A Ceramic Sensor for Prediction of Hydrogen Attack

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A ceramic sensor for monitoring the hydrogen permeated through steels at high temperatures using an electrochemical method has been developed. A new proton conductive solid electrolyte (5mol% Yb₂O₃-SrCeO₃) was used as an electrolyte in this sensor. It was found possible to measure the diffusivity and the content of hydrogen permeated through a plain carbon steel at 773 K and 0.101 MPa hydrogen gas by joining the sensor to the steel with a platinum past. However, the detectability of hydrogen was poor, because joining of ceramics/steel exerted a large influence on it. Joining of the ceramics to the platinum-plated steel with amorphous copper filler metal led to the great improvement of the detectability of hydrogen. This sensor will be useful for predicting hydrogen attack of steels in operating chemical plants.

KEY WORDS: hydrogen attack; ceramic sensor; proton conductive solid electrolyte; diffusivity of hydrogen; hydrogen content.

1. Introduction

Steels exposed to hydrogen gas at high temperatures and high pressures often suffer from a marked reduction in their mechanical properties. This phenomenon, well known as hydrogen attack,¹⁾ is caused primarily by nucleation, growth and coalescence of the methane bubbles along grain boundaries accompanied by concomitant internal decarburization.

There are many reports²⁻⁵⁾ on accidents and damage caused by hydrogen attack in petrorefining plants and ammonia production plants. However, there is no method in use for predicting or monitoring hydrogen attack. The only conventional method for avoiding hydrogen attack is to select materials adequate for the operating temperature and hydrogen pressure according to the Nelson chart,⁵⁾ which has been compiled from empirical data.

Hydrogen attack is closely related to the content of hydrogen brought in a steel from high temperature and high pressure hydrogen environments.⁶⁾ Thus, if a detector or sensor is developed to measure the hydrogen content at high temperatures, it will be useful for predicting hydrogen attack of steels. One of the authors has developed a detector for measuring the hydrogen content in steels at elevated temperatures using an electrochemical method.^{7,8)} However, since a molten salt (NaOH) was used as an electrolyte in the cell of this detector, argon gas had to be continuously flowed into the cell for preventing the cathodic reaction of air in the molten NaOH. In addition, the steel was severely corroded. We, therefore, attempted to develop a new detector using a solid electrolyte, or a ceramic sensor, to solve these problems.

This study shows an electrochemical technique for measuring hydrogen permeated through a plain carbon

steel at 773 K with this ceramic sensor.

2. Basic Concept to Measure Hydrogen Content

The principle of the present electrochemical technique is shown in Fig. 1. Hydrogen is introduced from one side (the entry side) of steel, while the other side (the extraction side) is held at an anodic potential sufficient to ionize the hydrogen permeated through the steel. From the detected ionization current, the permeation rate of hydrogen can be evaluated. In this study, a new type proton conductive solid electrolyte⁹⁾ (5mol% Yb₂O₃-SrCeO₃) was used. The following reaction occurs at the anode:

while the following reaction takes place at the cathode:

The hydrogen content in a specimen changes with time according to Fick's second law. Theoretical permeation curves during build-up and decay processes are calculated by applying the law under appropriate initial and boundary conditions.¹⁰⁾ The diffusivity of hydrogen in a specimen is obtained by comparing the theoretical curves with the build-up and decay transient curves that are measured by changing the hydrogen pressure as shown in Fig. 2.

Fig. 3 shows the change of hydrogen distribution with time through the thickness of a flat specimen. In the steady state, the hydrogen content C_0 (ppm)¹¹⁾ can be calculated from

$$C_0 = \frac{J_\infty \cdot L}{F \cdot D \cdot d} \dots\dots\dots(3)$$

where, J_∞ : the permeation current density in the

Fig. 1. Principle of the present electrochemical technique for measuring hydrogen permeated through steel using a solid electrolyte.

Fig. 2. Schematic representation of permeation transients in the build-up and decay processes.

$X=0, X=L$: the inner and outer surfaces, respectively

Fig. 3. Change in the concentration gradients of hydrogen in a flat specimen with time in the build-up and decay processes.

steady state ($A \cdot m^{-2}$)

L : the specimen thickness (m)

F : the Faraday constant

D : the diffusivity of hydrogen in the specimen ($m^2 \cdot s^{-1}$)

d : the density of the specimen ($7.86 \text{ Mg} \cdot m^{-3}$).

3. Experimental Procedures

The apparatus for the present experiment is shown schematically in Fig. 4. The specimen had a hollow cylindrical shape and the thickness of its top was about three times thinner than the side. The chemical composition of the specimen is given in Table 1. The inner and outer radii of the specimen were 12 and 18

Fig. 4. Schematic diagram of the experimental apparatus.

Table 1. Chemical composition of the specimens. (mass%)

Specimen	C	Si	Mn	P	S	Al
Carbon steel	0.19	0.22	1.00	0.018	0.012	0.015

mm, respectively. The top of the specimen, into which a steel pipe was bonded by electron beam welding, separated the entry side and extraction side of the hydrogen.

On the entry side, argon gas was replaced to hydrogen gas (build-up) and *vice versa* (decay) at a flow rate of $1.7 \times 10^{-6} \text{ m}^3 \cdot s^{-1}$ and at a gas pressure of 0.101 MPa. On the extraction side, the hydrogen permeated through the steel was detected with the solid electrolyte mounted to the top of the specimen. The ceramics was 10 mm in diameter and 2 mm in thickness. It was used as a reference and a counter electrodes; they were separated by a coating porous platinum on the one side of the solid electrolyte as shown in Fig. 1. The platinum paste with which the ceramics was coated was dried for 1.8 ks at 623 K and then sintered for 0.9 ks at 1 273 K. After the treatment, joining of the solid electrolyte to the steel was made with a platinum paste at 773 K.

Since it was difficult to get a good detectability of hydrogen by joining the solid electrolyte to the steels with the platinum past as will be described later, we tried to join the ceramics to the as-polished or metal-plated steel using amorphous copper filler metal at 923 K. The amorphous filler metal was about 0.03 mm in thickness and had the following chemical composition: Ni: 9.5, Sn: 4.0, P: 7.5 mass%, Cu: balance.

The hydrogen in the specimen was extracted at an anodic potential in the range of 0 to 160 mV *vs.*

$\text{O}_2(\text{SrCeO}_3)/\text{H}_2\text{O}(\text{air})$. The temperature was maintained at a given temperature within ± 3 K by a controller with a thermocouple close to the furnace. The permeated transient current during the built-up and the decay processes was recorded as a function of time.

4. Results and Discussion

4.1. Response of Solid Electrolyte to Hydrogen

First, we investigated the response of the solid electrolyte to the change in the atmosphere from argon to hydrogen and *vice versa*. In this experiments, one side of the solid electrolyte was exposed directly to the atmosphere by drilling a hole of about 2 mm in diameter in the top of the steel specimen as shown in Fig. 4. A graphite sheet was put around the hole between the steel and the solid electrolyte and the three were fastened together with bolts to prevent a gas leak. The permeation current density was measured during the built-up and decay processes in the same way as described above.

An example of the measurements is illustrated in Fig. 5. Fig. 5 shows that the solid electrolyte used is very sensitive to the change in the atmosphere or hydrogen pressure.

4.2. Relationship between Extraction Potential and Permeation Current Density

A typical relationship between the extraction potential and the permeation current density at the steady state (J_∞) in a hydrogen pressure of 0.101 MPa and in an argon pressure of 0.101 MPa are shown in Fig. 6. The values of J_∞ increased with increasing potential. Since the solid electrolyte used has only *p*-type conduction or hole conduction in an atmosphere free from hydrogen or water vapor,⁹⁾ this phenomenon is probably due to the increase in the residual anodic current by hole conduction. From the difference between the two steady state permeation currents (ΔJ_∞), or the net ionization current density, it can be seen that the most suitable potential range for detecting the permeated hydrogen is from 0 to 140 mV *vs.* $\text{O}_2(\text{SrCeO}_3)/\text{H}_2\text{O}(\text{air})$. Thus, we selected 80 mV as an anodic potential sufficient to ionize the

hydrogen permeated through the steel.

4.3. Permeation Curves and Diffusivity of Hydrogen

A typical permeation curve for hydrogen at 80 mV *vs.* $\text{O}_2(\text{SrCeO}_3)/\text{H}_2\text{O}(\text{air})$ polarization is shown in Fig. 7, where the arrows show the changes in the atmosphere from argon to hydrogen for buildup and from hydrogen to argon for decay.

Fig. 8 shows a comparison between the theoretical curves (solid lines) and experimental data. The ordinate was normalized in units of $\Delta J_i/\Delta J_\infty$, and the plots were shifted on the abscissa to coincide with the theoretical curves at $\Delta J_i/\Delta J_\infty=0.5$. The experimental data agreed fairly well with the theoretical curves. This indicates that the following initial and boundary conditions at the entry and extraction surfaces were adequate:

for the build-up process,

$$\begin{aligned} t = 0, 0 \leq X \leq L, C = 0 \\ t > 0, X = 0, C = C_0 \\ X = L, C = 0 \end{aligned} \quad \dots\dots\dots(4)$$

J_∞ : the steady state permeation current density
 ΔJ_∞ : the difference between the two steady state permeation current densities, or the net ionization current density

Fig. 6. Relationship between permeation current density and extraction potential.

Fig. 5. Response of the solid electrolyte to the change in hydrogen pressure.

Arrows denote the points at which the atmosphere is replaced from argon to hydrogen (build-up) and *vice versa* (decay).

Fig. 7. Typical permeation transients in the build-up and decay processes at an extraction potential of 80 mV *vs.* $\text{O}_2(\text{SrCeO}_3)/\text{H}_2\text{O}(\text{air})$.

Fig. 8.

Comparison between the theoretical permeation curves and experimental data in the build-up and decay transients.

and for the decay process,

$$\begin{aligned} t = 0, 0 \leq X \leq L, C = C_0(1 - X/L) \\ t > 0, X = 0, C = 0 \\ X = L, C = 0 \end{aligned} \quad \dots\dots(5)$$

The diffusivity obtained from build-up and decay runs is plotted against the reciprocal of temperature in Fig. 9. The values obtained from the electrochemical method⁸⁾ and the conventional gaseous methods such as the gaseous permeation¹²⁻¹⁶⁾ and evolution techniques¹⁶⁻¹⁸⁾ are also shown in the figure. The diffusion coefficients of hydrogen for the carbon steel obtained from the build-up and decay runs were 8.71×10^{-9} and $6.99 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, respectively. These values were close to the ones measured by the electrochemical method using a molten sodium hydroxide electrolyte⁸⁾ (1.27×10^{-8} and $9.90 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) as shown in Fig. 9.

4.4. Effect of Joining of Ceramics/Steel on Detectability of Hydrogen

The detectability of hydrogen can be evaluated by comparing the hydrogen content obtained from the permeation current density with that calculated from Sievert's law:

$$C_0(\text{ppm}) = a^* \sqrt{P_{\text{H}_2}} \exp(-\Delta H/RT) \quad \dots\dots(6)$$

where, a^* : a constant ($\text{ppm} \cdot \text{Pa}^{-1/2}$)

P_{H_2} : the hydrogen partial pressure (Pa)

ΔH : the enthalpy change associated with dissolution of hydrogen in steel ($\text{kJ} \cdot \text{mol}^{-1}$)

R : the gas constant ($8.31 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}$)

T : the reaction temperature (K).

Fig. 10 shows the values of C_0 (hydrogen content) and $\Delta J_{\infty} \cdot L$ (hydrogen permeability) obtained from several build up and decay runs at 773 K and 0.101 MPa hydrogen gas. Broken lines in the figure represent the values of C_0 and $\Delta J_{\infty} \cdot L$ calculated from Eqs. (3) and (6). In this case, from the published data¹⁹⁻²¹⁾ for a^* and ΔH and Fig. 9 for D , 0.133 $\text{ppm} \cdot \text{Pa}^{-1/2}$, 27.2 $\text{kJ} \cdot \text{mol}^{-1}$ and $1.1 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ were taken, respectively. The values obtained by joining the solid electrolyte to the as-polished steel using the platinum paste are much smaller than the calculated

Fig. 9. Arrhenius plots of hydrogen diffusivities in carbon steel.

---: the values of C_0 and $\Delta J_{\infty} \cdot L$ obtained from Eqs. (3) and (4)

Fig. 10. Effect of joining of ceramics/steel on the hydrogen content (C_0) and the hydrogen permeability ($\Delta J_{\infty} \cdot L$).

ones. This poor detectability of hydrogen is probably derived from the fact that most of atomic hydrogen permeated through the steels became hydrogen

molecules and water vapor on the surfaces of the steels and/or porous platinum and escaped in the atmosphere. We, therefore, attempted to join the ceramics to the as-polished or metal-plated steel using a filler metal to prevent the escape of hydrogen. Fig. 10 also shows typical examples of these results. Of these, the values obtained by joining the ceramics to the platinum-plated steel with the amorphous filler metal are in fairly good agreement with that calculated ones, indicating that this joining of ceramics/steel leads to the remarkable improvement of the detectability of hydrogen.

5. Conclusions

From these experiments, it was found possible to measure the diffusivity and the content of hydrogen permeated through the steel using the ceramic sensor. However, in order to put it into practical use, it will be required to monitor the hydrogen with high detectability for a long period. Thus, further improvement of joining of ceramics/steel is being made to meet the requirement.

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