1. Introduction

In water cooling process of steelmaking after hot rolling, strict temperature control is required to produce high quality steel. The steel plate is easily oxidized to form oxide scale. The oxide scale, which exists between the cooling water and the steel plate, is a heat resistance factor for the cooling process. Thus, thermophysical property data of the oxide scale are necessary for the process simulation. The typical oxide scale on the steel after hot rolling has a multi-layered structure, i.e., the oxide scale formed on the steel consists of FeO, Fe3O4, and Fe2O3, and the thickness ratio of the FeO/Fe3O4/Fe2O3 layers is approximately 95/4/1 at 1 273 K.1)

Since FeO is the main phase of the oxide scales, the thermal diffusivity of FeO is primarily required for estimating the effective thermal diffusivity of the multi-layered oxide scale. There have been several reports for thermal diffusivities of iron oxides.2–6) However, the values reported by different laboratories show large discrepancies among them. The discrepancies would be due to the difference in microstructures of samples originating from their preparation methods, i.e., sintering of iron oxide powders2,3) or thermal oxidation of iron or steel sheets.4–6) From the practical viewpoint, the measured data on iron oxide samples prepared by the thermal oxidation of iron would be more suitable as the input parameters used in the water-cooling-process simulation.

There are two reports on the thermal diffusivity for FeO scales formed on iron sheets as functions of temperature,4,5) where both reports applied the laser flash method. However, a large discrepancy exists between the values reported by Taylor et al.4) and Li et al., 5) which would be due to the compositional change of the sample during the experiment, as suggested by Taylor et al. According to the phase diagram of Fe–O system,7) FeO decomposes into Fe3O4 and Fe below 838 K. The decomposition of FeO increases the measured thermal diffusivity because the thermal diffusivity of iron is much greater than that of FeO. Li et al. reported that their measured value was greater than that reported by Taylor et al. at 673 K, and also noticed that their results had been influenced by the decomposition of FeO from the phase identification for the post-experiment samples using a Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) with the target of Co. Thus, the thermal diffusivity of FeO reported by Li et al. was determined by correcting the measured data on the basis of the volume ratio of existing phases in the post-experiment samples. Therefore, the thermal diffusivity of FeO scale without decomposition is still unknown at high temperature.

One solution to the problem of the decomposition of FeO...
is to minimize the duration of high temperature exposure of the sample in the thermal diffusivity measurement. This would be achieved by applying the electrical-optical hybrid pulse-heating method. Using this method, Watanabe et al. have measured thermal diffusivity of Mo at temperatures from 2,000 to 2,600 K. In their work, a coupon sample of Mo was heated from room temperature up to a temperature beyond 2,000 K within 300 ms by passing a large current through the sample, and then the thermal diffusivity was measured by the laser flash method just after the sample temperature was kept constant for several milliseconds by controlling the heating current. Thus, the present work aims to measure thermal diffusivity of thermally grown FeO scale formed on an iron coupon substrate at high temperature by the electrical-optical hybrid pulse-heating method without the compositional change during the experiment. In this work, FeO scale was indirectly heated by the resistive heating of the iron substrate, and the thermal diffusivity was determined based on the laser flash method together with a multi-layered analysis.

2. Experimental

2.1. Sample Preparation

The sample of FeO scale was prepared by oxidizing an iron coupon (99.99\% Fe) having a size of $0.5 \times 4 \times 40$ mm$^2$ at 1,123 K for 18 ks in the Ar-8.4\%H$_2$-15.6\%H$_2$O gas mixture with the calculated oxygen partial pressure of $1.7 \times 10^{-12}$ Pa at 1,123 K. The thickness of FeO layer formed on each of the 40 $\times$ 4 mm$^2$ face of the coupon was estimated to be ca. 90 $\mu$m from the mass change of the coupon after oxidation. To measure the temperature of the sample, an R-type thermocouple was welded at the center of a 40 $\times$ 4 mm$^2$ face of the iron coupon. The FeO scale around 4-mm length from the ends in the longitudinal direction was removed by 15\% HCl solution to form the terminals for current supply.

2.2. Experimental Apparatus and Measurement

Figure 1 shows a schematic diagram of the apparatus of the electrical-optical hybrid pulse-heating method$^9$ used in this work. The coupon was connected to the circuit consisting of the battery to supply the heating current, field-effect transistors to control the current, and the standard resistor to measure the current level. The experimental chamber, which was not shown in the figure, was evacuated to $2 \times 10^{-4}$ Pa. The coupon was rapidly heated up to a preset experimental temperature by passing a large current pulse through iron substrate based on the radiance temperature of the coupon. The apparent temperature ($T_a$) was measured by a pyrometer, which was calibrated in advance by the thermocouple welded on the coupon as follows: the sample was heated to a preset experimental $T_a$ and kept stable for about 100 ms, the system collected signals both from the pyrometer and the thermocouple, and the measured $T_a$ was considered to be equivalent to the temperature measured by thermocouple ($T_i$)$^9$. To maintain the coupon at the preset temperature for a brief interval, the heating current level was feed-back controlled by using the data acquisition and heating control system. Just after attaining the brief steady-state, thermal diffusivity measurement was conducted based on the laser flash method as follows: a partial area of the coupon surface opposite to the pyrometer was irradiated by a laser pulse from the Nd: glass laser and the temperature change of the rear surface was measured by the pyrometer. Just after obtaining the temperature profile for measuring the thermal diffusivity, the heating current was shut down to minimize the duration of high temperature exposure of the sample. Details of schemes for controlling such a multi-step experimental sequence have been mentioned elsewhere.$^9$ Using the measured temperature variation due to the laser irradiation, the effective thermal diffusivity of the coupon was calculated based on the half time analysis.$^{10}$ The post-experiment coupon was characterized by XRD and SEM to identify the phase of the sample and to determine the thicknesses of the iron layer and the FeO layers formed, respectively.

3. Results

3.1. Characterization of FeO Scales

Figure 2 shows the XRD results for the coupon before and after the thermal diffusivity measurement. The analysis was conducted for both the two surfaces focused on by the pyrometer and irradiated by the laser. Several peaks are found in each profile, and all the peaks belong to FeO; however, there are differences in heights of peaks at the same angle. This would be due to the large size of FeO grain because the XRD analysis was conducted directly for the coupon surface, not for the powder. Therefore, the thermally formed FeO scale is considered to be hardly decomposed during such a rapid experiment realized by the present heating method.

Figure 3 shows the cross-sectional SEM image of the oxidized coupon after the thermal diffusivity measurement. The coupon has a three-layered structure of FeO/Fe/FeO, the upper FeO layer was irradiated by the laser, and the bottom one was focused on by the pyrometer. Respective thicknesses of the three layers of the upper FeO, Fe and bottom FeO ($L_1$, $L_2$ and $L_3$) were evaluated to be 89.7 $\pm$ 5.9 $\mu$m, 382.0 $\pm$ 5.0 $\mu$m and 95.1 $\pm$ 6.7 $\mu$m by averaging 45 thickness measurements for different positions in each of the three layers shown in Fig. 3. The total thickness ($L_\text{T}$)
of the coupon was determined to be 566.8 μm ($L_s = L_1 + L_2 + L_3$). Since both the interfaces between the FeO and Fe layers are smooth as illustrated in Fig. 3, the uncertainties of thicknesses of FeO layers are mainly caused by the outer surface roughness of the FeO layers.

3.2. Effective Thermal Diffusivity of the Coupon

Figure 4 shows the time evolution of the apparent temperature ($T_a$) during the high-temperature thermal diffusivity measurement of the coupon. It can be seen that within 400 ms, the coupon was heated up and then maintained at the preset experimental temperature ($T_r$) of 932 K. The abrupt increase in $T_a$ around the time of 410 ms indicates the direct detection of the stray light of the laser emission for the laser flash method. The gradual temperature increase after the direct laser detection was due to the heat transfer from the rear surface heated by the laser, which is clearly shown in the middle of Fig. 4 as the enlarged curve of $T_a$ versus time, where the origin of the time axis is transferred to the time when the laser was emitted. The half time of thermal diffusion was estimated to be 18.6 ms. To determine the thermal diffusivity at 932 K, the total thickness of the coupon ($L_s$) at 932 K was estimated based on account of the following estimation of thermal expansion. Linear thermal expansion $\Delta L/L_0$ of FeO and Fe at 932 K are calculated to be 0.845% and 1.62%, respectively, where $L_0$ is the length at room temperature and $\Delta L$ is the difference between the length at 932 K and $L_0$. Using these values, the respective thicknesses of $L_1$, $L_2$, and $L_3$ at 932 K are estimated to be 90.5 μm, 386.9 μm, and 95.9 μm. Therefore, the effective thermal diffusivity of the oxidized coupon ($\alpha$) at 932 K was calculated to be $2.45 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$ on the case that $L_s$ at 932 K would be 573.3 μm.

4. Discussion

In this section, the thermal diffusivity of FeO scale at high temperature was derived by the measured values based on a three-layered analysis method. The validity of the obtained thermal diffusivity was discussed on two viewpoints of the experimental uncertainty mainly due to the thermal boundary resistance and of the comparison with previously reported results.

4.1. Thermal Diffusivity of FeO Scale

The thermal diffusivity of FeO scale ($\alpha_{\text{FeO,app}}$) was calculated according to ISO 18555 by the following three-layered analyzing equation:

$$\alpha_{\text{FeO,app}} = \frac{\left(\frac{C_1}{6} + \frac{C_2}{2} + \frac{C_3}{2}\right)L_1^2 + \left(\frac{C_1}{2} + \frac{C_2}{2} + \frac{C_3}{6}\right)L_2^2 + \left(\frac{C_1}{6} + \frac{C_2}{2} + \frac{C_3}{2}\right)L_3^2}{6\alpha_s \left(\frac{L_4 + L_2 + L_3}{L_1 + L_2 + L_3}\right)^2} \left(C_1 + C_2 + C_3\right) - \frac{L_2^2}{6\alpha_s} \left(\frac{L_1^3}{C_1} + \frac{L_2^3}{C_2} + \frac{L_3^3}{C_3}\right)$$

where $C_i = c_i \rho_i L_i$, in which $c_i$ is the heat capacity and $\rho_i$ is the density of substance $i$. The subscripts “2” means the Fe layer and “1” and “3” mean the two FeO layers in the coupon. Since the boundary resistance between FeO scale and Fe substrate is neglected in Eq. (1), $\alpha_{\text{FeO,app}}$ is considered as an apparent value. Since Eq. (1) has a symmetric
structure for the parameters with subscripts “1” and “3”, the two scale layers can be represented by either “1” or “3”. In this study, the two scale layers were assumed to have the same properties of $c$, $\rho$, and $\alpha$ but different $L$. The value of $\alpha_{FeO,app}$ was calculated by substituting measured values of $\alpha_s$, $L_1$–$L_3$, at 932 K into Eq. (1) with other parameters cited in literature\textsuperscript{12,14,16} as listed in Table 1. The density of FeO listed in Table 1 was estimated from the reported values of the density at room temperature (5 870 kg/m$^3$)\textsuperscript{15} and linear thermal expansion at 932 K (0.845%).\textsuperscript{11} The value of $\alpha_{FeO,app}$ was derived to be $5.27 \times 10^{-7}$ m$^2$ s$^{-1}$.

4.2. Uncertainties of Thermal Diffusivity of the Sample and FeO Scale

The standard combined uncertainty was calculated for the effective thermal diffusivity of the coupon ($\alpha_s$) at 932 K as well as that of FeO scale ($\alpha_{FeO,app}$) from the following equations based on the guide to the expression of uncertainty in the measurement (GUM):\textsuperscript{17}

$$Y = f(x_1, x_2, \ldots, x_N) \quad \ldots \quad (2)$$

$$u^2(Y) = \sqrt{\sum_{i=1}^{N} \left[ \frac{\partial f}{\partial x_i} u(x_i) \right]^2} \quad \ldots \quad (3)$$

where $Y$ is a measure and determined from $N$ other quantities $x_1, x_2, \ldots, x_N$ through a functional relation $f$, $u(Y)$ is the standard uncertainty of $Y$, and $u(x_i)$ is the standard deviation of the estimated input quantity $x_i$. The uncertainty budget of $\alpha_s$ at 932 K is listed in Table 2. The larger product of $s$ and sensitivity ($\partial f/\partial x$) has a greater contribution to $u(\alpha_s)$. The main factor for the uncertainty is related to the determination of $L_s$, the uncertainty of which results from the outer surface roughness of FeO layers.

Table 3 shows the uncertainty budget of $\alpha_{FeO,app}$ at 932 K. The standard uncertainty is determined to be $0.48 \times 10^{-7}$ m$^2$ s$^{-1}$ and is mainly caused by the uncertainties of $\alpha_s$, $L_1$ and $L_3$. The uncertainties of $L_1$ and $L_3$ mainly depend on the surface roughness as explained in Section 3.1., besides, the uncertainty of $\alpha_s$ is also significantly associated with the surface roughness as explained above. Therefore, the surface roughness of the FeO scale should be decreased to decrease the uncertainty of the thermal diffusivity of FeO scale.

4.3. Effect of Thermal Boundary Resistance on Thermal Diffusivity of FeO Scale

The value of $\alpha_{FeO,app}$ would be influenced by the thermal boundary resistance between FeO scale and Fe substrate. Li \textit{et al.}\textsuperscript{3} have suggested that the boundary resistance is not negligibly small for the FeO scale/Fe at room temperature and they have reported that the boundary resistance for the FeO scale/Fe was $8.3 \times 10^{-6}$ m$^2$ K$^{-1}$ W$^{-1}$ at room temperature. On the other hand, Lyeo \textit{et al.}\textsuperscript{13} have suggested that the boundary resistance decreased with increasing temperature for some oxide/metal interfaces, such as Al$_2$O$_3$/Al. Thus, the effect of the thermal boundary resistance on the apparent value of $\alpha_{FeO,app}$ would be estimated as $8.3 \times 10^{-4}$ m$^2$ K$^{-1}$ W$^{-1}$ at most. In this work, therefore, the effect of boundary resistance is neglected in the determination of the thermal diffusivity of FeO scale.

The relationship among the thermal resistance of FeO scale $(L_{feo}/k_{feo})$, the thermal boundary resistance $(h)$ and the apparent thermal resistance $(L_{feo}/k_{feo,app})$ is explained by the following equation,

$$\frac{L_{feo}}{k_{feo,app}} = \frac{L_{feo}}{k_{feo}} + 2h \quad \ldots \quad (4)$$

where $k$ is the thermal conductivity, which is derived from $k = \alpha pc$, where $\alpha$ is the thermal diffusivity, the subscripts of “FeO” and “Fe” represent the presence and absence of the effect of thermal boundary resistance of FeO scale/Fe interfaces, respectively, and $L_{feo}$ is the total thickness of FeO layers $(L_{feo} = L_1 + L_3)$. In addition, Eq. (4) can be transformed into another equation as follows,

$$\frac{1}{\alpha_{FeO,app}} = \frac{1}{\alpha_{feo}} - \frac{2h_{FeO,app}}{L_{feo}} \quad \ldots \quad (5)$$

where $\alpha_{feo}$ is the true value of thermal diffusivity of FeO scale, which involves no effect of thermal boundary resistance. By substituting the room temperature value of $h$ reported by Li \textit{et al.} into Eq. (5), the high temperature value of $\alpha_{feo}$ is estimated to be $6.74 \times 10^{-7}$ m$^2$ s$^{-1}$, which is 28.1% larger than that of $\alpha_{FeO,app}$. Since the thermal boundary resistance on $\alpha_{FeO,app}$ at 932 K would be smaller than

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>Referred data for calculation of $\alpha_{FeO,app}$ at 932 K.</th>
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<tbody>
<tr>
<td>Specific heat/J kg$^{-1}$ K$^{-1}$</td>
<td>Density/kg m$^{-3}$</td>
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<tr>
<td>Iron</td>
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</tr>
<tr>
<td>FeO</td>
<td>817$^{(3)}$</td>
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<th>Table 2.</th>
<th>Uncertainty budget of effective thermal diffusivity of $\alpha_{FeO,app}$ at 932 K.</th>
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<tbody>
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<td>Input</td>
<td>Type</td>
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<tr>
<td>quantity</td>
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<td>B</td>
</tr>
<tr>
<td>Thickness, $L_3$/m</td>
<td>B</td>
</tr>
<tr>
<td>Half time, $t_{1/2}$/s</td>
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<td>Type</td>
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<tr>
<td>quantity</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{FeO,app}/m^2s^{-1}$</td>
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<tr>
<td>$L_1$/m</td>
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<td>$\rho_s$/kg m$^{-3}$</td>
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<tr>
<td>$\rho_f$/kg m$^{-3}$</td>
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<tr>
<td>$\rho_s$/kg m$^{-3}$</td>
<td>A</td>
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</tbody>
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that at room temperature, the expected difference between $\alpha_{\text{FeO}}$ and $\alpha_{\text{FeO,app}}$ at 932 K (28.1%) may be overestimated.

4.4. Comparison with Reported Values

The thermal diffusivity obtained in this work is plotted with the previously reported values of thermally grown FeO scale\(^\text{4,5}\) as shown in Fig 5. The data reported by Taylor \textit{et al.} show hysteresis during the consecutive heating and cooling cycles. This should be caused by decomposition of FeO in the heating cycle, especially, from 600 K to 900 K. In the cooling cycle, the phases at high temperatures, mainly FeO, would be maintained in their sample because of the significantly fast cooling speed, suggesting that the ratio of phases in the scale exhibits the hysteresis. Similar thermal diffusivity hysteresis was also observed by Li \textit{et al.} (heating a and cooling a) as shown by the solid curves. Li \textit{et al.} have corrected the measured (apparent) data of thermal diffusivity to derive the true data for FeO on the basis of the volume ratio of existing phases in their post-experiment samples. The corrected thermal diffusivity obtained in the heating and cooling cycles exhibit the same temperature dependence as that of each other, shown as the broken curves in Fig. 5. The present value obtained without the consideration of thermal boundary resistance is placed between the reported values of Taylor \textit{et al.} and Li \textit{et al.} (heating b and cooling b). A possible reason why the present data is smaller than those reported by Taylor \textit{et al.} is because no decomposition of FeO scales has been occurred during the rapid heating and cooling process executed in this work. The discrepancy between our data and those reported by Li \textit{et al.} (heating b and cooling b) would be due to the uncertainty in the estimation of the volume fraction of existing phases conducted by Li \textit{et al.}, because of the experimental difficulties of the phase identification.

5. Conclusions

The thermal diffusivity of FeO scale, which had been thermally grown on high purity Fe, has been measured at 932 K by the electrical-optical hybrid pulse-heating method. The FeO scale was maintained during the measurement because the pulse-heating method can excessively decrease the duration of the high temperature exposure of the sample. Thermal diffusivity of thermally grown FeO at 932 K was determined to be $5.27 \pm 0.48 \times 10^{-7} \text{m}^2\text{s}^{-1}$, without considering the thermal boundary resistance between the scale and the substrate. The uncertainty of thermal diffusivity was mainly attributed to the uncertainty of the thicknesses of FeO scale layers. In order to further decrease the uncertainty, therefore, it is effective to reduce the surface roughness of FeO scales. In addition, the effect of the thermal boundary resistance of the FeO scale/Fe interfaces on the thermal diffusivity of the thermally grown FeO scale would be smaller than 28.1%.

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