temperature.

Recently, many studies have been carried out to investigate the heat transfer reduction by the crystallization of mold flux,3–5) and it could be summarized into two main categories: those which ascribe the decrease in heat transfer through crystallization as the enlargement of the air gap at the interface between the solid mold flux and the copper mold that enhances the interfacial thermal resistance;3,6–8) and those which suggest crystallization lowers the transmissivity of the mold flux, which in turn reduces the radiative heat flux.9–11)

Furthermore, some research has focused on the study of crystal compounds such as, cuspidine (Ca4Si2O7F2), which is the dominant phase in the crystalline flux films.12–14) Since cuspidine is the primary crystalline phase in almost all commercial mold fluxes; controlling the crystallization of cuspidine is a key component in adjusting the horizontal heat flux. Ozawa et al.15) has reported about the effect of slag crystallization on thermal conductive heat transfer in several annealed commercial fluxes. However, there are relatively few studies on the radiative heat transfer behavior for different solid mold fluxes and the difference of the heat transfer behavior of the solid crystalline fluxes to the knowledge of authors. Therefore, it is necessary to understand these different solid mold fluxes with various phases affect heat transfer in continuous casting.

In this study, an infrared heat emitter was used to irradiate the surface of a copper mold covered with various thicknesses of glassy or crystallized solid mold flux disks to...
determine the in-mold heat flux variance by analyzing the response of subsurface mold temperatures. The effect of mold flux chemistry on the heat transfer rate was also studied and the thermal diffusivity of the various mold flux was compared using the DHTT (Double Hot Thermocouple Technology).

2. Experimental Apparatus and Procedures

2.1. Heat Transfer Simulator

A schematic of the experimental apparatus is shown in Fig. 1, the details of which have been described elsewhere. The experimental apparatus mainly includes: a power controller, an infrared radiant heater capable of emitting 2.0 MW/m² heat flux at the rate of 380 voltages, a data acquisition system and a command-and-control unit.

The copper mold is simulated by a one-end water cooled copper cylinder, which acts as the radiation target, and its schematic figure is shown in Fig. 2. As the heat flux was applied on the top surface of the copper mold, which was covered with mold flux disk, the response temperatures could be measured by the sub-surface thermocouples.

2.2. Mold Flux Disk Preparation

Two commercial mold fluxes were studied in this paper. Flux1 was used for casting of low carbon steel (LC) and Flux2 was for medium carbon steel (MC) casting, and their main chemical composition were listed in Table 1. The mold fluxes were decarburized by placing them into a programmable furnace prior to the fusion process. The fused mold flux was melted at 1500°C in an alumina crucible placed on top of the aluminum crucible in an induction furnace for 300 s and then quenched from its molten state onto a stainless steel plate at room temperature to achieve a fully glass phase. A new cylindrical tube-like copper mold with the same diameter as the copper substrate was used to cast the mold flux before it solidified on the steel. The mold flux disks were polished with the SiC sand papers down to 1200 (grit size) to control its surface roughness and thickness. The pre-melted slags were analyzed by X-ray fluoroscopy (XRF), and the results were shown in Table 2. It suggested that the F evaporation could be neglected in our study, as there only resulted in a 2% loss, which was consistent with Sridhar’s study. Furthermore the basicity (CaO/SiO₂) value keeps relatively independent.

The polished glassy samples with various thicknesses were then annealed in a dried high purity (99.99%) argon atmosphere at the temperature of 900°C for 2 h to fully crystallize the disk. The samples were then taken out from the furnace and cooled to room temperature in air. The glassy or fully crystallized mold flux disks were then placed on the top of the copper mold individually for heat transfer experiments.

2.3. Thermal Diffusivity Tests

The double hot thermocouple technique (DHTT) was adopted here for the thermal diffusivity test and its schematic illustration was shown in Fig. 3. The principle of the

| Table 1. Chemical compositions of commercial mold fluxes (in mass%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | CaO  | SiO₂   | Al₂O₃ | MgO  | F    | Na₂O   | Li₂O  | CaO/SiO₂ |
| Flux1            | 33.5 | 42     | 7     | 2    | 6    | 9      | 0.5   | 0.8     |
| Flux2            | 44.5 | 37.1   | 7.8   | 2    | 3.4  | 4.9    | 0.5   | 1.2     |

| Table 2. Chemical compositions of pre-melted mold fluxes (in mass%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | CaO  | SiO₂   | Al₂O₃ | MgO  | F    | Na₂O   | Li₂O  | CaO/SiO₂ |
| Flux1            | 33.53| 42.05  | 7.02  | 2.00 | 5.88 | 9.02   | 0.50  | 0.8     |
| Flux2            | 44.51| 37.12  | 7.82  | 1.98 | 3.36 | 4.91   | 0.50  | 1.2     |
DHTT has been described in details elsewhere. The heating and cooling process was controlled by a computer program. The sample was heated between the tips of the two thermocouples at a rate of 150°C/s and held at 1500°C for at least 5 minutes to eliminate the bubbles, and homogenize its composition. After homogenization, the sample was rapidly cooled to room temperature to achieve a pure glassy phase. Then, the specimen was heated to a pre-set experimental temperature (900°C in this case) at the rate of 150°C/s for isothermal crystallization. Figure 4 shows the temperature profile of the process of pre-treating mold fluxes before conducting thermal diffusivity tests.

Finally, a temperature pulse of e.g. 200°C was applied to the left hand thermocouple creating a driving force for heat flux transfer across the solid crystalline flux towards the right end of the thermocouple. The right hand thermocouple recorded the temperature response. This response could be used to qualitatively evaluate the heat transfer capability of the slag.

3. Results and Discussion

3.1. Effect of Solid Mold Fluxes on Radiative Heat Transfer

In order to study the effect of solid mold flux on the radiative heat transfer, the top surface of the bare copper mold system was first pre-heated with a 200 KW/m² thermal radiation, and then subjected to a constant 500 KW/m² thermal radiation to establish the reference.

Figure 5 shows the subsurface temperature response when 500 KW/m² thermal radiation was incident to the bare copper mold. The thermocouples placed at 2, 5, 10, and 18 mm below the irradiated surface were recorded as T1, T2, T3, and T4 respectively. The cooling water inlet and outlet temperature were also recorded as Tin and Tout. The system reached steady state after 200–300 s, and the steady state heat flux was calculated by Fourier’s Law:

\[
q = -\frac{1}{n} \sum_j k \left( \frac{dT}{dx} \right)
\] ............................... (1)

Then the glassy disks of Flux1 and Flux2 were put on the top of the copper mold individually and subjected to constant 500 KW/m² thermal radiation. Five different mold flux disk thicknesses ranging from 2 mm to 5 mm were used. The measured heat fluxes histories through various thicknesses of Flux1 and Flux2 disks are shown in Figs. 6 and 7, respectively. As shown in Fig. 6, the measured heat flux stepped into steady state after 300 seconds. The steady state heat fluxes increased with the addition of the glassy disk thickness, which changed from 223 KW/m² at 2.06 mm to 263 KW/m² at 4.19 mm, and was relatively constant about 260 KW/m² at 5.08 mm. This could be explained by the Lambert-Beer Law, as indicated in previously published work:

\[
T = \exp(-\alpha d)
\] ............................... (2)

where \(T\) is the transmittance; \(\alpha\) stands for the extinction
coefficient; and \( d \) is the thickness of the flux disk. According to the Lambert-Beer Law, when the thickness of the sample increases, there will be more energy absorbed and this energy would heat the sample, leading to a higher heat flux being conducted and transmitted to the copper mold.

Figure 7 shows the similar results for Flux2 disks, where the thickness of disk has an exponential function of transferred heat transfer rate. The transferred heat flux at steady state was 226 KW/m² for 2 mm disk, and became to 260 KW/m² when the thickness changed to 5 mm. However, all the measured heat flux through the glassy disks from Figs. 6 and 7 are higher than the bare copper system, which confirmed that the solid mold flux film does enhance the radiative heat transfer rate in continuous casting.21)

An optical-process model to study the radiation energy through the solid mold flux layer to copper mold has been previously developed by Wang and Cramb,11) and Eq. (3) was given to compute the part of the radiation transferred through the solid flux to the mold, as follows:

\[
I_{\text{transfer}} = I_0 [1 - R(1 + \exp(-\alpha d)(1 - R)^2)] - R_{\text{system,copper}} [\exp(-\alpha d) - (1 - R)^2] \\
+ R_{\text{system,copper}} [\exp(-\beta d)(1 - R)^2] - R_{\text{system,copper}} [\exp(-\alpha d) - (1 - R)^2] \\
1 - R_{\text{system,copper}} [\exp(-\alpha d) - (1 - R)^2] - R_{\text{system,copper}} [\exp(-\alpha d) - (1 - R)^2] \quad \ldots \quad (3)
\]

where \( I_0 \) is the incident thermal radiation, \( R \) is the surface reflectivity of the mold flux, \( \alpha \) stands for the extinction coefficient values, and \( R_{\text{system,copper}} \) is the copper mold thermal heat reflectivity. The measured heat fluxes at steady state for above glassy samples and their values calculated through Eq. (3) were shown in Figs. 8(a) and 8(b). The values for the surface reflectivity of glassy mold flux, \( R \), and the surface reflectivity for bare copper mold, \( R_{\text{system,copper}} \), could be measured through the radiation tests, which was 0.474 and 0.683 respectively. The important adsorption/extinction coefficient values for Flux1 and Flux2 was calculated to be 280 m⁻¹ and 300 m⁻¹ through the model of the data fitting, details of which have been provided elsewhere.11,20)

As shown in Figs. 8(a) and 8(b), the transferred radiation part through the solid glassy mold flux was increasing with the increase of the disk thickness, and kept relatively constant when the thickness became larger than 4 mm, which show a good agreement with the calculated ones obtained from model.

Figure 9 shows the comparison of the radiation heat flux of glassy samples for Flux1 and Flux2 with identical thickness subjected to constant incident radiation of 500 KW/m². It could be found that there is no significant difference on the transferred heat flux for Flux1 and Flux2. Reasons for this was mainly due to: (1) there are no transition metal oxides in mold fluxes, which have a remarkable effect on absorption and extinction coefficients of mold fluxes samples;22,23) (2) the absorption coefficients for Flux1 and Flux2 are comparable. The absorption coefficient values calculated by Eq. (3) for Flux1 and Flux2 are 280 m⁻¹ and 300 m⁻¹ respectively. Both values for absorption coefficient are consistent with other researchers.2,21) Figure 9 also indicates that the basicity (mass% CaO/mass% SiO₂) of mold fluxes has no impact on the radiative heat transfer for glassy disks.

Crystallization of mold flux in the mold can significantly reduce the heat transfer between the solidified shell and copper mold, and lead to mild cooling of solidified shell, which was mainly due to the increase of the extinction coefficient resulting in a decreased energy transmittance and increased scattering of energy due to the developed crystal boundary and defects.5,22,23) Therefore, it is interesting to investigate the radiative heat transfer behavior of different crystalline samples.

Figure 10 shows that all measured heat fluxes through the crystalline Flux1 disks converged to 185 KW/m², when the disks were irradiated with 500 KW/m² thermal radiation. All transferred heat fluxes were higher than the bare copper system (150 KW/m²); however, they were lower than those of glassy ones, which was due to the larger extinction coefficient of crystalline mold flux. As illustrated in Fig. 10, the thickness of crystalline mold fluxes for Flux1 didn’t have significant effect on radiation heat transfer, which is consistent with our previous investigation.20)

As shown in Fig. 11, the transferred heat fluxes passing through crystallized Flux2 disks were around 193 KW/m² regardless of their thickness. Therefore, for both crystallized
mold fluxes, the thickness of crystalline mold fluxes didn’t have significant impact on radiation heat transfer. The extinction coefficients for crystalline Flux1 and Flux2 disks were calculated by Eq. (3) as: 2 000 m–1 and 2 200 m–1, respectively, where \( R_{\text{crystalline disks}} \) was determined as 0.64 through the radiation tests as indicated in reference. 20) The larger extinction coefficients led to a lower heat flux for crystalline samples than that for glassy ones (the absorption coefficients are only 280 m–1 or 300 m–1), and were responsible for the result that the thickness of crystalline disks doesn’t have an obvious effect on the radiative heat transfer rate according to Lambert-Beer Law as Eq. (2).

In order to compare the thermal properties of different solid crystallized mold fluxes, the measured steady state heat fluxes corresponding to each flux were plotted in Fig. 12. It is quite clear that all the measured heat fluxes through the crystallized Flux2 (medium carbon) samples are a little bit higher than those for Flux1, resulted in a 2% difference. It suggested that the solid crystallized phase of Flux2 has a better capability to transfer heat. It should be noticed that in the real continuous casting process, the flux with high basicity and crystallization temperature for medium carbon steel operation would introduce a thick solid crystal layer and larger flux/mold interface resistance, which are the two primary effects to control the heat transfer rate in the mold. The slight thermal property difference of above solid crystallized phase will not alter the general heat transfer rate in the casting. However it is interesting to explore this difference as well as its relationship with the crystal phase, morphology for the mold flux optimization.

3.2. Heat Transfer between Solid Mold Flux and Copper Mold

In order to study the heat transfer behavior of the two different mold fluxes, it is assumed that (1) heat is transferred in one direction from the mold fluxes to the copper mold; (2) the total heat flux is consisted of radiative and conductive heat flux; (3) there is no interaction between the radiation and conduction.

The total heat flux, \( q_{\text{tot}} \), through the mold flux film can be expressed by introducing effective thermal conductivity, \( K_{\text{eff}} \), as

\[
q_{\text{tot}} = K_{\text{eff}} \frac{\partial T}{\partial X} \quad ................. (4)
\]

where,

\[
K_{\text{eff}} = K_{\text{cond}} + K_{\text{rad}} \quad ................. (5)
\]

The total heat flux, \( q_{\text{tot}} \), could be calculated by the temperature gradient in the copper mold system. And the effective thermal conductivity, \( K_{\text{eff}} \), was determined by Eq. (6):

\[
K_{\text{eff}} = q_{\text{tot}} \frac{d}{(T_s - T_m)} \quad ................. (6)
\]

where \( d \) is the thickness of solid flux disk, \( T_m \) is the temperature of copper mold hot surface that could be calculated by the in-mold temperature gradient, \( T_s \) is the surface temperature of mold flux that was measured by placing a thermocouple on the top of the mold flux disk during the fabrication.

Figure 13 gives an example of measured temperature histories for the \( T_m \) and \( T_s \), when a constant thermal radiation of 500 KW/m² was applied to a crystalline Flux2 disk with the thickness of 4.12 mm. The steady state surface temperatures for copper mold and mold flux were determined to be 55°C and 580°C, respectively.

The radiation heat transfer through crystalline disks was calculated in Eq. (7) through gray gas approximation, which was also employed by other researchers. 24, 25
where $\beta$ stands for the radiative heat transfer coefficient; $n$ is refractive index, which was referred to be 1.6 in this case; $\sigma$, the Stefan-Boltzmann constant is $5.6705 \times 10^{-8}$ (W/(m$^2$K$^4$)); $\alpha$ is absorption coefficient that is 2 000 m$^{-1}$ for crystal of Flux1 and 2 200 m$^{-1}$ for Flux2 obtained from Eq. (3); $\varepsilon_{\text{crystalline}}$ and $\varepsilon_{\text{mold}}$ are the emissivity of the crystal and copper mold with the values of 0.7 and 0.4 individually.  

The radiative thermal conductivity $K_{\text{rad}}$ of the crystalline flux was then calculated with Eq. (8).

$$K_{\text{rad}} = \frac{\beta (T_i^4 - T_m^4)}{T_i - T_m} \text{ w/(m·K)}$$

The calculated heat transfer parameters are shown in Table 3. It is shown that the crystalline disk of Flux2 has larger effective thermal conductivity, which is consistent with Cho’s research. The lager effective thermal conductivity of crystalline sample for Flux2 was responsible for the higher transferred heat flux.

In order to study the variation of precipitated phases and the crystal micrographs, the crystalline samples for Flux1 and Flux2 after the experiments were analyzed by XRD and SEM.

**Figure 14** shows the SEM images for Flux1 and Flux2, respectively. It can be seen that a granular crystalline phase was formed for Flux1, while dendritic crystalline phase and some fine crystals precipitated for Flux2.

As shown in **Fig. 15**, the results of XRD indicated that the granular crystalline phase in Flux1 is Ca$_4$Si$_2$O$_7$F$_2$, the dendrite structure in Fig. 15(b) is also Ca$_4$Si$_2$O$_7$F$_2$ and the scattered fine crystals are Ca$_2$Al$_2$SiO$_7$.

The reason could be that Flux2 with higher basicity leads to a higher crystallization tendency, which may be favorable to form dendritic structure. The precipitation of Ca$_2$Al$_2$SiO$_7$ may be due to the higher alumina content in mold Flux2. Therefore, the formation of dendritic crystalline phase and the precipitation of Ca$_2$Al$_2$SiO$_7$ could be responsible for the
better heat transfer capability for Flux2, which was consistent with Taylor’s observation, who had studied the thermal conductivity of several crystalline phases and it was given in the following order: CaSiO3 > Ca2Al2SiO7 > Ca2Si2O7F2 > Na2Al2Si2O8.27)

3.3. The Comparison of Thermal Diffusivity by DHTT Measurement

The principle of using DHTT to study the heat transfer behavior of mold flux is similar to the laser-pulse technique. Previous study has shown the applicability of DHTT for the measurement of the thermal diffusivity of B2O3.18,19) The slag was mounted at the ends of two thermocouples and was kept at a certain temperature. Then a temperature pulse of e.g. 200°C was applied from one end, while the other thermocouple was recording the temperature response. This response could be used to evaluate the heat transfer through the slag and to calculate its thermal diffusivity. By using this method, heat transfer through the glassy sample and fully crystalline sample had been investigated by Lachman and Scheller.27)

The mold Flux1 and Flux2 were crystallized and kept at 900°C individually as indicated in Fig. 4, section 2.3; then a temperature pulse of 200°C (Fig. 16) was applied from the left end of the thermocouple, then passed through the crystallized flux and reached the right end of thermocouple; meanwhile the responding temperature was recording and shown in Fig. 17.

It was suggested from Fig. 17 that the responding temperatures for Flux2 were higher than those of Flux1; the highest temperature for Flux2 is 905°C and it is 903°C for Flux1. This indicates that the crystalline Flux2 film behaves better thermal transfer ability, leading to a higher level responding temperature system, which was consistent with the results of radiation heat transfer measurement.

4. Conclusions

Experiments were conducted to study the radiative heat transfer behavior for two different mold fluxes, i.e., Flux1 used for casting low carbon steel and Flux2 for medium carbon steel casting. The heat flux transferred through glassy disks and crystalline ones with various thicknesses were investigated, and the DHTT was also employed to analyze the heat transfer through the crystallized slag film. The important conclusions were made as follows:

(1) The transferred heat fluxes passing through glassy disks for Flux1 and Flux2 increases with the addition of the thickness and keeps relative constant when the thickness became more than 4 mm. Both glassy samples behave similar radiation heat transfer capability, which indicates that there is no direct effect of basicity of mold fluxes on radiative heat transfer for solid glassy fluxes.

(2) The crystallized solid mold flux disks appear different heat transfer capability, and the Flux2 has a better one, which in turn introduces a higher heat transfer rate compared with Flux1 samples.

(3) The precipitated crystalline phases are dendritic CaSiO3F2 and Ca2Al2SiO7 for Flux2, while it only forms granular CaSi2O7F2 in Flux1. The crystallization difference could be attributed to heat transfer behavior difference for these two mold fluxes.

(4) The DHTT measurement suggests that the responding temperatures through the solid crystallized Flux2 film are higher than those for Flux1, which suggests that the thermal diffusivity of fully crystalline Flux2 samples is higher than Flux1 under the same condition.

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