Hydrogen Permeability through n-type Cr₂O₃ Scale at 1273 K under the Oxygen Activities of 1.6 × 10⁻¹⁸ – 1.0 × 10⁻¹⁶

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(Received on October 12, 2010; accepted on December 22, 2010)

The effect of dissolution of hydrogen on the defect structure of Cr₂O₃ was studied. The hydrogen flux and permeability through Cr₂O₃ scale were measured at 1273 K in the oxygen activities of 1.6 × 10⁻¹⁸ – 1.0 × 10⁻¹⁶. The oxygen activities on the both sides of the sample were controlled by fixing the H₂/CO₂ and CO/CO₂ ratios to measure the hydrogen permeation without oxygen activity gradient through the sample. The measured hydrogen flux and permeability was proportional to $a_{H_2}^{1/2}$ and $a_{O_2}^{-1/8}$ respectively. The activity dependences indicate that dissolved hydrogen is the neutral hydrogen at oxygen site as a minor defect and does not affect the oxidation behavior of chromia-forming alloys.

KEY WORDS: hydrogen permeability; hydrogen flux; defect structure; Cr₂O₃ scale.

1. Introduction

The effect of water vapor on the high-temperature oxidation of Fe–Cr ferritic alloys have been studied by many researchers for various applications such as a boiler tube in steam power plants and interconnects of solid oxide fuel cell (SOFC). 1–8) These studies reported that the formation of protective Cr₂O₃ scale is retarded in humid atmosphere compared to in dry atmosphere.

Hanafi et al. 1) and Setiawan et al. 2) clarified that the critical Cr concentration for the formation of external Cr₂O₃ scale was increased in the humid atmosphere compared to in dry atmosphere in the study on the transition from internal to external oxidation of ferritic Fe–Cr alloys at 973 K and 1073 K. They have proposed that the dissolved hydrogen in the internal oxidation zone enhances the inward oxygen transport along the interface between metal and precipitated oxides and retards the formation of external Cr₂O₃ scale.

Once the external Cr₂O₃ scale is formed on the alloy, it is expected that hydrogen species present in the atmosphere may be dissolved as proton, neutral hydrogen or hydride ion, and may change the defect structure which affects the oxidation behavior. Tveten et al. 3) reported the influence of hydrogen in chromium on oxidation behavior in dry oxygen at 1173 K by two-stage oxidation used with oxygen isotopes. Hydrogen in chromium degraded the adherence of Cr₂O₃ scale. They suggested that hydrogen dissolution in Cr₂O₃ scale increases the concentration of metal vacancies and decreases the concentration of oxygen vacancies. Yang et al. 4) investigated the oxidation behavior of ferritic stainless steels under the SOFC simulated condition. When the sample was exposed to air on one side and moist hydrogen of fuel on the other side, nodules of Fe₂O₃ were formed on the air side and Cr₂O₃ layer was observed on the fuel side. They have suggested that hydrogen permeates from the fuel side to the air side and may dissolve as proton which increases the concentration of iron vacancy. Higher concentration of iron vacancy causes the accelerated iron transport.

Dissolution of hydrogen in Cr₂O₃ scale is directly related to the defect structure of Cr₂O₃ and may alter the defect concentration. The defect structure in oxides is affected by the oxygen activity. The oxide scale is always exposed to the oxygen activity gradient and defect structure varies through the scale. For the quantitative discussion on the high temperature oxidation in humid atmospheres, the information of the dissolved hydrogen in Cr₂O₃ is required as a function of oxygen activity.

The permeability of hydrogen is the products of its concentration and diffusion coefficient. The diffusion coefficient is reasonably assumed to be independent of hydrogen concentration which is low enough. Therefore the permeability is a useful measure of the concentration of dissolved hydrogen in oxides. In this study, a novel technique was developed to measure the hydrogen permeation in oxide without oxygen activity gradient and this technique was applied to Cr₂O₃ scales at 1273 K. The measurement was carried out at oxygen activities of 1.6 × 10⁻¹⁸ – 1.0 × 10⁻¹⁶.

2. Defect Structure

2.1. Intrinsic Defects in Cr₂O₃ Scale

Defect structure in oxides is dependent on oxygen partial pressure (oxygen activity, $a_{O_2}$) in the environment. Figure 1 shows Kröger-Vink diagram of Cr₂O₃ constructed based on previous report. 5 11) Major defects are electron and hole in the intrinsic region, vacancy of chromium ion and hole in the higher $a_{O_2}$ region, and interstitial ion of chromium and
electron in the lower \( a_{O2} \) region. The concentration of interstitial ion of chromium is proportional to \( a_{O2}^{-3/16} \) and that of vacancy of chromium ion is to \( a_{O2}^{3/16} \). Yurek\(^{11}\) has compiled reported data of chromium tracer diffusion coefficients in single crystal of \( \text{Cr}_2\text{O}_3 \), and has showed an approximate expression for the dependence of the chromium diffusion coefficient on temperature and oxygen activity as the following equation,

\[
\frac{D_{\text{Cr}}}{m^2s^{-1}} = A \cdot a_{O2}^{-3/16} + B \cdot a_{O2}^{3/16}
\]

\[
A/m^2s^{-1} = 1.2 \times 10^{-10} \exp \left( -\frac{398 [\text{kJ}mol^{-1}]}{RT} \right)
\]

\[
B/m^2s^{-1} = 1.5 \times 10^{-10} \exp \left( -\frac{502 [\text{kJ}mol^{-1}]}{RT} \right)
\]

...... (1)

where \( D_{\text{Cr}} (m^2s^{-1}) \) is the tracer diffusion coefficient of chromium in \( \text{Cr}_2\text{O}_3 \), \( R (\text{J}mol^{-1}K^{-1}) \) is the gas constant, \( T (K) \) is the absolute temperature. Based on Eq. (1), \( a_{O2} \) dependence of \( D_{\text{Cr}} \) at 1273 K is shown in Fig. 2. This figure also indicates the \( a_{O2} \) region examined in this study. \( D_{\text{Cr}} \) in the \( a_{O2} \) region is proportional to \( a_{O2}^{-3/16} \). This indicates that the major ionic defect in this region is the interstitial ion of chromium and \( \text{Cr}_2\text{O}_3 \) exhibits the n-type behavior.

2.2. Possible Hydrogen Defects in \( \text{Cr}_2\text{O}_3 \) Scale

Possible hydrogen-defects in \( \text{Cr}_2\text{O}_3 \) are proton, neutral hydrogen or hydride ion. The radii of proton, neutral hydrogen and hydride ion are \( 1.5 \times 10^{-6}, 5.3 \times 10^{-2} \) and \( 2.1 \times 10^{-1} \) nm, respectively.\(^{12}\) The radius of interstitial site can be calculated to be \( 4.6 \times 10^{-2} \) nm from the reported lattice parameter of \( \text{Cr}_2\text{O}_3 \)\(^{13}\) and that of oxygen vacancy is \( 1.3 \times 10^{-1} \) nm.\(^{12}\)

It is believed that a proton sits on an oxide ion as \( \text{OH}_2^+ \) and frequently described as interstitial hydrogen ion as \( \text{H}_i \). Taking account of the sizes of hydrogen-defects and sites in \( \text{Cr}_2\text{O}_3 \), a neutral hydrogen may locate at an interstitial site as \( \text{H}_i \) or an oxygen vacancy site as \( \text{H}_0^+ \). A hydride ion may sit at oxygen vacancy site as \( \text{H}_0^- \).

2.3. Proton in n-type \( \text{Cr}_2\text{O}_3 \)

In the case of dissolved hydrogen is proton at interstitial site, the reaction can be expressed as follows

\[
\text{H}_2 \rightarrow 2\text{H}_i^+ + 2e' \]

Equilibrium constant of reaction (2) is

\[
K_2 = \frac{[\text{H}_i^+]^2}{a_{H_i}} \]

...... (3)

where \( K \) is the equilibrium constant, \( a \) is activity and \([ ]\) (mol m\(^{-3}\)) is concentration. If the concentration of proton is high enough to be considered as a major defect, the electron-neutrality in \( \text{Cr}_2\text{O}_3 \) scale should be maintained by

\[
[\text{H}_i^+] = [e'] \]

...... (4)

Substitution of Eq. (4) into Eq. (3) gives

\[
[\text{H}_i^+] = K_2^{1/4} a_{H_i}^{1/4} \]

...... (5)

The concentration of proton at interstitial site is proportional to \( a_{H_i}^{1/4} \) and independent to \( a_{O2} \).

On the other hand, if the concentration of proton is low enough as a minor defect in n-type \( \text{Cr}_2\text{O}_3 \), the concentration of electron is proportional to \( a_{O2}^{-3/16} \) in n-type \( \text{Cr}_2\text{O}_3 \) so that the Eq. (3) gives the concentration of proton to be

\[
[\text{H}_i^+] \propto a_{H_i}^{1/2} a_{O2}^{3/16} \]

...... (6)

In this case, the concentration of proton is proportional to \( a_{H_0}^{1/2} \) and \( a_{O2}^{3/16} \).

2.4. Neutral Hydrogen in n-type \( \text{Cr}_2\text{O}_3 \)

The formation of neutral hydrogen at the oxygen site is expressed as

\[
\text{H}_2 + 2\text{O}_2^- \rightarrow 2\text{H}_0^+ + \text{O}_2 + 4e' \]

Equilibrium constant of reaction (7) is

\[
K_7 = \frac{[\text{H}_0^+]^{16} a_{H_i} [e']^4}{a_{H_i}} \]

...... (8)

If neutral hydrogen at the oxygen site is a major defect, electro-neutrality in \( \text{Cr}_2\text{O}_3 \) scale is maintained by

\[
2[\text{H}_0^+] = [e'] \]

...... (9)

Substitution of Eq. (9) into Eq. (8) gives

\[
[\text{H}_0^+] = (K_7^{1/16} a_{H_i}^{16} a_{O2}^{-1/6}) \]

...... (10)

The concentration of neutral hydrogen at the oxygen site as a major defect is proportional to \( a_{H_0}^{-1/6} \) and \( a_{O2}^{-1/6} \).

On the other hand, if neutral hydrogen at the oxygen site is a minor defect, the concentration of electron is propor-
tional to $a_{O_2}^{-3/16}$ in n-type Cr$_2$O$_3$ so that the Eq. (8) gives the concentration of neutral hydrogen to be

$$[H_2^+] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/18} \quad \text{............... (11)}$$

In this case, the concentration of neutral hydrogen is proportional to $a_{H_2}^{1/2}$ and $a_{O_2}^{-1/18}$.

### 2.5. Hydrogen Defects in n-type Cr$_2$O$_3$

The concentration of dissolved hydrogen in Cr$_2$O$_3$ exhibits various dependences of $a_{O_2}$ and $a_{H_2}$. All possible dissolution reactions are shown in Table 1 with activity dependence of concentration of hydrogen-defects.

### 3. Experimental

#### 3.1. Experimental Apparatus

**Figure 3** shows the apparatus for measurement of hydrogen flux ($J_H$) through the Cr$_2$O$_3$ scale without oxygen activity gradient. Gas mixtures of Ar–H$_2$–CO$_2$ and Ar–CO–CO$_2$ are fed to both sides of the specimen. The activity of oxygen at both sides can be fixed by the ratio of H$_2$/CO$_2$ or CO/CO$_2$. As shown in Fig. 3, oxygen pump made by CaO-stabilized zirconia were placed on the both paths. These pumps enable to adjust the ratio of H$_2$/CO$_2$ or CO/CO$_2$ and to keep the same oxygen activity at the both sides of the sample.

#### 3.2. Preparation of Thin Cr$_2$O$_3$ Scale with a Constant Thickness

To obtain the higher flux of permeating hydrogen, the thinner Cr$_2$O$_3$ scales are required as specimens. Complete oxidation of thin sheets of a Cr$_2$O$_3$-forming alloy offers a suitable specimen in which thin metal sheets are sandwiched with two thin Cr$_2$O$_3$ scales with constant thickness. Prior to the permeability measurement, oxidation test of an SUS430 sheet was carried out in order to evaluate the oxidation time long enough for the complete oxidation. A thin SUS430 sheet (20 × 20 × 0.01 mm) was oxidized at 1273 K in Ar–20%H$_2$–0.16%H$_2$O atmosphere. Table 2 shows chemical composition of SUS430 sheet. After oxidation, samples were analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Electron Probe Micro-analysis (EPMA).

#### 3.3. Measurement of Hydrogen Permeation without Oxygen Activity Gradient

**Figure 4** shows schematically the sequence of experimental procedure. A sheet of SUS430 (20 × 20 × 0.01 mm) was placed between two alumina tubes with rings of pyrex glass as sealants. During the permeation measurement, hydrogen permeates from the left compartment (refer to hydrogen provided side) to the right one (refer to hydrogen detected side). After substitution of air with Ar–20%H$_2$–0.16%H$_2$O in both compartments, the furnace is heated up to 1273 K. The sealing of compartments was performed around 1273 K by softening of glass rings. After temperature reached 1273 K, the sheet of SUS430 was oxidized for 60 ks at 1273 K. This condition of oxidation was pre-determined by a separated oxidation experiment and gave the complete oxidation of Cr in the SUS430 sheet.

### Table 1. Dissolution reactions of hydrogen and their activity dependences.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>as a minor defect</th>
<th>as a major defect</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2 \rightarrow 2H_2^+ + 2e^-$</td>
<td>$[H_2^+] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/18}$</td>
<td>$H_2 \rightarrow 2H_2^+$</td>
</tr>
<tr>
<td>$H_2 \rightarrow 2H_2^+$</td>
<td>$[H_2^+] \propto a_{H_2}^{1/2}$</td>
<td>$H_2 + 2O_2^{\cdot} \rightarrow 2H_2O^{\cdot}$</td>
</tr>
<tr>
<td>$H_2 + 2O_2^{\cdot} + 2e^- \rightarrow 2H_2O^{\cdot}$</td>
<td>$[H_2O^{\cdot}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/8}$</td>
<td>$H_2 + 2O_2^{\cdot} + O_2 + 4e^- \rightarrow 2H_2O + O_2$</td>
</tr>
<tr>
<td>$H_2 + 2O_2^{\cdot} \rightarrow 2H_2O^{\cdot} + O_2 + 4e^-$</td>
<td>$[H_2O^{\cdot}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/8}$</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Chemical composition of SUS430.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass %</td>
<td>Bal.</td>
<td>16.3</td>
<td>0.21</td>
<td>0.35</td>
<td>0.12</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. 3. Apparatus for measurement of hydrogen flux ($J_H$) through the Cr$_2$O$_3$ scale without oxygen activity gradient.

Fig. 4. Sequence of experimental procedure.
After the oxidation, Ar–20%H2–0.16%H2O were exchanged to Ar–10%CO–0.1%CO2 in both compartments to remove H2O adsorbed on the wall of apparatus. This treatment was conducted until the dew point of the hydrogen detected side decreased to the constant value of about 228 K. To start measurement of hydrogen permeation, the gas on the hydrogen provided side was finally changed from Ar–10%CO–0.1%CO2 to Ar–40%H2–1.2%CO2 or Ar–20%H2–0.6%CO2. The flow rate of both gases was 5.6 × 10−7 m3s−1. Oxygen activities of these gas mixtures were controlled in the region of 1.6 × 10−18 – 1.0 × 10−16 by adjusting H2/CO2 and CO/CO2 ratios with oxygen pumps and aO2 is kept identical on both sides during measurement of hydrogen permeation. Permeated hydrogen through the sample is led to the combustion furnace with platinum catalyst and combusted completely with oxygen into water vapor. The dew point of the gas was continuously monitored by a dew point hygrometer (General Eastern D-2-SR + Hygro M-4).

To terminate the permeability measurement, the gas in the hydrogen provided side was changed again from Ar–H2–CO2 gas to Ar–10%CO–0.1%CO2 and temperature was cooled down to room temperature.

3.4. Evaluation of Hydrogen Permeability

Figure 5 shows the schematic illustration of gas flow during the measurement of hydrogen permeation without oxygen activity gradient. The flowing gases on both sides of a specimen posses the identical oxygen activity but different hydrogen activities. The left compartment is fed with a gas mixture of Ar–H2–CO2 and the right with a mixture of Ar–CO–CO2. The oxygen activity was fixed by adjusting the ratio of H2/CO2 or CO/CO2. Hydrogen permeates from the left to the right. Permeated hydrogen through the sample is led to the combustion furnace with platinum catalyst and combusted completely with oxygen into water vapor. Dew point of the gas is continuously monitored by a dew point hygrometer.

The mass flow rate of hydrogen permeated through the sample and that of water vapor after combustion are identical

\[ \dot{n}_{H2(\text{permeation})} = \dot{n}_{H2O(\text{combustion})} \] .......................... (12)

where \( \dot{n} \) (mol s−1) is the mass flow rate. Because the gases fed from cylinders contain the trace of water vapor as an impurity, the correction is performed using the mass flow rate of impurity water vapor which is summed up, \( \dot{n}_{H2O(\text{impurity})} \). The partial pressure of water vapor, \( P_{H2O} \) (bar), in the hygrometer is calculated from the measured dew point,

\[
\frac{P_{H2O}}{P^*} = \frac{\dot{n}_{H2O}}{\dot{n}_H^{(\text{Total})}} = \frac{\dot{n}_{H2O(\text{combustion})} + \dot{n}_{H2O(\text{impurity})}}{\dot{n}_H^{(\text{Total})}} \] .......................... (13)

where \( P^* \) is the standard pressure of 1 bar and \( \dot{n}_H^{(\text{Total})} \) is the total mass flow rate in the hygrometer. The mass flow rate of hydrogen defect through Cr2O3 scale, \( \dot{n}_H^{(\text{sample})} \) is double of hydrogen molecule permeated,

\[ \dot{n}_H^{(\text{sample})} = 2\dot{n}_{H(\text{permeation})} \] .......................... (14)

The flux of hydrogen defect through Cr2O3 scale, \( J_H \) (mol m−2 s−1) is expressed as

\[ J_H = \frac{\dot{n}_H^{(\text{sample})}}{A} \] .......................... (15)

where \( A \) (m²) is the surface area of the sample for hydrogen permeation. Substitution of Eqs. (14) and (15) into Eq. (13) gives

\[
\frac{P_{H2O}}{P^*} = \frac{2A J_H}{P_{H2O}^{(\text{Total})}} + \frac{\dot{n}_{H2O(\text{impurity})}}{P_{H2O}^{(\text{Total})}} \] .......................... (16)

Because \( \dot{n}_{H2O(\text{impurity})} \) can be calculated by a measured dew point of gas on the hydrogen detected side, \( J_H \) also can be calculated from Eq. (16) without oxygen activity gradient.

4. Results

4.1. Oxidation of a Thin SUS430 Sheet and Morphology of the Oxide Scale

Figure 6 shows the mass gain during the oxidation test. The expected mass gain after complete oxidation is 5.8 gm−2. The mass increased in the parabolic manner and reached a constant value of 5.5 gm−2 at 43.2 ks. Figure 7 presents XRD patterns of the scale after oxidation for 64.8 ks. XRD detects the formation of Cr2O3 and MnCr2O4. Figure 8 shows the surface microstructure after oxidation for 64.8 ks. Whole surface of the sample was covered with Cr2O3 layer and a small amount of dispersed MnCr2O4. Because surface area of MnCr2O4 is less than 1%, one can reasonably neglect...
the effect of MnCr$_2$O$_4$ on the measurement of hydrogen permeation. Figure 9 shows the cross-sectional microstructure after oxidation for 64.8 ks. The dense and continuous Cr$_2$O$_3$ layers of around 1.5 μm thick were formed on the both surfaces.

4.2. Hydrogen Permeation at Various Oxygen Activities

Variations of measured dew points are shown in Fig. 10.
The oxygen activities of both compartments are almost the same during a measurement. This confirms that the permeation measurement is carried out without oxygen activity gradient. The measured dew point decreased gradually during gas exchange process and approached to about 228 K. This dew point is regarded as the amount of water vapor which is contained in Ar–CO–CO2 gas mixture as an impurity. After hydrogen started to permeate, the dew point drastically increased and reached steady values. To terminate the measurement, the atmosphere was changed from Ar–H2–CO2 to Ar–CO–CO2 and the measured dew point decreased down to impurity level again.

Figures 10(b) and 10(d) are the magnified Figs. 10(a) and 10(c). It is obvious that the dew point is lower in higher \( \alpha_{O2} \). Table 3 summarizes the calculated \( J_H \) from the obtained dew points and the Eq. (16).

<table>
<thead>
<tr>
<th>( \alpha_{O2} )</th>
<th>( J_H ) / mol m(^2) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6 ( \times ) 10(^{-14})</td>
<td>2.7 ( \times ) 10(^{-5})</td>
</tr>
<tr>
<td>1.0 ( \times ) 10(^{-17})</td>
<td>2.3 ( \times ) 10(^{-5})</td>
</tr>
<tr>
<td>1.0 ( \times ) 10(^{-16})</td>
<td>2.0 ( \times ) 10(^{-5})</td>
</tr>
</tbody>
</table>

5. Discussions

Figure 11 illustrates the distribution of the hydrogen activity gradient through the iron substrate and the two Cr2O3 layers with the thickness of \( l \). Kurokawa et al.\(^{14} \) studied hydrogen permeation through ferritic alloy interconnect under simulating SOFC atmosphere at 1073 K. The hydrogen permeability of Cr2O3 scale was about four orders of magnitude lower than that of the iron. This result indicates that the hydrogen activity gradient in the iron substrate is negligibly small as shown in Fig. 11(a). The obtained hydrogen permeability is for Cr2O3 scale with the thickness of 2\( l \) as shown in Fig. 11(b).

According to Fick’s first law, \( J_H \) through the sample can be described as follows

\[
J_H = -D_H \frac{d[H]}{dx} \quad \text{................................ (17)}
\]

where \( D_H \) (m\(^2\) s\(^{-1}\)) is diffusion coefficient of hydrogen defect and \([H]\) (mol m\(^{-3}\)) is the concentration of dissolved hydrogen. This Eq. is integrated as

\[
\int_0^L J_H dx = -\int_0^{\alpha_{H2}} D_H d[H]
\]

\[
J_H L = -D_H ([H]^i - [H]^0) \quad \text{........................ (18)}
\]

Fig. 11. Distribution of the hydrogen activity through the sample.
where $L$ is the thickness of the oxide scale and $[H]^p$ and $[H]^k$ are the concentrations of hydrogen defect on the hydrogen provided side and detected side, respectively.

$[H]^k$ is negligible because permeated hydrogen was continuously carried away by the flowing gas on the hydrogen detected side. Equation (18) can be simplified as

$$J_H = \frac{D_H}{L} [H]^p \tag{22}$$

On the other hand, $a_{H2}$ and $a_{H2}$ dependence of dissolved hydrogen in $\text{Cr}_2\text{O}_3$ scale, which is shown in Table 1, is expressed as follows

$$[H] = S_H a_{\text{O}_3}^{-q} a_{\text{H}_2}^{-r} \tag{20}$$

where $S_H$ (mol m$^{-3}$) is the solubility coefficient and $q$ and $r$ are given constants. Oxygen activity is assumed as constant because there is no oxygen activity gradient through the sample. Substitution of Eq. (20) into Eq. (19) gives

$$J_H = \left( \frac{D_H S_H a_{\text{O}_3}^{-q} a_{\text{H}_2}^{-r}}{L} \right) a_{\text{H}_2}^{1/2} \tag{21}$$

According to the Table 1, $J_H$ is proportional to $a_{H2}^{1/2}$, $a_{H2}^{1/4}$ or $a_{H2}^{1/6}$ at a constant oxygen activity. Figures 12(a), (b) and (c) show the plots of $J_H$ as a function of $a_{H2}^{1/2}$, $a_{H2}^{1/4}$ and $a_{H2}^{1/6}$, respectively. Although the available points are only three including the origin, the linear relationship is obtained only in Fig. 12(a). This fact strongly suggests that the $a_{H2}^{1/2}$ dependence is acceptable. Hydrogen permeability is defined as

$$\Phi_H = J_H L \tag{22}$$

where $\Phi_H$ (mol m$^{-1}$ s$^{-1}$) is hydrogen permeability in $\text{Cr}_2\text{O}_3$. Substitution of Eq. (21) and obtained $a_{H2}$ dependence into Eq. (22) gives

$$\Phi_H = D_H S_H a_{\text{O}_3}^{-q} a_{\text{H}_2}^{1/2} \tag{23}$$

$J_H$ at $a_{H2} = 1$ is calculated from the slope of the lines shown in Fig. 12. Calculated $\Phi_H$ are shown in Fig. 13. The hydrogen permeability in $\text{Cr}_2\text{O}_3$ exhibited the oxygen activity dependence of $a_{O2}^{-1/8}$. This result indicates that hydrogen defect in $n$-type $\text{Cr}_2\text{O}_3$ is neutral hydrogen as minor defects. If the hydrogen defect is the hydride ion at oxygen site, the oxygen activity dependence should be $a_{O2}^{-3/16}$. This is different from the experimentally obtained dependence. Hydrogen dissolution as a minor defect into $\text{Cr}_2\text{O}_3$ does not affect the defect structure and the oxidation behavior.

Kurokawa et al. studied oxidation behavior of ferritic alloy under hydrogen activity gradient by simulating condition of SOFC. The oxidation rate and morphology of oxide scale formed on both the air side and fuel side were almost similar to those which were oxidized in both atmospheres separately without hydrogen activity gradient. This fact suggested that hydrogen dissolves as a minor defect into $\text{Cr}_2\text{O}_3$ scale.

6. Conclusion

A novel technique was developed to measure the hydrogen permeation in oxide without oxygen activity gradient and was applied to $\text{Cr}_2\text{O}_3$ scale at 1273 K in the oxygen activity region of $1.6 \times 10^{-18}$ – $1.0 \times 10^{-16}$. The hydrogen permeability was proportional to $a_{H2}^{1/2}$ and $a_{O2}^{-1/8}$. This fact indicates that the dissolved hydrogen in $n$-type $\text{Cr}_2\text{O}_3$ is the neutral hydrogen atom at the oxygen site and the concentration is low enough to regard as a minor defect. The minor defect does not affect the oxidation behavior of chromia-forming alloys.

Acknowledgement

This research was partially supported by Japan Society for Promotion of Science under Grant-in-Aid for “Scientific Research (A) (General)” (21246108) and by Iron and Steel Institute of Japan under the 18th ISIJ Research Promotion Grant.

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