THE CONTRIBUTIONS OF THERMAL RADIATION AND THERMAL CONDUCTIVITY TO THE HEAT TRANSPORT IN THE SLAG 40% CAO - 40% SiO₂ - 20% Al₂O₃

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ABSTRACT

Measurements of phonon and photon conductivity have been carried out on metallurgical slags of the system CaO - SiO₂ - Al₂O₃. The results show that the values for photon conductivity lie considerably higher than those of phonon conductivity, indicating that the main energy transport in the slag takes place by radiation. This has been confirmed for other slags. Both photon and phonon conductivity show increased values within the melting range, which may be accounted for by the solid/liquid transformation.

INTRODUCTION

In metallurgical process technology a knowledge of the thermal properties of slags is of prime importance. The surface finish of continuous cast steel slabs, for example, is dependent on the heat transfer between mould and strand, which in turn is determined by the heat conductivity of the intermediate slag layer. Likewise, the Electroslag Remelting Process (ESR) and the recuperation of heat from slags are greatly influenced by the thermal conductivity of metallurgical slags.

Many investigations have already been carried out on the heat transport in metallurgical slags and a number of theoretical models put forward (1-5). However, new aspects come to light when novel measuring methods are applied, as in the measurement of photon conductivity, which is presented here and compared with the conventional phonon conductivity measurement.
EXPERIMENTAL

a) Measurement of phonon (conventional) conductivity

For this determination the instationary hot wire method was used. This is shown in principle in Fig. 1. The crucible {1} containing the slag sample {2} is initially brought up to temperature in a Tammann furnace and then carefully heated further by means of a centrally located, current carrying tungsten wire {5}.

The temperature profile in the slag is measured by a Pt/PtRh8 thermocouple {8}, adjacent to the heat source, and is recorded as a function of time. To satisfy the theoretical requirements of an infinitely extending temperature field and a linear heat source, a large testing space (60 mm diam.) together with a long thin heat wire (0.35 mm diam.) were selected. The calculation of the heat conductivity followed from the relevant equation for linear heat sources (6). The expression $\frac{dT}{d \ln(t)}$ was evaluated using the method of linear regression.

\[
k_{\text{cond}} = \frac{C \cdot q_e \cdot d\ln(t)}{4\pi \cdot dT}
\]

with

- $k_{\text{cond}}$ = thermal conductivity (phonon conductivity) [W/(m·K)]
- $q_e$ = electrical/thermal power per unit length of wire over the measuring distance [W/m]
- $C$ = correction factor for heat losses in axial direction of the wire
- $T$ = measured temperature [K]
- $t$ = time [sec]

b) Measurement of the photon conductivity

The determination of photon conductivity was based on a method proposed by Keene and Quinn for measuring the emissivity of slags (7), and further developed here for measuring photon conductivity. The principle involves the simultaneous spectroscopic determination of the real and imaginary terms of the complex refractive index (9) of slags between 800°C and 1600°C and within the wavelength range of 550 nm to 850 nm (this being restricted by the apparatus available). Fig. 2 shows a sketch of the apparatus. The sample graphite crucible {1} was provided with a stepped insert to receive two reference emitters (black body radiators), a molybdenum disc as radiation reflector and a cover. Three apertures in the cover permitted the passage of three ray bundles:

- slag emission above the molybdenum disc
- slag emission plus reference emitter
- emission of the reference emitter
With the aid of an optical bank these three ray bundles are focused onto the entry slit of a monochromator \( \{2\} \) and their spectrum registered at the particular temperature. To eliminate as far as possible the background emission of the Tammann furnace \( \{3\} \), two additional sites of the crucible cover were spectroscopically observed. After subtraction of the background emission and the setting up of the relationships between the ray bundle intensities at each wave-length, the complex refractive index can be calculated as a function of wavelength.

\[
n_c = n_R - i \cdot n_I = \left( \frac{c}{\nu} \right) - i \cdot \left( \frac{k \cdot \lambda}{4 \pi} \right)
\]

with \( n_R \) = real term of the complex refractive index
\( n_I \) = imaginary term of the complex refractive index
\( c \) = velocity of light in vacuo = \( 2.99792 \times 10^8 \) m/sec
\( \nu \) = velocity of light in the slag
\( k \) = absorption coefficient \([\text{m}^{-1}]\)
\( \lambda \) = wave length \([\text{m}]\)

The quantity \( n_C \) contains not only information about the absorption coefficients and the reflection, emission and transmission powers of a substance, but also provides the link with fundamental electrical data, the dielectric constants and the electrical conductivity. With the aid of the complex refractive index, all optical material constants of slags may be expressed, including the photon conductivity. The relation between radiation flow and temperature gradient during radiation transport in hot media was originally investigated by Rosseland (8), and the approximation named after him for photon conductivity \( (k_{\text{rad}}) \), in terms of the complex refractive index, is written as

\[
k_{\text{rad}} = \frac{4 \sigma}{3 \pi} \left( \frac{n_R^2}{n_I / \lambda} \right) \cdot T^3
\]

As \( n_R \) and \( n_I \) are wavelength dependent, the expression inside brackets must be averaged over the wavelength.

**RESULTS**

A comparison of the two conductivities, phonon and photon, is shown in fig. 3 for a slag of composition 40% CaO - 40% SiO\(_2\) - 20% Al\(_2\)O\(_3\) as a function of temperature. To enable both conductivities to be included in the same graph, a logarithmic scale has been applied, which, in part, is responsible for the apparent wide scatter of the phonon values.
It is evident that, the photon conductivity is considerably higher than the phonon conductivity, the ratio $k_{rad}$ to $k_{cond}$ being, on average, 20 to 1. Such high values for photon conductivity have also been found for other compositions of the CaO-SiO$_2$-Al$_2$O$_3$ system (9). In general, slags at high temperatures exhibit similar conductivity behaviour to glass. In the case of a time independent or stationary temperature field in the slag, the 1st Fourier heat theorem may be applied to the transported energy flux density in the $x$-direction, namely

$$Q = -k \cdot \frac{dT}{dx} \quad [4]$$

with $Q$ = heat flux or heat flux density [W/m$^2$], $k$ = heat conductivity or coefficient of heat conductivity [W/m-K], $T$ = Temperature [K].

If several mechanisms (as heat conductivity and heat radiation) contribute to the heat transfer, the heat conductivity expressed in the 1st Fourier heat theorem may be written as a simple sum, but only where there is strong interaction between the individual transfer mechanisms i.e alternating heat conduction and radiation, as in the case of slags.

Not only in their additive behaviour in energy transport is there similarity between the two conductivities, but also with respect to the phenomena exhibited in the melting range of the 40%CaO-40%SiO$_2$-20%Al$_2$O$_3$ slag. Both show a discontinuity or conductivity peak. In fig. 4 the measured $k_{rad}$ and $k_{cond}$ curves are plotted for the temperature range 1200°C - 1500°C, the differential scaling of the ordinate axis being a consequence of the considerably higher absolute values of the photon conductivity.

There is a striking difference in the absolute widths and heights of the two peaks. The $k_{rad}$ discontinuity is high and narrow (amplitude 40W/(mK), FWHM 15K) whereas the $k_{cond}$ discontinuity is flat and wide (amplitude 1.5W/(mK), FWHM 100K). The photon peak can be described approximately by a Gauß profile with a maximum at 1360°C, but the phonon peak is asymmetric with a maximum at 1335°C.

The occurrence of these peaks may be ascribed to a phase change in the slag 40%CaO-40%SiO$_2$-20%Al$_2$O$_3$ in passing from solid to liquid state. This phase change, which occurs at 1355°C, absorbs energy and thus reduces the transported heat flux density. Here the 1st Fourier heat theorem (equation 4), relating transported heat flux density, heat conductivity and temperature gradient, no longer applies. The relevant DTA (Differential Thermal Analysis) curve dips below the equilibrium line (endothermic process). This means that, for the same time interval $t$, the temperature rise $dT$ is less than equilibrium, which in equation [1] is indicative of a higher heat conductivity. The converse applies for an exothermic process. A simple relationship can be obtained between the peak surface, the specific heat of fusion and the mean specific heat $<c_p>$ by deriving the following expression from the 2nd Fourier heat theorem:
\[ \int \left( \frac{k_{\text{cond}}}{<k_{\text{cond}}>} - 1 \right) dT = \frac{h}{<c_p>} \]

in which the mean specific heat is given by \(<c_p> = (c_p^S + c_p^L)/2\). \(k_{\text{cond}}\) describes the conductivity underlying the peak i.e. without the peak and \(h\) is the specific heat of fusion.

According to a model put forward by K.C. Mills and B.T. Keene (10), \(c_p^S\) and \(c_p^L\), as well as the latent heat, can be calculated for the slag 40%CaO-40%SiO₂-20%Al₂O₃, giving \(c_p^S(1355°C) = 1.20 \text{ J/(g-K)}\), \(c_p^L = 1.44 \text{ J/(g-K)}\) and \(h = 496.9 \text{ J/g}\). The mean value \(<c_p>\) in the region of the phase change is then 1.32 J/(g-K). The integral in equation [5] represents a value of \((388 \pm 29) \text{ K}\), which yields a value for \(h\), the latent heat, of \((512 \pm 38) \text{ J/g}\). Within the limits of accuracy for graphical integration, this gives excellent agreement with the value \(h = 496.9 \text{ J/g}\) of Mills and Keene.

The phase change solid/liquid is also responsible for the photon peak. The principal factors in the photon conductivity are the real and imaginary terms of the refractive index, the mean values of which are shown in fig. 5 for the melting region of the slag 40%CaO-40%SiO₂-20%Al₂O₃.

The real term remains practically constant in the region 1325°C - 1455°C, but the imaginary term shows a clear minimum. In the calculation of the photon conductivity as in equation [3], the imaginary term of the refractive index is in the numerator, leading to an increased value for \(k_{\text{rad}}\) in the melting region. It is noteworthy that N. Neuroth (11) found in the melting region of window glass a minimum in the absorption coefficient, which, according to equation [2], is proportional to the imaginary term of the refractive index.

CONCLUSIONS

With the aid of two different measuring methods, the instationary hot-wire method and optical spectroscopy, the phonon and photon conductivity of slags could be measured. Of importance is that the instationary wire method can only register the contribution to heat conductivity made by atomic vibrations (phonon conductivity). This is evident from the fact that, with the instationary hot-wire method, temperature is recorded by thermocouples, which are insensitive to radiant heat. Furthermore, the measurement of heat conductivity is based on the recording of temperature differences of the order of less than 1°C in a temperature medium of 1000-1500°C, i.e. \(\Delta T/T \approx 10^{-3}\). According to the Stefan-Boltzmann-Law, the radiation flux \(\Phi\) is proportional to \(T^4\), so that \(\Delta \Phi/\Phi \approx 4 \cdot 10^{-3}\). Thermocouples cannot detect these relatively minute changes in \(\Phi\), as they are ineffective radiation detectors.

Photon and phonon conductivity of the slag 40%CaO-40%SiO₂-20%Al₂O₃ in the temperature and wavelength range under consideration are related to one another by the ratio of 20:1. Even if this ratio is reduced to 10 or 5:1 for slags of other chemical com-
position, the fact remains that, as long suspected, that heat transport within a slag layer is largely determined by the heat radiation.

Both photon and phonon conductivity show increased values within the melting range, which may be accounted for by the solid/liquid transformation. The phonon peak can be directly related to the latent heat of transformation, whereas the photon peak is a result of a drastic reduction in the absorption coefficients of the slag.

An extension of the measurable wavelength range of the spectroscopic equipment into the IR-region up to approx. 4.5μm would be great value, as the temperatures that most concern the metallurgist lie between 1000°C and 1700°C. The main portion of radiant heat is to be found in this wavelength range.

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Fig. 1 Experimental set-up for the hotwire method

Fig. 2 Experimental set-up for measuring the photon conductivity of metallurgical slags
Fig. 3 General comparison of the measured phonon conductivity (lower values) with photon conductivity (upper values).

Fig. 4 Measured photon (left) and phonon (right) conductivity near the melting range for the slag 40%CaO-40%SiO₂-20%Al₂O₃.

Fig. 5 Mean values of the real term (straight line) and the quotient of imaginary term / wave-length of the refractive index.