Controllability of Radiative Heat Flux across Mould Flux Films by Cuspidine Grain Size

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Apparent reflectivities and transmissivities have been measured as functions of cuspidine grain diameter for mould fluxes having constant degrees of crystallinity. Samples used were two types of synthesised mould flux with the basicity of 1, one of which samples contained 1 mass% of Fe₂O₃, and the grain diameter was varied in the range 1–3.5 μm. The optical measurements were carried out in the wavelength range 300–2600 nm at room temperature using a spectrophotometer with an integrating sphere. With increasing grain diameter, the apparent reflectivity tended to increase and the apparent transmissivity tended to decrease at higher wavelengths for iron oxide free mould fluxes; it seemed that the apparent reflectivity showed a maximum value and the apparent transmissivity showed a minimum value in the grain diameter range 2–3 μm. In contrast, there was less significant dependence on grain size for mould fluxes containing iron oxides. The total radiative heat flux which may reach the mould from the steel shell has been evaluated using apparent reflectivity and transmissivity data on the basis of an optical process model. It has been found that the total radiative heat flux would be smallest in iron oxide free mould fluxes having the highest apparent reflectivity and the lowest apparent transmissivity at higher wavelengths. Effects of grain size on the radiative heat flux are smaller for mould flux containing iron oxides. Comparison of the total radiative heat flux with the total heat flux including conductive contribution suggests that control of cuspidine grain diameter would lead to reduction of the total heat flux by 7–8% for iron oxide free mould fluxes. In addition, the air gap layer would affect the total heat flux more efficiently where the volume fraction of air in the layer exceeds 85%.

KEY WORDS: mould flux; reflectivity and transmissivity; cuspidine grain size; radiative and conductive heat fluxes; air gap.

1. Introduction

During continuous casting, the mould flux forms a slag film consisting of a liquid layer (typically 0.1 mm thick) next to the steel shell and a solid layer (typically 1–2 mm thick) next to the mould; in time, the solid layer is partially crystallised to form cuspidine. The liquid layer provides lubrication between the mould and the strand, and the solid layer primarily controls horizontal heat transfer across the mould flux film. It has also been known that crystallisation of mould flux is very effective for mild cooling to avoid longitudinal cracking. The mechanisms of mild cooling proposed so far include (a) conductive heat transfer reduction due to enlargement of an air gap at the interface between the mould flux and the mould and (b) radiative heat transfer reduction due to increase in the reflectivity of mould fluxes. The predominant mechanism is considered to depend on the characteristics of mould fluxes.

To examine the reasonability of the latter mechanism, the authors have measured apparent reflectivities and transmissivities of mould fluxes with systematic variations in two factors, (i) the degree of crystallinity and (ii) the concentration of iron oxides, and evaluated radiative heat transfer characteristics using the measured data on the basis of an optical process model. As a result, it has been found that the increase in the degree of crystallinity causes reflectivity increase and transmissivity decrease, leading to radiative heat transfer reduction. Another finding is that the presence of iron oxides in mould fluxes is not suitable for radiative heat transfer reduction because of absorptivity increase leading to reflectivity decrease via the following relationship

\[ R + A + T = 1 \]............................... (1)

where \( R \) is the reflectivity, \( A \) is the absorptivity and \( T \) is the transmissivity.

The previous work assumed that the optical characteristics of crystallised mould fluxes were dependent only on the degree of crystallinity, actually, crystallised mould fluxes are polycrystalline, and their optical characteristics should depend on the size and shape of crystal grains as well. On the basis of the Lambert-Beer law, for example, the transmissivity is expressed by the following equation:

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

where \( \alpha \) is the absorption coefficient, \( S \) is the scattering coefficient, and \( d \) is the thickness of the mould flux layer.
coefficient – the sum of \( \alpha \) and \( S \) is called the extinction coefficient – and \( d \) is the thickness of a sample and, furthermore, it is known that the value of \( S \) depends on grain size. As an example, Thiele and French have investigated the scattering coefficient of TiO\(_2\) particles\(^6\) for a wavelength of 560 nm and found that the value of \( S \) becomes higher at particle diameters around 300 nm which is close to the wavelength, as suggested by theory of Mie scattering. Accordingly, particle size control results in higher values of \( S \), leading to lower values of \( T \), which can also affect values of \( R \) and \( A \).

In mould fluxes as well, it is likely that the grain size of cuspidine modulates the optical characteristics, by which radiative heat flux can be reduced. From this viewpoint, Diao \textit{et al.} have studied the dependence of radiative heat flux on grain size using mould fluxes containing MnO,\(^8\) and found that the radiative heat flux decreases with increasing grain diameter up to 20 \( \mu \)m and then increases slightly. In continuous casting, it is assumed that the steel shell exists around the melting point of iron (1 809 K) at the initial stage of solidification, at which temperature the strongest radiation occurs at about 1.6 \( \mu \)m in wavelength from Wien’s displacement law. Thus, control of grain size to the magnitude close to this wavelength would be more relevant to the modulation of the optical characteristics, in turn, radiative heat flux. However, there is no report available for the dependence of radiative heat flux on grain diameter in the range around 1.6 \( \mu \)m.

Against this background, the present work focuses on the effect of cuspidine grain size on the radiative heat flux across the mould flux film, and consequently aims:

\begin{itemize}
  \item to measure apparent reflectivities and transmissivities of mould fluxes having constant degrees of crystallinity as functions of cuspidine grain diameter.
  \item to clarify the effect of grain size control on the magnitude of radiative heat flux across the mould flux film on the basis of the measured optical characteristics.
\end{itemize}

In the previous work,\(^6\) the radiative heat transfer characteristic of mould fluxes was evaluated as the ratio of radiative energy which may reach the mould to energy radiated from the steel shell. In contrast, the present work attempts to derive the absolute value of radiative heat flux which may reach the mould from the steel shell, which attempt is another objective of the present work.

2. Experimental

2.1. Sample Preparation

The basic chemical composition of mould flux samples (Flux A) is the same as used in the previous work.\(^6\) \( T \text{CaO}/\text{SiO}_2 = 1, \text{Al}_2\text{O}_3 + \text{MgO} = 3.3 \text{ mass\%} \) and \( \text{Na}_2\text{O} + \text{F} = 20.0 \text{ mass\%} \) where \( T \text{CaO}/\text{SiO}_2 \) represents the basicity on a mass basis including CaO originating from CaF\(_2\). The sample was prepared from reagent grade \( \text{SiO}_2, \text{Al}_2\text{O}_3, \text{MgO}, \text{Na}_2\text{CO}_3, \text{CaF}_2 \) and CaO powders, the last being made by heating CaCO\(_3\) at 1 323 K for 12 h. In addition, another type of sample (Flux B) was prepared by adding 1 mass\% of Fe\(_2\text{O}_3\) to Flux A. Weighed mixtures of these powders were melted in platinum crucibles in air at 1 673 K for 5 min, and the melts were poured into brass moulds at room temperature to obtain glassy samples \~ 5 mm thick. The glassy samples were heat-treated at temperatures 913–1 143 K for 30 min so as to have different crystal grain sizes: these temperatures were higher than 903 K which was crystallisation temperature of Flux A determined by differential scanning calorimetry (DSC).

2.2. Sample Characterisations

X-ray diffraction (XRD) analysis was applied to know the crystal phase precipitated and the degree of crystallinity, the latter being determined by the internal standard method.\(^9\) To evaluate the crystal grain size, the cross section of the samples was observed using a scanning electron microscope (SEM), and the diameter of grains was measured using the micrographs. The apparent reflectivity \( (R_a) \) and transmissivity \( (T_a) \) of the samples were measured at room temperature using a spectrophotometer with an integrating sphere in the wavelength range 300–2 600 nm. Prior to the optical measurement, the thickness of each sample was measured using a micrometer. To investigate the dependence of the sample thickness on the optical characteristics, the sample heat-treated at 1 073 K was thinned down to thicknesses of 3.36, 2.85, 2.15 and 1.65 mm, and at each thickness the optical measurements were made.

3. Results

3.1. Degree of Crystallinity

X-ray diffraction analysis has confirmed that both Fluxes A and B crystallise to form only cuspidine by heat treatment. Figure 1 shows the change with time in the degree of crystallinity for Flux A samples during the heat treatment at 933 K. It can be seen that the degree of crystallinity started to increase about 5 min after the heat treatment was made, and reached 63% with uncertainty of \pm 5\% in 30 min. This percentage is not unreasonable since the degree of crystallinity has been estimated to be \~ 65\% assuming that all CaO contained joins to form cuspidine. On the basis of this result, the heat treatment time for crystallisation was determined to be 30 min at each temperature except for 913 K, at which temperature the heat treatment was made for 1 h to avoid lower degrees of crystallinity.

Figure 2 shows the relation between the heat treatment time and the degree of crystallinity for Fluxes A and B. In consideration of uncertainty in the measurements, the
degree of crystallinity is supposed to be ~ 58% for Flux A and ~ 53% for Flux B, irrespective of heat treatment temperature, and iron oxides seem to retard crystallisation. The degree of crystallinity was not determined for a Flux A sample heat-treated at 913 K; on the other hand, a Flux B sample heat-treated at 913 K has the same degree of crystallinity as those heat-treated at higher temperatures. Thus, all the Flux A samples are likely to have a degree of crystallinity of about 58%.

3.2. Grain Diameter

Figures 3 and 4 show micrographs for samples of Fluxes A and B heat-treated at various temperatures, respectively, where for Flux A six samples have been selected from eleven due to limitations of space. For Flux A, the crystals precipitated are needle-shaped at 913 K, becoming spheroidal

Fig. 2. Relation between heat treatment temperature and degree of crystallinity for Fluxes A and B: The heat treatment was made for 1 h at 913 K and for 30 min at other temperatures.

Fig. 3. Micrographs of cuspidine grains formed in Flux A samples annealed at (a) 913 K, (b) 933 K, (c) 1 053 K, (d) 1 073 K, (e) 1 113 K and (f) 1 143 K: The heat treatment was made for 1 h at 913 K and for 30 min at other temperatures.

Fig. 4. Micrographs of cuspidine grains formed in Flux B samples annealed at (a) 913 K, (b) 933 K, (c) 1 053 K, (d) 1 073 K, (e) 1 113 K and (f) 1 143 K: The heat treatment was made for 1 h at 913 K and for 30 min at other temperatures.

Fig. 5. Dependencies of diameters in minor and major axes (D₁ and D₂) and corrected diameter (D_cor) on heat treatment temperature for (a) Flux A and (b) Flux B.
at higher temperatures. For Flux B, in contrast, the crystals precipitated are more granulated at 913 K, becoming spheroidal at higher temperatures. Using these micrographs, the grain diameter of each sample was evaluated as follows: The diameters in the minor and major axes were measured on about 80 grains for each sample, and the respective averages were calculated as $D_1$ and $D_2$, which were converted to the corrected diameter $D_{cor}$ from the following equation.

$$D_{cor} = 2 \left( \frac{D_1}{2} \right) \left( \frac{D_2}{2} \right)^{\frac{3}{2}} \text{ (3)}$$

where it is assumed that the sphere with the diameter $D_{cor}$ has the same volume as the spheroid. Figures 5(a) and 5(b) show the dependencies of $D_1$, $D_2$ and $D_{cor}$ on heat treatment temperature for Fluxes A and B, respectively. It is found that in both fluxes the diameters on the whole increase with increasing temperature and that the diameters of Flux A are roughly two times larger than those of Flux B, the latter finding suggesting that iron oxides have an effect of fining cuspudine crystals. To express the diameter of samples, the value of $D_{cor}$ is used in the present paper for convenience.

3.3. Reflectivity and Transmissivity

Figures 6(a) and 6(b) show apparent reflectivities ($R_a$) and transmissivities ($T_a$) as functions of wavelength ($\lambda$) for Flux A samples having various corrected grain diameters, respectively, and Fig. 6(c) shows the corresponding apparent absorptivities ($A_a$) derived from Eq. (1). In each spectrum, data below 400 nm in wavelength may not be reliable because of the lower limit of the measurable range by the apparatus. The spectra are very complex; at the same time, the apparent reflectivities on the whole decrease and the
apparent transmissivities increase with increasing wavelength. In addition, the apparent absorptivities roughly range between 0.05 and 0.2. With increasing grain diameter, the apparent reflectivities tend to increase and the apparent transmissivities tend to decrease at higher wavelengths. To examine these tendencies in more detail, these optical characteristics have been plotted against corrected diameter, resulting in Fig. 7, in which only the data for wavelengths of 1 200 nm, 1 600 nm and 2 200 nm are focused on because wavelengths around 1 600 nm are more relevant to radiation at the melting point of iron – Wien’s displacement law says that blackbody at the melting point of iron emits the strongest radiation around 1 600 nm; in addition, the temperature of steel shell in continuous casting can be assumed to lie around the melting point of iron. The apparent reflectivity has a maximum value for each wavelength, and the diameter showing the maximum is larger as wavelength is higher. In contrast, the apparent transmissivity and absorptivity have minimum values, and the diameters showing the minima are also larger as wavelength is higher. These findings suggest that formation of crystal grains having various diameters would enable one to produce mould fluxes having high apparent reflectivity and low apparent transmissivity and absorptivity in a wider range of wavelength, which leads to possible reduction of radiative heat transfer across the mould flux film.

Figures 8(a) and 8(b) show apparent reflectivities and transmissivities as functions of wavelength for Flux B samples having various corrected grain diameters along with the data for Flux A having a corrected grain diameter of 2.55 μm, and Fig. 8(c) shows the corresponding apparent absorptivities. Flux A is iron oxide free, whereas Flux B contains 1 mass% of Fe₂O₃, which causes considerable changes in absolute values of the optical characteristics.

Fig. 8. (a) Apparent reflectivities, (b) apparent transmissivities and (c) apparent absorptivities as functions of wavelength for Flux B samples: The sample is specified by the corrected diameter $D_{cor}$ which has been derived from Eq. (3) using average diameters in the minor and major axes ($D_1$ and $D_2$).

Fig. 9. (a) Apparent reflectivities, (b) apparent transmissivities and (c) apparent absorptivities for wavelengths of 1 200 nm, 1 600 nm and 2 200 nm for Flux B samples plotted against corrected diameter: The sample is specified by the corrected diameter $D_{cor}$ which has been derived from Eq. (3) using average diameters in the minor and major axes ($D_1$ and $D_2$).
Roughly speaking, the apparent reflectivity decreases from 0.8 to 0.4, the apparent transmissivity decreases from 0.1 to below 0.05 and the apparent absorptivity increases from 0.1 to 0.6; the absorption is due to Fe$^{2+}$ ions. In comparison with the effects by iron oxides, the grain diameter gives only small effects. Figure 9 shows maximum or minimum values distinctly in the range investigated.

Figures 10(a) and 10(b) show apparent reflectivities and transmissivities as functions of wavelength for Flux A samples of 2.55 μm in corrected grain diameter having different sample thicknesses, and Fig. 10(c) shows the corresponding apparent absorptivities. The spectra of apparent reflectivities are close to each other, which is also applicable to the spectra of apparent transmissivities and absorptivities. With decreasing sample thickness, the apparent reflectivity decreases and the apparent transmissivity increases probably due to the decrease in scattering frequency inside the sample, and the apparent absorptivity is the greatest at 2.85 mm in sample thickness.

4. Discussion

4.1. Calculation of Total Radiative Heat Flux

The total radiative heat flux across the mould flux film is calculated on the basis of the optical process model proposed in the previous report. This model assumes:
- There exists a mould flux film consisting of molten and solid flux layers between the steel shell and the mould. The molten flux layer is next to the steel shell, and the solid flux layer is next to the mould.
- There is no absorption within the molten flux layer since the thickness is as thin as 0.1 mm; instead, multiple reflections of radiation from the steel shell are taken into account.
- The whole system reaches a steady state.

According to the calculation of the previous work, the radiative heat flux (I) which may reach the mould from the steel shell can be considered as

\[ I = [I_s + I_f - I^0] \{1 - (1 - \epsilon_s)R_s\}^{-1} \] ........................ (4)

where \( I_s \) is the heat flux radiated from the steel shell, \( I_f \) is the heat flux radiated from the solid flux layer, \( \epsilon_s \) is the emissivity of the steel shell: it is assumed that the emissivity of solid flux is equal to its apparent absorptivity (\( A_s \)). Using Eq. (4), the previous work approximately evaluated the ratio of radiative energy which may reach the mould to energy radiated from the steel shell using the Stefan-Boltzmann law for the terms \( I_s \) and \( I_f \). In contrast, the present attempt is to derive the absolute value of the total radiative heat flux which may reach the mould and, thus, the terms \( I_s \) and \( I_f \) are replaced by Planck’s law of radiation, respectively, as follows:

\[ I_s = \epsilon_s n^2 C_1 \lambda^{-5} \left\{ \exp \left( \frac{C_2}{\lambda T_s} \right) - 1 \right\}^{-1} \] ........................ (5)

\[ I_f = A_s n^2 C_1 \lambda^{-5} \left\{ \exp \left( \frac{C_2}{\lambda T_f} \right) - 1 \right\}^{-1} \] ........................ (6)

where \( n \) is the refractive index of the molten flux, \( C_1 \) and \( C_2 \) are Planck’s radiation constants (\( C_1 = 3.7469 \times 10^{-16} \text{ Wm}^2 \text{K}^{-5} \) and \( C_2 = 0.014398 \text{ mK} \)), and \( T_s \) and \( T_f \) are assumed to be 1800 K and 1400 K, respectively, since the former is a temperature close to the melting point of iron and the latter is a typical liquidus temperature of mould fluxes. Substituting Eqs. (5) and (6) into Eq. (4) results in

\[ I = \frac{n^2 C_1}{\lambda^5 \{1 - (1 - \epsilon_s)R_s\}} \left\{ \frac{(1 - R_s) \epsilon_s}{\exp(C_2/\lambda T_s) - 1} - \frac{A_s \epsilon_s}{\exp(C_2/\lambda T_f) - 1} \right\} \] ........................... (7)

where the term \( (1 - R_s) \) has arisen from the term \( (T_s + A_s) \). In addition, the terms \( n, R_s, A_s \) and \( \epsilon_s \) are also functions of
wavelength, and the integration of Eq. (7) over wavelength gives the total radiative heat flux ($I_{\text{Total}}$). The detail of this calculation is mentioned in the following.

The value of $n$ for glassy SiO$_2$ has been reported as a function of wavelength and temperature by Wray and Neu.\cite{11} For glassy SiO$_2$ at room temperature, the value of $n$ decreases very steeply from 1.52 to 1.47 with increasing wavelength from 200 nm to 350 nm and then decreases slightly from 1.47 to 1.42 with increasing wavelength from 350 nm to 3300 nm. The latter wavelength range is more relevant to the integration of Eq. (7), in which range the refractive index shows only a three percent decrease. In addition, the refractive index shows an increase only by $ca$ 0.7% with an increase in temperature from room temperature to 1100 K over the wavelength range investigated. On the other hand, there have been no data reported for molten mould fluxes as a function of wavelength and temperature: only Firoz et al.\cite{12} have measured refractive indices for simulated mould fluxes in molten state at temperatures between 1400 K and 1650 K for a wavelength of 632 nm, and reported that the refractive index for a molten flux having CaO/SiO$_2$ = 1 is 1.610 for 1450 K and 1.605 for 1650 K. It should be noted that the temperature dependence is very small. In the present work, a value of 1.6 has been used as the refractive index of molten flux for the integration, assuming that the variation in $n$ with wavelength is as small as that for glassy SiO$_2$.

The emissivity of solid iron at its melting point has been reported over wavelength ranges between 650 nm and 800 nm and between 1000 nm and 1900 nm by Watanabe et al.\cite{8} For the integration of Eq. (7), the reported emissivity data have been regressed to the following equations:

$$\epsilon_1 = -1.80 \times 10^{-10} \lambda^3 + 9.15 \times 10^{-7} \lambda^2 - 1.55 \times 10^{-3} \lambda + 1.15 \quad (\lambda \leq 1500 \text{ nm})........ (8)$$

$$\epsilon_2 = -1.00 \times 10^{-5} \lambda + 0.298 \quad (\lambda \geq 1500 \text{ nm})........ (9)$$

The values of $R_a$ and $A_e$ determined in the present work are also used for the integration; however, it should be noted that these values have been determined only in the wavelength range between 300 nm and 2600 nm. To avoid this problem, the following approximation is made in the integration.

Figure 11 shows the value of $I$ as a function of wavelength along with the radiative heat flux ($I_b$) from blackbody at 1800 K calculated from Planck’s law of radiation, where the thick solid line represents the value of $I_b$, the thin solid line represents the value of $I$ derived from Eq. (7) using measured $R_a$ and $A_e$ data of a Flux A sample heat-treated at 973 K and the dashed line at wavelengths higher than 2600 nm represents the value of $I$ approximated by multiplying $I_b$ by the ratio of $I_b(2600 \text{ nm})/I_b(2600 \text{ nm})$. Generally, silicate glasses have strong absorptions due to Si-OH and Si-O bonds around 3.6 nm, and 4.5 $\mu$m, respectively,\cite{10} and the actual value of $I$ may not be as simple as drawn by the dashed line. However, it is supposed that these absorptions do not give considerable error since steep changes in $R_a$, $T_a$, and $A_e$ observed around 500 nm and 1900 nm in Fig. 6 do not appear distinctly in Fig. 11. Consequently, the function of $I$ obtained as above is integrated over wavelength to obtain the total radiative heat flux ($I_{\text{Total}}$). This integration must be made from 0 to $\infty$; however, the value of $I$ is almost zero below 300 nm, and thus the integration is conducted in the wavelength range from 300 nm to $\infty$ by quadrature at intervals of 1 nm.

4.2. Effect of Cuspidine Grain Size on Total Radiative Heat Flux

Figure 12 shows values of $I_{\text{Total}}$ obtained as functions of corrected diameter of crystal grains for Fluxes A and B. The values obtained are $\sim 10^5$ Wm$^{-2}$; in contrast, Diao et al.\cite{9} have reported values of $\sim 10^4$ Wm$^{-2}$. This difference would be because they overestimated the extinction coefficient probably due to measurements using an FTIR spectrometer without an integrating sphere. It can be seen from Fig. 12 that the value of $I_{\text{Total}}$ for Flux B is greater than that for Flux A. Flux B contains Fe$_2$O$_3$, and its apparent reflectivity is smaller and its apparent absorptivity is greater, as shown in Fig. 8. The latter factor is considered to contribute to greater values of $I_{\text{Total}}$ since the re-emission from the solid flux layer is increased, as discussed in the previous report.\cite{9} Figure 12 also suggests that Flux A has the lowest value in $I_{\text{Total}}$ in the corrected diameter range 2–3 $\mu$m, which value is smaller by
ca 30% than the value of $I_{\text{Total}}$ at corrected diameters around 1 μm. For Flux B as well, the value of $I_{\text{Total}}$ tends to decrease with increasing corrected diameter; however, this dependence is weaker, which is a reflection of Fig. 8. It is likely that the effect by absorption due to iron oxides is stronger than that by scattering due to grains; as a result, reflection of light in Flux B would occur more efficiently at the sample surface and be less affected by scattering inside the sample than in Flux A. In short, the total radiative heat flux in mould fluxes containing iron oxides is less dependent on grain diameter of crystal grains; in contrast, control of crystal grain diameter to 2–3 μm is effective to reduce the total radiative heat flux in iron oxide free mould fluxes.

4.3. Effect of Sample Thickness

Figures 13(a), 13(b) and 13(c), respectively, show apparent reflectivities, transmissivities and absorptivities for a wavelength of 1 600 nm as functions of thickness for Flux A samples of 2.55 μm in corrected diameter, where measured data have been taken from Fig. 10. For comparison, Fig. 13 also includes values calculated in the following way:

i) For a Flux A sample 5 mm thick of 2.55 μm in corrected grain diameter, the values of $R_a$ and $T_a$ have been derived using the values of $R$ and $\alpha$ from Eqs. (10) and (11).

\[ R_a = R + \frac{R(1-R) \exp(-2\alpha d)}{1-R^2 \exp(-2\alpha d)} \]  \hspace{1cm} (10)  
\[ T_a = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \]  \hspace{1cm} (11)  

where $R$ is the reflectivity for single reflection at the sample surface, $\alpha$ is the absorption coefficient of the sample and $d$ is the thickness of the sample.

ii) Using the values of $R$ and $\alpha$ derived, values of $R_a$ and $T_a$ for different thicknesses have been calculated from Eqs. (10) and (11).

With decreasing sample thickness, the measured $R_a$ values decrease and the measured $T_a$ values increase, whereas the calculated $R_a$ and $T_a$ values show only weak dependencies. This finding suggests that Eqs. (10) and (11) are not suitable to be applied to media in which scattering occurs. Thus, calculation of the total radiative heat flux requires $R_a$ and $T_a$ values of samples having the thickness close to those of actual mould flux films. However, it is likely that the dependence of $I_{\text{Total}}$ on corrected diameter in Fig. 12 is not altered even if the sample thickness is different.

Figure 14 shows the total radiative heat flux ($I_{\text{Total}}$) derived as a function of thickness for Flux A samples of 2.55 μm in corrected diameter, where the value of $I_{\text{Total}}$ has been derived using measured values of $R_a$ and $T_a$ shown in Fig. 10 as well as using $R_a$ and $T_a$ values calculated from Eqs. (10) and (11) using measured data for a Flux A sample 5 mm thick in Fig. 10. The values of $I_{\text{Total}}$ derived using the

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**Fig. 13.** (a) Apparent reflectivities, (b) apparent transmissivities and (c) apparent absorptivities for wavelength of 1 600 nm as functions of thickness for Flux A samples of 2.55 μm in corrected diameter, where measured data have been taken from Fig. 10, and calculated data have been derived from Eqs. (10) and (11) using measured data for a Flux A sample 5 mm thick in Fig. 10.

**Fig. 14.** Total radiative heat flux ($I_{\text{Total}}$) derived as function of thickness for Flux A samples of 2.55 μm in corrected diameter, where the value of $I_{\text{Total}}$ has been derived using measured values of $R_a$ and $T_a$ shown in Fig. 10 as well as using $R_a$ and $T_a$ values calculated from Eqs. (10) and (11) using measured data for a Flux A sample 5 mm thick in Fig. 10.
calculated values of $R_a$ and $T_a$ is almost independent of sample thickness, similar to the calculated $R_a$ and $T_a$ values. In contrast, the values of $I_{\text{total}}$ derived using the measured values of $R_a$ and $T_a$ increases linearly with decreasing sample thickness due to decreased $R_a$ and increased $T_a$ values: $I_{\text{total}}$ is $\sim 2.8 \times 10^5$ Wm$^{-2}$ for a sample 1.65 mm thick, which is greater by ca 65% than $I_{\text{total}}$ for a sample 5 mm thick. The thickness of actual mould flux films usually ranges between 1 mm and 2 mm, and the total radiative heat flux for mould flux film 1 mm thick can be estimated to be $\sim 2.9 \times 10^5$ Wm$^{-2}$ from Fig. 14. This value of 0.29 MWm$^{-2}$ is used for comparison with the value of total conductive heat flux in the following.

4.4. Comparison between Heat Fluxes Transported by Radiation and Conduction

Figure 15 shows a temperature profile in a mould flux model to calculate the total conductive heat flux across the mould flux film. This model is almost the same as the model used in 4.1 except for the presence of an air gap layer. The air gap layer affects the conductive heat flux because the thermal conductivity of air is about two orders of magnitude smaller than that of mould fluxes. On the contrary, the air gap layer does not affect the radiative heat flux because air is much more transparent than mould fluxes and the air gap layer is as thin as 10–30 $\mu$m. Thus, the model in Fig. 15 is considered to be equivalent to the model in 4.1 from the viewpoint of radiation. In a steady state, the sum of radiative and conductive heat fluxes is kept constant at every position and, strictly, the radiative and conductive heat fluxes must be determined so as to meet the above-mentioned condition, which is very difficult in actuality. As a first step, in the present work, the total radiative heat flux derived based on the discussion in 4.1 and 4.3 is compared with the total heat flux including the total conductive heat flux derived based on the temperature profile in Fig. 15 assuming the steel shell temperature ($T_s$) and the mould temperature ($T_m$). The total conductive heat flux ($q_c$) in the above-mentioned system can be expressed by the following equation:\(^{(16)}\)

$$q_c = \frac{T_m - T_s}{d_l / \lambda_l + d_c / \lambda_c + d_a / \lambda_a} \quad \text{............ (12)}$$

where $d$ and $\lambda$ are the thickness and thermal conductivity of each layer, respectively, and the suffices ‘l’, ‘c’ and ‘a’ represent the molten flux layer, the crystallised flux layer and the air gap layer, respectively. In this calculation, the following parameters are used:

- $T_s = 1800$ K, $T_m = 400$ K
- $d_l = 100 \mu$m, $d_c = 895 - 870 \mu$m, $d_a = 5 - 30 \mu$m
- $\lambda_l = 0.25$ Wm$^{-1}$K$^{-1}$\(^{(5)}\), $\lambda_c = 1.63$ Wm$^{-1}$K$^{-1}$\(^{(5)}\)

where the total thickness of mould flux film is assumed to be 1 mm. The thermal conductivity of the air gap layer is estimated on the basis of an air gap model in Fig. 16. In actuality, the mould flux film is expected to touch the mould partly as shown in Fig. 16(a). Thus, the value of $\lambda_a$ should be estimated for a composite of air and crystallised mould flux. Figure 16(b) shows a model for thermal conductivity estimation. In case conductive heat flow occurs in a parallel direction to the layers, the effective conductivity ($\lambda_{a eff}$) of the composite can roughly be estimated from the following equation:\(^{(17)}\)

$$\lambda_{a eff} = \lambda_a f_a + \lambda_c f_c$$

where $f_a$ and $f_c$ are the volume fractions of crystallised mould flux and air, respectively, and a value of 0.024 Wm$^{-1}$K$^{-1}$ has been used as thermal conductivity of air.\(^{(18)}\) The value of $\lambda_{a eff}$ derived is used for $\lambda_a$ in Eq. (12) after all.

Figure 17 shows the total conductive heat flux ($q_c$) calculated for various thicknesses of the air gap layer as a function of volume fraction of air. The value of $q_c$ is roughly 1.45 MWm$^{-2}$ in the range $f_a < 0.6$, irrespective of air gap thickness; in contrast, where $f_a > 0.6$, the value of $q_c$ decreases with increasing $f_a$ and the degree of decrease depends on the thickness of an air gap layer. According to Eq. (13), the value of $\lambda_{a eff}$ becomes 0.26 Wm$^{-1}$K$^{-1}$ at $f_a = 0.85$. Where $f_a$ exceeds 0.85, the value of $\lambda_{a eff}$ becomes smaller than the thermal conductivity of molten flux layer, and the air gap layer would affect the value of $q_c$ more efficiently via Eq. (12) although stricter examination should be made for the terms $d/d_{a eff}$ and $d_a/d_{a eff}$. In other words, to attain mild cooling by formation of an air gap, the volume fraction of air in the air gap layer should be controlled to be more than 0.85.

As mentioned above, stricter analysis requires the condition that the sum of radiative and conductive heat fluxes is kept constant at every position, which also enables one to

![Fig. 15. Temperature profile in mould flux model to calculate total conductive heat flux.](image)

![Fig. 16. (a) Schematic diagram of air gap layer and (b) its model for estimation of effective thermal conductivity.](image)
derive the interface temperatures between the molten and crystallised flux layers and between the crystallised flux and air gap layers. However, the present work does not use this condition and roughly compares between the total conductive and radiative heat fluxes obtained independently. Now the interface temperature \( T_{\text{ic}} \) between the molten and crystallised flux layers is estimated just for reference using \( q_c = 1.45 \text{ MWm}^{-2} \) from Fourier’s law, as follows:

\[
q_c = -\lambda_f \frac{T_{\text{ic}} - T_i}{d_i} \quad \text{(14)}
\]

Substitution of the parameters as mentioned above into Eq. (14) gives \( T_{\text{ic}} = 1220 \text{ K} \). In the same way, the interface temperature between the crystallised flux and air gap layers can be derived as 446 K for a crystallised flux layer 870 \( \mu \text{m} \) thick, which temperature would be reasonable for the actual situation. On the contrary, the temperature of \( T_{\text{ic}} \) is different from \( T_i \) which has been assumed to be 1400 K as a typical liquidus temperature of mould fluxes for calculation of Eq. (7). As shown in the previous work, however, the total radiative heat flux is not sensitive to \( T_i \) at temperatures between 1000 K and 1500 K for iron oxide free mould flux – the difference is a few percents in the temperature range. Thus, rough comparison between \( I_{\text{total}} \) and the total heat flux including \( q_c \) is considered to have its place to a certain extent and is made for \( f_a = 0.6 \) and \( f_a = 0.9 \) in case of an air gap layer 30 \( \mu \text{m} \) thick.

For \( f_a = 0.6, q_c = 1.45 \text{ MWm}^{-2} \) and \( I_{\text{total}} = 0.29 \text{ MWm}^{-2} \); as a result, the total heat flux is 1.74 \text{ MWm}^{-2}, where the value of \( I_{\text{total}} \) has been estimated in 4.3 for a mould flux film 1 mm thick having crystal grains of 2.55 \( \mu \text{m} \) in corrected diameter, which should give the minimum value of \( I_{\text{total}} \) according to Fig. 12. This figure also suggests that, where the grain diameter is controlled not to 2.55 \( \mu \text{m} \) but to 1 \( \mu \text{m} \), the value of \( I_{\text{total}} \) could increase by 40% to become 0.41 \text{ MWm}^{-2}. In this case, the total heat flux would be 1.86 \text{ MWm}^{-2}, which is greater by about 7%. In addition, for \( f_a = 0.9, q_c = 1.25 \text{ MWm}^{-2} \) and \( I_{\text{total}} = 0.29 \text{ MWm}^{-2} \); as a result, the total heat flux is 1.54 \text{ MWm}^{-2}. Where the grain diameter is 1 \( \mu \text{m} \), the value of \( I_{\text{total}} \) could become 0.41 \text{ MWm}^{-2} and the total heat flux would be 1.66 \text{ MWm}^{-2}, which is greater by about 8%. As a consequence, control of cuspidine grain diameter in iron oxide free mould fluxes would lead to reduction of the total heat flux by 7–8%. As pointed out in 3.3, formation of cuspidine grains having various diameters would enable the apparent reflectivity to increase in a wider range of wavelength, which would result in further reduction of the total heat flux. In contrast, control of grain size is less effective for mould fluxes containing iron oxides.

5. Conclusions

Apparent reflectivities and transmissivities have been measured as functions of cuspidine grain diameter in the wavelength range 300–2600 nm for mould fluxes having constant degrees of crystallinity.

- With increasing grain diameter, the apparent reflectivity tends to increase and the apparent transmissivity tends to decrease at higher wavelengths for iron oxide free mould flux: it seems that the apparent reflectivity shows a maximum value and the apparent transmissivity shows a minimum value at grain diameters 2–3 \( \mu \text{m} \). In contrast, there is less distinct dependence on grain diameter for mould fluxes containing iron oxides.
- The total radiative heat flux would be smallest in iron oxide free mould flux having the highest apparent reflectivity and the lowest apparent transmissivity at higher wavelengths. Effects of grain size on the radiative heat flux are smaller for mould flux containing iron oxides.
- Comparison of the total radiative heat flux with the total heat flux including conductive contribution suggests that control of cuspidine grain diameter would lead to reduction of the total heat flux by 7–8% for iron oxide free mould fluxes. In addition, the air gap layer would affect the total heat flux more efficiently where the volume fraction of air in the layer exceeds 85%.

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