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Hydrogen dissolution into zirconium oxide

S. Yamanaka*, T. Nishizaki, M. Uno, M. Katsura

Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565, Japan

Abstract

The hydrogen dissolution behavior of monoclinic ZrO_2 oxide has been examined in the temperature range of 500–1100°C in oxygen/water vapor atmosphere using a thermal desorption method. Thermal desorption of H_2O gas from hydrogenated ZrO_2 oxide was observed. The hydrogen solubility in the ZrO_2 oxide evaluated from the thermal desorption spectra ranged from 10^{-5} to 10^{-4} mol H/mol oxide and decreased with increasing temperature. The equilibrium between the atmosphere and the ZrO_2 oxide was explained on the basis of reaction involving oxygen and hydrogen defects.

Keywords: Zirconium oxide; Hydrogen dissolution; Oxide; Hydrogen; Thermal desorption

1. Introduction

Zirconium alloys such as Zircaloy and Zr–Nb have been used as the cladding materials of light water reactors (LWRs). The renewed interest in the corrosion of the cladding under high burn up conditions of LWRs promotes reassessment of hydrogen absorption of the cladding. Surface ZrO_2 oxide formed on the cladding serves as a hydrogen diffusion barrier. A sound understanding of hydrogen diffusion, solubility and permeability in ZrO_2 oxide is required for minimizing the hydrogen embrittlement of the cladding.

Although several studies on the hydrogen behavior in ZrO_2 oxide [1–4] have been carried out, literature data for hydrogen solubility and diffusivity show some uncertainty and discrepancies. This may result from difficulties of detecting a small amount of hydrogen dissolved in the oxides. In the present work, thermochemical studies on the hydrogen dissolution into ZrO_2 oxide have been carried out using a thermal desorption method.

2. Experimental

The sintered ZrO_2 oxide (99.96% in purity) was selected as a specimen in the form of a disk (6.5 mm $\phi \times 1.2$ mm). It was found from X-ray diffraction analysis that all the specimens have the monoclinic structure. Oxygen gas (99.999 vol% in purity) was used.

The experimental apparatus consisted of a hydrogen analyzing system and a hydrogenating system. A hydrogenated ZrO_2 specimen was able to be transferred from the hydrogenating system to the hydrogen analyzing system without air exposure, which enabled us to avoid surface contamination of the ZrO_2 specimen. The ultimate pressure of the hydrogen analyzing system was 1×10^{-7} Pa. The specimen was heated with a constant heating rate of 5°C/s from room temperature to 1000°C by an infrared light furnace. The gaseous species released from the specimen were detected by means of a quadrupole mass spectrometer.

The ZrO_2 specimen was exposed to a flow of wet oxygen in the temperature range of 500–1000°C in the hydrogenating system. The water vapor pressure was controlled to be 872 Pa, and the total pressure of the gas mixture of oxygen and water vapor was 10^5 Pa. After equilibration, the specimen was quenched and then transferred from the hydrogenating system to the hydrogen analyzing system. The total amount of hydrogen absorbed in the specimen was evaluated from integration of the thermal desorption spectra of chemical species containing hydrogen.

3. Results and discussion

Fig. 1 shows a typical example of desorption spectra from the ZrO_2 specimen hydrogenated at 700°C under a water vapor pressure of 872 Pa. The hydrogen-containing species released from the specimen was H_2O gas. A

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*Corresponding author.

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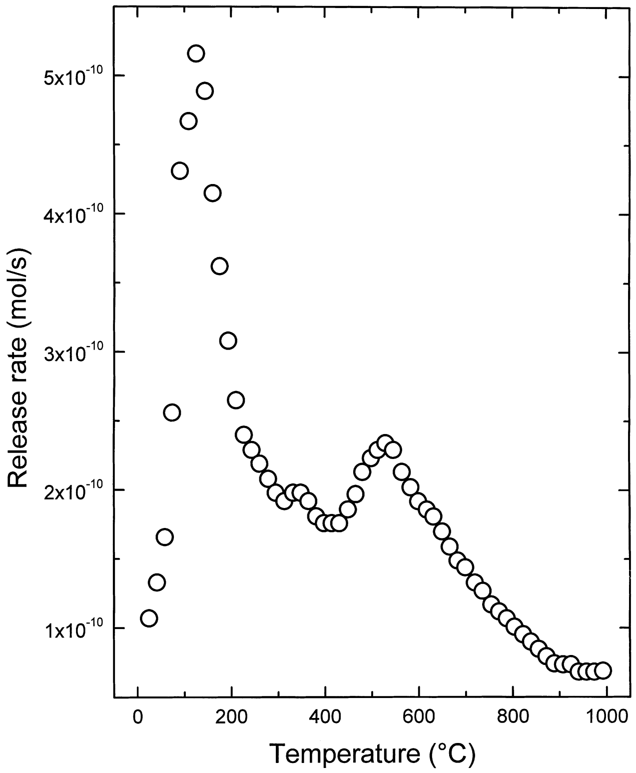

Fig. 1. Thermal desorption spectra of ZrO_2 hydrogenated at a temperature of 700°C at a water vapor pressure of 872 Pa.

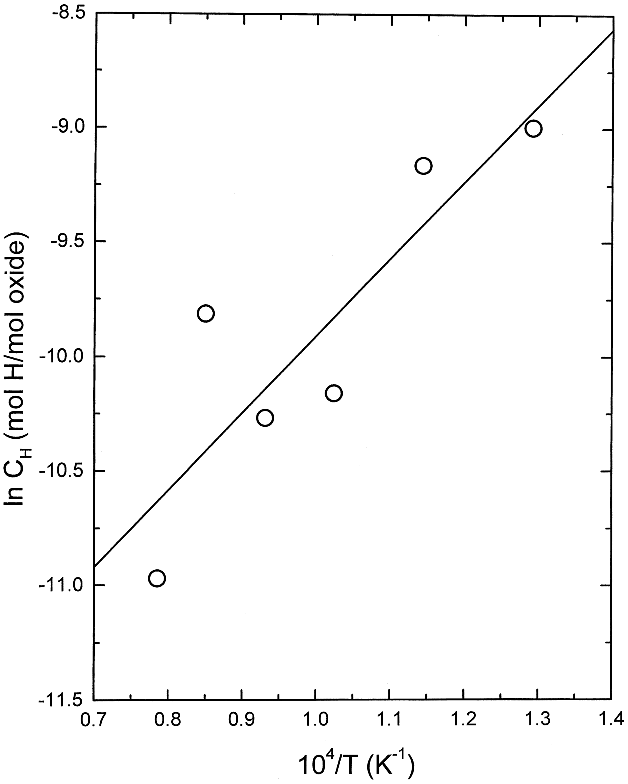

Fig. 2. Temperature dependence of hydrogen solubility in ZrO_2.

negligibly small amount of H_2 gas was found to be released.

As evidenced by Fig. 1, there exist two desorption peaks in the desorption spectrum of H_2O. For H_2O gas release around 100°C, the amount of the released gas and the peak temperature was not markedly affected by the hydrogenating temperature. The H_2O gas release below 200°C appears to be desorption of H_2O adsorbed on the surface of the specimen. The H_2O gas release around 600°C strongly depended on the hydrogenating temperature and was inferred to result from the hydrogen dissolved inside the specimen. The hydrogen dissolved in the specimen was almost all released up to 1000°C.

The total amount of dissolved hydrogen inside the ZrO_2 specimen was evaluated from the thermal desorption spectra, and the hydrogen solubility was estimated from the result. The dependence of the hydrogen solubility in the ZrO_2 on the hydrogenating temperature is illustrated in Fig. 2. As shown in this figure, the hydrogen solubility in the monoclinic ZrO_2 oxide ranges from 10^{-5} to 10^{-4} mol H/mol and decreases with the hydrogenating temperature.

Under high oxygen partial pressure conditions, the equilibrium between oxygen gas and ZrO_2 can be expressed as,

$$\tfrac{1}{2}\,O_2(g) = O_i'' + 2h^{\cdot} \tag{1}$$

where O_i'' is the interstitial oxygen with -2 effective valence charge and $h^{\cdot}$ is the hole. Assuming that hydrogen is dissolved interstitially in ZrO_2 in equilibrium with the oxygen/water vapor atmosphere, the following equilibrium appears to be established:

$$H_2O(g) + 2h^{\cdot} = 2H_i^{\cdot} + O_2(g) \tag{2}$$

where $H_i^{\cdot}$ is the interstitial hydrogen defect. The equilibrium constants K_1 and K_2 for the above reactions are written by

$$K_1 = [O_i'']p^2/P_{O_2}^{1/2} \text{ for Eq. (1)} \tag{3}$$

$$K_2 = [H_i^{\cdot}]^2 P_{O_2}^{1/2}/(p^2 P_{H_2O}) \text{ for Eq. (2)} \tag{4}$$

where $[O_i'']$, p and $[H_i^{\cdot}]$, are the concentrations of the interstitial oxygen, the hole and the interstitial hydrogen, and P_{O_2} and P_{H_2O} are the partial pressures of oxygen and water vapor. The electrical neutrality condition can be expressed as,

$$[H_i^{\cdot}] + p - 2[O_i''] = 0 \tag{5}$$

On the assumption that under high water vapor pressures, the interstitial hydrogen concentration is much higher than hole concentration:

$$[H_i^{\cdot}] \gg p. \tag{6}$$

we obtain the following equation:

$$[H_i^{\cdot}] = 2[O_i'']. \tag{7}$$

Hence, the concentration of the interstitial hydrogen and hole can be given by the following equations:

$$[H_i^{\cdot}] = K_3 P_{H_2O}^{1/3}, \quad K_3 = (2K_1K_2)^{1/3} \tag{8}$$

$$p = K_4 P_{O_2}^{1/4} P_{H_2O} - 1/6, \quad K_4 = 2K_1^{2/3} K_2^{-1/3} \tag{9}$$

Applying the experimental data to above equation, we can estimate the equilibrium constant K_3. Fig. 3 demonstrates the temperature dependence of the equilibrium constant thus estimated. As shown in this figure, plots of the equilibrium constant K_3 vs. the reciprocal temperature exhibits a straight line, which is expressed by

$$\ln K_3 = -15.57 + 3391/T. \tag{10}$$

Under the water vapor pressure $P_{H_2O} = 80$, 872 and 8000 Pa, the temperature dependence of hydrogen solubility was estimated, as indicated by the broken, dotted and solid lines in Fig. 4. It is obvious from this figure that the estimated line for $P_{H_2O} = 872$ Pa reasonably agrees with the experimental values and that the hydrogen solubility decreases with the temperature under both water vapor pressures of 80 and 8000 Pa. Hence, the ZrO_2 appears to equilibrate with the wet oxygen atmosphere, and the equilibrium can be expressed by the above equations.

In Fig. 5, the hydrogen solubility in the monoclinic ZrO_2 oxide is compared with those in other oxide reported in the

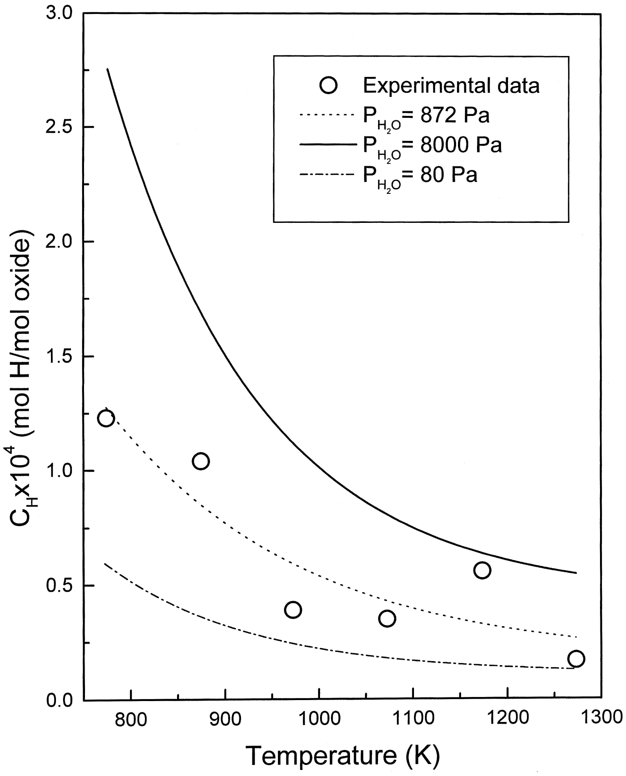

Fig. 4. Influence of water vapor pressure on the hydrogen solubility in ZrO_2.

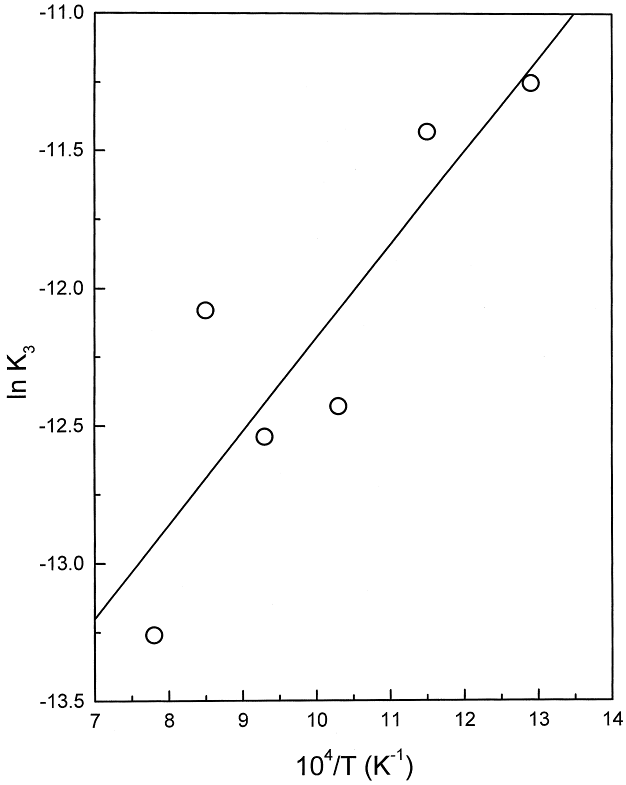

Fig. 3. Temperature dependence of equilibrium constant for hydrogen dissolution into ZrO_2.

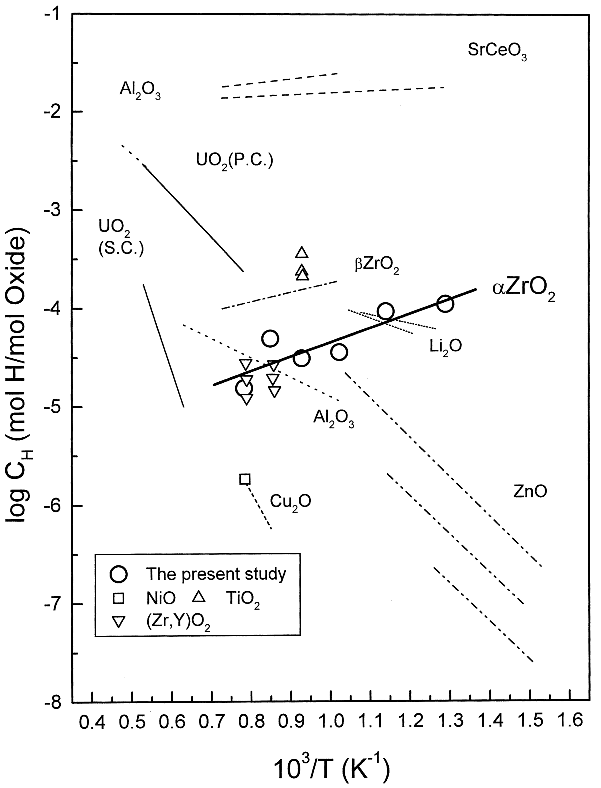

Fig. 5. Comparison of the hydrogen solubility in ZrO_2 with those in other oxides.

literature [1,5–11]. Our solubility data for the ZrO_2 oxide are two orders of magnitude lower than the solubility data for $SrCe_{0.95}Yb_{0.05}O_3$ [9] (above 10^{-2} mol H/oxide mol). The hydrogen solubility in the monoclinic ZrO_2 oxide obtained in the present study is close to the solubility data for cubic and tetragonal ZrO_2 [1,6]. Other oxides such as ZnO have lower solubility than ZrO_2 oxide. As shown in Fig. 5, there exist marked differences in the temperature dependence of hydrogen solubility in oxides.

4. Conclusions

The hydrogen dissolution into the monoclinic ZrO_2 sintered oxide has been studied in the temperature range of 500–1000°C in oxygen/water vapor atmosphere using a thermal desorption method. The thermal desorption of H_2O gas from the hydrogenated ZrO_2 specimen was observed, whereas a negligibly small amount of H_2 gas was released from the hydrogenated ZrO_2 specimen.

The hydrogen solubility in the ZrO_2 oxide was estimated from the thermal desorption spectra to be from 10^{-5} to 10^{-4} mol H/mol oxide and found to decrease with increasing temperature. The equilibria between the ZrO_2 and the atmosphere was discussed in terms of reaction involving interstitial hydrogen defects.

Acknowledgements

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References

[1] K. Park, D.R. Olander, J. Am. Ceram. Soc. 74 (1991) 72.
[2] D. Khatamian, J. Alloys Comp. 253–254 (1997) 471.
[3] D. Khatamian, J. Alloys Comp. 231 (1997) 722.
[4] D. Khatamian, F.D. Manchester, J. Nucl. Mater. 166 (1989) 300.
[5] T.S. Elleman, D. Rao, K. Verghese, L. Zumawalt. DE-AS05-76-ET52022, DOE.
[6] C. Wagner, Ber. Bunsenges. Phys. Chem. 72 (1968) 778.
[7] S. Stotz, C. Wagner, Ber. Bunsenges. Phys. Chem. 70 (1966) 778.
[8] D.G. Thomas, J.J. Lander, J. Chem. Phys. 25 (1956) 1143.
[9] S. Yamanaka, M. Okada, S. Komatuki, M. Miyake, J. Alloys Comp. 231 (1995) 713.
[10] D.F. Sherman, D.R. Olander, J. Nucl. Mater. 166 (1989) 307.
[11] O. Johnson et al., J. Appl. Phys. 46 (1975) 1026.