Hydrogen Permeability through n-type Cr_2O_3 Scale at 1273 K under the Oxygen Activities of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$

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The effect of dissolution of hydrogen on the defect structure of Cr_2O_3 was studied. The hydrogen flux and permeability through Cr_2O_3 scale were measured at 1273 K in the oxygen activities of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$. The oxygen activities on the both sides of the sample were controlled by fixing the H_2/CO_2 and CO/CO_2 ratios to measure the hydrogen permeability without oxygen activity gradient through the sample. The measured hydrogen flux and permeability was proportional to $a_{\text{H}_2}^{1/2}$ and $a_{\text{O}_2}^{-1/8}$ 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; Cr_2O_3 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 Cr_2O_3 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 Cr_2O_3 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 Cr_2O_3 scale.

Once the external Cr_2O_3 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 Cr_2O_3 scale. They suggested that hydrogen dissolution in Cr_2O_3 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 Fe_2O_3 were formed on

the air side and Cr_2O_3 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 Cr_2O_3 scale is directly related to the defect structure of Cr_2O_3 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 Cr_2O_3 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 Cr_2O_3 scales at 1273 K. The measurement was carried out at oxygen activities of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$.

2. Defect Structure

2.1. Intrinsic Defects in Cr_2O_3 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 Cr_2O_3 constructed based on previous report.^{9–11)} 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

 Fig. 1. Kröger-Vink diagram of Cr_2O_3 scale.

 Fig. 2. a_{O_2} dependence of D_{Cr} in Cr_2O_3 .

electron in the lower a_{O_2} region. The concentration of interstitial ion of chromium is proportional to $a_{\text{O}_2}^{-3/16}$ and that of vacancy of chromium ion is to $a_{\text{O}_2}^{3/16}$. Yurek¹¹⁾ has compiled reported data of chromium tracer diffusion coefficients in single crystal of Cr_2O_3 , and has showed an approximate expression for the dependence of the chromium diffusion coefficient on temperature and oxygen activity as the following equation,

$$D_{\text{Cr}} / \text{m}^2 \text{s}^{-1} = A \cdot a_{\text{O}_2}^{-3/16} + B \cdot a_{\text{O}_2}^{3/16}$$

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

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

where D_{Cr} ($\text{m}^2 \text{s}^{-1}$) is the tracer diffusion coefficient of chromium in Cr_2O_3 , R ($\text{Jmol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) is the absolute temperature. Based on Eq. (1), a_{O_2} dependence of D_{Cr} at 1273 K is shown in Fig. 2. This figure also indicates the a_{O_2} region examined in this study. D_{Cr} in the a_{O_2} region is proportional to $a_{\text{O}_2}^{-3/16}$. This indicates that the major ionic defect in this region is the interstitial ion of chromium and Cr_2O_3 exhibits the n-type behavior.

2.2. Possible Hydrogen Defects in Cr_2O_3 Scale

Possible hydrogen-defects in Cr_2O_3 are proton, neutral hydrogen or hydride ion. The radii of proton, neutral hydrogen

and hydride ion are 1.5×10^{-6} , 5.3×10^{-2} and 2.1×10^{-1} nm, respectively.¹²⁾ The radius of interstitial site can be calculated to be 4.6×10^{-2} nm from the reported lattice parameter of Cr_2O_3 ¹³⁾ and that of oxygen vacancy is 1.3×10^{-1} nm.¹²⁾

It is believed that a proton sits on an oxide ion as $\text{OH}_\text{O}^\bullet$ and frequently described as interstitial hydrogen ion as $\text{H}_\text{i}^\bullet$.^{3,4)} Taking account of the sizes of hydrogen-defects and sites in Cr_2O_3 , a neutral hydrogen may locate at an interstitial site as $\text{H}_\text{i}^\times$ or an oxygen vacancy site as $\text{H}_\text{O}^\bullet$. A hydride ion may sit at oxygen vacancy site as $\text{H}_\text{O}^\bullet$.

2.3. Proton in n-type Cr_2O_3

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

Equilibrium constant of reaction (2) is

$$K_2 = \frac{[\text{H}_\text{i}^\bullet]^2 [\text{e}']^2}{a_{\text{H}_2}} \quad \dots (3)$$

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 electro-neutrality in Cr_2O_3 scale should be maintained by

$$[\text{H}_\text{i}^\bullet] = [\text{e}'] \quad \dots (4)$$

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

$$[\text{H}_\text{i}^\bullet] = K_2^{1/4} a_{\text{H}_2}^{1/4} \quad \dots (5)$$

The concentration of proton at interstitial site is proportional to $a_{\text{H}_2}^{1/4}$ and independent to a_{O_2} .

On the other hand, if the concentration of proton is low enough as a minor defect in n-type Cr_2O_3 , the concentration of electron is proportional to $a_{\text{O}_2}^{-3/16}$ in n-type Cr_2O_3 so that the Eq. (3) gives the concentration of proton to be

$$[\text{H}_\text{i}^\bullet] \propto a_{\text{H}_2}^{1/2} a_{\text{O}_2}^{3/16} \quad \dots (6)$$

In this case, the concentration of proton is proportional to $a_{\text{H}_2}^{1/2}$ and $a_{\text{O}_2}^{3/16}$.

2.4. Neutral Hydrogen in n-type Cr_2O_3

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

Equilibrium constant of reaction (7) is

$$K_7 = \frac{[\text{H}_\text{O}^\bullet]^2 a_{\text{O}_2} [\text{e}']^4}{a_{\text{H}_2}} \quad \dots (8)$$

If neutral hydrogen at the oxygen site is a major defect, electro-neutrality in Cr_2O_3 scale is maintained by

$$2[\text{H}_\text{O}^\bullet] = [\text{e}'] \quad \dots (9)$$

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

$$[\text{H}_\text{O}^\bullet] = \left(\frac{K_7}{16} \right)^{1/6} a_{\text{H}_2}^{1/6} a_{\text{O}_2}^{-1/6} \quad \dots (10)$$

The concentration of neutral hydrogen at the oxygen site as a major defect is proportional to $a_{\text{H}_2}^{1/6}$ and $a_{\text{O}_2}^{-1/6}$.

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_2O_3 so that the Eq. (8) gives the concentration of neutral hydrogen to be

$$[H_O^{\bullet}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/8} \dots\dots\dots (11)$$

In this case, the concentration of neutral hydrogen is proportional to $a_{H_2}^{1/2}$ and $a_{O_2}^{-1/8}$.

2.5. Hydrogen Defects in n-type Cr_2O_3

The concentration of dissolved hydrogen in Cr_2O_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_2O_3 scale without oxygen activ-

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

as a minor defect	$H_2 \rightarrow 2H_i^{\bullet} + 2e'$	$[H_i^{\bullet}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{3/16}$
	$H_2 \rightarrow 2H_i^{\times}$	$[H_i^{\times}] \propto a_{H_2}^{1/2}$
	$H_2 + 2V_O^{\bullet\bullet} \rightarrow 2H_O^{\bullet\bullet}$	
	$(H_2 + 2O_O^{\times} \rightarrow 2H_O^{\bullet\bullet} + O_2 + 4e')$	$[H_O^{\bullet\bullet}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-1/8}$
	$H_2 + 2V_O^{\bullet\bullet} + 2e' \rightarrow 2H_O^{\bullet}$	
as a major defect	$(H_2 + 2O_O^{\times} \rightarrow 2H_O^{\bullet} + O_2 + 2e')$	$[H_O^{\bullet}] \propto a_{H_2}^{1/2} \cdot a_{O_2}^{-5/16}$
	$H_2 \rightarrow 2H_i^{\bullet} + 2e'$	$[H_i^{\bullet}] \propto a_{H_2}^{1/4}$
	$H_2 \rightarrow 2H_i^{\times}$	$[H_i^{\times}] \propto a_{H_2}^{1/2}$
	$H_2 + 2O_O^{\times} \rightarrow 2H_O^{\bullet\bullet} + O_2 + 4e'$	$[H_O^{\bullet\bullet}] \propto a_{H_2}^{1/6} \cdot a_{O_2}^{-1/6}$
	$H_2 + 2O_O^{\times} \rightarrow 2H_O^{\bullet} + O_2 + 2e'$	$[H_O^{\bullet}] \propto a_{H_2}^{1/4} \cdot a_{O_2}^{-1/4}$

Fig. 3. Apparatus for measurement of hydrogen flux (J_H) through the Cr_2O_3 scale without oxygen activity gradient.

ity 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_2O_3 Scale with a Constant Thickness

To obtain the higher flux of permeating hydrogen, the thinner Cr_2O_3 scales are required as specimens. Complete oxidation of thin sheets of a Cr_2O_3 -forming alloy offers a suitable specimen in which thin metal sheets are sandwiched with two thin Cr_2O_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 ($20 \times 20 \times 0.01$ mm) was oxidized at 1273 K in $Ar-20\%H_2-0.16\%H_2O$ 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 ($20 \times 20 \times 0.01$ 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 $Ar-20\%H_2-0.16\%H_2O$ in both compartments, the furnace is heated up to 1273 K. The sealing of compartments was performed around 1073 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 2. Chemical composition of SUS430.

Composition	Fe	Cr	Mn	Si	Ni	Al
Mass %	Bal.	16.3	0.21	0.35	0.12	0.11

Fig. 4. Sequence of experimental procedure.

After the oxidation, Ar–20% H_2 –0.16% H_2O were exchanged to Ar–10%CO–0.1% CO_2 in both compartments to remove H_2O 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% CO_2 to Ar–40% H_2 –1.2% CO_2 or Ar–20% H_2 –0.6% CO_2 . The flow rate of both gases was $5.6 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$. Oxygen activities of these gas mixtures were controlled in the region of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$ by adjusting H_2/CO_2 and CO/CO_2 ratios with oxygen pumps and a_{O_2} 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– H_2 – CO_2 gas to Ar–10%CO–0.1% CO_2 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 possess the identical oxygen activity but different hydrogen activities. The left compartment is fed with a gas mixture of Ar– H_2 – CO_2 and the right with a mixture of Ar–CO– CO_2 . The oxygen activity was fixed by adjusting the ratio of H_2/CO_2 or CO/CO_2 . 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

$$\dot{n}_{H_2(\text{permeation})} = \dot{n}_{H_2O(\text{combustion})} \quad \text{..... (12)}$$

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, $\dot{n}_{H_2O(\text{impurity})}$. The partial pressure of water vapor, P_{H_2O} (bar), in the hygrometer is calculated from the measured dew point,

$$\begin{aligned} \frac{P_{H_2O}}{P^*} &= \frac{\dot{n}_{H_2O}}{\dot{n}_{(\text{Total})}} = \frac{\dot{n}_{H_2O(\text{combustion})} + \dot{n}_{H_2O(\text{impurity})}}{\dot{n}_{(\text{Total})}} \\ &= \frac{\dot{n}_{H_2(\text{permeation})} + \dot{n}_{H_2O(\text{impurity})}}{\dot{n}_{(\text{Total})}} \quad \text{..... (13)} \end{aligned}$$

where P^* is the standard pressure of 1 bar and $\dot{n}_{(\text{Total})}$ is the total mass flow rate in the hygrometer. The mass flow rate of hydrogen defect through Cr_2O_3 scale, $\dot{n}_{H(\text{sample})}$ is double of hydrogen molecule permeated,

$$\dot{n}_{H(\text{sample})} = 2\dot{n}_{H_2(\text{permeation})} \quad \text{..... (14)}$$

The flux of hydrogen defect through Cr_2O_3 scale, J_H ($\text{mol m}^{-2} \text{ s}^{-1}$) is expressed as

$$J_H = \frac{\dot{n}_{H(\text{sample})}}{A} \quad \text{..... (15)}$$

where A (m^2) is the surface area of the sample for hydrogen permeation. Substitution of Eqs. (14) and (15) into Eq. (13) gives

$$\frac{P_{H_2O}}{P^*} = \frac{AJ_H}{2\dot{n}_{(\text{Total})}} + \frac{\dot{n}_{H_2O(\text{impurity})}}{\dot{n}_{(\text{Total})}} \quad \text{..... (16)}$$

Because $\dot{n}_{H_2O(\text{impurity})}$ 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 Cr_2O_3 and $MnCr_2O_4$. **Figure 8** shows the surface microstructure after oxidation for 64.8 ks. Whole surface of the sample was covered with Cr_2O_3 layer and a small amount of dispersed $MnCr_2O_4$. Because surface area of $MnCr_2O_4$ is less than 1%, one can reasonably neglect

Fig. 5. Schematic illustration of gas flow during measurement of hydrogen permeation.

Fig. 6. Mass gain during oxidation test at 1273 K in Ar–20% H_2 –0.16% H_2O atmosphere.

Fig. 7. X-ray diffraction patterns of scale grown on sample after oxidation for 64.8 ks.

Fig. 8. Surface microstructure after oxidation for 64.8 ks.

Fig. 9. Cross-sectional microstructure after oxidation for 64.8 ks.

the effect of MnCr_2O_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_2O_3 layers of around $1.5\ \mu\text{m}$ 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**.

Fig. 10. Variation of dew point during hydrogen permeation.

Table 3. Calculated J_H at various conditions.

a_{O_2}	$J_H / \text{mol m}^2 \text{s}^{-1}$	
	Ar-20%H ₂ -0.6%CO ₂	Ar-40%H ₂ -1.2%CO ₂
1.6×10^{-18}	2.7×10^{-5}	4.1×10^{-5}
1.0×10^{-17}	2.3×10^{-5}	3.3×10^{-5}
1.0×10^{-16}	2.0×10^{-5}	2.5×10^{-5}

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 a_{O_2} . **Table 3** summarizes the calculated J_H from the obtained dew points and the Eq. (16).

5. Discussions

Figure 11 illustrates the distribution of the hydrogen activity 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 $2l$ as shown in Fig. 11(b).

According to Fick's first law, J_H through the sample can be described as follows

Fig. 11. Distribution of the hydrogen activity through the sample.

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

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

$$\int_0^L J_H dx = -\int_{[H]^0}^{[H]^L} D_H d[H] \quad (18)$$

$$J_H L = -D_H ([H]^L - [H]^0) \quad (18)$$

Fig. 12. a_{H_2} dependence of J_H in the a_{O_2} region of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$.

where L is the thickness of the oxide scale and $[H]^0$ and $[H]^L$ are the concentrations of hydrogen defect on the hydrogen provided side and detected side, respectively.

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

$$J_H = \frac{D_H}{L} [H]^0 \quad (19)$$

On the other hand, a_{H_2} and a_{O_2} dependence of dissolved hydrogen in Cr_2O_3 scale, which is shown in Table 1, is expressed as follows

$$[H] = S_H a_{O_2}^q a_{H_2}^r \quad (20)$$

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

$$J_H = \left(\frac{D_H S_H a_{O_2}^q}{L} \right) a_{H_2}^r \quad (21)$$

According to the Table 1, J_H is proportional to $a_{H_2}^{1/2}$, $a_{H_2}^{1/4}$ or $a_{H_2}^{1/6}$ at a constant oxygen activity. **Figures 12(a), (b) and (c)** show the plots of J_H as a function of $a_{H_2}^{1/2}$, $a_{H_2}^{1/4}$ and $a_{H_2}^{1/6}$, 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 dependence of $a_{H_2}^{1/2}$ is acceptable. Hydrogen permeability is defined as

$$\Phi_H = J_H L \quad (22)$$

where Φ_H ($\text{mol m}^{-1} \text{s}^{-1}$) is hydrogen permeability in Cr_2O_3 . Substitution of Eq. (21) and obtained a_{H_2} dependence into Eq. (22) gives

$$\Phi_H = D_H S_H a_{O_2}^q a_{H_2}^{\frac{1}{2}} \quad (23)$$

J_H at $a_{H_2} = 1$ is calculated from the slope of the lines shown

Fig. 13. a_{O_2} dependence of Φ_H in the a_{O_2} region of $1.6 \times 10^{-18} - 1.0 \times 10^{-16}$.

in Fig. 12. Calculated Φ_H are shown in **Fig. 13**. The hydrogen permeability in Cr_2O_3 exhibited the oxygen activity dependence of $a_{O_2}^{-1/8}$. This result indicates that hydrogen defect in n-type Cr_2O_3 is neutral hydrogen as minor defects. If the hydrogen defect is the hydride ion at oxygen site, the oxygen activity dependence should be $a_{O_2}^{-5/16}$. This is different from the experimentally obtained dependence. Hydrogen dissolution as a minor defect into Cr_2O_3 does not affect the defect structure and the oxidation behavior.

Kurokawa *et al.*⁵⁾ 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 Cr_2O_3 scale.

6. Conclusion

A novel technique was developed to measure the hydrogen permeation in oxide without oxygen activity gradient and was applied to Cr_2O_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 $a_{H_2}^{1/2}$ and $a_{O_2}^{-1/8}$. This fact indicates that the dissolved hydrogen in n-type Cr_2O_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.

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