Radiative Heat Transfer in Transition Metal Oxides contained in Mold Fluxes

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Transition metal oxides FeO, MnO and TiO$_2$ contained in mold fluxes were prepared and measured by a FTIR spectrometer. Characteristics of absorption/extinction coefficient were obtained through infrared spectrum analysis. Relation between radiative heat transfer and the transition oxides was calculated by a heat exchange model. The result indicates that the transition oxides have the great negative effect on radiative heat transfer during the wavelength of 1–6 µm. Radiation heat flux, $q_{12}$ decreases from 5.5–6.3 × 10$^4$ W m$^{-2}$ to 4.3–5.1 × 10$^4$ W m$^{-2}$, 3.4–4.2 × 10$^4$ W m$^{-2}$ and 3.9–5.4 × 10$^4$ W m$^{-2}$ with 2–8% MnO, 1–3% FeO and 2–8% TiO$_2$ added, respectively. Due to the great refraction and scattering at surface and grain boundaries, the negative effect in crystalline samples was much larger than that happened in the glassy ones. MnO and TiO$_2$ have great influence on viscosity and melting temperature of mold fluxes, but FeO has little influence. XRD results show that Mn$_2$SiO$_4$, Fe$_2$SiO$_4$, CaTiO$_3$ and other minor phases were precipitated after transition oxides added. Grain size of crystals enlarges from 12.5 to 100 µm with increasing of holding temperature. At 800°C, the radiation heat flux is 1.25 × 10$^4$ W m$^{-2}$, and decreases to 0.84 × 10$^4$ W m$^{-2}$ at 900°C. Above 900°C, the radiation heat flux increased on the contrary. The radiation heat flux increased from to 0.84 × 10$^4$ W m$^{-2}$ to 1.0 × 10$^4$ W m$^{-2}$. Industrial trial shows that the transition oxides contained in mold fluxes are good at coordination of heat transfer controlling and strand lubricating, and the occurrence of longitudinal cracks is greatly decreased. Further studies in the transition metal oxides contained in mold fluxes will be valuable for improving strand surface quality of crack sensitive peritectic steels.

KEY WORDS: continuous casting; mold fluxes; radiative heat transfer; radiation heat flux; transition oxides; absorption/extinction coefficient; crystalline.

1. Introduction

Occurrence of surface defects on continuously cast steel slabs is strongly influenced by the heat transfer during initial solidification of the slabs in casting mold. Excessively large heat transfer near the meniscus from steel shell across infiltrated mold flux film to copper mold causes longitudinal surface cracks on slabs, and hence the suppress of the heat flux in the mold is an important issue to produce high quality slabs. With the development and wide application of the high-speed continuous casting, hypo-peritectic steel become a bottleneck of casting due to contraction on peritectic solidification which causes an uneven strand surface in the mold. The non-uniformity results in uneven heat transfer, and hence the occurrence of longitudinal crack causes a breakout in the mold.

Many efforts have been concentrated on reducing the heat transfer by increasing crystallizing temperature and crystallinity of mold flux film which infiltrates between the mold and solidifying steel shell. Although these methods could suppress heat flux in the mold, but the problem of strand stroller breakout was brought as a result of excessive crystallizing temperature and crystallinity as well. It is reported that the radiative heat transfer, as one of the two heat transfer ways in the mold, contributes 20–50% to the total heat transfer from the steel shell to the mold.$^{[1-3]}$ In the research of flux film and infrared glass, it was found that the addition of transition metal oxides such as MnO, FeO, Cr$_2$O$_3$, NiO etc. could increase infrared absorption coefficient of flux film and decrease infrared radiometric force.$^{[4-6]}$ Therefore, it is possible to decrease infrared radiative heat transfer through selecting proper components of mold fluxes. The radiative heat transfer characteristics of transition oxides contained in mold fluxes are discussed, and other physic-chemical properties are also mentioned in this study.

2. Methodology

In the previous study,$^{[7]}$ a radiative heat exchange model in the mold was developed based on the Planck’s radiation law and radiative heat transfer between two infinite plates. Infrared characteristics of mold flux samples were measured by a FTIR spectrometer and calculated through this model.
where \( q_{12} \) is the radiation heat flux from the strand to the mold; \( \alpha_1, \alpha_2 \) are absorptivity of the strand and the mold; \( \tau_\lambda \) describes the transmittance; \( T_1, T_2 \) are temperature of the strand and the mold, respectively; \( \lambda \) is the wavelength; \( C_1, C_2 \) are constant.

The chemical compositions of mold flux samples are summarized in Table 1. In order to reveal the effect of transition oxides on the radiative heat transfer, MnO, FeO and TiO\(_2\) were added into the samples through the change of the ratio of calcium oxide and silicon dioxide.

A simple schematic flowchart of the FTIR measurement is provided in Fig. 1. Samples were first pre-melted in a carbon crucible at 1 573 K, and then poured into a steel container for naturally cooling. Samples obtained were mainly glassy phases. In order to investigate the influence of crystallization, a portion of glassy samples were annealed at 800°C in a muffle furnace to obtain crystalline phases. Both glassy and crystalline samples were sliced and polished into thin discs, whose thickness was controlled at 0.3 ± 0.02 mm.

3. Results and Discussion

3.1. Characteristics of Absorption/Extinction Coefficient

Because 91.48% of the radiant energy between the strand and the mold is in the wavelength range of 1–6 \( \mu \)m, other wave band are not discussed in this study. Absorption and extinction spectra at room temperature calculated by Beer’s Law were shown in Figs. 2 and 3. Absorption coefficients and extinction coefficients for the glassy and the crystalline samples at the wavelength of 1–6 \( \mu \)m are 2 500–9 000 m\(^{-1}\) and 3 000–18 000 m\(^{-1}\), respectively. There is good agreement between the results by previous studies. Due to the strong scattering of crystalline phase at surface and grain boundaries, the extinction coefficients of crystalline samples are much larger than the absorption coefficients of glassy samples. In Figs. 2 and 3, there are two “shoulders” in the spectra beyond \( \lambda \) of 2.7 \( \mu \)m and 4.5 \( \mu \)m. These are owing to the stretching vibration of Si–OH bonds and Si–O bonds, respectively.

Transition metal oxides, MnO, FeO and TiO\(_2\) have a marked effect on absorption coefficients and extinction coefficients of mold fluxes samples. As illustrated in Figs. 2 and 3, absorption coefficients and extinction coefficients increase rapidly with the transition oxides addition in the wavelength range of 1–6 \( \mu \)m. The upper bounds are increased from 5 800 to 8 800 m\(^{-1}\) in glassy sample and from 9 000 to 18 000 m\(^{-1}\) in crystalline sample, respectively.

3.2. Characteristics of Radiative Heat Transfer

Radiation heat flux, \( q_{12} \) from the steel shell to the mold calculated by Eq. (1) at room temperature in the wavelength range of 1–6 \( \mu \)m are given for both glassy and crystalline mold fluxes films in Fig. 4. Characteristic of transition element is that electrons could transit form low-level trajectory \( d_e \) to high-level trajectory \( d_g \) after obtain energy due to the reason of unfilled in the \( d \) trajectory. This transition goes by the name of \( d-d \) transition, and the energy absorbed in the transition is so-called break-up energy. In the range of infrared (1–25 \( \mu \)m), transmittance of infrared light decreased as a result of phonons absorption by coordinate ions through \( d-d \) transition. Wavelength range selective absorbed are different owing to the different break-up energy. It can be interpreted as “coloring” effect of transition element to mold flux films. In this
study, the wavelength range of 1–6 μm is emphasized on account of the continuous casting process, and actually, the absorption spectrum of transition elements always expands to near ultraviolet band and infrared band, at the wavelength range of 200–25,000 nm.10)

As illustrated in Fig. 4, with MnO, FeO and TiO₂ addition, there is a remarkable radiation heat flux decrease in the mold flux samples. In glassy samples, the radiation heat flux, \( q_{12} \) decreased from 5.5–6.3×10⁴ W m⁻² to 4.3–5.1×10⁴ W m⁻² and 3.4–4.2×10⁴ W m⁻² while 2–8% MnO, 1–3% FeO and 2–8% TiO₂ are added, respectively. The radiative heat transfer from the strand to the mold in the crystalline samples is much smaller than that in the glassy samples. This difference is attributed to the opaque surface of the crystalline samples that reflects incident photons, and the grain boundary in crystalline samples that scatters radiation photons. Figure 5 shows XRD results of crystalline samples. The crystalline portion of transition oxides free sample was mainly Cuspidine (Ca₄Si₂O₇F₂). After transition oxides MnO, FeO and TiO₂ added, Mn₂SiO₄, Fe₂SiO₄, CaTiO₃, Ca₂SiO₄ and other minor phases were also present. The radiation heat flux, \( q_{12} \) decreased from 1.2–4.8×10⁴ W m⁻² to 0.03–4.0×10⁴ W m⁻² in the crystalline samples, and the maximum decrease reached up to 54%, 65% and 95% with the addition of 8% MnO, 3% FeO and 8% TiO₂, respectively.

### 3.3. Effect of Crystal Grain Size on Radiative Heat Transfer

In order to study the effect of grain size on radiative heat transfer, sample (R1.1, 4% MnO) was held for 1 h at different temperature in the crucible furnace. As illustrated in Fig. 6, with increasing of holding temperature, the grain size of crystals enlarged. When the sample was treated at 800°C, crystals represent as small grain size, and mainly around 12.5 μm; while the sample was held at 900°C and 1000°C, grain size were enlarged, mainly around 20 μm and 25 μm respectively; while the holding temperature are 1100°C and 1200°C, the crystals were grown up, mainly around 35 μm and 100 μm.

Radiation heat flux of the sample held at different temperature is shown in Fig. 7. Current research indicated that the crystallization behavior does not always the negative effect on radiative heat transfer. Ozawa et al.11) reported that the radiation conductivities decrease with increasing the degree of crystallinity and become almost constant where the degree of crystallinity exceeded about 15%. Figure 7 shows that at the holding temperature of 800°C, the radiation heat flux is 1.25×10⁴ W m⁻²; when the holding temperature is increased to 900°C, the radiation heat flux decreased to 0.84×10⁴ W m⁻², the reduction of which reached 33%. Above 900°C, the radiation heat flux increased on the contrary. The radiation heat flux increased from to 0.84×10⁴ to 1.0×10⁴ W m⁻². Under the condition of the same crystallinity, radiation heat flux should increase with the crystal grain size increasing, however, the radiation heat flux at the holding temperature of 800°C in present study is excessively high as a result of the low crystallinity in the microscopy observation.
3.4. Viscosity and Melting Characteristics

Figures 8 and 9 show the measured melting and viscosity characteristics of mold flux samples. MnO is known as network modifier. When MnO is added into mold fluxes, O\(^{2-}\) is provided to disintegrate large size silicate network and reduce viscosity of mold fluxes. Under the condition of low basicity, the effect of MnO on viscosity is more obvious than that of high basicity. When the basicity is 0.9 and 1.0, the viscosity of the samples reduces 0.21–0.22 Pa·s with 8% MnO addition, while the basicity is 1.1, viscosity reduces 0.07 Pa·s with the same MnO addition. The effect of MnO on melting temperature is also notable. When the basicity is 0.9 and 1.0, the melting temperature of the samples reduces 60°C with 8% MnO addition, while the basicity is 1.1, the melting temperature increases on the contrary when the MnO addition exceeds 6%, because of the precipitation of high-melting substance, such as melilite.

General mold flux base materials is free of TiO\(_2\), however, the TiO\(_2\) inclusion can emerge into mold fluxes during casting, and influence mold flux properties. As illustrated in Fig. 9, the viscosity of mold flux samples reduces with TiO\(_2\) addition. With the increase of basicity, the reducing tendency of viscosity becomes gradually weak. Under the condition of high basicity and high content of TiO\(_2\), TiO\(_2\) is easy to precipitate as the form of CaTiO\(_3\), which leads to viscosity and melting temperature increasing as shown in Figs. 8 and 9.

FeO has little influence on melting temperature of mold fluxes. When the basicity is 0.9 and 1.0, the melting temperature of the samples reduces 13–20°C with 1% FeO added, but have no marked variations with the continuous FeO increasing. The viscosity variation range of FeO containing mold fluxes is 0.03–0.06 Pa·s, and it is stable during the experiment.

4. Industrial Practice

Several commercial mold fluxes were designed and have been applied to industrial production. Chemical composition of mold fluxes and industrial trials parameters are listed in Tables 2 and 3.

Transition oxide MnO was added to adjust microcrystalline precipitation in mold flux film, and reduces the ra-
diative heat transfer in the mold. Crystallinity is controlled less than 50% and 30% for the 1# and 2# mold fluxes, respectively. The strong lubricating ability can reduce thermal stress in the steel shell, and hence, decreases generation of longitudinal cracks and surface micro-cracks. In the industrial trial, longitudinal crack ratio decreased 20–30% compared with initial mold fluxes.12)

5. Conclusion

Relation between the radiative heat transfer and the transition metal oxides FeO, MnO and TiO$_2$ were obtained by the FTIR spectrum measuring of the mold flux samples and the heat exchange calculating. In summary, transition metal oxides have a great negative effect on radiative heat transfer through mold flux samples during the wavelength of 1–6 $\mu$m. X-ray analysis revealed that Mn$_2$SiO$_4$, Fe$_2$SiO$_4$, CaTiO$_3$ and other minor phases were found in MnO, FeO and TiO$_2$ containing mold fluxes, respectively. The negative effect on the radiative heat flux in crystalline samples were much larger than that happened in glassy ones. Industrial trial shows that the transition oxides contained in mold fluxes are good at coordination of heat transfer controlling and strand lubricating, and occurrence of longitudinal cracks is greatly decreased. Further studies in the transition metal oxides contained in mold fluxes will be valuable for improving strand surface quality of crack sensitive peritectic steels.

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