Calculations of Internal Oxidation Rate Equations and Boundary Conditions between Internal and External Oxidation in Silicon Containing Steels

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The rate constants for internal oxidation of Si containing steels (Fe-Si alloys) at 850 °C were calculated in order to clarify the formation mechanism of fayalite scale, which can form as a “sub-scale” in Si containing steels. The diffusion coefficient of oxygen in the oxide layer, $D_O$, and the oxygen concentration at specimen surface, $N_O(s)$, which are constituents of the internal oxidation rate constant, $(2D_O N_B^0/N_B^{0\infty})$, were calculated under various oxidation conditions, and the rate equation for the internal oxide layer was derived. Comparing the calculated and the measured values of $(2D_O N_B^0/N_B^{0\infty})$, we confirmed that the rate equation determined for the internal oxide layer was reasonable. The conditions at the boundary between internal to external oxidation of Si containing steels (Fe-Si alloys) at 850 °C were also calculated by substituting the calculated values of $D_O$ and $N_O(s)$ at the boundary into the rate equation. [doi:10.2320/matertrans.M2009256]

(Received July 24, 2009; Accepted December 4, 2009; Published January 27, 2010)

Keywords: internal-oxidation, fayalite, scale, silicon containing steel, high-temperature oxidation, transition from internal to external oxidation, rate constant, oxygen permeability

1. Introduction

The iron oxide scale that forms on billets and slabs of hot-rolled steel is usually removed using a hydraulic descaling process. However, any residual primary or secondary scale that forms after the descaling process can remain on the surface of the final product through subsequent hot- and cold-working steps. This residual scale greatly influences the surface quality of the steel by modifying its mechanical properties. Deformation, fracture and spalling of the steel can occur. Hence, it is of great importance to understand the physical and mechanical properties of iron oxide scale in order to control its formation and properties, and ultimately to improve the surface quality of the steel.

The composition of the oxide scale that forms on steel is principally $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, and $\text{FeO}$, which forms in lamellar strata from the substrate towards the outer layer. In the case of Si-containing steels, which are widely used in the manufacture of automobile bodies and frames in the form of high-tensile steel sheets, fayalite scale ($\text{Fe}_2\text{SiO}_4$) can form as a “sub-scale” beneath the external wustite ($\text{FeO}$) layer. Since the bottommost layer of scale is fayalite scale, the properties and formation mechanism of this need to be clarified in order to optimize the properties of iron oxide scale on Si containing steels.\(^1\)\(^-\)\(^8\)

This paper focuses on internal oxidation, which is the first stage of sub-scale formation, and on calculating the internal oxidation rate constants of Si containing steels in order to clarify the formation mechanism of fayalite scale. The validity of their calculations was confirmed by comparing the results with experimental values. Furthermore, the conditions at the boundary between internal to external oxidation were also calculated on the basis of the kinetics theory of internal oxidation.

2. Internal Oxidation Kinetics

2.1 Internal oxidation rate

Internal oxidation can be defined as the formation of a dispersed metal oxide layer near to the surface of an alloy. This layer consists of very fine metal oxide particles composed of one or more alloy elements and oxygen. In the case of Si containing steels (Fe-Si alloys), because the affinity for oxygen of Si is higher than that of Fe, the Si oxidizes preferentially and very fine $\text{SiO}_2$ particles become dispersed near the surface forming an internal oxide layer.

Rate equations for the internal oxidation of flat specimens have been derived using the quasi-steady state approximation. Figure 1 shows approximate concentration profiles for oxygen and Si in the internal oxide layer of Fe-Si alloys.

Fig. 1 Approximate concentration profiles for oxygen and silicon in the internal-oxide layer of Fe-Si alloys.
depth, the flux of oxygen permeating into the internal oxidation layer, \( J_O \), can be expressed by

\[
J_O = \frac{D_O N_O^{(s)}}{V_m x}
\]

where \( D_O \) is the diffusion coefficient of oxygen in the oxide layer, \( N_O^{(s)} \) is the oxygen concentration at the specimen surface, \( V_m \) is the molar volume of the A-B binary alloy, and \( x \) is the thickness of the internal oxide layer. \( J_O \) can be also expressed as the following equation because the amount of oxygen accumulated at the interface of the internal oxide layer and the A-B alloy (Fe-Si alloy) is equivalent to \( J_O \).

\[
J_O = \frac{D_O N_O^{(s)}}{V_m x} = (N_B^{(O)}/V_m) (dx/dt)
\]  

(2)

By transposing and integrating eq. (2), we obtain a rate equation for internal oxidation in the absence of an external oxide layer as follows

\[
x = \left(2D_O N_O^{(s)}/N_B^{(O)n}\right)^{1/2} \tau^{1/2}
\]  

(3)

where \( N_B^{(O)} \) is the initial concentration of the alloy element, B (the initial Si concentration of the Fe-Si alloy) in the oxide layer, and \( n \) is the atomic ratio of oxygen to B (Si) in the oxide. From eq. (3), the thickness of the internal oxidation zone, \( x \), is estimated to be a parabolic function of time, \( t \). Substituting values for the constants \( D_O, N_O^{(s)}, N_B^{(O)} \) and \( n \) in the internal oxidation rate constant, \( (2D_O N_O^{(s)}/N_B^{(O)n}) \), we obtain the rate equation for internal oxidation of an A-B binary alloy (Fe-Si binary alloy).

### 2.2 Transition from internal to external oxidation

As shown in eq. (3), the internal oxidation rate decreases with decreasing \( N_O^{(s)} \) or increasing \( N_B^{(O)} \). Above a critical concentration of \( N_O^{(s)} \), continuous scale layers composed of \( BO_n \) form on A-B binary alloys, and internal oxidation is suppressed. The transition from internal to external oxidation begins to occur in this stage.

Wagner’s theory for the transition from internal to external oxidation is developed as follows.\(^9\) The ratio of \( N_O^{(s)} \) to \( N_B^{(O)} \) is expressed by the following equation

\[
N_O^{(s)}/N_B^{(O)n} = \exp(\gamma^2) \text{erf}(\gamma)/\theta^{1/2} \exp(\gamma^2 \theta) \text{erfc}(\gamma\theta^{1/2})
\]  

(4)

where \( n \) is the atomic ratio of oxygen to B (Si) in the oxide, \( \theta \) is the ratio of the diffusion coefficient of oxygen, \( D_O \), to the diffusion coefficient of B (Si), \( D_B \), and \( \gamma \) is a dimensionless parameter defined by \( x = 2\gamma(D_B t)^{1/2} \).

In the case of low Si alloys (i.e. \( N_B^{(O)} \) is small),

\[
\gamma \ll 1 \ \text{and} \ \gamma\theta^{1/2} \gg 1, \ D_B/D_O < N_O^{(s)}/N_B^{(O)} < 1,
\]

the internal oxidation rate is expressed by eq. (3).

On the other hand, in case of high Si alloys (i.e. \( N_B^{(O)} \) is large),

\[
\gamma \ll 1 \ \text{and} \ \gamma\theta^{1/2} \ll 1, \ N_O^{(s)}/N_B^{(O)} < D_B/D_O < 1
\]

whereupon eq. (3) becomes

\[
x = (\pi^{1/2}D_O N_O^{(s)}/N_B^{(O)n} D_B^{1/2} n)^{1/2}
\]  

(5)

In this case, B concentrates as \( BO_n \) in the oxide layer, and the molar concentration, \( f \), of \( BO_n \) is given by

\[
f/N_B^{(O)} = 2nN_B^{(O)}/\pi N_O^{(s)}/D_O
\]  

(6)

Furthermore, the volume fraction of \( BO_n \), \( g^{*} \), can be expressed as

\[
g^{*} = f(V_{OX}/V)
\]  

(7)

where \( V \) is the molar volume of the A-B alloy and \( V_{OX} \) is the molar volume of \( BO_n \).

If the value of \( g^{*} \) exceeds the critical value of 0.3, the internal oxidation begins to change to external oxidation.\(^10\)

Substituting eq. (7) into eq. (6), the concentration of the alloy element, B (Si), at which external oxidation begins to occur can be found and is given by

\[
N_B^{(O)} \geq (\pi g^{*} N_O^{(s)}/D_O)/2nD_B V_{OX}^{1/2}
\]  

(8)

### 2.3 Boundary conditions between internal and external oxidation

If the internal diffusion rate of oxygen is higher than the external diffusion rate of the alloy element, B (Si), internal oxidation occurs, and if internal diffusion rate of oxygen is lower or \( N_B^{(O)} \) is higher, the external oxidation is disrupted by internal oxidation. Equation (9) is obtained by rearranging eq. (8).

\[
N_O^{(s)} = 2n(N_B^{(O)})^2 V_{OX} D_B/\pi g^{*} V D_O
\]  

(9)

\( N_O^{(s)} \) seems to follow Sievert’s law depending on temperature and is expressed as eq. (10).

\[
N_O^{(s)} = A(T) P_{O_2}^{1/2}
\]  

(10)

where \( A(T) \) is the function fixed by specifying temperature. The boundary conditions between internal and external oxidation can be obtained by combining eqs. (9) and (10). The most appropriate \( g^{*} \) value is reported to be 0.3.\(^10\)

### 3. Experimental Procedure

Ingots of Fe-Si alloy were prepared using vacuum induction furnace. The chemical compositions of these alloys are shown in Table 1. The ingots were soaked at 1100°C for 10 h, hot-forged at 1100°C for 2 h, hot-rolled at 1100°C for 1.5 h, and descaled by sand blasting. Cylindrical samples with a diameter of 6 mm and height of 10 mm were prepared for use in the oxidation experiments. The sides of the specimens were polished with emery paper and finished by buffing. Each specimen was cleaned ultrasonically in acetone and ethanol before being oxidized.

Internal oxidation of Fe-Si alloys occurs below the equilibrium oxygen pressure of Fe/FeO (2.76 \times 10^{-13} Pa at 850°C). The tests were conducted under a fixed partial oxygen pressure at 850°C and the partial oxygen pressure was controlled by using \( N_2-3\%H_2 \) gas with the dew point.

### Table 1 Chemical compositions of Si containing steels. (mass%)

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-0.2 mass%Si</td>
<td>0.09</td>
<td>0.20</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>0.0023</td>
</tr>
<tr>
<td>Fe-0.5 mass%Si</td>
<td>0.10</td>
<td>0.50</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>0.0006</td>
</tr>
<tr>
<td>Fe-1.0 mass%Si</td>
<td>0.11</td>
<td>1.00</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>0.0031</td>
</tr>
<tr>
<td>Fe-2.0 mass%Si</td>
<td>0.10</td>
<td>2.01</td>
<td>&lt;0.01</td>
<td>&lt;0.03</td>
<td>&lt;0.005</td>
<td>0.0018</td>
</tr>
</tbody>
</table>
The oxidised cylindrical specimens were mounted and sectioned perpendicular to the cylinder axis, and the exposed sections were polished to a mirror finish with abrasive paper (#220–#1500) and alumina paste. The depth of internal oxidation was measured using a SEM.

4. Results and Discussion

4.1 Calculation of internal oxidation rate constants

Whereas the values of $N_0^{(i)}$ and $n$ are known, the values of $D_0$ and $N_0^{(i)}$ are unknown, so the most appropriate values were substituted in the internal oxidation rate constant, $(2D_0N_0^{(i)}/N_B^{(0)2}n)$, to obtain the most accurate internal oxidation rates. Takeda et al. reported the following equation for $D_0$ by measuring the diffusion coefficients of oxygen in Fe-0.06–90.274 mass%Si alloys. In this study, the value of $D_0$ was obtained by using eq. (11).

$$D_0 = 2.91 \times 10^{-7} \exp(-89.5 \text{ (kJ/mol)}/RT) \text{ (m}^2/\text{s}) \quad (11)$$

Figure 2 shows SEM images of internally oxidized Fe-0.2 mass%Si alloy specimens oxidized for 10 min at 850°C in fixed oxygen partial pressures. The internal oxide layers, in which very fine SiO$_2$ particles are dispersed, can be observed near the surfaces of specimens. The thickness of these internal oxide layers increases with increasing oxygen partial pressure. From the results, it is estimated that $N_0^{(i)}$ increases with increasing oxygen partial pressure.

The equation of $N_0^{(i)}$ is set up as follows. The solubility of oxygen in Fe seems to follow Sievert’s law depending on temperature and is expressed as eq. (10). Takeda et al. evaluated $N_0^{(i)}$ on the basis of thermodynamic data and reported that the temperature dependence of $N_0^{(i)}$ under the equilibrium oxygen pressure with Fe and FeO is shown to be given by eq. (12). Substituting the equilibrium oxygen pressure with Fe and FeO given in Table 2 for $P_{O_2}$ in eq. (10), and combining eqs. (10) and (12), an expression for $A(T)$ can be obtained. This is given in eq. (13).

$$N_0^{(i)} = 0.381 \exp[-104 \text{ (kJ/mol)}/RT] \quad (12)$$

$$A(T) = 9.67 \times 10^{-5} \exp[161.95 \text{ (kJ/mol)}/RT] \quad (13)$$

4.2 Comparison of calculated values with experimental values for internal oxidation rate

Figures 3 to 6 show SEM images of internally oxidized Fe-0.2 mass%Si alloy and Fe-0.5 mass%Si alloy specimens oxidized at 850°C in oxygen partial pressures of $7.61 \times 10^{-14}$Pa and $2.76 \times 10^{-13}$Pa. Very fine SiO$_2$ particles dispersed in the internal oxide layers are observed near the surfaces in all cases. The thickness of the internal oxide layer increases parabolically with increasing oxidation time.

4.3 Comparison of calculated values with experimental values for internal oxidation rate

Figures 7 to 10 show the internal oxidation rates in Fe-Si alloys. The calculated rates are also shown in Figs. 7 to 10.
Fig. 3  SEM images of internally oxidized Fe-0.2 mass%Si alloy specimens oxidized at 850°C for (a) 10 min, (b) 30 min and (c) 60 min in oxygen partial pressures of $P_{O_2} = 7.61 \times 10^{-14}$ Pa.

Fig. 4  SEM images of internally oxidized Fe-0.5 mass%Si alloy specimens oxidized at 850°C for (a) 10 min, (b) 30 min and (c) 60 min in oxygen partial pressures of $P_{O_2} = 7.61 \times 10^{-14}$ Pa.

Fig. 5  SEM images of internally oxidized Fe-0.2 mass%Si alloy specimens oxidized at 850°C for (a) 10 min, (b) 30 min and (c) 60 min in oxygen partial pressures of $P_{O_2} = 2.76 \times 10^{-13}$ Pa.

Fig. 6  SEM images of internally oxidized Fe-0.5 mass%Si alloy specimens oxidized at 850°C for (a) 10 min, (b) 30 min and (c) 60 min in oxygen partial pressures of $P_{O_2} = 2.76 \times 10^{-13}$ Pa.
Close agreement between the experimental and calculated values is obtained for both Fe-0.2 mass%Si alloy and Fe-0.5 mass%Si alloy. From these results, it is concluded that the calculation of the internal oxidation rate constant, \( \frac{N_{O}}{B(O)^{n}} \), using eqs. (10), (11) and (13) is valid, and the following values of \( D_{O} \) and \( N_{O}(s) \) are appropriate for internal oxidation at 850°C:

\[
D_{O} = 1.99 \times 10^{-11} \text{ (m}^{2}/\text{s}) \\
N_{O}(s) = 3.32 \times 10^{3} \text{ (}P_{O}/P_{O_{2}})^{1/2}
\]

### 4.3 Calculation of boundary conditions between internal and external oxidation

As described in the section 2.3, the boundary conditions between internal and external oxidation can be calculated by solving eqs. (9) and (10) simultaneously. The boundary conditions at 850°C are calculated using the two parameters of \( N_{B(O)} \) and \( P_{O_{2}} \). The following values of the atomic ratio of oxygen to Si, \( n \), the molar volume of SiO\(_2\), \( V_{OX} \), the diffusion coefficient of Si in Fe, \( D_{X} \), the value of \( g^{*} \) and the molar volume of Fe, \( V_{Fe} \), were used in this calculation: \( n = 2 \), \( V_{OX} = 2.311 \times 10^{-5} \text{ m}^{3}/\text{mol} \), \( D_{X} = 4.28 \times 10^{-15} \text{ m}^{2}/\text{s} \), \( g^{*} = 0.3 \), \( V_{Fe} = 7.096 \times 10^{-6} \text{ m}^{3}/\text{mol} \).

The calculated boundary conditions between internal and external oxidation in Fe-Si alloys at 850°C are shown in Fig. 11. The oxygen partial pressure is plotted on the ordinate and the composition of the Fe-Si alloy is plotted.
on the abscissa. The range of oxygen partial pressure in which internal oxidation occurs decreases with increasing Si concentration, and vanishes for Si concentrations of 1.0 mass% or more.

Figure 12 shows schematic representations of the scale structure of specimens for the regions labeled in Fig. 11. Internal oxidation is restricted to region (c); external oxidation occurs in region (d) in which the oxygen partial pressure is lower and the diffusion rate of oxygen slower than in region (c). A very thin SiO$_2$ layer forms on the alloy surface in region (d), because, in this region, the diffusion rate of Si is relatively high compared with that of oxygen. No oxidation occurs in region (e), in which the oxygen partial pressure is lower than in region (d). On the other hand, fayalite, Fe$_2$SiO$_4$, or wustite, FeO, form in regions (b) and (a), respectively. No internal oxidation occurs in regions (b) and (a), in which the oxygen partial pressure is lower than in region (c).

Thus, oxidation behavior of Fe-Si alloy strongly depends on the Si concentration and the oxygen partial pressure. The oxidation situation determined by metallographic observation is also shown in Fig. 11. Internal oxidation is limited to region (c), and external oxidation or surface oxidation is limited to region (d) and (b). From these results, the boundary conditions between internal and external oxidation as shown as Fig. 11 are confirmed to be valid.

5. Conclusion

In the present study, the rate constants of internal oxidation of Si containing steels (Fe-Si alloys) at 850°C were calculated in order to clarify the formation mechanism of fayalite scales, which can form as a “sub-scale” in Si containing steels. The internal oxidation rate equation, $x = (2D_ON_O(s)/N_O^{(0)}n)^{1/2}t^{1/2}$, was used. The diffusion coefficient of oxygen in the oxide layer, $D_O$, and the oxygen concentration at the specimen surface, $N_O^{(0)}$, which are constituents of internal oxidation rate constant, $(2D_ON_O^{(0)}/N_B^{(0)}n)$, were selected, and the internal oxidation rates were calculated under various oxidation conditions. The validity of the values of $D_O$ and $N_O^{(0)}$ was confirmed by comparing the calculated results with experimental data.

The boundary conditions between internal and external oxidation were calculated using the values of two parameters, $D_O$ and $N_O^{(0)}$, determined in this study. From the results, it was confirmed that internal oxidation occurs in a limited oxygen partial pressure range and is limited to Si concentrations below 1.0 mass%. The oxygen partial pressure range, in which internal oxidation can occur, decreases with increasing Si concentration, and vanishes if the Si concentration is 1.0 mass% or more.

Acknowledgements

The authors wish to express their thanks to Professor T. Maruyama and Assistant Professor M. Ueda at Tokyo Institute of Technology for their useful advice on this work.

REFERENCES


Fig. 12 Schematic representation of several scale structures of Fe-Si alloys. (a) formation of FeO scale, (b) formation of internal-oxide layer of SiO$_2$ and Fe$_2$SiO$_4$, (c) formation of internal-oxide layer of SiO$_2$, (d) formation of external scale of SiO$_2$, (e) no oxidation.