1. Introduction

The water-cooling rate in the hot-rolling process should strictly be controlled to obtain qualified steels in high-grade steel making.1) Actually an oxide scale is formed on the surface of slab during the hot-rolling process and more or less affects the cooling rate. The oxide scale is frequently removed by de-scaling water; however, it still grows to tens of micrometers thickness because the oxidation rate of steel is very fast.

Figure 1 shows a backscattered electron (BE) image of a cross-section of an oxide scale on a steel substrate.2) The oxide scale roughly has a multiple-layered structure such as FeO/Fe3O4/Fe2O3 from the steel substrate side; silicon-rich iron oxide and pores also exist in the oxide scale.3) Another feature of this system is that it exists under a steep temperature gradient in the actual process: temperature shows a drop by several hundred Kelvin within the thickness of oxide scale between the hot steel and the cooling water.

The thermal conductivity of oxide scales has been reported to be smaller than that of steel.4) This suggests that the oxide scale is a considerable resistance factor for the heat transfer from the hot steel to the cooling water. Thus, to control the cooling rate during the hot-rolling process, important factors are the heat transfer characteristics such as thermal conductivity and diffusivity of oxide scales formed on the steel surface.5)

In recent years, there are some researches focusing on the thermal diffusivity of iron oxide; however, only Taylor et al. have measured on an FeO sheet prepared by thermal oxidation of an iron sample, at temperatures ranging from 623 to 753 K.6) Other reports have used sintered substances of FeO, Fe3O4 and Fe2O3 as samples to simulate the oxide scale;7–10) however, the recorded thermal diffusivity values differ very much from each other, for example, the thermal diffusivity value of FeO ranges from 4 to 7×10−7 m2s−1 at room temperature. This difference would be caused by the different sample preparation procedures such as sintering temperature, atmosphere and time, purities and sizes of starting materials grains and so on. In addition, there is another problem whether the sintered samples are reasonable or not as stimulants for actual iron oxide scales. On the other hand, the thermal conductivity and diffusivity of oxide scale are also very difficult to estimate from the chemical compositions and temperature using the extant data only, because of (i) the paucity of extant data and (ii) the complicated situation where the oxide scale lies, including the phase structures and the temperature gradient.

A new apparatus to measure a heat flux across a sheet sample has been proposed to determine its apparent thermal conductivity. The heat flux was derived from the volume change caused by melting of ice utilizing the principle of the Bunsen Ice Calorimeter. Measurements were conducted using Ni-base super alloy (Inconel 600), alumina and Teflon as samples to confirm the reasonability of this method, in addition to a simulation study. The apparent thermal conductivity values obtained are 14.7±0.4 Wm−1K−1 for Inconel at 281 K–287 K, 24.8±0.7 Wm−1K−1 for alumina at 281 K–287 K and 0.313±0.004 Wm−1K−1 for Teflon at 285 K–411 K, which are in very good agreement with the respective reported values. Discussion has been made on error factors of this method and a feasibility of this method being applied to measurements of apparent thermal conductivities of oxide scales formed on the steel surface under steep temperature gradient in the actual hot-rolling process.

KEY WORDS: Bunsen Ice Calorimeter; heat flux; apparent thermal conductivity; sheet sample; oxide scale.
thermore, the conventional measurement methods such as the laser flash method cannot be applied to a system under a steep temperature gradient because they use a rather small temperature gradient. Accordingly, it is strongly required to develop a new method to measure apparent thermal conductivities and diffusivities of oxide scales attached to steel substrates under steep temperature gradients.

Bunsen\(^{12}\) has reported an ice-calorimeter that can determine a quantity of heat transferred to an ice/water mixture by measuring the volume change of the mixture due to melting of ice. Jessup\(^{13}\) has applied this technique to obtain a heat quantity of the magnitude of 160 J with a precision of about 0.05%, and also succeeded in measuring the heat quantity change associated with chemical reaction using a Bunsen Ice Calorimeter. Thus, there is a possibility of measuring a heat flux across the oxide scale from a measurement of the heat quantity change with time utilizing this method, leading to determination of its apparent thermal conductivity using the temperature gradient in the oxide scale on the basis of Fourier’s law.

Consequently, as a first step to application to oxide scales formed on the steel surface, the present work aims to establish a new heat flux measurement apparatus based on the principle of the Bunsen Ice Calorimeter, and to measure the heat flux across sheet samples, finally to determine their apparent thermal conductivities.

2. Experimental

2.1. Heat Flux Measurement

The Bunsen Ice Calorimeter is an apparatus to measure a heat quantity from the change in volume of an ice/water mixture caused by melting of ice. The main principle is the density difference between water and ice at 273.15 K: its volume shrinks by 0.0907 cm\(^3\) in case 1 g ice melts. Thus, the measured reduction in volume of the mixture indicates the number of moles of ice which has melted, and thereby the amount of energy deposited in the calorimeter.\(^{25}\)

Figure 2 shows a schematic diagram of the heat flux measurement apparatus developed in the present work utilizing the principle of the Bunsen Ice Calorimeter. A vertical barrel container (calorimeter) that was filled with an ice/water mixture inside was placed in an ice box to reduce the effect of surrounding conditions. Ice was made by an ice-making machine from distilled water, and crushed to small pieces sized around 10×10×10 mm\(^3\). The container was hermetically sealed with a copper lid, which had 77 fins 50 mm long at the downside to promote the heat transmission from the sample to the ice/water mixture. In addition, there was a stirrer placed at the bottom of the container to keep the temperature more uniform. The sheet sample was placed upon the copper lid. Two aluminium blocks sized 20×20×10 mm\(^3\) weighing ca. 11 g were positioned on the sample: the lower was used to accommodate a thermocouple and the upper was used as heat source. In principle, heat transmits from the heat source to the ice/water mixture across the sample and melts parts of ice; thereby the volume of the mixture changes. The volume change was detected by a laser displacement meter as the liquid height decrease in the pipe that was connected to the container.

The liquid height change provides the number of moles of melted ice, \(\Delta n_{\text{H}_2\text{O}}\), as follows:

\[
\Delta n_{\text{H}_2\text{O}} = \frac{\pi r^2 \cdot \Delta h}{M_{\text{H}_2\text{O}}} \left( \frac{1}{\rho_{\text{water}}} - \frac{1}{\rho_{\text{ice}}} \right) \quad (1)
\]

where \(r\) is the radius of the pipe, \(\rho\) is the density of each substance, \(h\) is the liquid height and \(M_{\text{H}_2\text{O}}\) is the molar mass of water. The relevant physical property values are given in Table 1.\(^4\) The number of moles of melted ice, in turn, provides the heat deposited to the ice/water mixture as follows:

\[
Q = \Delta n_{\text{H}_2\text{O}} \cdot \Delta H_{\text{H}_2\text{O}} \quad (2)
\]

where \(Q\) is the heat quantity and \(\Delta H_{\text{H}_2\text{O}}\) is the enthalpy of fusion of ice at 273.15 K.

Thus, the heat flux (\(q_{\text{ice}}\)) across the sample is derived from the derivative of the liquid height with respect to time as follows:

\[
q_{\text{ice}} = \frac{\Delta H_{\text{H}_2\text{O}}}{A \cdot M_{\text{H}_2\text{O}}} \cdot \left( \frac{\rho_{\text{ice}}}{\rho_{\text{water}}} - 1 \right) \frac{dh}{dt} \quad (3)
\]

where \(A\) is the surface area of the sample across which area heat transmits, and the heat losses from sample to atmosphere is neglected because the sample is thin.

2.2. Determination of Apparent Thermal Conductivity

As shown in Fig. 2, a sheathed K-type thermocouple (φ 0.5 mm×200 mm, sheath part/SUS 316, lead wire/nickel plate with Teflon coat) was positioned inside the aluminium block 1.3 mm away from its bottom surface and a platinum thermometry resistance element (size: 1.7×1.25×0.8 mm\(^3\)) was placed at the lower surface of the copper lid to monitor temperatures \(T_{\text{up}}\) and \(T_{\text{down}}\), respectively. Using Fourier’s law, the relationship between the temperature difference and the heat flux \(q_{\text{app}}\) can be given as follows:

\[
\text{Table 1. Values of physical properties used in the present research.}^{4}
\]

<table>
<thead>
<tr>
<th>physical property</th>
<th>Value</th>
<th>physical property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho_{\text{water}})</td>
<td>0.917 gcm(^{-3})</td>
<td>(\Delta H_{\text{H}_2\text{O}})</td>
<td>6.01 kJmol(^{-1})</td>
</tr>
<tr>
<td>(\rho_{\text{ice}})</td>
<td>1.0 gcm(^{-3})</td>
<td>(k_{\text{copper}})</td>
<td>397 Wm(^{-1})K(^{-1})</td>
</tr>
<tr>
<td>(M_{\text{H}_2\text{O}})</td>
<td>18 gmol(^{-1})</td>
<td>(k_{\text{app}})</td>
<td>0.024 Wm(^{-1})K(^{-1})</td>
</tr>
</tbody>
</table>
\[ q_{\text{temp}} = \left( \frac{T_{\text{up}} - T_{\text{down}}}{x_{\text{sample}} / k_{\text{sample}} + x_{\text{Al}} / k_{\text{Al}} + x_{\text{Cu}} / k_{\text{Cu}}} \right) \] ........................ (4)

where \( x \) is the thickness of each substance and \( k \) is the apparent thermal conductivity or thermal conductivity of each substance and the term for air represents the contribution from the interfaces.

The contributions from parts other than the sample are integrated into a heat resistance factor (\( R \)), and thus the heat flux (\( q_{\text{temp}} \)) can be given as follows:

\[ q_{\text{temp}} = \left( \frac{T_{\text{up}} - T_{\text{down}}}{x_{\text{sample}} / k_{\text{sample}} + R} \right) \] ........................ (5)

Now consider measurements of heat fluxes for two same samples with different thicknesses but the same surface roughness value. The heat resistance factor is originated from the aluminium block, the two interfaces and the copper plate, and thus values of \( R \) should be the same with each other as long as samples with the same surface roughness are used. The temperature difference between the two positions in Eq. (5) is related to the differences in thickness and \( q_{\text{temp}} \) between two samples in the following expression.

\[ \frac{x_{\text{sample}1} - x_{\text{sample}2}}{k_{\text{sample}}} = \left( \frac{T_{\text{up}} - T_{\text{down}}}{q_{\text{temp}1} - q_{\text{temp}2}} \right) \] ........................ (6)

where symbols 1 and 2 represent thick and thin samples, respectively. It has been confirmed by simulation results that this heat-transfer system instantaneously reaches a quasi-steady state, in a short time of 25 s, which will be described in 2.5. As a consequence, the term \( q_{\text{temp}} \) can be replaced by \( q_{\text{us}} \), and finally the apparent thermal conductivity of the sample can be derived by the following equation:

\[ k_{\text{sample}} = \frac{x_{\text{sample}1} - x_{\text{sample}2}}{(T_{\text{up}} - T_{\text{down}}) \cdot \left( \frac{1}{q_{\text{us}1}} - \frac{1}{q_{\text{us}2}} \right)} \] ........................ (7)

### 2.3. Liquid Height Fitting Equation

In the present work, the liquid height measurement is necessary to obtain the heat flux; however, there was sometimes instability seen in the liquid height change curve in experiment. To avoid such an influence, a fitting equation is formulated, for which the present experimental system is approximated to a semi-infinite medium with one surface which is kept at a constant temperature.

According to the error function solution on linear flow of heat, \(^{13}\) the temperature (\( T_{\text{up}} \)) is given by the following equation:

\[ T_{\text{up}} = T_0 \cdot \text{erfc} \left( \frac{x_{\text{Al}}}{2 \sqrt{\alpha_{\text{Al}} \cdot t}} \right) \] ........................ (8)

where \( T_0 \) is the temperature of the heat source, \( \alpha_{\text{Al}} \) is the thermal diffusivity of aluminium and \( x_{\text{Al}} \) is the distance between the upper surface of the aluminium block and the upper thermocouple. The temperature (\( T_{\text{down}} \)) is assumed to be 273.15 K. Apply Eq. (8) to Eq. (5) and the heat flux (\( q_{\text{temp}} \)) can be given by the following equation:

\[ q_{\text{temp}} = \frac{T_0 \cdot \text{erfc} \left( \frac{x_{\text{Al}}}{2 \sqrt{\alpha_{\text{Al}} \cdot t}} \right) - T_{\text{down}}}{x_{\text{sample}} / k_{\text{sample}} + R} \] ........................ (9)

Replace the term \( q_{\text{temp}} \) by \( q_{\text{us}} \), and finally the liquid height can be expressed by the following equation:

\[ h = \frac{A \cdot M_{\text{H}_2 \text{O}} \cdot \left( \rho_{\text{us}} - \rho_{\text{water}} \right)}{\Delta T \cdot H_{\text{H}_2 \text{O}} \cdot \pi r^2 \cdot \rho_{\text{Cu}} \cdot \rho_{\text{water}}} \cdot \frac{1}{x_{\text{sample}} / k_{\text{sample}} + R} \int \left( T_0 \cdot \text{erfc} \left( \frac{x_{\text{Al}}}{2 \sqrt{\alpha_{\text{Al}} \cdot t}} \right) - T_{\text{down}} \right) \, dt \] ........................ (10)

However, in the present work the temperature of the heat source \( T_0 \) is not kept constant. In order to ensure the temperature \( T_0 \) as a function of time, heat loss \( (Q_{\text{loss}}) \) arising from heating the system is required and can be expressed by the following equation:

\[ Q_{\text{loss}} = \int \frac{T_0(t)}{R'} \cdot A \cdot dt \] ........................ (11)

where \( R' = \frac{x_{\text{sample}}}{k_{\text{sample}} + R} \), which means the heat resistance for this whole system. The initial heat quantity \( (Q_0) \) of the heat source is derived as follows:

\[ Q_0 = T_0(0) - C_P \cdot m_h \] ........................ (12)

Therefore, the temperature of the heat source at \( t \) is given by the following equation:

\[ T_0(t) = \frac{Q_0 - Q_{\text{loss}}}{C_P \cdot m_h} \] ........................ (14)

Apply Eqs. (11) and (12) to Eq. (14) and the following equation is obtained:

\[ \int_0^T \frac{Q_0(t)}{A} \cdot \left[ T_0(0) - T_0(t) \right] \, dt \] ........................ (15)

Only the function form of time is of interest in the present work, and finally the temperature of the heat source at \( t \) is simplified into the following equation:

\[ T_0(t) = \frac{A}{C_P \cdot m_h \cdot R'} \cdot \left( 1 - e^{-A \cdot \frac{t}{C_P \cdot m_h \cdot R'}} \right) + T_0(0) \] ........................ (16)

Apply Eq. (16) to Eq. (10) and the liquid height is expressed by the following equation:
angle change by a laser displacement meter where a plastic disc was placed on the water surface to make laser reflection stronger. In order to make sure the value of the radius of the pipe (r), prior to experiment, 1.00 ml distilled water was put into the pipe and the liquid height change was measured to obtain 9.49 mm; thus the average radius was determined to be 5.79 mm, which is in good agreement with a value of 5.83 mm measured by a caliper.

2.5. Feasibility of Measurements

In order to examine the feasibility of the measurement system, a two-dimensional model is used with COMSOL simulation software. The experimental system is described as the 2D axisymmetrical geometry in Fig. 3. The top rectangle is a heat source 20×10 mm² sized, the next rectangle is a block 20×10 mm² sized, which is placed between the heat source and the sample to accommodate a thermocouple, the next thin layer is a sample 20×1 mm² sized, and the bottom rectangle is a container 54×150 mm² sized, the last being sealed with a lid 54×1 mm² sized. It should be noted that there are no fins and stirrer provided in this simulation system.

2.5.1. Model Definition

The top two rectangles are made of aluminium, the thin layer is made of Inconel 600, and the lid is made of copper. The container is filled with an ice/water mixture. The thermophysical properties of the materials used were obtained from the COMSOL Multiphysics Material Library. The whole system is governed by transient heat transport in each part is described by the equation.

\[ d_t \rho C_v \frac{\partial T}{\partial t} + \nabla \cdot (\rho C_v u \cdot \nabla T) + \nabla \cdot q = d_t (q + q_0 + d_t \rho C_v u \cdot \nabla T) \]  

where \( d_t \), \( \rho \), \( C_v \), \( T \), \( u \) and \( Q \) denote the distance in \( z \) direction, density, specific heat, temperature, fluid velocity and heat with respect to each part, respectively. In the simulation system, well-insulation, no fins and stirrer are considered so convection and radiation is negligible in this system. Therefore, the heat flux \( q \) is derived from the following:

\[ q = -d_t \rho C_v \frac{\partial T}{\partial z} \]

The initial temperature of the heat source is set at 873.15 K, whereas the other parts are set at 273.15 K; the top boundary is in contact with air at 298.15 K. The boundary condition in the bottom contacted with the ice/water mixture is set at 273.15 K.

2.5.2. Simulation Results

Figure 4 shows the simulation results of the temperature distribution and the heat flux in the system from 0 to 200.0 s after the sample is set up. The numerical results of time-dependent heat flux indicate that heat mainly transfers from the heat source to the ice/water mixture across the sample within 1 s and continually transfers along the surface of the ice/water mixture horizontally. To further investigate the time required to reach a quasi-steady state and the direction of heat flux across different interfaces, Figs. 5 and 6 are demonstrated. Figure 5 shows the heat flux changes in the block and the sample \( q_{block} \) and \( q_{sample} \) with time, where the negative sign means that heat flows downwards.
The numerical results predict that \( q_{\text{block}} \) equals \( q_{\text{sample}} \) in 25 s, representing the system approaches a quasi-steady state in 25 s. In Fig. 6, the temperature change in different directions at times 0–200.0 s. The temperature change in \( y \)-coordinate at \( x=0.0 \) mm and in \( x \)-coordinate at a depth of 0.5 mm in the ice/water mixture are shown in Figs. 6(a) and 6(b), respectively. The numerical results present that there is a temperature gradient (around 150 K) in the ice/water mixture near the lid. The simulation results proves the feasibility of apparent thermal conductivity measurements by our proposed new method. In addition, as mentioned above, the simulation system provides no fins and stirrer, the use of which would be of help to improve the situation. The simulation model provides real-time prediction for further adjusting the apparatus and measurement methods.

3. Results

Figure 7 shows the temperature changes \( (T_{\text{up}} \text{ and } T_{\text{down}}) \) with time obtained in experiments for (a) an Inconel sample
0.5 mm thick, (b) an Inconel sample 0.1 mm thick, (c) an alumina sample 0.5 mm thick, (d) an alumina sample 0.2 mm thick, (e) a Teflon sample 0.5 mm thick and (f) a Teflon sample 0.2 mm thick. It can be seen that in each experiment $T_{\text{up}}$ increases significantly and rapidly just after the heat source is placed and then starts to decrease after reaching the maximum. The maxima of $T_{\text{up}}$ for the thinner samples are higher than those for the thicker samples, which is because the thicker samples have larger thermal resistances. It can also be seen that the maxima of $T_{\text{up}}$ for the Teflon samples are higher than those for the Inconel samples, which in turn are higher than those for the alumina samples. This order corresponds to that in thermal conductivity values of the samples; namely, Teflon has the smallest and alumina has the largest thermal conductivity, as given in Table 2. It is noted that $T_{\text{down}}$ is not kept at 273.15 K, which might affect the apparent thermal conductivity value. However, the increase in $T_{\text{down}}$ is 10 K at largest and is much smaller than predicted by the simulation probably due to the use of a stirrer and fins.

Figure 8 shows the liquid height change with time obtained in experiments: (a) comparison between raw data and fitted data for Inconel 0.5 mm thick, (b) fitted data for the Inconel samples, (c) fitted data for the alumina samples and (d) fitted data for the Teflon samples. It is found that the raw liquid height change is slightly instable but the overall trend is steadily and that the difference between raw data and fitted data is on average as small as 0.0047 mm. Thus, it is reasonable that the liquid height is fitted to Eq. (18). It can also be seen that the liquid height decreases slowly before the heat source is placed, drastically immediately after the heat source is placed and then slowly again. Similar to the temperature changes shown in Fig. 7, the thinner samples exhibit larger liquid height changes than the thicker samples, which indicates that more heat is transmitted across the thinner samples. This height decrease rate provides the value of heat flux $q_{\text{ice}}$ via Eq. (3).

Figure 9 compares values of $q_{\text{ice}}$ determined from the liquid height decrease after fitting for (a) the Inconel samples 0.5 mm and 0.1 mm thick, (b) the alumina samples 0.5 mm and 0.2 mm thick and (c) the Teflon samples 0.5 mm and 0.2 mm thick. The values of $q_{\text{ice}}$ increase quickly at about 100 s, namely, just after the heat source is placed, and then decrease after reaching the maxima. There can be seen a difference between the values of $q_{\text{ice}}$ for the two samples with different thicknesses, which is the most remarkable in Teflon. This difference leads to the apparent thermal conductivity of the sample.

Table 3 shows surface roughness values for all the samples measured by a laser scanning microscope. The same material samples with different thicknesses have almost the same average roughness values. Thus, the heat resistant factor $R$ in Eq. (5) derived from Eq. (4) can be assumed to be constant for the same materials. This is a basis for Eqs. (6) and (7), the latter being modified into Eq. (21).

$$
\left( \frac{1}{q_{\text{ice}1}} - \frac{1}{q_{\text{ice}2}} \right)^{-1} = k_{\text{sample}} \cdot \frac{T_{\text{up}} - T_{\text{down}}}{x_{\text{sample1}} - x_{\text{sample2}}} \quad \ldots (21)
$$
Figure 10 shows relations between the heat flux and the temperature difference plotted on the basis of Eq. (21) for (a) Inconel, (b) alumina and (c) Teflon, using $q_{ice}$ data having the same value of $(T_{up} - T_{down})$ in Fig. 9. It is considered that before the calculation region the sample is just heated up by the heat source and the system has not yet reached a quasi-steady state. On the other hand, after the calculation region the temperature difference is too small to use for analysis. There can be seen linear portions in Fig. 10, which correspond to the data within the calculation region. This linearity guarantees the reasonability of Eq. (21) and the slope of the linearity provides the apparent thermal

<table>
<thead>
<tr>
<th></th>
<th>Front surface (µm)</th>
<th>Back surface (µm)</th>
<th>Total roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel</td>
<td>0.5 mm thick</td>
<td>28.57</td>
<td>24.12</td>
</tr>
<tr>
<td></td>
<td>0.1 mm thick</td>
<td>30.18</td>
<td>23.58</td>
</tr>
<tr>
<td>Alumina</td>
<td>0.5 mm thick</td>
<td>25.90</td>
<td>21.39</td>
</tr>
<tr>
<td></td>
<td>0.2 mm thick</td>
<td>24.19</td>
<td>23.50</td>
</tr>
<tr>
<td>Teflon</td>
<td>0.5 mm thick</td>
<td>23.68</td>
<td>24.96</td>
</tr>
<tr>
<td></td>
<td>0.2 mm thick</td>
<td>19.47</td>
<td>27.07</td>
</tr>
</tbody>
</table>

Fig. 8. Change with time in liquid height: (a) comparison between raw data and fitted data for Inconel 0.5 mm thick; (b) fitted data for Inconel samples; (c) fitted data for alumina samples; (d) fitted data for Teflon samples.

Fig. 9. Comparison between heat flux changes with time for samples with different thicknesses: (a) Inconel samples; (b) alumina samples; (c) Teflon samples.

Fig. 10. Plots based upon Eq. (21): (a) Inconel samples; (b) alumina samples; (c) Teflon samples.
conductivity of the sample. In comparison with the reported values, Table 2 also gives the apparent thermal conductivity values derived for the three kinds of sample along with their standard deviations which comes from the regression for Fig. 10. The experimental scatter of apparent thermal conductivity values is less than 5%, and all the experimental values are in good agreement with the reported values. Consequently, this apparatus can be applied to sheet samples with thermal conductivity ranging between 0.25 Wm$^{-1}$K$^{-1}$ and 30 Wm$^{-1}$K$^{-1}$.

4. Discussion

4.1. Experimental Uncertainty

The present heat flux measurement apparatus seems a simple system but the apparent thermal conductivity determination requires complicated procedures. The apparent thermal conductivity is derived on the basis of Eq. (7) and thereby values of heat flux and temperature affect the uncertainty in apparent thermal conductivity values. The heat flux value is calculated from Eq. (3) assuming $T_{down}$ = 273.15 K; thus the liquid height and the actual temperature of the ice/water mixture would be error factors. In addition, the heat conduction from the heat source to the mixture would also be affected by the surface roughness of each interface. Accordingly, the experimental uncertainty of this method is discussed using the Inconel 600 sample as an example from the viewpoints of (1) instability of liquid height, (2) temperature of ice/water mixture, (3) precision of temperature measurements and (4) surface roughness.

4.1.1. Instability of Liquid Height

The liquid height was measured by a laser displacement meter; however, the liquid height did not decrease completely smoothly, as shown in Fig. 8(a), probably because of the surface tension of liquid water and its wettability to the acryl tube wall. To evaluate the instability, the liquid height change with time was measured for natural ice melting, which decreases linearly with a slope of $-0.011 \pm 6.0 \times 10^{-6}$ mms$^{-1}$. Applying this finding to a liquid height change rate of about 0.060 mms$^{-1}$ for Inconel 600 and it is supposed that its standard deviation is $\pm 3.3 \times 10^{-5}$ mms$^{-1}$. Applying this standard deviation to Eq. (3) suggests that the heat flux value with experimental uncertainty is $(0.068 \pm 3.2 \times 10^{-5})$ Wmm$^{-2}$, providing the apparent thermal conductivity as $(14.7 \pm 0.14)$ Wm$^{-1}$K$^{-1}$. Consequently, the instability of liquid height gives only about 1% error to the apparent thermal conductivity value.

4.1.2. Temperature of Ice/Water Mixture

In the present calculation, the temperature of ice/water mixture ($T_{down}$) has been assumed to be 273.15 K but the actual temperature was higher than this assumption, as shown in Fig. 7, which would affect the heat flux as well as the apparent thermal conductivity. There are two possibilities of explaining this temperature increase: (i) the heat transmitted to the ice/water mixture was not only for melting ice but also for heating liquid water itself and (ii) $T_{down}$ was measured by a platinum thermometry resistance element, which produced some heat during the measurement. Possibility (i): it is assumed that some heat transmitted to the ice/water mixture heats liquid water, causing the increase of $T_{down}$. Now Eq. (3) for calculation of $q_{ice}$ is tentatively modified to Eq. (22) including the term to express heat necessary for heating liquid water.

$$q_{ice} = \frac{\Delta n'_{H_2O} \cdot \Delta m_{H_2O} + \Delta n'_{H_2O} \cdot C_{P,H_2O} \cdot T_{down}}{A} \frac{dh}{dt} \cdots (22)$$

where $\Delta n'_{H_2O}$ is the amount of liquid water in mol heated from 273.15 K and $C_{P,H_2O}$ is the molar heat capacity of liquid water at temperature $T_{down}$. Table 4 gives values of the density and molar heat capacity of liquid water at different temperatures. As shown in Fig. 7, $T_{down}$ did not exceed 282.15 K, in which temperature range the density change of liquid water is negligibly small, and thus its volume change is neglected. To evaluate the influence of heating liquid water, the heat quantities for melting ($Q_n$) and heating ($Q_h$) are calculated by the following equations:

$$Q_n = \Delta n_{H_2O} \cdot \Delta m_{H_2O} \cdot \Delta H_{trs} \cdots (23)$$

$$Q_h = \Delta n'_{H_2O} \cdot C_{P,H_2O} \cdot T_{down} \cdots (24)$$

Values of $Q_n$ and $Q_h$ have been derived as 6.01 kJ and 0.69 kJ, respectively, assuming that both $\Delta n_{H_2O}$ and $\Delta n'_{H_2O}$ equal 1 mol and that $T_{down}$ equals 282.15 K. Comparison between the values of $Q_n$ and $Q_h$ suggests that it is difficult to neglect the effect of $Q_h$; thus it is considered that the increase of $T_{down}$ affects the apparent thermal conductivity results to some extent. In actually, however, it is very difficult to evaluate the amount of $\Delta n'_{H_2O}$ accurately and thus the extent of this error factor is still unclear.

Possibility (ii): it is assumed that the platinum thermometry resistance element used in the present work produces heat during the measurement. The element has a resistance ($R_p$) of 100 m$\Omega$, which has been obtained from the platinum resistance bulb synthesis catalogue of its manufacturer, and the current ($I$) applied is 0.97 mA. Thus, the produced heat ($Q_p$) is derived from the following equation:

$$Q_p = I^2 \cdot R_p \cdot t \cdots (25)$$

The calculation region in the present work is less than 200 s; thus, applying the data above to Eq. (25) results in a value of $1.88 \times 10^{-3}$ kJ for produced heat, which is negligible compared with $Q_n$. Consequently, it is considered that the temperature change of the ice/water mixture would cause some error, which requires improvement of copper fin design so as to control $T_{down}$ as close to 273.15 K as possible in the future work.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Density (gcm$^{-3}$)</th>
<th>Heat capacity (kJmol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15 K</td>
<td>0.99994 3.92×10$^{-3}$</td>
<td>278.15 K 1.40×10$^{-3}$</td>
</tr>
<tr>
<td>274.15 K</td>
<td>0.99893 3.14×10$^{-4}$</td>
<td>279.15 K 1.66×10$^{-3}$</td>
</tr>
<tr>
<td>275.15 K</td>
<td>0.99994 5.89×10$^{-4}$</td>
<td>280.15 K 1.93×10$^{-3}$</td>
</tr>
<tr>
<td>276.15 K</td>
<td>0.99996 8.61×10$^{-4}$</td>
<td>281.15 K 2.19×10$^{-3}$</td>
</tr>
<tr>
<td>277.15 K</td>
<td>0.99997 1.13×10$^{-3}$</td>
<td>282.15 K 2.45×10$^{-3}$</td>
</tr>
</tbody>
</table>
4.1.3. Precision of Temperature Measurements

The temperatures ($T_{\text{up}}$ and $T_{\text{down}}$) were measured, respectively, by a sheathed K-type thermocouple inside the aluminium block and by a platinum thermometry resistance element under the copper lid. The sheathed K-type thermocouple has a 0.08 s response time and a wide measurement range of 223.15–923.15 K according to its manufacturer and can be applied to the present work. To ensure the precision, the temperature of aluminium block was recorded for 100 s without a heat source using this thermocouple, and the temperature measured is $(273.04 \pm 0.058)$ K. This precision is high enough to measure the change in temperature measured is $(273.12 \pm 0.047)$ K. This precision is also high enough to measure the change in $T_{\text{down}}$.

4.1.4. Surface Roughness

The surface roughness of samples directly affects the thickness of air gap at the interfaces. The reported thermal conductivity value of air is as small as 0.024 Wm$^{-1}$K$^{-1}$, which is nearly four orders of magnitude smaller than that of the sample. In the present work, the roughness values were around 90 μm; thus, the heat resistance factor of the air gap ($\kappa_{\text{roughness}}/k_\text{air}$) is estimated to be two orders of magnitude higher than that of the sample ($\kappa_\text{sample}/k_\text{sample}$), which suggests that the roughness is a crucial error factor of apparent thermal conductivity values. To minimize this effect, in the present work, silver paste was applied to each interface. The reported thermal conductivity value of silver paste is 9.1 Wm$^{-1}$K$^{-1}$ according to the catalogue of its manufacturer, in which case the heat resistant factor of the air gap can be reduced to be roughly the same as that of the sample. As a result of this improvement, the surface roughness has not affected the experimental results considerably. In the calculation of apparent thermal conductivity as well, the heat resistant factor (R) has been crossed out as given by Eq. (21) because the roughness values are the same for the two samples with different thicknesses. As expected from this equation, very good linearity has been obtained in Fig. 10. Thus, the surface roughness would not affect the apparent thermal conductivity as long as the roughness values are the same for the two samples with different thicknesses.

4.2. Applicability of the Present Method to Apparent Thermal Conductivity Measurements of Oxide Scales

According to the above, it has been confirmed that the present method can be applied to samples 0.1–0.5 mm thick with thermal conductivities in the range 0.25–30 Wm$^{-1}$K$^{-1}$. The reported thermal conductivity values of iron oxide do not exceed 30 Wm$^{-1}$K$^{-1}$ and basically the apparent thermal conductivity of oxide scale can be measured using the present method. The present method requires two same samples with different thicknesses and the same surface roughness. Thus, it is a key factor to prepare steel samples with different scale thicknesses in the range 0.1–0.5 mm and with the same roughness in scale surface. The FeO scales will be produced by thermal oxidation of steel plate in future work.

As shown in Fig. 9, in addition, higher thermal conductivity leads to shorter calculation time region, which probably results in larger error. In that case, the measurement system should be improved so as to extend the calculation time region. This improvement include: (i) the increase in the initial temperature of heat source, (ii) the use of high heat capacity material as heat source and (iii) the increase in the mass of heat source. These improvements would also enable apparent thermal conductivity measurements to be made for thinner sample at higher temperatures and under greater temperature gradients.

Simulation is applied to ensure the feasibility of the measurement of oxide scale. Figure 11 shows the simulation geometry, where the lower aluminium block in Fig. 3 has been removed to give a much higher temperature to the upper surface of the sample. The top block is a steel plate (20×20×5.1 mm$^3$ sized) with an FeO layer where the FeO layer 0.1 mm thick exists at the downside of the steel plate. The steel part corresponds to the heat source and the FeO layer to the sample in Fig. 3. The bottom block is a container φ27 mm×120 mm sized, sealed with a copper lid (1 mm thick) which has one fin 30-mm-long, four 28-mm-long, four 24-mm-long and 24 20-mm-long positioned inside a 30×30 mm$^2$ square. The thermophysical properties of the materials used in this simulation were also obtained from the COMSOL Multiphysics Material Library. The simulation is calculated corresponding to planned experimental conditions as follows: the initial temperature of the steel plate with FeO is fixed at 873.15 K, whereas those of the other parts are fixed at 273.15 K; the top boundary is in contact with air at 298.15 K and the bottom boundary is in contact with the ice/water mixture at 273.15 K. Temperature changes are calculated for $T_{\text{up}}$ and $T_{\text{down}}$, respectively, in the steel plate 1 mm above the FeO layer and in the ice/water mixture 1 mm below the lid.

Figure 12 shows temperatures of $T_{\text{up}}$ and $T_{\text{down}}$ as a function of time. It can be seen that $T_{\text{up}}$ decreases in the whole time region; in contrast, $T_{\text{down}}$ increases in the first 1 s and reaches the maximum and then starts to decrease. These tendencies are the same as obtained in the present work. However, it should be noted that $T_{\text{up}}$ quickly decreases down to about 580 K when the calculation time region starts. It would be required to heat the steel plate at higher tempera-
tures if data for the actual steel temperature are needed. It should also be noted that $T_{\text{down}}$ increases by about 200 K, which is greater than the increase of $T_{\text{down}}$ (150 K) predicted for the present work by the simulation, as mentioned in 2.5. This suggests that the actual temperature increase of $T_{\text{down}}$ obtained in measurement on oxide scale be smaller than the simulated temperature but be larger than that in the present experiment. Thus, another key factor to apply the present method to oxide scale at higher temperatures is to control the temperature of the ice/water mixture as close to 273.15 K as possible by optimizing the fin design.

5. Conclusions

For future measurements of apparent thermal conductivities of iron oxide scale on steel, a new heat flux measurement apparatus has been developed utilizing the principle of the Bunsen Ice Calorimeter and the procedure to derive the apparent thermal conductivity has also been established.

The method proposed has been applied to sheet samples of Inconel, alumina and Teflon, and the apparent thermal conductivity values have been obtained as 14.7 ± 0.4 Wm$^{-1}$K$^{-1}$ for Inconel at 281 K–287 K, 24.8 ± 0.7 Wm$^{-1}$K$^{-1}$ for alumina at 281 K–287 K and 0.313 ± 0.004 Wm$^{-1}$K$^{-1}$ for Teflon at 286 K–412 K, which are in good agreement with the respective reported values.

Discussion has been made on the uncertainty of the measurements. To minimize the uncertainty, key factors are (i) to control the temperature of the ice/water mixture as close to 273.15 K as possible by optimizing the fin design and (ii) to use samples with the same surface roughness.

The applicability of the present method to oxide scale on steel at higher temperature under a steeper temperature gradient has also been discussed using simulation as well. In conclusion, the method would be applicable to the scale if the above two key factors are optimized.

Acknowledgements

This work has been conducted as one of the projects in Research Group II for “Investigation on Factors Controlling Heat Transfer Characteristics of Scales” in Rolling Theory Committee, The Iron and Steel Institute of Japan. The authors are grateful for the financial support from the Institute and useful advices from the Committee members. The authors are also grateful for financial support to Nippon Steel & Sumitomo Metal Corporation.

REFERENCES


Appendix

The repeated integrals of the error function have been studied in relation to problems on conduction of heat and derived as follows:

$$i^n\text{erfc}x = \int_0^x (i^n\text{erfc}z)dz = \pi(n+1)!\text{erfc}x$$  (26)

with $i^n\text{erfc}x = \frac{1}{\sqrt{\pi}} e^{-x^n} - x^n\text{erfc}x$  (27)

The integral of the error function from 0 to $t$ can be given as follows:

$$\int_0^t \text{erfc}dt = \int_0^t \text{erfc}dt - \int_0^t \text{erfc}dt$$  (28)

so that

$$\int_0^t \text{erfc}dt = \frac{1}{\sqrt{\pi}} - \frac{1}{\sqrt{\pi}} e^{-t^2} - t\text{erfc}t$$  (29)

Thus Eq. (17) can be simplified into

$$h = a'\int_0^t \left[-b' \cdot e^{-bt} \cdot \text{erfc} \frac{c'}{\sqrt{t}} + d' \cdot \text{erfc} \frac{c'}{\sqrt{t}} - T_{\text{down}} \right]dt$$  (30)

where $a'$, $b'$ and $c'$ are constants expressed by the following:

$$a' = \frac{A \cdot M_{H,O} \cdot (\rho_{\text{exc}} - \rho_{\text{water}})}{\Delta_{\text{heat}} H_{H,O} \cdot \pi r^2 \cdot \rho_{\text{exc}} \cdot \rho_{\text{water}}} \frac{1}{x_{\text{sample}} / l \cdot k_{\text{sample}} + R}$$

$$b' = \frac{A}{C_r \cdot m_h \cdot R}$$

$$c' = \frac{x_{\text{refl}}}{2\sqrt{\Delta u}}$$

$$d' = T_0(0) + \frac{A}{C_r \cdot m_h \cdot R}$$

Using Eqs. (29), (30) can be integrated and the liquid height is derived as Eq. (18).