Physical Properties of Iron-Oxide Scales on Si-Containing Steels at High Temperature

Mikako Takeda¹, Takashi Onishi¹, Shouhei Nakakubo¹ and Shinji Fujimoto²

¹Materials Research Laboratory, Kobe Steel, Ltd., Kobe 651-2271, Japan
²Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The mechanical properties of oxide scales at high-temperature were studied in order to improve the surface quality of commercial Si-containing high strength steels. Specific oxides of Fe3O4, Fe4O9, FeO and Fe3SiO4 were synthesized by powder metallurgy. The Vickers hardness, thermal expansion coefficient and thermal conductivity were measured at high-temperatures. A series of measurements confirmed that the physical properties of the synthesized oxides were different each other. From the Vickers hardness measurements, it was verified that the hardness of each synthesized oxide was identical with the naturally-formed iron oxide, as observed in the cross-section of oxide scales on steels. The influence of the Fe3SiO4 formed on Si-containing steels on the scale adhesion at high temperature and the surface property is discussed on the basis of the physical properties of the oxides. [doi:10.2320/matertrans.M2009097]

Keywords: high-temperature oxidation, oxide hardness, oxide thermal expansion coefficient, oxide thermal conductivity, silicon-containing steel, FeO, Fe3O4, Fe4O9, Fe3SiO4, adhesion, surface property

1. Introduction

The iron oxide scales that form on billets and slabs of hot-rolled steels are usually detached using a hydraulic descaling process. However, residual primary scales or secondary scales that form after the descaling process remain on the steel surface through subsequent hot- and cold-working, then influence the surface quality of the final products by modifying its mechanical properties, such as deformation, fracture and spalling. The residual scales may induce non-uniform surface temperature, which affects the final scale structure and mechanical properties of the steel. Hence, it is of great importance to examine/understand the physical and mechanical properties of iron oxide scales in order to control their formation and properties, and ultimately to improve the quality of steels.

The oxide scales that form on steels include Fe3O4, Fe4O9, FeO, which form in lamellar strata from the substrate towards the outer layer. In the case of Si-containing steels, which are widely used for automobile bodies and frames in the form of high-tensile steel sheets, the inner-most layer, mainly composed of fayalite (Fe2SiO4) and FeO, can form at the interface between scale and steel.1–4 Therefore, the high-temperature physical properties such as hardness, thermal expansion coefficient, thermal conductivity, etc. of each oxide species need to be clarified in order to understand the deformation and fracture behaviour of scale and its influence on the surface properties after rolling.

The high-temperature deformation and fracture behaviour of these oxide species are not yet well summarised in the literature. Amano et al.5–8 reported the Vickers hardness of Fe3O4, Fe4O9, FeO and Fe3SiO4 at RT (room temperature) and at 1000°C, as measured by employing micro-indentation.9 In this study, Vickers hardenesses were measured for the lamellar constituent oxides in cross-sections of Si-containing steels. In terms of the deformation behaviour of oxides, Hidaka et al. reported on the deformation of Fe3O4, Fe4O9 and FeO at 600–1250°C by measuring stress-strain curves.7,8 In these studies, tensile-test specimens of pure iron were completely oxidized under fixed conditions and tensile tests at fixed strain rates were conducted to obtain the deformation and fracture behaviour.

Although knowledge of such high-temperature mechanical properties of oxide scales is beneficial, their mechanical properties have been less extensively studied because high-purity specimens of specific iron oxides are required in order to measure these parameters with sufficient accuracy.

This paper focuses on the hardness, thermal expansion coefficients and thermal conductivities at high-temperatures of Fe3O4, Fe4O9, FeO and Fe3SiO4 which were prepared by powder metallurgy and oxidation under a controlled atmosphere. Sintered compacts of each oxide were used as test specimens to measure the physical properties at high temperature. Each synthesized specific oxide of iron-oxide was prepared using the following process.

FeO forms on Fe under limited oxygen partial pressures, ranging from 2.8 × 10⁻¹³ Pa (equilibrium oxygen pressure of Fe3SiO4/FeO at 850°C) to 2.6 × 10⁻¹³ Pa (equilibrium oxygen pressure of FeO/Fe3O4 at 850°C). FeO is the stable phase at temperatures of 570°C and above, but is not stable below 570°C. Therefore, FeO may decompose into Fe and Fe3O4 at RT. FeO that is formed at high temperature can be ‘frozen-in’ by quenching, but this type of material is not suitable for measuring the mechanical properties in the high-temperature phase because numerous pores are present in such FeO specimens.

2. Experimental

2.1 Preparation of specific oxide specimens

In this study, pure high-density FeO, Fe3O4, Fe4O9 and Fe3SiO4 were prepared by powder metallurgy and oxidation under a controlled atmosphere. Sintered compacts of each oxide were used as test specimens to measure the physical properties at high temperature. Each synthesized specific oxide of iron-oxide was prepared using the following process.

FeO forms on Fe under limited oxygen partial pressures, ranging from 2.8 × 10⁻¹³ Pa (equilibrium oxygen pressure of Fe3SiO4/FeO at 850°C) to 2.6 × 10⁻¹³ Pa (equilibrium oxygen pressure of FeO/Fe3O4 at 850°C). FeO is the stable phase at temperatures of 570°C and above, but is not stable below 570°C. Therefore, FeO may decompose into Fe and Fe3O4 at RT. FeO that is formed at high temperature can be ‘frozen-in’ by quenching, but this type of material is not suitable for measuring the mechanical properties in the high-temperature phase because numerous pores are present in such FeO specimens.
In order to prepare an FeO specimen, finely-powdered Fe and Fe$_3$O$_4$ were mixed in the ratio 8:10 by weight, and were then formed into blocks, 55 mm square by 8 mm thick. The shaped blocks were compacted by cold isostatic pressing under a constant load of 150 MPa, and then sintered at 1100°C for 3.6 ks in an Ar atmosphere. The sintered blocks were pressed in a graphite mould at 900°C for 3.6 ks in vacuum, under a constant load of 50 MPa. Dense sintered compacts of pure FeO were finally obtained.

On the other hand, Fe$_3$O$_4$ forms on Fe over a wide range of oxygen pressures from $2.6 \times 10^{-13}$ Pa (equilibrium oxygen pressure of FeO/Fe$_3$O$_4$ at 850°C) to $4.1 \times 10^{-3}$ Pa (equilibrium oxygen pressure of Fe$_3$O$_4$/Fe$_2$O$_3$ at 850°C). Fe$_3$O$_4$ is relatively stable, but can be oxidized to Fe$_2$O$_3$ under high partial pressures of oxygen, and is reduced to FeO under low oxygen partial pressures. In addition, Fe$_2$O$_3$ forms on Fe under limited partial pressures of oxygen above $4.1 \times 10^{-3}$ Pa (equilibrium oxygen pressure of Fe$_2$O$_3$/FeO at 850°C). Fe$_2$O$_3$ is stable in high partial pressures of oxygen, but is unstable and can be reduced to Fe$_3$O$_4$ under low partial pressures of oxygen, e.g., in an inert atmosphere. The blocks of finely-powdered Fe$_2$O$_3$ and Fe$_3$O$_4$ were compacted by cold isostatic pressing under a constant load of 300 MPa, and then sintered at 1100°C for 3.6 ks. The Fe$_2$O$_3$ and Fe$_3$O$_4$ were sintered in atmospheres of Ar and air, respectively.

Si-containing steels promote the formation of lamellar fayalite: Fe$_2$SiO$_4$ forms between the FeO layer and the steel substrate. Fe$_5$SiO$_4$ forms in a narrow range of oxygen pressures between $2.7 \times 10^{-14}$ Pa (equilibrium oxygen pressure for SiO$_2$/Fe$_5$SiO$_4$ at 850°C) and $2.8 \times 10^{-13}$ Pa (equilibrium oxygen pressure for Fe$_5$SiO$_4$/FeO at 850°C), and therefore it is difficult to obtain pure Fe$_5$SiO$_4$ by the oxidation of Si-containing steels. Therefore, Fe$_2$SiO$_4$ was prepared by the sintering of fayalite powder.

The natural fayalite minerals were powdered and classified into the appropriate fineness (below 150 mesh), then formed into blocks. The shaped blocks were compacted by cold isostatic pressing under a constant load of 150 MPa, and were sintered at 1130°C for 3.6 ks in vacuum.

### 2.2 Quantitative analysis of purity and sintering density of synthesized specific oxide specimens

The synthesized oxide specimens were identified and were quantitatively analyzed by X-ray diffraction. In the quantitative analysis of the synthesized oxides, the main peaks of the X-ray diffraction spectra were fitted to Gaussian curves, and the intensities of the main peaks were obtained. The relative concentrations of the synthesized specific oxide were calculated by substitution in the following equation for the peak intensity.

$$C_n = \frac{A_n \times Y_n}{\Sigma(A_i \times Y_i)}$$  \hspace{1cm} (1)

where $C_n$ is the relative concentration of component $n$, $A_n$ is the relative sensitivity coefficient of component $n$, and $Y_n$ is the peak intensity of component $n$.

The synthesized oxide specimens were machined and their densities were obtained at room temperature by measuring the volume-to-weight ratio.

### 2.3 Measurements of physical properties

#### 2.3.1 Hardness

The synthesized oxides, Fe$_2$O$_3$, Fe$_3$O$_4$, FeO and Fe$_2$SiO$_4$, were machined into work-pieces with dimensions of $10 \times 20 \times 3$ mm$^3$, and then polished with a series of emery papers up to 1500 grit, buffed, finally degreased in acetone. The hardnesses of the work pieces were measured by a high-temperature micro indenter (Nikon MQ type) at temperatures up to 1000°C using square-based diamond and sapphire pyramids. A load of 50 g was applied for 30 s, and 3 impressions were recorded for each sample.

Oxide scales that were formed on iron and steel substrates were also prepared as reference standards, and the hardnesses of these scales were also measured similarly. 10 mm × 20 mm × 2 mm work-pieces of high-purity Fe (99.99%) and an Fe-3.0 mass%-Si alloy were oxidized at 1000°C for 1.8 ks in an O$_2$ atmosphere. Oxide scales of about 600 μm in thickness were formed under the oxidation condition. The hardnesses of oxide scales were measured using the square-based diamond and sapphire pyramids as indenters for the lamellar oxides in a cross section.\(^5\)

#### 2.3.2 Thermal expansion coefficient

The synthesized oxides were formed into 3.5 mm × 3.5 mm × 18 mm blocks, and were degreased in acetone. The thermal expansion coefficients of the work pieces were measured between room temperature and 1000°C using a thermo-mechanical analyzer (Rigaku TMA8140 type) at a heating rate of 5°C/min. A fused quartz bar was used as a reference in this measurement. The thermal expansion coefficients of the synthesized oxides were measured in the air for Fe$_3$O$_4$, in an Ar atmosphere for Fe$_2$O$_3$ and FeO, and in a He atmosphere for Fe$_2$SiO$_4$.

#### 2.3.3 Thermal conductivity

The synthesized oxides were machined into work pieces with dimensions of φ10 mm × 1.5 mm, and were degreased in acetone prior to measurements. The thermal conductivities were measured at up to 1000°C using a laser flash analyzer (ULVAC-RIKO TC-7000 type). The specific heats were measured by differential scanning calorimetry in an Ar atmosphere. The thermal conductivities of the synthesized oxides were calculated using the thermal diffusion coefficient, the specific heat and the sintering density.

### 3. Results and Discussion

#### 3.1 Purity and sintering density of iron oxide specimens

The synthesized oxides were identified from X-ray diffraction spectra. Typical X-ray diffraction patterns of the synthesized oxides are shown in Figs. 1 to 4. It was confirmed that the synthesized Fe$_3$O$_4$, Fe$_2$O$_3$ and Fe$_2$SiO$_4$ were composed of a pure single phase. Although, slight inclinations of residual α-Fe and Fe$_3$O$_4$ were indicated for the synthesized FeO as shown in Table 1, FeO was the predominant compound because the concentration of Fe$_3$O$_4$ was below 2.0 mass%. From these results, we could assume that the synthesized oxides were essentially composed of single oxide species.

The densities of the synthesized oxides of Fe$_2$O$_3$, Fe$_3$O$_4$, FeO and Fe$_2$SiO$_4$ were 4.69 g·cm$^{-3}$, 5.08 g·cm$^{-3}$, 6.27 g·cm$^{-3}$ and 4.08 g·cm$^{-3}$, respectively. Considering that
the densities of Fe₂O₃, Fe₃O₄, FeO and Fe₂SiO₄ noted in the literature are 5.27 g/cm³, 5.18 g/cm³, 5.70 g/cm³ and 4.34 g/cm³ respectively, the sintering density of our synthesized Fe₂O₃ was slightly low and that of the synthesized FeO was slightly high compared with the values available in the literature.

3.2 Hardness

The hardnesses of synthesized iron oxides at room- and high-temperatures are shown in Fig. 5. The hardnesses of all of the oxides decrease with increasing temperature, with the magnitude of the decrease occurring approximately in the following order: Fe₂SiO₄, Fe₂O₃, Fe₃O₄ and FeO. In particular, the hardnesses of Fe₂SiO₄ and Fe₂O₃ are remarkably high at room temperature, but are equivalent to the other oxides above 400°C. The hardness of FeO is lower than the other oxides in the range between room temperature and 1000°C. The hardness of Fe₂SiO₄ can not be exactly measured at 1000°C because the melting point of Fe₂SiO₄ is 1170°C and the material begins to soften at 1000°C.

In order to confirm the validity of these results, they were compared with the hardnesses of oxide scales formed on steels. The hardnesses of the synthesized iron oxides and of cross-sectional oxide scales on pure Fe and a Fe-3.0 mass%Si alloy are listed in Table 2. Variation of hardness of the synthesized oxides is similar to that of scales formed on steels. Furthermore, the order of magnitude of the hardness

Table 1 Concentration of oxide phase in FeO specimen (vol%).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Concentration (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>86.8</td>
</tr>
<tr>
<td>FeO</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 2 Comparison of Vickers hardness (GPa) of the respective iron oxide scales and the cross-sectional oxide scales on iron.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample form</th>
<th>Sintered specimen</th>
<th>Scale formed on iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>RT</td>
<td>1.67</td>
<td>3.50</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td>0.0436</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>RT</td>
<td>1.64</td>
<td>4.00</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td>0.0505</td>
<td>0.08</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>RT</td>
<td>3.27</td>
<td>6.70</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td>0.0734</td>
<td>0.53</td>
</tr>
<tr>
<td>Fe₂SiO₄</td>
<td>RT</td>
<td>3.29</td>
<td>5.50</td>
</tr>
<tr>
<td>1000°C</td>
<td></td>
<td>---</td>
<td>0.63</td>
</tr>
</tbody>
</table>
of the synthesized oxides is consistent with that formed on the steels. However, the hardness of Fe$_2$O$_3$ formed on the steel is much larger than synthesized Fe$_2$O$_3$ at 1000°C. It is considered that the hardness of Fe$_2$O$_3$ formed on the steel could not be measured precisely because its thickness is a few or several tens of μm. Therefore, it is concluded that the properties of synthesized iron oxides that had been fabricated with high purity and density corresponds to that of oxide scales formed on steels.

3.3 Thermal expansion coefficient

As shown in Fig. 6, the thermal expansion coefficients of all of the synthesised oxides increase with increasing temperature, with magnitudes approximately in the following ascending order: FeO, Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe$_2$SiO$_4$. In particular, FeO exhibits the highest thermal expansion coefficient in the temperature range below 400°C. The thermal expansion coefficient of FeO abruptly increases at 600–700°C. This phenomenon may be caused by a stabilization of FeO, because FeO is becomes stable above 570°C.

3.4 Thermal conductivity

The temperature dependence of the thermal conductivity of the synthesized iron oxides is shown in Fig. 7. The thermal conductivity is reduced approximately in the following ascending order: FeO, Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe$_2$SiO$_4$. A prominent feature is that FeO has the highest conductivity and Fe$_2$SiO$_4$ shows the lowest in the temperature range between room temperature and 1000°C. The following is also noteworthy. The thermal conductivity of Fe$_2$O$_3$ is the highest at RT, but changes remarkably smaller at high-temperature, while Fe$_2$SiO$_4$ exhibits extremely reduced thermal conductivity compared with FeO.

3.5 Influence of the physical properties of iron-oxide scales at high temperature on the surface properties of the Si-containing steel

It was shown in section 3.1–3.4 that the high-temperature physical properties, such as hardness, thermal expansion coefficient, and thermal conductivity, are significantly different for each oxide species.

The scale structure and oxidation behaviour on the Si-containing steel have been described in many literatures. On the Si-containing steel, inner-most layer consisting of FeO–Fe$_2$SiO$_4$ mixture is formed beneath the outer FeO layer. However, Fe$_2$SiO$_4$ in the inner-most layer, the amount of which increases as the Si content increases, suppresses the outward diffusion of Fe ions from steels and hence the inner diffusion of oxygen ions predominates in the oxide growth. Therefore, as the Si content increases, the composition of outer scale layer changes from FeO to Fe$_2$O$_3$ and Fe$_3$O$_4$. These results show that the fayalite (Fe$_2$SiO$_4$) affects the structure of the outer and inner scale layers on Si-containing steel.

In the following section, the influence of the fayalite (Fe$_2$SiO$_4$) formed on the high-Si steel on the scale adhesion at high temperature and surface properties are discussed on the basis of physical properties of iron-oxide scale.

3.5.1 The scale adhesion at high temperature of the Si-containing steel

The thermal stress generated by the difference in the thermal expansion coefficient between inner-most layer and steel causes a spalling and cracking of the scale during the hot-rolling process. As described above, the inner-most layer on the high-Si steel is mainly composed of Fe$_2$SiO$_4$. Therefore, the scale adhesion of high-Si steel is influenced by the difference in the thermal expansion coefficient between the Fe$_2$SiO$_4$ and steel.

As shown in Fig. 6, the thermal expansion coefficient of Fe$_2$SiO$_4$ increases as the temperature increases. The thermal expansion coefficient of Fe$_2$SiO$_4$ at 1000°C is nearly equal to that of Fe (14.6 × 10$^{-6}$/°C at 800°C). By contrast, the difference in the thermal expansion coefficient of FeO and Fe is large at 1000°C. It is also reported that the scale adhesion of Fe$_2$SiO$_4$ on steel at high temperature is greater than that of FeO. Therefore, the Fe$_2$SiO$_4$ might strongly adhere to the substrate steel and is not detached by the descaling process.
3.5.2 Surface property of the Si-containing steel after rolling

As described above, the Fe$_2$SiO$_4$ strongly adheres to the substrate steel, resulting in the deterioration of the descaling ability. The remaining Fe$_2$SiO$_4$ suppresses the outward diffusion of Fe ions from the steel and hence the inner diffusion of oxygen ions predominates in the oxide growth.\textsuperscript{11} It is also shown in Fig. 7 that the thermal conductivity of Fe$_2$SiO$_4$ is lower than that of other oxides. This result suggests that the remaining Fe$_2$SiO$_4$ on the substrate steel brings about a reduction in the cooling rate and a rising of the surface temperature. As a result, the thick Fe$_2$O$_3$, which is a higher order oxide, is formed as the outer-most scale layer on the Fe$_2$SiO$_4$-coated substrate steel. Therefore, the fracture and deformation behaviour of Fe$_2$O$_3$ may directly affect the surface properties of high-Si steel.

It is shown in Fig. 5 that the hardness of Fe$_2$O$_3$ is greater than that of the other oxides at 800°C. It is also reported that the ability to deform Fe$_2$O$_3$ is lower than that of FeO.\textsuperscript{7,8} As a result, the outer-most scale surface, mainly composed of Fe$_2$O$_3$, is crushed because of its hardness and stiffness at 800°C, corresponding to the hot-rolling temperature. Finely-ground Fe$_2$O$_3$ is often observed on high-Si steels, which frequently form red scales on their surfaces and degrade the surface property of the high-Si steel.

4. Conclusion

In the present study, we measured the high temperature physical properties of various iron oxides, constituents of oxide scales on steels, in order to clarify the dynamic behavior of the oxide scales that occur on practical steels.

We selected FeO, Fe$_3$O$_4$, Fe$_2$O$_3$ and Fe$_2$SiO$_4$ as typical oxide species that formed on Si-containing steels, and synthesized artificial specimens of each type of oxide. The specimens were composed of a single oxide species, and were used to measure the hardness, the thermal expansion coefficient and the thermal conductivity over the temperature range between RT and 1000°C. As a result, it was found that the physical properties of the synthesized iron oxides differed significantly from each other. The hardness of the synthesized iron oxides was identical with the naturally-formed corresponding iron oxide observed in cross-sectional oxide scales on practical steels. The experimental results from this study are confirmed as reflecting the physical properties of the oxide scales that form on practical steels.

Moreover, we discussed the relationship between the physical properties of oxides at high temperature and surface property after rolling the Si-containing steel. It is possible that Fe$_2$SiO$_4$ affects the high-temperature adhesion, surface temperature, and surface property of the Si-containing steel after rolling.

REFERENCES