Strain Development in Oxide Scale during Phase Transformation of FeO

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Development of a strain in oxide scale during phase transformation of FeO was investigated by a flexure method. A pure iron foil was oxidized on only one side, and the formed FeO was transformed at 400 or 500°C. *In-situ* observation of the bending behavior of the foil-formed specimen during the phase transformation of FeO was performed. Compressive strain develops in the scale in the early stage of the phase transformation, following which a significantly large expansion strain develops. Such a strain development corresponds to the two-step phase transformation of FeO and can be explained by the volume change of the scale considering the non-stoichiometry of FeO.

KEY WORDS: oxide scale; phase transformation; transformation strain; flexure method; non-stoichiometry.

1. Introduction

An oxide scale formed on iron in air comprises an outermost hematite layer (Fe_2O_3), an intermediate magnetite layer (Fe_3O_4), and a wustite layer (FeO) in contact with the iron. Among them, the FeO transforms to a mixture of Fe_3O_4 and Fe below 570°C, and the phase transformation behavior and the microstructure have been reported.^{1–9)} Because the phase transformation of FeO goes through the precipitation of Fe_3O_4 in FeO matrix and eutectoid transformation, considerable stress and strain can occur in the scale, which has a possibility to affect the mechanical properties or adhesiveness of the scale. Especially, since the low scale adhesiveness results in the scale defects and deteriorates the surface quality of the hot-rolled steel-sheet products, understanding the stress or strain development in the scale during the phase transformation is industrially important.

Several studies concerning stress and strain development in the oxide scale have been reported to date.^{10–15)} In the case of cooling of steel with an oxide scale from a high temperature, the difference of thermal expansion coefficients between the scale and substrate steel causes a stress in the scale, resulting in scale fracture or detachment.^{12,14)}

Oxide-growth stress has also been reported.^{10–13,15)} It occurs because of a difference in volume change between the oxide scale and substrate steel (Pilling–Bedworth ratio) and a lattice misfit at the scale/steel interface. Taniguchi *et al.*¹⁰⁾ measured the oxide-growth stress of iron using flexure method and observed that the specimens showed considerable bending. They attributed the bending of the specimen during oxidation to the volume changes accompanying phase reactions at the oxide interface and shrinkage of sub-

strate iron due to vacancy injection.

In contrast, stress or strain development during the phase transformation of FeO has not been studied. The scale adhesiveness can be affected by the stress or strain in the scale caused by the oxidation, cooling, and phase transformation. The volume change of phase transformation of FeO to Fe_3O_4 and Fe can be estimated to be significant and cannot be neglected. In this study, we investigated strain development during the phase transformation of FeO using the flexure method.

2. Experimental

The vacuum-melting pure iron (99.99%) was cut into a thin foil shape of 5 mm × 30 mm × 0.1 mm, following which surface polishing was performed. A 0.1- μm -thick SiO_2 film was sputtered on only one side of the pure iron specimen as an oxidation-resistant coating, allowing one-side oxidation of the specimen (an oxide scale grows on the uncoated side).

The one end of the specimen was rigidly fixed in an infrared heating furnace and its longitudinal direction is parallel to vertical direction. The specimen was heated to 750°C in nitrogen gas and oxidized in air for 10 min, enabling the growth of an oxide scale with approximately 30- μm thickness on only the uncoated side of the specimen. After oxidation, the specimen was cooled down to 400 or 500°C for 1 min and isothermally soaked at the temperature in nitrogen gas for 120 min for the phase transformation of FeO.

If the oxide scale expands or contracts compared with the iron substrate during the above heat treatment, the specimen will bend because the scale exists on only one side and the substrate iron is sufficiently thin to release the moment; scale contraction will bend the specimen to the direction of the scale side, whereas scale expansion will bend the

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specimen to the direction of iron (SiO_2 coating) side. The bending behavior of the specimen during heat treatment was observed using a video camera through the window of the furnace.

3. Results

The observed bending behavior in the case of 400°C soaking is shown in **Fig. 1**. The position of the specimen is indicated by down arrows. The SiO_2 coating is located at the left-hand side of the specimen and the oxide scale grows on the right-hand side. When the temperature reaches 750°C, the specimen is almost straight (Fig. 1(a)). At the end of the 10-min oxidation, the specimen shows subtle bending to the left-hand side (Fig. 1(b)). The bending amount slightly increases after cooling down to 400°C (Fig. 1(c)). When the 400°C soaking starts, the specimen bends to the right-hand side for approximately 6 min (Fig. 1(d)). The bending direction then changes to the left-hand side again and the specimen shows drastically large bending for the next 20 min (Fig. 1(e)). The specimen then maintains the position until the end of the 2-hr heat treatment at 400°C (Fig. 1(f)). In the case of soaking at 500°C, the bending behavior of the specimen is similar to the case of 400°C soaking, but its progress is relatively slow; when the 500°C soaking starts, the specimen slightly returns to the right-hand side for 18 min, and then bends to left-hand side for next 60 min. The bending amount is also smaller than that at 400°C soaking.

Figure 2 shows the form of the specimen after extraction from the cooled furnace. The curvature change with time is shown in **Fig. 3** along with the heat history. The developed strain in the scale is also shown in this figure as a second vertical axis, which is briefly calculated using the

elastic theory.

4. Discussion

The oxidation and cooling can develop a stress or strain in the scale. The expansion strain or compressive stress has been shown to arise in the scale during the scale growth.^{10,15)} In our results, the specimen slightly bends to the left-hand side corresponding to scale expansion during oxidation at 750°C, which can be explained by the oxide-growth stress. The increase in the expansion strain during cooling from 750°C to 400 or 500°C can be considered as a thermal stress. The linear expansion coefficient of the iron and scale are reported as 16.5×10^{-6} and $14 \times 10^{-6}/\text{K}$, respectively.¹⁶⁾ Therefore, when the iron/scale specimen is cooled

Fig. 2. Form of the specimen after extraction from the furnace.

Fig. 1. Observed form of the specimen during heat treatment in the case of 400°C soaking. The down arrows show the position of the specimen. The SiO_2 coating is located at the left-hand side of the specimen, and the scale grows on the right-hand side. (a) Before oxidation, (b) after 10 min oxidation at 750°C, (c) after cooling down to 400°C, (d) after 6 min soaking at 400°C, (e) after 14 min soaking at 400°C, (f) after 120 min soaking at 400°C.

down, the scale relatively expands because the contraction of iron substrate is larger than that of the scale.

In contrast, during soaking especially at 400°C, the strain becomes lower than zero (compressive strain) and then increases again, finally becoming a very large expansion strain. Such unusual strain development cannot be explained by the oxide-growth stress and thermal stress; during soaking at 400 or 500°C, the scale-growth stress cannot be developed because of the low temperature and non-oxidation

atmosphere, and the cooling stress also cannot be developed because of the isothermal soaking.

Thus, the phase-transformation strain of the scale causes unusual strain development. The phase transformation of FeO undergoes the following two-step reactions:²⁾

In the above reactions, x and y represent the non-stoichiometry parameter of FeO ($x < y$). At the first step of the phase transformation, reaction (1), the Fe concentration in FeO increases from x to y and Fe_3O_4 precipitates. Then, the Fe-rich FeO (Fe_yO) changes to a eutectoid structure of Fe and Fe_3O_4 in reaction (2). Previously, we investigated the microstructure change during the phase transformation of FeO. **Figure 4** shows typical examples of the microstructure change during the phase transformation at 400°C. This temperature corresponds to the nose temperature of TTT diagram of FeO.⁷⁾ Before soaking at 400°C, the scale comprises surface Fe_3O_4 layers (dark gray parts) and an FeO layer (light gray parts). After soaking at 400°C for 5 min, the surface Fe_3O_4 layer becomes thicker, corresponding to the precipitation of Fe_3O_4 as in reaction (1). After soaking for 30 min, the eutectoid structure comprising Fe and Fe_3O_4 with lamellar structure appears, which corresponds to reaction (2).

Now, we consider the volume change during the phase transformation of FeO. To evaluate the volume change, the volume of FeO considering non-stoichiometry is required. Foster *et al.*¹⁷⁾ reported that the lattice parameter of Fe_xO has an almost proportional relationship with the non-

Fig. 3. (a) Heat history and (b) curvature and the corresponding strain change of the specimen with time. The typical plots corresponding to Fig. 1 are pointed.

Fig. 4. Typical examples of cross-sectional SEM images of the transformed scale at 400°C. Dark gray parts, light gray parts, and white parts represent Fe_3O_4 , FeO, and Fe, respectively. (a) Before phase transformation (only oxidation), (b) after 5 min phase transformation, (c) after 30 min phase transformation, (d) enlarged image of enclosed area of (c) showing lamellar structure of Fe and Fe_3O_4 .

stoichiometry, and they are approximated by the following formula:

$$l = 0.458x + 3.88 \quad (3)$$

Here, x and l are the non-stoichiometry index and lattice parameter of Fe_xO , respectively. FeO shows NaCl structure, and the number of atoms per unit cell is 4; the volume per mol of Fe_xO V can be given by the following formula using the lattice parameter l and the Avogadro number Na :

$$V = l^3 Na / 4 \quad (4)$$

The density calculated from the above volume and the molecular weight are shown in **Fig. 5**. The calculated line is consistent with the reported values,^{18,19} which indicates the validity of formula (4).

The volume changes of FeO before and after the phase transformation can be calculated. In reaction (1), the volume of 1-mol Fe_xO is 11.88 cm^3 and the total volume of the right hand is 11.84 cm^3 ; the volume change is approximately -0.34% . The x and y values are 0.9 and 0.97, respectively, which were previously determined by high-temperature X-ray diffraction measurement,⁷⁾ and the volume per mol of Fe and Fe_3O_4 were referred to from the database. In reaction (2), the volume change can be similarly obtained as $+4.9\%$. The volume change through the phase transformation of FeO : $\text{Fe}_x\text{O} \rightarrow 1/4\text{Fe}_3\text{O}_4 + (x-3/4)\text{Fe}$ is $+3.1\%$. These volume changes during the phase transformation of FeO are

Fig. 5. Relationship between the calculated density of Fe_xO and non-stoichiometry index x . The line represents the calculated density in this study and the two plots are reference values.^{18,19)}

summarized in **Table 1**.

Thus, these volume changes can explain the unusual strain development observed in the experiment. The compressive strain in the early stage of soaking at 400 or 500°C corresponds to the decrease in the scale volume during the precipitation of Fe_3O_4 , as in reaction (1). The subsequent expansion strain corresponds to the increase in the scale volume at the eutectoid transformation, as in reaction (2). As the phase transformation of FeO almost completes in approximately 30 min as shown in **Fig. 4(c)**, the specimen maintains its position in the latter stage of soaking.

As previously reported,^{4,5,7)} the phase transformation of FeO at 500°C undergoes with slow rate compared with 400°C. This is consistent with the slow bending progress in the case of 500°C soaking. **Figure 6** shows typical scale structures before and after phase transformation of FeO at 500°C. The transformed scale consists of large volume fraction of Fe_3O_4 and small volume fraction of Fe precipitations.

Table 1. Volume change in the reactions of phase transformation of FeO . The non-stoichiometry index x and y are 0.9 and 0.97, respectively. The values of volume change were obtained by dividing total volume of the right-hand side by that of the left-hand side in each reaction.

$\text{Fe}_x\text{O} \rightarrow (4x-3)/(4y-3)\text{Fe}_y\text{O} + (y-x)/(4y-3)\text{Fe}_3\text{O}_4$			
	Fe_xO	Fe_yO	Fe_3O_4
Mole number (mol)	1	0.68	0.08
Volume (cm ³)	11.9	8.28	3.56
Volume change	-0.34%		
$\text{Fe}_y\text{O} \rightarrow (4y-3)/4\text{Fe} + 1/4\text{Fe}_3\text{O}_4$			
	Fe_yO	Fe	Fe_3O_4
Mole number (mol)	0.68	0.15	0.17
Volume (cm ³)	8.28	1.06	7.62
Volume change	+4.9%		
$\text{Fe}_x\text{O} \rightarrow 1/4\text{Fe}_3\text{O}_4 + (x-3/4)\text{Fe}$			
	Fe_xO	Fe_3O_4	Fe
Mole number (mol)	1	0.25	0.15
Volume (cm ³)	11.9	11.2	1.06
Volume change	+3.1%

Fig. 6. Typical examples of cross-sectional SEM images of before and after phase transformation of FeO at 500°C. (a) Before phase transformation (only oxidation), (b) after 120 min phase transformation.

In that case, the most part of FeO transforms with reaction (1), precipitation of Fe₃O₄ with volume shrinkage, and then the small part of FeO changes to Fe₃O₄ and Fe as reaction (2) with volume expansion. Thus, it is considered that the relatively small final strain at 500°C shown in our experiment is attributed to such a transformation behavior.

For the steel products with oxide scale on both the surfaces, the expansive volume change of the scale acts as a compressive stress because free expansion of the scale is not allowed by the substrate steel. The expansive strain of 0.17–0.26% obtained in this experiment is converted to a compressive stress of 380–620 MPa using the formula:²⁰⁾

$$\sigma = \frac{E_s t_s (t_s + t_f)}{6 R t_f} = \frac{E_s t_s}{3 t_f} \varepsilon \quad \text{..... (5)}$$

Here, E , t , and R are Young's modulus, thickness, and curvature radius, respectively, and index s and f indicate the substrate and oxide scale, respectively, and an isotropic phase transformation and no lattice correspondence are assumed.

The stress caused by the phase transformation of the order of 0.1% is too large to ignore in the evaluation of the total stress in the scale of steel products. The possible stress development in the scale is summarized in **Table 2**. The phase transformation stress is of the same order or larger than the growth stress and thermal stress. Therefore, the phase transformation stress should be considered for the evaluation of strain of the oxide scale. For example, Kobayashi *et al.*²¹⁾ reported that the transformed scale shows high adhesiveness, which has a possibility to be affected by the phase transformation stress.

The final strain shown in our experiment is up to 0.26%, which is smaller than the value estimated from volume change, 1.0%. This can be attributed to the larger bending rigidity of the substrate iron than that of the scale, which decreases the bending degree caused by the volume change of the scale. Therefore, it is difficult to have a quantitative

argument; however, this study experimentally clarifies that two types of strain develop in the scale during the phase transformation of FeO. The quantitative evaluation of total strain in the scale including transformation strain and its effect on the scale adhesiveness are required as a future work.

5. Conclusions

Strain development during the phase transformation of FeO is observed as a bending behavior in the flexure method. The results show that compressive and expansion strain develop in turn during the phase transformation of FeO, and the final strain reaches 0.26%, corresponding to a compressive stress of –620 MPa. Because the transformation strain is sufficiently large compared with the reported origins such as oxidation growth and thermal contraction, it should be considered for evaluating total strain or residual stress in the oxide scale.

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Table 2. Comparison of the estimated stress in the scale caused by phase transformation with growth stress and thermal stress.

	Phase transformation	Scale growth	Cooling ^{*)}
Stress (MPa)	–380~–620	–100 ¹⁰⁾ –300 ¹⁵⁾	–420

*) Assuming 750°C to 30°C.