

## 論文

### ZrC の水素吸収放出挙動

波多野 雄治, 野崎 天生, 本間 啓史, 松山 政夫

富山大学水素同位体科学研究センター  
〒930-8555 富山市五福 3190

### Absorption and Release of Hydrogen Isotopes by ZrC

Yuji Hatano, Teo Nozaki, Hirofumi Homma and Masao Matsuyama

Hydrogen Isotope Research Center, University of Toyama  
Gofuku 3190, Toyama 930-8555, Japan

(Received January 10, 2008; accepted March 13, 2008)

#### Abstract

Interaction between hydrogen isotopes and ZrC powder was examined at 873 K and pressure from 0.89 to 99 Pa. Reversible absorption and release of hydrogen isotopes were observed. The equilibrium concentrations of hydrogen isotopes in the above pressure range were from 82 to 120 mol ppm; the pressure dependence observed was much weaker than that expected from Sieverts' law. The diffusivity of hydrogen was evaluated to be  $3 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  by assuming that powder particles were spherical with diameters of 1  $\mu\text{m}$ .

#### 1. Introduction

Zirconium carbide, ZrC, is a potential candidate of coating material for fuel particles in high temperature gas-cooled reactors [1]. Hydrogen production from water

by thermo-chemical processes is one of the main objectives of the development of this type of nuclear reactor [2]. The contamination of product hydrogen by tritium produced by ternary fission of uranium is a critical issue for this application [3], and hence the permeability of hydrogen isotopes through coating materials has to be carefully evaluated. It is known that ZrC in carbon deficient composition,  $ZrC_{1-x}$ , absorbs hydrogen [4]. The solubility of hydrogen isotopes at/near stoichiometric composition, however, has been scarcely reported. In addition, no data on diffusivity is available in literature.

The authors have previously carried out hydrogen absorption experiments for TiC having near-stoichiometric composition and successfully evaluated diffusion coefficients of hydrogen in a temperature range from 773 to 973 K [5]. In the present study, the absorption and desorption of hydrogen and deuterium by ZrC were examined by the similar technique at 873 K and pressure from 0.89 to 100 Pa. The diffusion coefficient was evaluated from absorption curves.

## 2. Experimental

Specimen used in the present study was powder of ZrC supplied by Kojundo Chemical Laboratory Co., Japan. The nominal purity of the specimen was 95%. According to the supplier, the main impurity was Hf. The specimen powder was analyzed by X-ray diffraction (XRD) before and after hydrogen absorption experiments. The size distribution of powder particles were examined with a scanning electron microscope (SEM).

The hydrogen absorption experiments were carried out at 873 K using a vacuum apparatus which was similar one used in the previous study [6]. The specimen

powder of 2 g was installed in a quartz tube attached to the apparatus and heated in vacuum for degassing. Elevation of specimen temperature resulted in significant release of gas whose mass number was 28, i. e. CO and/or N<sub>2</sub>. The specimen temperature was raised gradually to keep the pressure in the apparatus lower than 10<sup>-3</sup> Pa. The degassing was stopped when the pressure in the apparatus became lower than 10<sup>-5</sup> Pa at 1373 K. Then, absorption of hydrogen (or deuterium) was examined in a closed vacuum system, in which the hydrogen absorption was indicated by pressure drop [6]. The initial pressure of H<sub>2</sub> (or D<sub>2</sub>) gas was adjusted to be 5.2 or 105 Pa, and the specimen temperature to be 873 as described above. The rate of hydrogen absorption was evaluated from the change in pressure with time. After the attainment of equilibrium, the specimen was cooled down to room temperature, and H<sub>2</sub> gas remaining in gas phase was evacuated by a turbo-molecular pump. Then the apparatus was isolated again from the pump, and the specimen was heated to 873 K in a closed system to examine desorption.

### 3. Results

#### 3.1 Characteristics of Specimen Powder

Fig. 1 shows XRD pattern of powder particles after hydrogen absorption experiments as an example. No significant difference was observed between the powder under as-received conditions and after hydrogen absorption experiments. All peaks in the XRD pattern could be assigned to ZrC (NaCl structure) and Si added as an internal standard; no peaks of other phases such as metallic Zr and Zr oxides were observed. The lattice parameter of ZrC was evaluated to be 0.4696 nm. Fig. 2 shows SEM micrograph of the specimen powder. Majority of particles was in a range of size from 0.5 to 3 μm.

The size of 55 particles was measured randomly, and the average value of particle size was evaluated to be 1.6  $\mu\text{m}$ .

### 3.2 Hydrogen Absorption

Figs. 3 (a) and (b) shows typical examples of the absorption curves obtained at initial  $\text{H}_2$  pressure of 5.2 and 105 Pa, respectively. In the former case, the majority of introduced  $\text{H}_2$  was absorbed by the specimen powder, while only small portion was

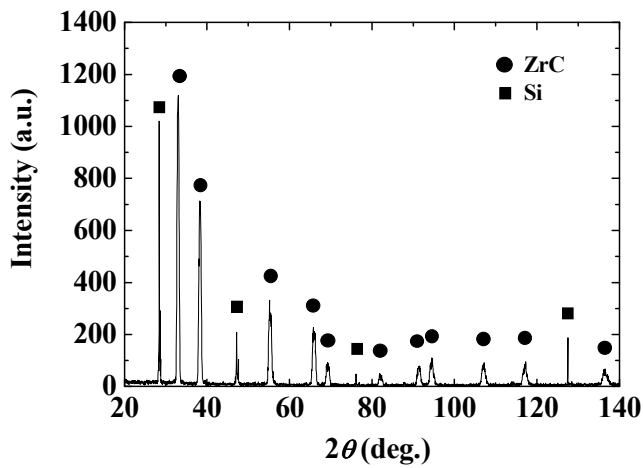


Fig. 1 XRD pattern of ZrC powder.

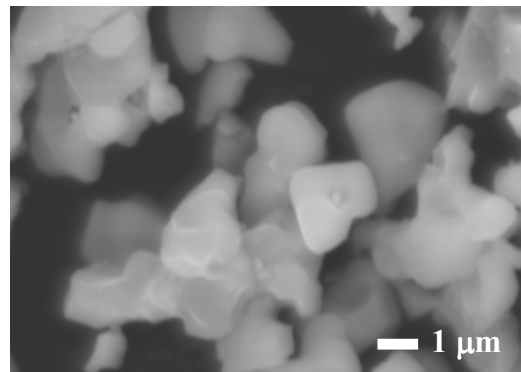


Fig. 2 SEM micrograph of ZrC powder.

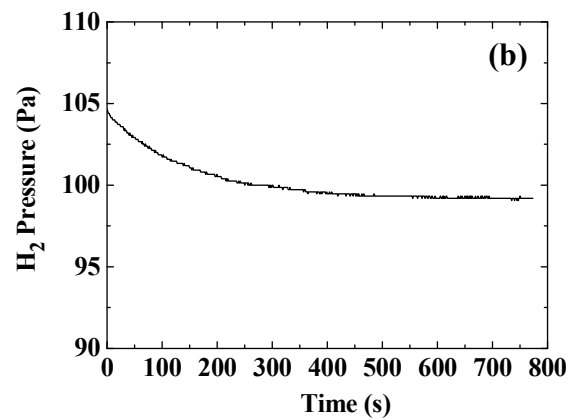
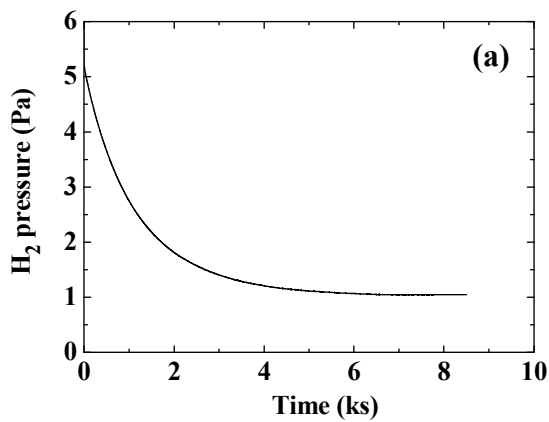


Fig. 3 Typical examples of  $\text{H}_2$  absorption curves at 873 K and initial pressures of 5.2 Pa (a) and 105 Pa (b).

dissolved in the latter case. The equilibrium pressures of H<sub>2</sub> in these absorption experiments were 1.1 and 99 Pa, respectively. The extent of pressure reduction corresponded to H concentration in ZrC of 82 and 120 mol ppm ( $[H]/[ZrC] = 8.2 \times 10^{-5}$  or  $1.2 \times 10^{-4}$ ).

The correlation between hydrogen concentration in ZrC and gas pressure is shown in Fig. 4 together with the data obtained by absorption experiments with D<sub>2</sub> and desorption experiments. The results of desorption experiments agreed well with those of absorption experiments. This observation suggests that ZrC reversibly absorbs and releases hydrogen isotopes. In other words, ZrC can permeate hydrogen isotopes under gradient of chemical potential of hydrogen isotopes. The solubility of deuterium was comparable to that of hydrogen. The number of data points, however, is not enough to derive decisive conclusion

on the isotope effect.

Further investigation is necessary to understand the solubility of tritium.

One of the important features of

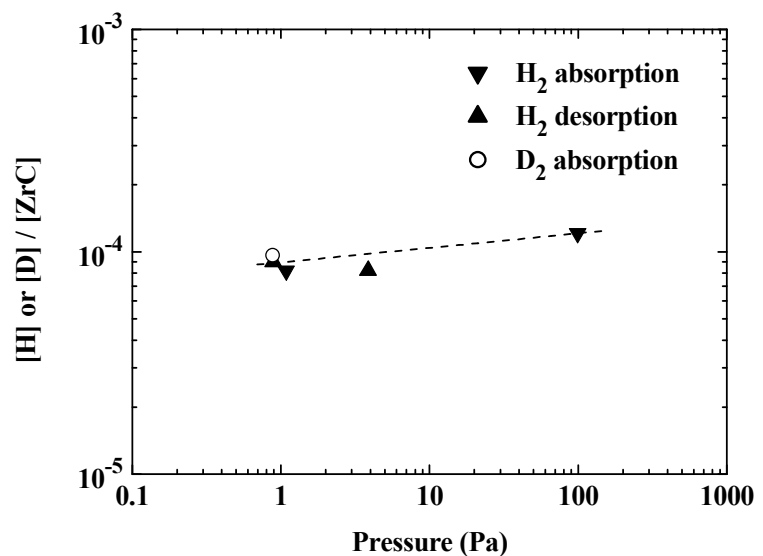


Fig. 4 Pressure dependence of H or D concentrations in ZrC.

Fig. 4 is very weak pressure dependence of hydrogen concentration. Although the pressure of hydrogen was varied by two orders of magnitude, the concentration of hydrogen in ZrC increased only by factor 1.5. Such weak pressure dependence can be explained by the saturation of the sites for hydrogen dissolution at high pressure (99 Pa). Results of neutron diffraction analysis for  $\text{ZrC}_{0.62}\text{D}_{0.28}$  showed that both deuterium and carbon atoms occupied octahedral sites of FCC type arrangement of Zr atoms [7]. In other words, deuterium occupies carbon vacancies in this system. Samsonow and Morosow [4] examined the hydrogen absorption of  $\text{ZrC}_{1-x}$  and reported that the concentration of absorbed hydrogen roughly corresponded to the amount of carbon vacancy. For examples,  $\text{ZrC}_{0.64}$  and  $\text{ZrC}_{0.81}$  absorbed hydrogen up to  $\text{ZrC}_{0.64}\text{H}_{0.31}$  and  $\text{ZrC}_{0.81}\text{H}_{0.12}$ , respectively. Their observations also indicate the occupancy of carbon vacancies by hydrogen atoms. Hence, it is appropriate to consider that hydrogen and deuterium occupied carbon vacancies also in the present specimen, and the concentration of hydrogen under 99 Pa  $\text{H}_2$  (120 mol ppm) roughly correspond to that of carbon vacancies. Measurements of pressure-composition isotherms of TiC-H system are currently under progress. In this system, hydrogen concentration under equilibrium obeyed Sieverts' law at  $\text{H}_2$  pressure below 10 Pa but ceased to increase in higher pressure range ( $\sim 1000$  Pa) at the concentration close to that of carbon vacancy

evaluated by chemical analysis. Detailed results in TiC-H system will be reported in a separate paper.

The present results lead to two important predictions. First, solubility of tritium, and consequently permeability, should be reduced by the reduction in the carbon vacancy concentration. Second, the measurement of solubility of hydrogen isotopes is a sensitive method to determine the concentration of carbon vacancy, especially in a low concentration range where precise measurement by chemical analysis is impossible. It is known that ZrC contains certain concentration of carbon vacancies even under coexistence of elemental carbon [8,9]. The concentration of carbon vacancy may influence not only on the transport of tritium but also on that of other hazardous fission products. Hence, it is important to develop the techniques to control and evaluate the concentration of carbon vacancies in ZrC. Further investigation is necessary to derive decisive conclusions on the correlation between carbon vacancy concentration and solubilities of hydrogen isotopes in ZrC.

The rate-limiting step of hydrogen absorption was evaluated in the manner described in the previous paper [5]. All absorption curves indicated that the rate-limiting step is the bulk diffusion process. The diffusion coefficient of hydrogen  $D$  in ZrC was evaluated by fitting the solution of diffusion equation to the absorption curves obtained

at initial pressure of 105 Pa by assuming that the powder particles are spherical with diameters of 1  $\mu\text{m}$  for simplicity. The surface concentration of hydrogen was assumed to be constant during the absorption since the extent of pressure change was small as mentioned above. Under such conditions, the amount of absorbed hydrogen at time  $t$ ,  $M_t$ , is described as [10]

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t/a^2), \quad (1)$$

where  $a$  is the radius of powder particle. The result of fitting is shown in Fig. 5. The experimentally-obtained absorption curve was well reproduced at  $D = 3 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$ .

Fig. 6 shows the comparison with the values of hydrogen diffusivity in TiC obtained in the previous study. The obtained value of diffusion coefficient of hydrogen in ZrC is close to that in TiC. It is necessary to examine the dependence of diffusivity on the carbon vacancy concentration.

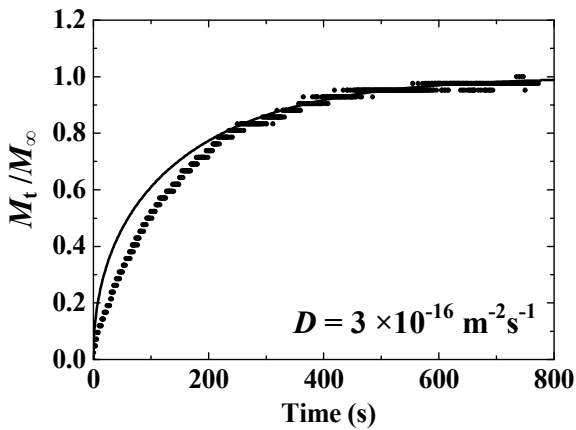


Fig. 5 Example of fitting of Eq. (1) (line) to absorption curve corresponding to Fig. 3 (b) (dots).

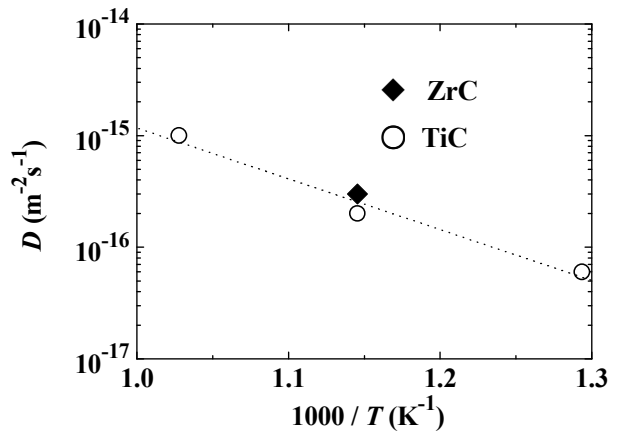


Fig. 6 Comparison between diffusion coefficients of hydrogen in ZrC and TiC.



#### 4. Conclusions

The absorption and release of hydrogen isotopes by ZrC powder was examined at 873 K and pressure from 0.89 to 99 Pa. Reversible absorption and release of hydrogen isotopes were observed. The equilibrium concentrations of hydrogen isotopes in the above pressure range were from 82 to 120 mol ppm; the pressure dependence observed was much weaker than that expected from Sieverts' law. Such weak pressure dependence was attributed to the saturation of carbon vacancies by hydrogen isotopes at high pressure. The diffusivity of hydrogen was evaluated to be  $3 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  from absorption curves.

#### Acknowledgements

This study was supported in part by a Grant-in-Aid for Scientists Research (C) of Ministry of Education, Culture, Sports, Science and Technology of Japan, No. 17560613.

#### References

- [1] K. Minato, T. Ogawa, K. Fukuda, H. Nabelek, H. Sekino, Y. Nozawa and I. Takahashi, *J. Nucl. Mater.*, **224** (1995) 85-92.
- [2] K. Onuki, Y. Inagaki, R. HINO and Y. Tachibana, *Progress in Nucl. Energy*, **47** (2005) 496-503.
- [3] D. Yook, K.-J. Lee, Y. Lee and D. Hong, *J. Nucl. Sci. Technol.*, **43** (2006) 1522-1529.
- [4] G. W. Samsonow and W. W. Morosow, *Mh. Chem.*, Bd. **102** (1971) 1667-1678.

- [5] Y. Hatano, T. Nozaki, H. Homma and M. Matsuyama, Annual Report of Hydrogen Isotope Research Center, University of Toyama, **26** (2006) 31-43.
- [6] R. Hayakawa, Y. Hatano, A. Pisarev, K. Watanabe, Phys. Scr., **T108** (2004) 38-41.
- [7] K. Yvon, H. Nowotny and R. Kieffer, Mh. Chem., **98** (1967) 2164-2172.
- [8] E. K. Storms, *The Refractory Carbides*, Academic Press, New York, NY, USA, 1967.
- [9] H. O. Pierson, *Handbook of Refractory Carbides and Nitrides*, Noyes Publications, Westwood, NJ, USA, 1996.
- [10] J. Crank, *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, Oxford, UK, 1975, p. 89-93.