Intergranular and Internal Oxidation during Hot-rolling Process in Ultra-low Carbon Steel

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1. Introduction

Recently, demand for high surface quality of steel sheet has become more intense. Many kinds of defects caused in hot-rolling process can be related to oxidation in a reheating furnace. For example, it has been reported that the root cause of a red scale defect was melting of eutectic compound of FeO/Fe₂SiO₄ during reheating at over 1446 K on Si-added steel sheet.¹⁻³) Since the melted eutectic compound forms complicated scale/substrate interface, the scale remains to cause the defect even after descaling.⁴) Uneven impact force distribution of descaling could accelerate heterogeneous red scale occurrence.⁴) A sliver-type scale defect originating from a surface crack or pinhole in a continuously cast slab has also been reported to be promoted by internal oxidation during reheating which increases hardness of the substrate surface and deteriorates hot ductility of the slab.⁴⁻⁵)

There are two types of oxidation occurring at subsurface of substrate; intergranular oxidation and internal oxidation. As for the intergranular oxidation, several permeation mechanisms have been reported. With nickel alloy, intergranular oxide may permeate into grain boundaries due to opening stress generated by intergranular oxide formation and resulting local volume increase.⁶⁻⁷) Voids concentrated in grain boundaries may also accelerate permeation of intergranular oxide by promoting oxygen transportation.⁷) With steel, melted eutectic compound of FeO/Fe₂SiO₄ may permeate preferentially into grain boundaries due to obstruction of oxidation by nickel segregation at the substrate surface.⁸⁻⁹) A liquid oxysulfide may also penetrate to substrate grain boundaries.¹⁰⁻¹¹) However, there have been few studies on kinetics of the intergranular oxidation.

Kinetics of internal oxidation has been investigated by several researchers.¹²⁻¹³) Wagner assumed that the formation of internal oxide is controlled by oxygen diffusion within substrate in the case of no external scale formation.¹⁴) Stott et al. considered oxygen diffusion around the interface between internal oxide and substrate in their calculation.¹⁵) With oxidation accompanied by external scale formation, it has been suggested that the permeation of internal oxide is determined by competition between external scale formation and internal oxidation.¹⁶) There is, however, no conclusive result to explain the internal oxidation with external scale formation.

The purpose of this study is to clarify oxidation behavior within subsurface of substrate during reheating process for hot-rolling. In particular, the effects of oxidation temperature, oxidation time and partial pressure of oxygen on the intergranular and internal oxidation are investigated in this paper. The generation mechanism and kinetics of the intergranular and internal oxidation are also discussed.

2. Experimental Procedure

The steel used in this investigation was commercially
produced interstitial free steel (IF-steel) slab in which solute carbon and nitrogen was scavenged by titanium and contained following impurities: 0.01 mass% Si, 0.2 mass%Mn–0.015 mass%P–0.01 mass%S–0.03 mass%sol. Al–0.02 mass%Ni–0.04 mass%Cr. Oxidation test specimens, 25×50×50 mm³, were cut from subsurface of the 230 mm thick slab and the surface was finished to 0.5 μm of average surface roughness, Ra. These specimens were heated at temperatures of 1423–1563 K in a N₂ atmosphere in an electric furnace. Subsequently, coke oven exhaust gas was introduced mixed with air to achieve a partial pressure of oxygen of 1–10%, and the specimens were held isothermally for 1 800–5 400 sec in this atmosphere. After oxidation, the specimens were quenched to preserve the interface between scale and substrate.

The thickness of oxidized specimens was measured after pickling to estimate scale loss of steel.

Cross sections of oxidized specimens were observed by an optical microscope to measure the permeation depth of intergranular oxides from the interface between scale and substrate and the thickness of internal oxidation layer extending beyond the furthest point of permeation by intergranular oxide. The permeation depth of intergranular oxides was measured in a range of 10 mm length at 50-power, and the thickness of internal oxidation layer was measured at 1000-power. Also, the intergranular and internal oxides were observed by Scanning Electron Microscope (SEM) and analyzed by Energy Dispersive X-ray Spectrometer (EDS).

In order to study the intergranular oxidation, austenite grains were observed at high temperature by a confocal laser microscope. The specimens were cut into 4.2×2 mm³ with 5 μm-Al₂O₃ surface finish. The specimens were heated in an infrared image furnace and held isothermally at temperatures of 1 423–1 623 K for 6 000 sec in a deoxidized argon gas atmosphere passed through heated magnesium ribbon. The image was obtained by Charge Coupled Device (CCD) and shown on Cathode Ray Tube (CRT). The resulting image was recorded on videotape during heating and isothermal holding.

3. Results

3.1. Effect of Oxidation Temperature, Time and Partial Pressure of Oxygen on the Formation of Intergranular and Internal Oxides

**Figure 1** shows the secondary electron image of a cross section of the specimen oxidized at 1 563 K for 5 400 sec in a 3% partial pressure of oxygen. Here, d was measured from the interface between scale and substrate, and ξ was measured from the furthest point of permeation by intergranular oxide. Both d and ξ are represented by average values. Total depth means the sum of d and ξ. As for the intergranular oxidation, the d was as small as 20 μm at 1 423 K, and as large as 70 μm at 1 473 K. The d decreased as oxidation temperature increased at above 1 473 K. As for the internal oxides, the ξ was almost zero at 1 423 K and increased up to 90 μm as oxidation temperature increased to 1 563 K. The total depth was 20 μm at 1 423 K and increased up to 140 μm as oxidation temperature increased to 1 563 K. The sharp increase in the intergranular oxidation depth at above 1 473 K may be attributed to melting of Fe–Si–O complex oxides.

**Figure 4** shows the effect of partial pressure of oxygen, P_O₂, on d and ξ for 5 400 sec oxidation at 1 503 K and 1 563 K. At 1 503 K, the effect of P_O₂ was slight. At 1 563 K, both d and ξ decreased as P_O₂ increased. In particular, the ξ decreased greatly from 90 to 45 μm as P_O₂ increased from 1 to 10%.

![Secondary electron image of a cross section of the specimen oxidized at 1 563 K for 5 400 sec in a 3% partial pressure of oxygen.](image)
Figure 5 shows the effect of oxidation time, \( t \), on \( d \) and \( \xi \) at 1 503 K and 1 563 K in 3% and 10% \( P_{O_2} \). As for the intergranular oxidation, the \( d \) increased as oxidation time increased. At the oxidation of 1 563 K in 3% \( P_{O_2} \), the increase in \( d \) was not significant. As for the internal oxidation, the \( \xi \) increased noticeably as oxidation time increased at 1 503 K. The \( \xi \) was less than 15 \( \mu m \) after 1 800 sec oxidation and was more than 45 \( \mu m \) after 5 400 sec oxidation at 1 503 K in 3% and 10% \( P_{O_2} \). At 1 563 K, the \( \xi \) increased greatly from 50 to 90 \( \mu m \) as oxidation time increased in 3% \( P_{O_2} \), and the increase in \( \xi \) was slight in 10% \( P_{O_2} \).
Figure 6 shows the relationship between the interval between intergranular oxidation, I, and the permeation depth, d. Here, I is represented by a mean value. The I decreased from 210 to 90 μm as d increased from 40 to 70 μm. The relationship between intergranular oxide generation and scale generation is illustrated in Fig. 7. With large scale generation, shallower intergranular oxidation is expected to disappear by being taken in the scale, therefore, the interval becomes large and the permeation depth becomes small as shown in Fig. 6.

3.2 Effect of Oxidation Conditions on Scale Growth

The intergranular oxidation depth may be influenced by scale growth as shown in Fig. 7. Next, we estimate oxidation loss of substrate, X. Figure 8 shows the effect of oxidation time, t, and temperature, T, on X in a 3% partial pressure of oxygen. X increased by increasing t and T. The rate of increase of X decreased by increasing t. Figure 9 shows the effect of partial pressure of oxygen, P_{O_2}, and T on X at 5400 sec oxidation. X increased by increasing P_{O_2} and T. The increase ratio of X by increasing P_{O_2} was very small.

As it is well known, scale grows on the scale surface. Here, iron ions are provided at the scale surface by diffusion within the scale layer. The scale growth rate is in proportion to the concentration gradient of iron ions within the scale layer which is in inverse proportion to the scale thickness, and the oxidation loss rate of substrate can be estimated.
pressed as follows,\(^2\)

\[ \frac{dX}{dt} = A/X \] ..........................(1)

Here, \( A \) is a constant. The Eq. (1) is written as follows.

\[ X = (2A)^{1/2} \cdot t^{1/2} \] ..........................(2)

Since \( A \) can be expressed by the Arrhenius relationship, the oxidation loss of substrate is expressed as follows,

\[ X = A' \left( \exp\left( \frac{-Q}{RT} \right) \right)^{1/2} \] ..........................(3)

Here, \( A' \) is a constant, \( Q \) is activation energy and \( R \) is gas constant.

The effect of partial pressure of oxygen on scale growth rate is expressed below. The reaction between FeO and oxygen gas is written as follows,

\[ \frac{1}{2} \text{O}_2 = \text{FEO} + \text{Fe}^{2+} + 2h \] ..........................(4)

Here, \( \text{Fe}^{2+} \) is Fe\(^{2+} \) vacancy and \( h \) is electron vacancy. Concentration of \( \text{Fe}^{2+} \) is so small that we can adapt the mass action law to Eq. (4) as ideal solution,

\[ \text{CFe}^{2+} \cdot \text{Ch}^2 = K \cdot P_{\text{O}_2}^{1/2} \] ..........................(5)

Here, \( \text{CFe}^{2+} \) is concentration of \( \text{Fe}^{2+} \) vacancies, \( \text{Ch} \) is concentration of electron vacancies and \( K \) is an equilibrium constant. On the basis of electric neutrality,

\[ \text{Ch} = 2 \text{CFe}^{2+} \] ..........................(6)

Therefore,

\[ \text{CFe}^{2+} = (K/4)^{1/3} \cdot P_{\text{O}_2}^{1/6} \] ..........................(7)

\( \text{Fe}^{2+} \) diffuses by way of \( \text{Fe}^{2+} \) vacancies within the scale layer, so the scale growth rate is in proportion to the concentration of \( \text{Fe}^{2+} \), and the oxidation loss of substrate can be expressed as follows,

\[ X = A'' \exp\left( \frac{-Q}{RT} \right) \cdot t^{1/2} \cdot P_{\text{O}_2}^{1/6} \] ..........................(8)

Here, \( A'' \) is a constant.

**Figure 10** shows the data for 5400 sec oxidation in a 3% partial pressure of oxygen plotted as \( \ln X \) vs. \( T^{-1} \) in the temperature range of 1473–1563 K. The \( \ln X \) decreased linearly with increasing \( T^{-1} \), and the effect of oxidation temperature on oxidation loss of substrate is written as follows.

\[ \ln X = -1.63 \cdot 10^4 \cdot T^{-1} + 10.4 \] ..........................(9)

From the Eqs. (8) and (9), \( Q \) is calculated to be 1.35\(^{\times}\)10\(^3\) J/mol. So far, it has been reported that the activation energy of FeO formation is 1.25\(^{\times}\)10\(^5\) J/mol in the temperature range of 973–1273 K,\(^2\) so the above value of \( Q \) in this study is reasonable.

**Figure 11** shows the data for 5400 sec oxidation plotted as \( X \) vs. \( \exp\left( -1.63 \cdot 10^4 \cdot T^{-1} \right) \cdot P_{\text{O}_2}^{1/6} \) in the temperature range of 1473–1563 K and in the partial pressure of oxygen range of 1–10%. The \( X \) increased linearly with increasing the value of \( \exp\left( -1.63 \cdot 10^4 \cdot T^{-1} \right) \cdot P_{\text{O}_2}^{1/6} \), and the oxidation loss of substrate is written as follows.

\[ X = 3.48 \cdot 10^2 \cdot \exp\left( -1.63 \cdot 10^4 \cdot T^{-1} \right) \cdot P_{\text{O}_2}^{1/6} \cdot t^{1/2} \] ..........................(11)
3.3. Direct Observation of Grain Boundary of Austenite

In this study, the maximum interval between the intergranular oxidation was 210 μm. Considering the grain growth of the substrate at high temperature, the value of 210 μm seems to be too small for the grain size of austenite. Figure 13 shows the CCD images of the polished steel surface during heating and holding at 1623 K in a non-oxidizing atmosphere. In the ferrite region, the grain boundary began to appear slightly, and just after transformation from ferrite to austenite, the boundary appeared clearly. The grain size ranged from 100 to 300 μm, and these grains did not change during holding for 6000 sec at 1623 K. After 600 sec holding, a new grain shown by an arrow in this figure began to appear. This new grain was so large that we could not observe the whole figure in the observation field of about 1×1 mm². During holding at 1623 K, this grain boundary moved gradually, and the displacement was about 150 μm for 5400 sec. As same as at 1623 K, the grains which appeared visually just after transformation did not change during holding in the temperature range of 1423–1563 K. At temperatures below 1473 K, however, the new grain was not observed during holding.

Figure 14 shows the optical image of as-cast steel etched by nital solution. The ferrite grain size ranged from 100 to 300 μm. These grain sizes were almost the same as those observed at high temperature by CCD. The grains observed clearly just after transformation to austenite may be the sites of ferrite grains, and we call them “quasi-austenite”. The large grains which appeared during holding at high temperature may be the true austenite grains. Since the maximum interval between intergranular oxidation was 210 μm, oxides may permeate into the quasi-austenite grain boundary. With the true austenite grains, the grain boundary moves during holding at high temperature, and the permeation of oxides is thought to be difficult.

4. Discussion

4.1. Generation Mechanism of Intergranular Oxidation

It is expected that the intergranular oxidation proceeds due to the permeation of melted Fe–Si–O complex oxides which are developed significantly at temperatures over 1446 K and accelerate oxygen ion supply to the reaction front. Scale grows simultaneously on the substrate during the growth of intergranular oxides, so the observed intergranular oxidation depth is considered to be the depth subtracted by the oxidation loss of substrate as shown in Fig. 15. That is, the true depth should be estimated by taking the oxidation loss of substrate into consideration.

Next, we estimate the true maximum depth of intergranular oxidation. During oxidation at 1503 K in a 10% partial
pressure of oxygen, the observed maximum depth, \(d_{\text{max}}\), for 1800, 3600 and 5400 sec oxidation was 80, 100 and 120 \(\text{m}\) respectively. The oxidation loss of substrate in the time range from \(t_A\) to \(t\), \(X_A\), is calculated from the Eq. (11) as follows.

\[
X_A = 3.48 \times 10^5 \cdot \exp(-1.63 \times 10^4 \cdot T^{-1}) \cdot P_{O_2}^{1/6} \cdot (t^{1/2} - t_A^{1/2})
\] ................................................(12)

Figure 16 shows the data plotted as \((d_{\text{max}}+X_A)\) vs. \((t_A-t)\) at 1503 K in 10% \(P_{O_2}\).

Figure 16. Relationship between \((d_{\text{max}}+X_A)\) and \((t_A-t)\) at 1503 K in 10% \(P_{O_2}\).

\[d_{\text{max}} = 150 - 3.48 \times 10^5 \cdot \exp(-1.63 \times 10^4 \cdot T^{-1}) \cdot P_{O_2}^{1/6} \cdot (t^{1/2} - (t - 500)^{1/2})
\] ................................................(13)

Figure 17 shows the relationship between the calculated \(d_{\text{max}}\) and the measured \(d_{\text{max}}\) in the temperature range of 1473–1563 K, for the oxidation time range of 1800–5400 sec and in the partial pressure of oxygen range of 1 to 10%. The calculated \(d_{\text{max}}\) was consistent with the measured \(d_{\text{max}}\).

The intergranular oxides are thought to repeat the process of permeation and disappearance as increasing amount of oxidation loss of substrate. When the intergranular oxides of \(d_{\text{max}}\) disappear in the time range from \(t_B\) to \(t\), the average depth of intergranular oxidation, \(d\), is estimated as follows.

\[d = \int_t^{t_B} X_A \partial t_A \quad \text{................................................}(14)\]

Here, the relation between \(d_{\text{max}}\) and \(t_B\) is expressed as follows.

\[d = \frac{1}{(t - t_B)} \int_0^{t_B} X_A \partial t_A \quad \text{................................................}(15)\]

From the Eqs. (14) and (15), \(d\) is expressed as follows,

\[d = \frac{1}{(t - t_B)} \int_0^{t_B} X_A \partial t_A \quad \text{................................................}(16)\]

we assume \(t_B \gg 0\) and \(t_B \approx t_B\).

\[d \approx 1/2 \cdot d_{\text{max}} \quad \text{................................................}(17)\]

Figure 18 shows the relationship between the calculated and measured value of \(d\) in the temperature range of 1473–1563 K, for the oxidation time range of 1800–5400 sec and in the partial pressure of oxygen range of 1–10%. The calculated value of \(d\) was consistent with the measured value.

The permeation of the intergranular oxides was promoted with increasing oxidation time and with decreasing oxidation temperature and partial pressure of oxygen. As shown above, these behaviors can be understood from the restraint of the oxidation loss rate of substrate.

4.2. Generation Rate of Internal Oxides

The generation kinetics of the internal oxidation layer is expressed by adapting a quasi-stationary state approximation to a plane sample of Fe–A system.\(^{22}\) Here, we assume that partial pressure of oxygen is too small to oxidize Fe, but enough to oxidize alloy element A. Furthermore, we assume that solute oxygen concentration changes linearly within the internal oxidation layer. Oxygen flux in the internal oxidation layer, \(J\), is expressed by Fick’s first law as fol-
follows,

$$J = \frac{\partial m}{\partial t} = D_O \cdot N_O / \xi \quad \cdots \quad (18)$$

here, $m$ is atomic fraction of oxygen in the internal oxidation layer, $D_O$ is diffusivity of oxygen in austenite and $N_O$ is atomic fraction of dissolved oxygen at the interface between scale and substrate. Also, $m$ is expressed as follows,

$$m = N_A \cdot v \cdot \xi \quad \cdots \quad (19)$$

here, $N_A$ is atomic fraction of solute metal of A in Fe and $v$ is the number of oxygen ions per A ion in a solute metal oxide of AO$_n$. From the Eq. (19),

$$\frac{\partial m}{\partial t} = N_A \cdot v \cdot \frac{\partial \xi}{\partial t} \quad \cdots \quad (20)$$

From the Eqs. (18) and (20),

$$\xi = \left( C \cdot N_O \cdot t_i \right)^{1/2} \quad \cdots \quad (21)$$

here, $C$ is a constant of $2/(v \times N_A)$ and $t_i$ is the generation time of internal oxides. In this study, $t_i$ is considered to be the time in which the intergranular oxidation depth changes from maximum depth to average one. The generation time of internal oxides, $t_i$, is expressed as follows.

$$t_i = (t-t_0) / 2 \quad \cdots \quad (22)$$

$D_O$ is expressed as follows.\(^{23)\}

$$D_O = 2.14 \times 10^{-8} \cdot \exp(-8840 \cdot T^{-1}) \quad \cdots \quad (23)$$

$t_i$ is expressed from the Eqs. (15) and (22) as follows.

$$t_i = \frac{1}{2} \left( t - (t_0 - d_{\text{max}} / \left( 3.48 \times 10^4 \cdot T^{-1} \cdot P_{O_2}^{1/6} \right) \right) \quad \cdots \quad (24)$$

Next we evaluate $N_O$. \textbf{Figure 19} shows the data in a 3% partial pressure of oxygen plotted as $\xi$ vs. $(D_O \cdot t_i)^{1/2}$. The gradient, $g$, apparently depended on the temperature. From the Eq. (21),

$$N_O = g(T)^2 / C \quad \cdots \quad (25)$$

here, $N_O$ is thought to depend on the diffusion of oxygen and has the Arrhenius relationship. \textbf{Figure 20} shows the data in 3% $P_{O_2}$ plotted as $\ln(g^2)$ vs. $T^{-1}$. The gradient of this figure, $N_O$, is expressed as follows,

$$N_O = \exp(29.9) \cdot \exp(-67500 \cdot T^{-1}) / C \quad \cdots \quad (26)$$

The $\xi$ can be calculated from the Eqs. (21), (23), (24) and (26) in 3% $P_{O_2}$. As for the effect of partial pressure of oxygen, \textbf{Figure 21} shows the relationship between the calculated and measured value of $\xi$ in the temperature range of 1473–1563 K, for the oxidation time range of 1800–5400 sec and in the partial pressure of oxygen range of 1–10%. The calculated value of $\xi$ was consistent with the measured value irrespec-
The depth of the internal oxidation was promoted with increasing oxidation time and temperature and with decreasing partial pressure of oxygen. As shown above, these behaviors can be understood from increases in the diffusion rate of oxygen and the diffusion time.

Figure 22 shows the effect of $T$ and $t$ on the total depth, $d + \xi$, in a 3% partial pressure of oxygen. Figure 23 shows the effect of $T$ and $P_{O_2}$ on $d + \xi$ at 1503 K. Here, lines show the calculated value, and the numbers in circles show the measured value. The calculated value of $d + \xi$ was consistent with the measured value. We can express the increase of $d + \xi$ with increasing $T$ and $t$, and decreasing $P_{O_2}$ by theoretical calculation.

5. Conclusions

The effects of oxidation temperature, oxidation time and partial pressure of oxygen on the intergranular and internal oxides permeation into the substrate were studied and the following conclusions were obtained.

1) The intergranular oxidation depth significantly increased at 1473 K because of melting of Fe–Si–O complex oxides and decreased with increasing oxidation temperature at above 1473 K.

2) The internal oxides formed underneath the scale and around the intergranular oxides. The thickness of internal oxidation layer extending beyond the furthest point of permeation by intergranular oxide increased with increasing oxidation temperature.

3) The intergranular and internal oxidation was accelerated by increasing oxidation time and by decreasing partial pressure of oxygen.

4) The size of quasi-austenite grains considered sites of ferrite grains were found to be close to the maximum interval between intergranular oxidation. A repeated sequence of oxide permeation into the quasi-austenite grain boundary and disappearance by oxidation loss of substrate may be a possible oxidation process.

5) The intergranular oxidation depth and the thickness of internal oxidation layer can be calculated by using the oxidation loss rate of substrate and the oxygen diffusion rate in austenite.

6) The intergranular oxidation behavior can be understood as related to restraint of the oxidation loss rate of substrate. The internal oxides can be understood as related to increases in the diffusion rate of oxygen and the diffusion time.

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