Temperature Dependence of Thermal Diffusivity and Conductivity of FeO Scale Produced on Iron by Thermal Oxidation

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(Received on May 30, 2017; accepted on August 3, 2017)

1. Introduction

After hot rolling, strict control over the water spray cooling process is essential to obtain high-quality steel products.1) In this process, heat is extracted from the hot steel to the water coolant via the iron oxide scale that is produced on the steel surface during hot rolling. The oxide scale is continually removed by hydraulic descaling using water during hot rolling; However, steel can easily be oxidised at high temperatures and possesses an oxide scale tens of micrometres thick, even after treatment with a finishing rolling machine. In addition, the thickness of the oxide scale is inhomogeneous, which causes a non-uniformity in the steel cooling rate. For example, Shoji et al.3) have reported that thicker oxide scales are prone to give higher water quench points (the transition temperature from film to nucleate boiling). This suggests that portions having thicker oxide scales cool faster at higher temperatures because the heat extraction due to nucleate boiling is one order of magnitude greater than that due to film boiling.3) As a result, the non-uniformity of the cooling rate may bring about distortion and cracking in the final products. To understand the distortion and crack-generation mechanisms, mathematical modelling has been carried out to aid steel-based industries. For such mathematical simulations, the thermal conductivity and diffusivity of the iron oxide scale are the most important thermophysical properties.4)

To date, to the best of the authors’ knowledge, there have been six reports on the thermal conductivity/diffusivity of iron oxide scales;5–10) each has reported that the thermal conductivities/diffusivities of iron oxide scales are smaller than those of steel. Three of these studies have obtained the thermal diffusivities of single-phase samples of sintered iron oxides as functions of temperature.5–7) However, there are large discrepancies between the values and temperature dependencies. With respect to FeO, for example, Slowik et al.5) and Akiyama et al.6) have reported that the thermal diffusivity shows a positive temperature dependence, whereas Takeda et al.11) find a negative temperature dependence. This may be due to the non-stoichiometric nature and porosity differences of the samples. In contrast to the sintered iron oxide samples, actual iron oxide scale has a multilayered structure of Fe2O3, Fe3O4, and FeO phases, and also contains pores.12) Even if accurate thermal conductivity/diffusivity values are known for single-phase iron oxides, it

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DOI: http://dx.doi.org/10.2355/isijinternational.ISIJINT-2017-301

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is extremely difficult to predict the values of an actual iron oxide scale. Thus, sintered iron oxide samples are not suitable representatives of an actual iron oxide scale.

In contrast, the other three reports determine the thermal conductivities/diffusivities of iron oxide scales produced on iron/steel substrates by thermal oxidation. Taylor et al. have measured the thermal diffusivities of iron oxide scales on iron substrates from 450 to 1 250 °C using the laser flash method. The scale phase composition and amounts of Fe₃O₄ and Fe produced by the FeO decomposition are not considered, although they are thermodynamically possible below 843 K. In fact, these form easily and very rapidly at 623 to 723 K in dynamics, as shown in a study of FeO decomposition dynamics by Tanei and Kondo. Baud et al. have also reported that significant numbers of magnetite seams are generated in the temperature range of 648 to 748 K. More recently, Endo et al. have measured the thermal diffusivity of an actual oxide scale formed on a steel slab during hot rolling using the laser flash method following the analysis proposed by Baba. Also, Li et al. have sought to measure the thermal conductivities of FeO scales produced on iron substrates by thermal oxidation using a newly developed quasi-steady-state hot plate method. At present, the latter two techniques have been limited to measurements at room temperature only. Thus, a method to determine the temperature-dependent thermal conductivities/diffusivities of iron oxide scales produced on iron/steel substrates by thermal oxidation is still required, alongside a close examination of the FeO decomposition.

Recently, the laser flash method combined with a new analysis technique to determine the thermal diffusivities of solid planar multilayered samples above room temperature has been published in ISO 18555. Akoshima et al. have applied this method to Ni-based super-alloy samples coated with CoNiCrAlY and YSZ layers, and succeeded in measuring the thermal diffusivities of both coatings. Thus, this method would enable the measurement of thermal diffusivities of iron oxide scales on iron/steel substrates at high temperatures. As a first step towards understanding the entire system, the present work focuses on FeO scales as this is a major part of actual iron oxide scales. Consequently, the thermal conductivities/diffusivities of FeO scales produced on iron substrates by thermal oxidation are obtained using the laser flash method to clarify their temperature dependencies, whilst close attention is paid to the FeO decomposition.

2. Experimental

2.1. Sample Preparation and Characterisation

Iron plates (99.99% purity, 10 × 10 × 0.5 mm³) were used as substrates, on which FeO scales were produced on both surfaces according to the method reported by Tanei and Kondo. First, the iron substrates were oxidised at 973 K in air for 1.5–5.5 h to give an oxide scale consisting of FeO, Fe₃O₄, and Fe₂O₃. To reduce the latter two to FeO, the samples were then heated at 1 273 K in a nitrogen atmosphere for 1.5–3 h. In the present work, 14 samples were prepared: samples A–H were used for the laser flash measurements and samples H–N were used to investigate FeO decomposition. In addition, samples A–C were prepared using the same iron substrates under oxidation for 1.5 h followed by reduction for 1.5 h, whereas samples D–N were prepared using the same iron substrates under oxidation for 5.5 h followed by reduction for 3 h. To be more specific, samples A–H were prepared to have different FeO scale thicknesses in the range of 40 to 100 μm; these thicknesses were adjusted by controlling the heating time for scale formation and successive polishing, the latter being conducted on both surfaces using #800 abrasive papers. The thickness of the FeO scale (d FeO) was measured from cross-sectional scanning electron microscopy (SEM) images, the total sample thickness (d) was measured using a micrometer before the laser flash measurements, and the thickness of the iron substrate (d iron) was the difference between d and d FeO. On the other hand, samples I–M were prepared by heating to 298, 460, 676, 859, or 1 005 K, respectively, and then cooling to room temperature in the furnace; these samples possess the same temperature history as those used in the laser flash measurements, as described later. SEM analyses of samples I–M were performed to observe the cross-sections of the FeO scales, as well as for sample H to measure the scale chemical composition. These samples were mounted in epoxy resin and polished with #2000 abrasive paper and then with a diamond abrasive with a ~0.25 μm particle diameter. Lastly, sample N, which had a 100 μm-thick FeO scale, was used for high-temperature X-ray diffraction. This analysis was conducted at intervals of ~200 K during heating from room temperature to 1 173 K and also after cooling to room temperature. This temperature history was also the same as that for the samples used in the laser flash measurements.

2.2. Density Measurements

The density of the FeO scale was estimated by the mass to volume ratio, determined at room temperature before the laser flash measurements, from the following equation.

\[
\frac{\Delta m_{\text{Sample}} \times M_{\text{FeO}}}{V_{\text{FeO}}} \left/ \right. M_0 = \rho_{\text{FeO}} \quad \text{(1)}
\]

where \(\Delta m_{\text{Sample}}\) is the mass change of the iron substrate induced by thermal oxidation, measured by an electronic balance before and after oxidation; \(M_{\text{FeO}}\) and \(M_0\) are the molar masses of FeO and O, respectively; and \(V_{\text{FeO}}\) is the volume of the FeO scale, which was estimated as the product of the FeO scale thickness and the whole sample surface area.

2.3. Laser Flash Measurements

The thermal diffusivities of the FeO scales of samples A–H were measured by the laser flash method with the analysis method proposed by Baba. Figure 1(a) shows a schematic of the method along with an iron plate sample: the front surface is heated by a laser pulse, and the resulting temperature change at the back surface is recorded by a radiation thermometer. The temperature rise curve obtained was analysed by curve fitting (CF) method according to the equireal method due to the following reason. Ideally, in the laser flash method, the temperature rise curve provides the value of the apparent heat diffusivity time (the time when the temperature rises to the maximum value, \(\tau\)), \(\tau\) is converted to the apparent thermal diffusivity for the whole
Sample (α) by the following equation.

\[ \alpha = \frac{d^2}{\tau} \]  

However, in actual measurements, heat loss from the sample may occur and affect the temperature rise curve, which makes it difficult to obtain the apparent heat diffusion time. In multilayer model calculations, the areal heat diffusion time (\( \tau_d \)) is applied to evaluate the thermal diffusivity of each layer, where \( \tau_d \) is defined as the hatched area on the temperature rise curve, as shown in Fig. 1(b). \( \tau_d \) is related to \( \tau \) as follows:18

\[ \tau_d = \frac{\tau}{6} \]  

This value leads to the heat diffusion time of the FeO scale (\( \tau_{scale} \)) as follows:15

\[ \tau_{scale} = \frac{3\alpha_d}{2C_{FeO} + C_{Fe}} - \frac{3\alpha_d}{2C_{FeO} + C_{Fe} / 6 + C_{FeO}^2 / C_{Fe}} \]

\[ = \frac{3C_{Fe} + 4C_{FeO}}{3C_{Fe} + 4C_{FeO}} \]

where \( C \) is the product of the heat capacity, density, and thickness of each substance, and the subscripts of FeO and Fe represent the FeO scale and iron substrate. The relevant physical property values are given in Table 1.20–23 In addition, \( \alpha_{scale} = \frac{d_{scale}^2}{\tau_{scale}} \), where \( \alpha_{scale} \) is the thermal diffusivity of iron. Finally, the thermal diffusivity of the FeO scale (\( \alpha_{FeO} \)) was derived from \( \alpha_{scale} = \frac{d_{scale}^2}{\tau_{scale}} \).

Before thermal diffusivity measurements, both surfaces of the samples were sprayed coated with high-emissivity carbon powders to improve the temperature response.

Measurements were conducted from room temperature up to 1 164 K, since \( \alpha \)-Fe transforms into \( \gamma \)-Fe above 1 184 K.24 For the high-temperature measurements, sample H was placed in a furnace evacuated to pressures lower than 1.2 Pa to avoid further oxidation. Figure 1(c) shows the temperature history for the laser flash measurement on sample H. This was heated at ~4 K min\(^{-1}\) except when in the temperature range of FeO decomposition (473–873 K) where ~15 K min\(^{-1}\) was employed, and thermal equilibrium was maintained for ~10 min at each temperature. Data were also recorded for reference during the cooling cycle.

### 3. Results

#### 3.1. Sample Details

Table 2 gives the \( d_{scale} \) and \( d_{Fe} \) values for samples A–N. The heating-induced mass change was 0.28 g for samples A–C (54 × 38 × 0.5 mm\(^3\)) and 0.40 g for samples D–N (50 × 30 × 0.5 mm\(^3\)). The density of the FeO scale was derived from Eq. (1) as 6.05 g cm\(^{-3}\) for samples A–C and 5.85 g cm\(^{-3}\) for samples D–N.

Figures 2(a)–2(f) show cross-sectional SEM images of the iron oxide scales of samples I–M and H, and Fig. 2(g) shows a magnified view of image (c). In these figures, the light grey parts represent FeO, the dark grey parts represent Fe\(_3\)O\(_4\), and the white parts represent Fe. These figures indicate that the scale consists only of FeO after measurements at room temperature to 460 K; contains granular FeO precipitates and eutectoid structures of Fe\(_3\)O\(_4\) and Fe at 676 K, as shown more clearly in Fig. 2(g); and contains granular Fe precipitates instead of the eutectoid structures at 859 to 1 164 K, which can be regarded as a model system consisting of a matrix (FeO) and two elliptic dispersed phases (Fe\(_3\)O\(_4\) and Fe), as described later in Section 4.3. Figure 3 shows the X-ray diffraction profiles of sample N after being heated and cooled following the same temperature history as that of the laser flash measurement samples. Only FeO exists up to 473 K, whilst FeO\(_2\) is present above 676 K but disappears above 1 023 K. However, FeO\(_2\) and Fe may remain in the deep regions of the scale, which the X-rays cannot reach, at high temperatures.

#### 3.2. Scale Thermal Diffusivity

Figures 4(a) and 4(b) show the temperature rise curves recorded for sample H at room temperature and 1 164 K, respectively. The temperature at the back surface of the sample rises quickly after the laser pulse input and reaches the maximum in about 0.141 s and 0.192 s at the respective temperatures, after which there is no obvious decrease to indicate heat loss in either case. The absolute temperature rise is about 0.43 K in the measurement at room tempera-

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**Table 1.** Values of physical properties used in this work.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R.T. 460 K 676 K 859 K 1 005 K 1 164 K</td>
</tr>
<tr>
<td>( c_{FeO} ) (J kg(^{-1}) K(^{-1}))</td>
<td>699.3 732.2 773.1 804.7 828.0 851.4</td>
</tr>
<tr>
<td>( c_{Fe} ) (J kg(^{-1}) K(^{-1}))</td>
<td>495.3 481.3 577.9 755.9 968.8 751.9</td>
</tr>
<tr>
<td>( \rho_{Fe} ) (g cm(^{-3}))</td>
<td>7.87 7.81 7.74 7.68 7.63 7.57</td>
</tr>
<tr>
<td>( \alpha_{Fe} ) (m(^2) s(^{-1}))</td>
<td>2.22 1.67 1.06 0.66 0.38 0.85</td>
</tr>
<tr>
<td>( k_{FeO} ) (W m(^{-1}) K(^{-1}))</td>
<td>80.1 62.9 49.2 39.0 28.0 48.5</td>
</tr>
<tr>
<td>( k_{Fe} ) (W m(^{-1}) K(^{-1}))</td>
<td>– – 9.3 5.4 7.2 6.9</td>
</tr>
</tbody>
</table>

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tecture. These curves are regressed by the CF method, and the areal heat diffusion time ($A_d$) is evaluated using the apparent heat diffusion time, providing the thermal diffusivity of the iron oxide scale via Eqs. (3) and (4). The thermal diffusivity ($\alpha$) can also be converted to thermal conductivity ($k$) using the relation $k = \alpha \rho c_p$ where $\rho$ is the density and $c_p$ is the specific heat capacity.

Figures 5(a)–5(c) respectively show the apparent thermal diffusivities ($\alpha$) of the whole sample, measured thermal diffusivities ($\alpha_{\text{scale-meas}}$), and conductivities ($k_{\text{scale-meas}}$) of the iron oxide scales obtained from the room temperature measurement. These curves are regressed by the CF method, and the areal heat diffusion time ($A_d$) is evaluated using the apparent heat diffusion time, providing the thermal diffusivity of the iron oxide scale via Eqs. (3) and (4). The thermal diffusivity ($\alpha$) can also be converted to thermal conductivity ($k$) using the relation $k = \alpha \rho c_p$ where $\rho$ is the density and $c_p$ is the specific heat capacity.

Table 2. Samples used for (a) laser flash measurements and (b) analysis: measurement temperatures were 298 K for sample A–G and 298–1 164 K for sample H.

(a)

<table>
<thead>
<tr>
<th>Samples</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{scale}}$/μm</td>
<td>37.59</td>
<td>40.47</td>
<td>50.88</td>
<td>62.55</td>
<td>82.45</td>
<td>83.86</td>
<td>94.50</td>
<td>103.65</td>
</tr>
<tr>
<td>$d_{\text{Fe}}$/mm</td>
<td>0.406</td>
<td>0.408</td>
<td>0.406</td>
<td>0.364</td>
<td>0.364</td>
<td>0.379</td>
<td>0.377</td>
<td>0.364</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Samples</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{scale}}$/μm</td>
<td>103.65</td>
<td>83.90</td>
<td>80.44</td>
<td>83.58</td>
<td>94.50</td>
<td>94.82</td>
<td>92.02</td>
</tr>
<tr>
<td>$d_{\text{Fe}}$/mm</td>
<td>0.364</td>
<td>0.373</td>
<td>0.373</td>
<td>0.388</td>
<td>0.361</td>
<td>0.374</td>
<td>0.366</td>
</tr>
</tbody>
</table>

Analysis

- SEM-EDS
- XRD

Fig. 2. Cross-sectional SEM images of FeO scales of samples I–M and H heated at (a) room temperature (I), (b) 460 K (J), (c) 676 K (K), (d) 859 K (L), (e) 1 005 K (M), (f) 1 164 K (H), and (g) a magnified view of image (e) showing enclosed eutectoid structure.

Fig. 3. High-temperature X-ray diffraction profiles of sample N.

Fig. 4. Normalised temperature rise curves of sample H at (a) room temperature, and (b) 1 164 K.
The apparent thermal diffusivity values decrease from $6.6 \times 10^{-6}$ to $2.6 \times 10^{-6}$ m$^2$ s$^{-1}$ with increasing scale thickness from 40 to 100 μm, because the thermal diffusivity of FeO is much smaller than that of Fe, as given in Table 1. In addition, the thermal diffusivity/conductivity values increase, respectively, from $3.2 \times 10^{-7}$ to $4.9 \times 10^{-7}$ m$^2$ s$^{-1}$ and from 1.3 to 2.0 W m$^{-1}$ K$^{-1}$ with increasing scale thickness. This is due to the interfacial heat resistance between the scale and the iron substrate, which is discussed later in more detail.

**Table 3.** Thermal diffusivity ($\alpha_{\text{scale-meas}}$) and conductivity ($k_{\text{scale-meas}}$) values obtained from measurements of sample H at each temperature, along with the volume fractions of the existing phases.

<table>
<thead>
<tr>
<th>Phases (Vol%)</th>
<th>Heating (298 K)</th>
<th>460 K</th>
<th>676 K</th>
<th>859 K</th>
<th>1 005 K</th>
<th>1 164 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>4.68</td>
<td>4.86</td>
<td>5.55</td>
<td>4.72</td>
<td>4.54</td>
<td>3.83</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>1.91</td>
<td>2.08</td>
<td>2.59</td>
<td>2.22</td>
<td>2.20</td>
<td>1.91</td>
</tr>
<tr>
<td>α-Fe</td>
<td>(100%)</td>
<td>(100%)</td>
<td>(78.12%)</td>
<td>(95.74%)</td>
<td>(96.97%)</td>
<td></td>
</tr>
<tr>
<td>Cooling (1 120 K)</td>
<td>3.84</td>
<td>3.95</td>
<td>3.99</td>
<td>4.10</td>
<td>4.55</td>
<td>4.47</td>
</tr>
<tr>
<td>FeO</td>
<td>1.90</td>
<td>1.90</td>
<td>1.88</td>
<td>1.85</td>
<td>1.96</td>
<td>1.83</td>
</tr>
<tr>
<td>Phases (Vol%)</td>
<td>(96.97%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>(2.78%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Fe</td>
<td>(0.25%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 6.** (a) Thermal diffusivity ($\alpha_{\text{scale-meas}}$), and (b) conductivity ($k_{\text{scale-meas}}$) values of iron oxide scale of sample H, plotted against temperature.
diffusivity and conductivity values increase until 676 K is reached. Beyond this, they decrease until 859 K and level off but decrease again above 1 005 K. During the cooling cycle, both properties show a hysteresis between 1 100 and 500 K, though return to their initial values at room temperature. In particular, the values obtained at 676 K during the heating cycle are almost 1.5 times larger than those during the cooling cycle. This is because all the FeO decomposed into Fe and Fe₃O₄, as given in Table 3.

4. Discussion

4.1. Reasonability of Measurements Made During the Cooling Cycle

Thermal conductivity/diffusivity should be measured after thermal equilibrium is established; however, this was not established in the measurements made during the cooling cycle, as shown in Fig. 1(c). Now, the reasonability of the data recorded during the cooling cycle is examined with COMSOL simulation software. The experimental system is described by a 2D axisymmetric geometry, as shown in Fig. 7; the schematic shows a magnified view of the sample part. The outer frame corresponds to the furnace, which is assumed to be 150 × 200 mm² in the simulation. The sample (10 × 0.5 mm²) is an iron plate with FeO scale layers on both surfaces, which is placed at the centre of the furnace. The initial temperature of the whole system is set at 1 164 K. Under the above conditions, the temperature change after the sample starts to cool is calculated for four different positions: position 1 is that of the thermometer placed in the actual laser flash apparatus, positions 2 and 4 are the front and back surfaces of the sample, and position 3 is the centre of the sample.

Figure 8(a) shows the temperatures calculated for the four positions against time, T₁–T₄, which are represented in order by the solid, dotted, dashed, and dot-dashed lines, and Fig. 8(b) shows T₁–T₄ against position at various time points. These figures indicate that, overall, the differences between T₁ and T₂ and between T₂ and T₃ are smaller than 0.16 K and 2.8 × 10⁻⁴ K, respectively. The largest difference between T₃ and T₂ is obtained at 1 min as 0.02 K. For comparison, the temperature rise in the laser flash measurement at 1 076 K can be approximated from the laser pulse energy (Q) absorbed by the sample. Q is assumed to be the same for a sample at different temperatures, and hence can be estimated using the following equation with the data collected at room temperature for sample H.

\[ Q = \Delta T \cdot c_{p,Fe} \cdot m_{Fe} + \Delta T \cdot c_{p,FeO} \cdot m_{FeO} \]  

where \( \Delta T \) is the temperature rise due to the laser pulse input. \( \Delta T \) is 0.43 K for sample H at room temperature, as mentioned in Section 3.2. The values of \( c_{p,Fe} \) and \( c_{p,FeO} \) are given in Table 1, and the values of \( m_{Fe} \) and \( m_{FeO} \) are estimated to be 0.29 and 0.12 g from the initial mass of the iron substrate and the mass increase due to oxidation. Thus, the laser pulse energy is estimated to be 0.09 J. Consequently, the temperature rise at 1 076 K can be calculated with the laser energy and heat capacity values of each substance at 1 076 K using Eq. (5). The derived value of 0.23 K is about 12 times greater than the maximum difference between T₃ and T₂. This suggests that the temperature distribution in the present sample does not significantly affect the laser flash measurements. Accordingly, the thermal diffusivity/conductivity values measured in the cooling cycle are also physically meaningful. In addition, the sample was cooled to 640 K from 893 K for 5 min, which would be too short for FeO to decompose to Fe and Fe₃O₄. Thus, the data recorded during the cooling cycle in Fig. 6 closely reflect the thermal conductivity/diffusivity behaviours of the FeO scale. However, future work should include an experiment to guarantee that the observed scale microstructure is the same as that of the scale measured at high temperatures.
4.2. Effect of FeO Decomposition on the Laser Flash Measurements

As shown in Fig. 2 and Table 3, FeO decomposed to Fe and Fe₃O₄ during the heating cycle of the measurement; in particular, no FeO was detected at 676 K. The decomposition generates heat, and the physical properties of the resultant Fe₃O₄ and Fe are different from those of FeO. Both may influence the result. However, the laser flash method is focused on the temperature rise only, which means the external energy will not affect the measurement. Thus, the effect of FeO decomposition on the laser flash measurement itself is only discussed in terms of the phase change.

The physical properties such as density and heat capacity of Fe₃O₄ and Fe are different from those of FeO, which may affect the thermal diffusivity results. Based on the principles of the laser flash method and the CF method, the phase change does not affect the apparent thermal diffusivity of the whole sample. However, as shown in Eq. (4), the density and specific heat capacity of the scale layer really affect the conversion of the apparent thermal diffusivity to thermal conductivity, as well as the thermal diffusivity of the scale itself.

As shown in Table 3, the most significant decomposition occurred at 859 K, except 676 K where no FeO was detected. The volume fractions of Fe₃O₄ and Fe are 21.38% and 0.50%, respectively. Thus, the product of the scale density and specific heat capacity used in Eq. (4) is different from that of FeO, which can be calculated from the following equation.

\[ \rho_{\text{scale}} \cdot c_{p,\text{scale}} = \rho_{\text{FeO}} \cdot c_{p,\text{FeO}} \cdot f_{\text{FeO}} + \rho_{\text{Fe₃O₄}} \cdot c_{p,\text{Fe₃O₄}} \cdot f_{\text{Fe₃O₄}} + \rho_{\text{Fe}} \cdot c_{p,\text{Fe}} \cdot f_{\text{Fe}} \]  

where \( c_{p,\text{FeO}} \) is 837.63 J kg\(^{-1}\) K\(^{-1}\) at 859 K, \( \rho_{\text{FeO}} \) is 5.18 g cm\(^{-3}\), and \( f \) is the volume fraction of each substance as shown in Table 3. The other values used are shown in Table 1.

In this case, the value of \( \rho_{\text{scale}} \cdot c_{p,\text{scale}} \) changes from 4.71 to 4.64 J cm\(^{-3}\) K\(^{-1}\), which changes the thermal diffusivity and conductivity from 4.7 \( \times \) 10\(^{-7}\) to 4.7 \( \times \) 10\(^{-7}\) m\(^2\) s\(^{-1}\) and from 2.2 \( \times \) 10\(^{-6}\) to 2.1 \( \times \) 10\(^{-6}\) W m\(^{-1}\) K\(^{-1}\), respectively. This suggests that the effect of FeO composition is also negligibly small.

4.3. FeO Scale Thermal Diffusivity/Conductivity

As shown in Fig. 5, the thermal diffusivity/conductivity values for the scales obtained in the present work increase with increasing scale thickness, which suggests that there is an interfacial heat resistance between the scale layer and iron substrate. In addition, as shown in Fig. 2, the FeO scale decomposed to Fe and Fe₃O₄ at high temperatures, which dispersed in the scale. Thus, the data plotted in Figs. 6(a) and 6(b) will be influenced by these two factors. In this part, the thermal diffusivity/conductivity values obtained are corrected by considering the presence of the interfacial heat resistance and dispersed phases to derive the thermal diffusivity/conductivity values of the FeO scale.

4.3.1. Correction of the Interfacial Heat Resistance

Consider that the total heat resistance of the scale consists of the heat resistance of the scale layer itself and the interfacial heat resistance. This situation can be expressed by the following equation:

\[ \frac{d_{\text{scale}}}{k_{\text{scale-meas}}} = \frac{d_{\text{scale}}}{k_{\text{scale}}} + h \]  

where \( k_{\text{scale-meas}} \) is the thermal conductivity of the scale directly converted from the measured scale thermal diffusivity \( (\alpha_{\text{scale-meas}}) \), \( k_{\text{scale}} \) is the thermal conductivity of the scale layer itself, and \( h \) is the interfacial heat resistance. It is noted that \( k_{\text{scale-meas}} \) includes the interfacial effect but \( k_{\text{scale}} \) does not. Plotting the data shown in Fig. 5(c) according to Eq. (7) gives Fig. 9, where the slope represents the reciprocal of the thermal conductivity of the scale itself and the intercept represents the interfacial heat resistance. Figure 9 gives \( k_{\text{scale}} = 2.3 \) W m\(^{-1}\) K\(^{-1}\) and \( h = 8.3 \times 10^{-6} \) m\(^2\) K\(^{-1}\). These values are based on room temperature data, but in the present work it is assumed that \( h = 8.3 \times 10^{-6} \) m\(^2\) K\(^{-1}\) can be applied even at high temperatures. Hence, the thermal conductivity/diffusivity of the scale itself can be expressed by the following equations, respectively:

\[ k_{\text{scale}} = \frac{d_{\text{scale}}}{d_{\text{scale}} / k_{\text{scale-meas}} - h} \]  

\[ \alpha_{\text{scale}} = \frac{k_{\text{scale}}}{\rho_{\text{scale}} \cdot c_{p,\text{scale}}} \]

where \( \alpha_{\text{scale}}, \rho_{\text{scale}}, \) and \( c_{p,\text{scale}} \) are the thermal diffusivity, density, and specific heat capacity of the scale. Here, the values for FeO are used for \( \rho_{\text{scale}} \) and \( c_{p,\text{scale}} \) because using the values of Fe₃O₄ and Fe does not affect the thermal conductivity/diffusivity results, as discussed above. Eq. (8) is applied to the data shown in Fig. 6(b), producing Fig. 10(a), which in turn produces Fig. 10(b) via Eq. (9). The values of \( k_{\text{scale}} \) and \( \alpha_{\text{scale}} \) increase only slightly after correction, and the temperature dependencies remain similar.

4.3.2. Correction of the Dispersed Phases

The values of \( k_{\text{scale}} \) and \( \alpha_{\text{scale}} \) derived above still include the effect of the dispersed Fe and Fe₃O₄ phases. To obtain the thermal conductivity \( k_{\text{FeO}} \) and diffusivity \( \alpha_{\text{FeO}} \) values of FeO itself, the effects of these dispersed phases are removed using the model proposed by Hatta and Taya. They have assumed a model system consisting of dispersed phases within a matrix and derived a predictive equation for the effective thermal conductivity \( k_{\text{eq}} \) of the whole system.

![Fig. 9. Relationship between \( d_{\text{scale}} \) and \( d_{\text{scale}} / k_{\text{scale-meas}} \).](image-url)
based on the equivalent inclusion method, as follows.

\[
k_{\text{eff}} = \frac{k_0 + 2f_0 (k_0 - k_i)}{3k_0 - f_0 (k_0 - k_i)}
\]

where the subscript ‘0’ represents the matrix and ‘1’ represents the dispersed phase. Ohta and Tomota have confirmed that this technique can also be applied to composite materials containing multiple dispersed phases, as shown in Fig. 11, which is a schematic of the scale system corresponding to the cross-sectional SEM images of the scale shown in Figs. 2(d)–2(f). According to Ohta and Tomota, Eq. (10) can be extended to the present system as Eq. (11).

\[
k_{\text{scale}} = \frac{f_{\text{FeO}} + 3f_{\text{Fe}_{3}\text{O}_4}k_{\text{Fe}_{3}\text{O}_4}(2k_{\text{FeO}} + k_{\text{Fe}_{3}\text{O}_4})^{-1} + 3f_{\text{Fe}}k_{\text{Fe}}(2k_{\text{FeO}} + k_{\text{Fe}})^{-1} - k_{\text{FeO}}}{f_{\text{FeO}} + 3f_{\text{Fe}_{3}\text{O}_4}k_{\text{FeO}}(2k_{\text{FeO}} + k_{\text{Fe}_{3}\text{O}_4})^{-1} + 3f_{\text{Fe}}k_{\text{Fe}}(2k_{\text{FeO}} + k_{\text{Fe}})^{-1} - k_{\text{FeO}}}
\]

Figure 12 shows the thermal conductivity values of FeO \((k_{\text{FeO}})\) derived from Eq. (9) using the \(k_{\text{scale}}\) data in Fig. 10(a) and the volume fractions given in Table 3; the thermal conductivities of Fe and Fe3O4 used for this calculation are given in Table 1. In Fig. 12, the correction was not applied to the value corresponding to 676 K during the heating cycle because there was no residual FeO at this temperature. Figure 12 indicates that the correction brings the heating and cooling cycle thermal conductivity data closer to each other, in particular at higher temperatures. In addition, the thermal conductivity of FeO increases up to 460 K, beyond which it decreases and then levels off above 859 K. It is likely that the thermal conductivity of thermally grown FeO ranges between 1.8 and 2.5 \(\text{W m}^{-1}\text{K}^{-1}\).

Figure 13 shows the thermal diffusivity values of FeO \((\alpha_{\text{FeO}})\) converted from the \(k_{\text{FeO}}\) values in Fig. 12, compared with reported values. As mentioned in the Introduction, Slowik et al. and Akimya et al. have measured the thermal diffusivities of sintered FeO samples. In contrast, Taylor et al. have used thermally grown iron oxide scales mostly comprised of FeO, which are comparable to the samples used in the present work. The thermal diffusivities of the sintered FeO samples have mostly positive temperature coefficients. In contrast, thermally grown FeO scales have negative temperature coefficients, based on the present data and that obtained during heating as reported by Taylor et al. Currently, it remains unclear what the main factor affecting the differences in temperature coefficients is. The report by Taylor et al. did not mention the temperature history of the measurement; however, the abundance of data suggests that the measurements were collected almost continuously during both heating and cooling cycles. This scale sample as well as those in the present study would consist of Fe and Fe3O4 at around 600 K during the heating cycle. In the work by Taylor et al., when the temperature was increased beyond 600 K, the sample would not completely transform to FeO if the thermal equilibrium was not established during
the measurement. Thus, it is thought that the sample used by Taylor et al. contained more Fe and Fe$_3$O$_4$ phases than the present samples, which explains why their values are greater than those determined here. Also, during the cooling cycle, there is the possibility of their sample remaining as it was under high temperatures. As a consequence, the present data on the thermal diffusivity of thermally grown FeO scale is more reliable, which ranges approximately between $3.7 \times 10^{-7}$ and $5.8 \times 10^{-7}$ m$^2$ s$^{-1}$.

It is also of scientific interest to evaluate the thermal conductivity/diffusivity values of FeO with varying stoichiometry and porosity. Consequently, further work will be required to measure the thermophysical properties of FeO to evaluate the differences between the values obtained from FeO and thermally grown FeO. In addition, future work should also include the temperature dependence of the interfacial heat resistance, and the effect of the interphase heat resistance of the dispersed phases, on the thermal conductivity/diffusivity.

### 4.4. Factors Dominating the Temperature Dependence of Thermal Conductivity/Diffusivity

The thermal conductivity of an opaque solid is expressed by the following equation:

$$k = \frac{1}{3} \sum (c_{i}v_{i}l_{i}) \quad \text{(12)}$$

where $c_{i}$ is the heat capacity at a constant volume per unit volume, $v_{i}$ is the average velocity, $l_{i}$ is the mean free path, and $i$ represents excitations, such as of electrons and phonons. Metals contain numerous free electrons and have an electrical conductivity as high as $\sim 10^{7}$ Ω$^{-1}$ m$^{-1}$, thereby, free electrons dominate thermal conduction in metals. In contrast, FeO is a p-type semiconductor and its electrical conductivity is $\sim 10^{5}$ Ω$^{-1}$ m$^{-1}$ at around 500 K. Thus, for FeO, the electronic contribution can be neglected and Eq. (12) can be approximated by Eq. (13) for phonon thermal conductivity.

$$k \approx k_{ph} = \frac{1}{3} c_{i}v_{i}l_{i} \quad \text{(13)}$$

where $c_{i}$ is the phonon heat capacity per unit volume, $v_{i}$ is the average phonon group velocity, and $l_{i}$ is the phonon mean free path.

The phonon heat capacity per unit volume can be expressed by the following equation:

$$c_{ph} = \frac{\rho c_{V}}{T} \quad \text{(14)}$$

where $c_{V}$ is the specific heat capacity at constant volume, which is confirmed to be almost constant at high temperatures, and $\rho$ can be expressed by the coefficient of linear thermal expansion ($\beta$) as in Eq. (15).

$$\rho = \frac{\rho_{0}}{(1 + \beta T)} \quad \text{(15)}$$

where $\rho_{0}$ is the density at room temperature. The value of $\beta$ is $\sim 10^{-5}$ K$^{-1}$ for FeO and does not change significantly with temperature. Accordingly, the density does not notably change with temperature, suggesting that the phonon heat capacity per unit volume is almost constant.

On the other hand, the average phonon group velocity approximately equals the speed of sound in solids, which is assumed to be independent of temperature. Thus, the thermal conductivity should be dominated by the phonon mean free path and be proportional to $T^{-1}$ at high temperatures.

**Figure 14** shows the relationship between the thermal conductivity of FeO and the reciprocal of the temperature $T^{-1}$. It is noted that the thermal conductivity is approximately proportional to $T^{-1}$ above 470 K ($T^{-1} < 2.1 \times 10^{-3}$ K$^{-1}$), which is in agreement with the above discussion. However, the values obtained around room temperature do not fall around the straight line. This is because the specific heat capacity decreases dramatically as a function of $T^{3}$ at temperatures lower than the Debye temperature, which has been reported to be 494 K for FeO. This agreement between the temperatures of 470 and 494 K also supports the above discussion suggesting that the negative temperature coefficient is due to the mean free path of the phonons.

### 5. Conclusions

The thermal diffusivity and conductivity values of the
FeO scales produced on iron substrates by thermal oxidation have been determined as functions of temperature (room temperature–1 164 K) using the laser flash method.

• The density of the prepared FeO scale is in the range of 5.85–6.05 g cm\(^{-3}\) at room temperature.

• With an increase of the scale thickness from 40 to 100 \(\mu m\), the apparent thermal diffusivity of the whole sample, measured scale thermal diffusivity, and conductivity change respectively from 6.6 \(\times\) 10\(^{-6}\) to 2.6 \(\times\) 10\(^{-6}\) m\(^2\) s\(^{-1}\), from 3.2 \(\times\) 10\(^{-7}\) to 4.9 \(\times\) 10\(^{-7}\) m\(^2\) s\(^{-1}\), and from 1.3 to 2.0 W m\(^{-1}\) K\(^{-1}\) at room temperature. The latter two changes suggest the presence of an interfacial heat resistance, estimated to be about 8.3 \(\times\) 10\(^{-6}\) m\(^2\) K W\(^{-1}\) from the thickness dependence of the scale thermal conductivity.

• During the heating cycle, the thermal diffusivity/conductivity increase up to 676 K, beyond which they mostly decrease up to 1 164 K. During the cooling cycle, they show a hysteresis between 1 100 and 500 K and return to their respective initial values at room temperature. The values recorded during heating are affected by the Fe and Fe\(_3\)O\(_4\) phases generated by FeO decomposition.

• By applying corrections relating to the interfacial heat resistance and volume fractions of the Fe and Fe\(_3\)O\(_4\) phases, the FeO scale thermal diffusivity was derived as 3.7 \(\times\) 10\(^{-7}\)–5.8 \(\times\) 10\(^{-7}\) m\(^2\) s\(^{-1}\) and the thermal conductivity as 1.8–2.5 W m\(^{-1}\) K\(^{-1}\) in the range between room temperature and 1 164 K. These values were based on the following assumptions:

  i. The interfacial heat resistance is independent of temperature;
  ii. The measured volume fractions of the dispersed phases are the same as those in the scale at high temperatures;
  iii. The interphase heat resistance can be ignored.

• The temperature coefficients of the thermal conductivity are largely negative and dominated by the phonon mean free path.

Acknowledgements

This study was supported by the 25th ISIJ Research Promotion Grant, and has also been conducted as one of the projects in Research Group II for the “Investigation on Factors Controlling Heat Transfer Characteristics of Scales” in the Rolling Theory Committee, The Iron and Steel Institute of Japan. The authors are grateful for the financial support from the Institute and useful advice from the Committee members. The authors are also grateful to Professor Hiromichi Ohta for his valuable discussions and advice about the interphase heat resistance.

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