論文

TiC 中の水素の拡散挙動

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Diffusion of Hydrogen in TiC

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Abstract

The diffusion coefficient of hydrogen in commercially supplied TiC powder was measured at 773, 873 and 973 K by hydrogen absorption experiments. The pre-exponential factor and activation energy were evaluated to be 10^{-11} $m^2 \cdot s^{-1}$ and 87 ± 13 $kJ \cdot mol^{-1}$, respectively.

1. Introduction

Carbides of group 4 and 5 metals have unique properties such as refractoriness, extreme hardness and good resistance against chemical corrosion [1,2]. Hence, systematic studies on the interactions between these carbides and hydrogen isotopes may lead to the development of new functional materials for handling of hydrogen isotopes. Indeed, the present authors have found that the intermediate layers of Nb

carbides improve high temperature stability of Pd coating prepared on Nb to form a composite membrane for hydrogen separation [3,4]. Accumulation of data on hydrogen diffusivity is important for material selection in this application. In addition, ZrC is a potential candidate of coating material for fuel particles used in high temperature gas-cooled reactors [5]. The data on diffusivity are necessary also in this application to evaluate the rate of tritium release from fuel core to coolant He gas. The diffusivity of hydrogen isotopes in the carbides, however, has been scarcely reported.

In the present study, the hydrogen absorption of commercially supplied TiC powder was examined at 773, 873 and 973 K. The analysis of absorption curves indicated that the rate of absorption was controlled by the diffusion process in the bulk. The diffusion coefficient evaluated was in a rage from 6×10^{-17} to 1×10^{-15} $m^2 \cdot s^{-1}$.

2. Experimental

2.1. Specimen

Specimen used in the present study was powder of TiC supplied by Kojundo Chemical Laboratory Co., Japan. The nominal purity of the specimen was 99%, and the concentrations of metallic impurities measured by the supplier are summarized in Table 1. The specimen power 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).

Table 1   Concentrations of metallic impurities in TiC specimen.

Element	Al	Cr	Fe	Mn	Ni
Conc. (mass%)	0.3	0.007	0.005	0.001	0.001

The hydrogen absorption experiments were carried out at 773, 873 and 973 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_2. The specimen temperature was raised gradually to keep the pressure in the apparatus lower than 10^{-3} Pa. The degassing was stopped when the pressure in the apparatus became lower than 10^{-5} Pa at 1373 K. Then, hydrogen absorption was examined in a closed vacuum system, in which the hydrogen absorption was indicated by pressure drop [6]. The initial pressure of H_2 gas was adjusted to be 20-50 kPa, and the specimen temperature to be 773, 873 or 973 K. The absorption rate was too small at temperatures lower than 773 K, while the pressure change by degassing from the specimen was not negligible at temperatures higher than 973 K even after the degassing treatment in vacuum at 1373 K. Hence, it was difficult to examine in a wider temperature range.

3. Results

3.1 Characteristics of Specimen Powder

Fig. 1 shows XRD patterns of powder particles before and after hydrogen absorption tests. All peaks in these patterns could be assigned to TiC (NaCl structure) and Si mixed with the specimen powder as standard reference material; no peaks of other phases such as metallic Ti and Ti oxides were observed. The lattice parameter of TiC was evaluated to be 0.4324 nm. This value of lattice parameter is slightly smaller

than that for high purity TiC (0.4328 nm)[1,2]. It is known that oxygen and nitrogen present in TiC as impurities lower the lattice parameter [1]. The specimen used in the present study contained these impurities at total concentration of 2 at% as described below. Thus the slightly small lattice

Fig. 1   X-ray diffraction patters of TiC powder before (a) and after (b) hydrogen absorption experiments.

parameter can be ascribed to the influence of these impurities. No noticeable difference was observed between diffraction patterns before and after hydrogen absorption experiments.

The concentrations of carbon, oxygen and nitrogen in the specimen powder subjected to hydrogen absorption experiments were examined in Horiba Co., Japan; carbon concentration was measured by combustion in O_2 gas flow and that of oxygen
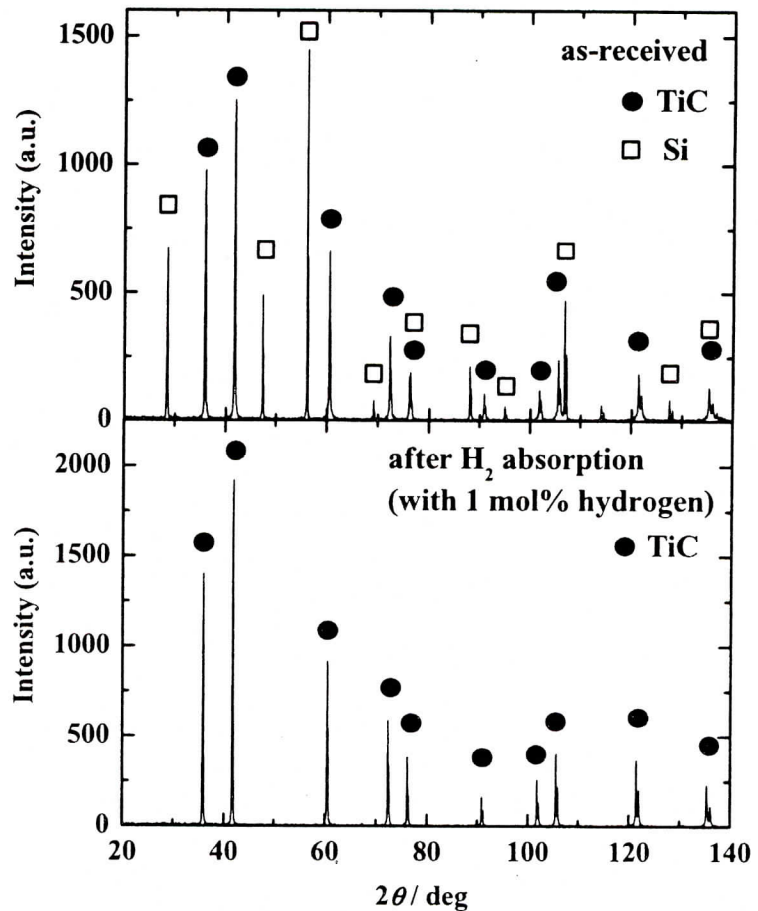
and nitrogen by fusion in Ar gas flow. The composition of the specimen powder thus

determined was $TiC_{0.958\pm0.001}N_{0.0172\pm0.0002}O_{0.0219\pm0.0002}$ or $Ti(C,N,O)_{0.997\pm0.001}$. Namely, the

TiC specimen used was in carbon deficient type non-stoichiometric composition.

Fig. 2 shows SEM micrograph of the specimen powder. Majority of particles was in a range of size 1 to 10 μm. The size of ca. 200 particles was measured randomly, and the average value of particle size was evaluated to be 4 μm.
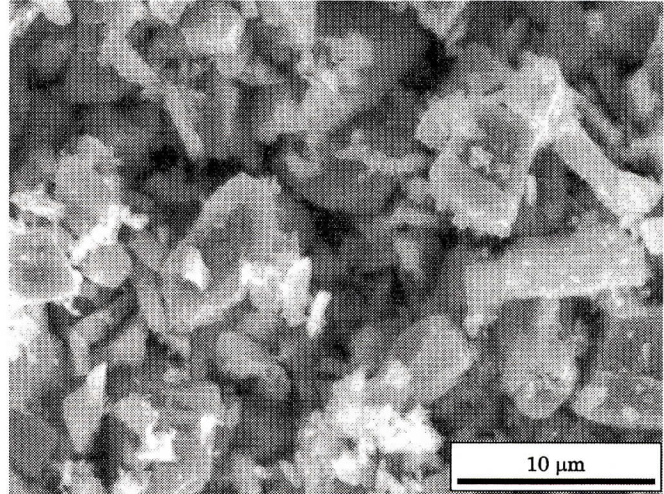

Fig. 2   SEM image of TiC specimen powder.

3.2   Hydrogen Absorption by TiC

Typical example of absorption curves obtained at 873 K is shown in Fig. 3. The
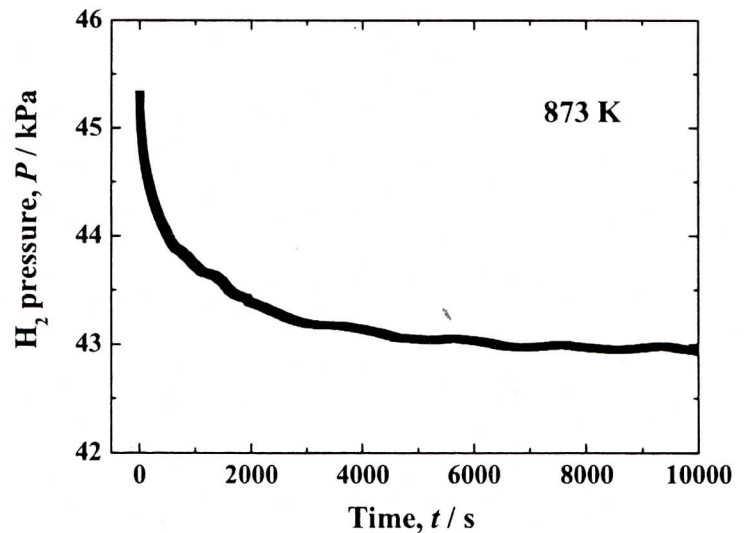

Fig. 3   Typical hydrogen absorption curve obtained at 873 K.

initial and equilibrium pressure of H_2 in this absorption experiment were 45.3 and 43

35

kPa, respectively. This extent of pressure reduction corresponded to H concentration in TiC of 1 mol% ([H]/[TiC] = 0.01).

The rate-limiting step of hydrogen absorption was evaluated by plotting $(dP/dt)/(dP/dt)|_{t=0}$ against $C(t)/C_\infty$ where P is the hydrogen pressure, t is time, $C(t)$ is average hydrogen concentration in TiC at t, and C_∞ is the concentration in equilibrium. If the dissociation at the surface is the rate-limiting step, $-(dP/dt)$ is described as follows:

$$-\frac{dP}{dt} = -\frac{dn}{dt}\frac{RT}{V} = \left\{ \frac{A\alpha P}{\sqrt{2\pi MRT}} - Ak_r C(t)^2 \right\}\frac{RT}{V}, \quad (1)$$

where n is the amount of gas in the reaction chamber, R is gas constant, T is the temperature of gas, V is the volume of reaction chamber, A is the total surface area of TiC, k_r is the rate constant for recombinative release of hydrogen on TiC surface, α is the sticking coefficient, M is the molar mass of hydrogen molecule. Since the initial concentration of hydrogen in TiC is negligibly small, $-(dP/dt)|_{t=0}$, can be expressed as $\frac{A\alpha P_i}{\sqrt{2\pi MRT}}\frac{RT}{V}$ where P_i is the initial pressure of H_2. In equilibrium, the sticking and desorption flux are balanced, and hence $\frac{A\alpha P_\infty}{\sqrt{2\pi MRT}} = Ak_r C_\infty^2$ where P_∞ is equilibrium pressure. Under the present conditions, the extent of pressure change during absorption experiment was small. By assuming $P = P_i = P_\infty$, one would obtain from Eq. (1)

$$\left(\frac{dP}{dt}\right)/\left(\frac{dP}{dt}\right)\Big|_{t=0} = 1 - (C(t)/C_\infty)^2. \quad (2)$$

If a first order surface reaction process, such as dissolution of adatom into subsurface, is the rate-limiting step, similar approach easily gives

$$(\frac{\mathrm{d}P}{\mathrm{d}t})/(\frac{dP}{dt})\big|_{t=0} = 1 - C(t)/C_\infty. \tag{3}$$

Namely, rather simple correlation would be obtained between $(\mathrm{d}P/\mathrm{d}t)/ (\mathrm{d}P/\mathrm{d}t)|_{t=0}$ and $C(t)/C_\infty$ for the surface-limited absorption. On the other hand, in the case of diffusion-limited absorption, $-(\mathrm{d}P/\mathrm{d}t)$ is proportional to the concentration gradient of hydrogen near the surfaces of TiC particles. Hence, $-(\mathrm{d}P/\mathrm{d}t)$ should decrease sharply in the initial stage of absorption with increasing penetration depth of hydrogen, i.e. increasing $C(t)/C_\infty$. According to calculation based on the diffusion model in a sphere at constant surface concentration [7], $-(\mathrm{d}P/\mathrm{d}t)$ should decrease by factor 10 when $C(t)/C_\infty$ increases from 0.022 to 0.22. These values of $C(t)/C_\infty$ correspond to $Dt/a^2 = 5\times10^{-4}$ and 5×10^{-2}, respectively, where D is the diffusion coefficient and a is the radius of sphere. The absorption curve shown in Fig. 3 is replotted in the above-mentioned manner in Fig. 4. The change in $(\mathrm{d}P/\mathrm{d}t)/ (\mathrm{d}P/\mathrm{d}t)|_{t=0}$ with $C(t)/C_\infty$ clearly shows the characteristics of diffusion-limited absorption.

The diffusion coefficient of hydrogen D in TiC was evaluated by fitting the solution of diffusion equation to the absorption curves by assuming that the powder particles are spheres whose diameter is 4 μm 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 t, M_t, is described as

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2\pi^2 t / a^2) \ [7].$$ (4)

Fig. 5 shows the results of fitting for absorption curve obtained at 873 K as an example. The experimentally-obtained absorption curves was well reproduced at $D = 2 \times 10^{-16}$ $m^2 \cdot s^{-1}$.

The diffusion coefficient thus evaluated was plotted against reciprocal temperature in Fig. 6. The activation energy for hydrogen diffusion was derived as 87±13 kJ·mol^{-1} and the pre-exponential factor as 10^{-11} m^2·s^{-1}.
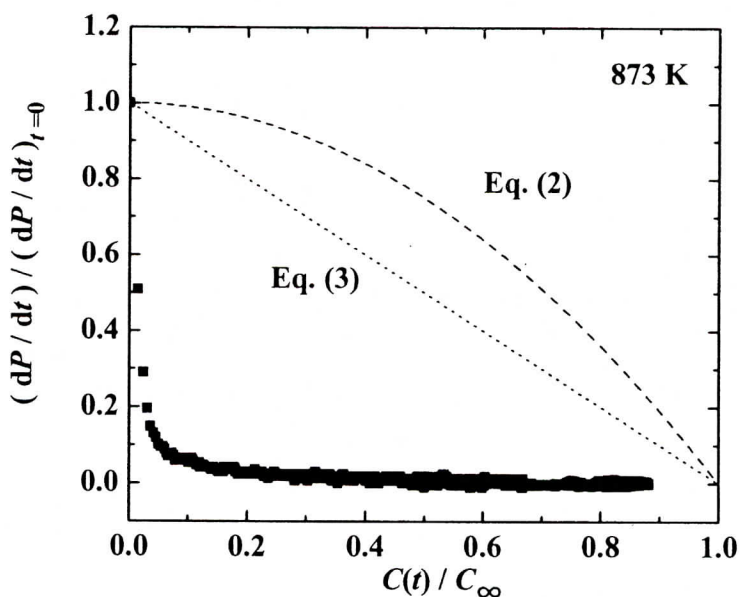
Fujita and Masuda [8] have examined hydrogen

Fig. 4 Plot of $(dP/dt)/(dP/dt)|_{t=0}$ against $C(t)/C_\infty$. Solid symbol indicates the experimental data. Dashed and dotted lines correspond to Eqs. (2) and (3), respectively.

absorption of Ti covered by TiC and reported that the apparent activation energy for absorption was 114 kJ·mol^{-1}. In contrast to the present observations, Fujita and Masuda [8] concluded that the rate-limiting step of absorption was the dissolution process of adatoms into TiC layer and not the diffusion through TiC because the value of activation energy was significantly higher than that for
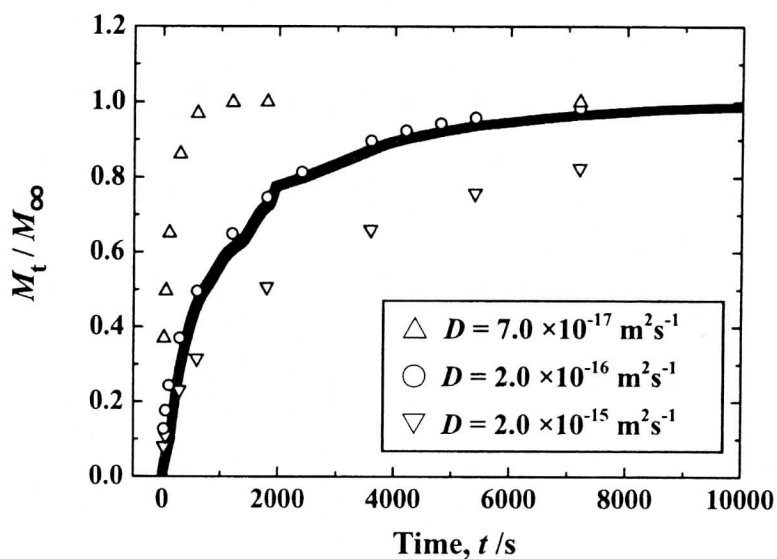

Fig. 5   Typical result of fitting of Eq. (4) to absorption curve obtained at 873 K.
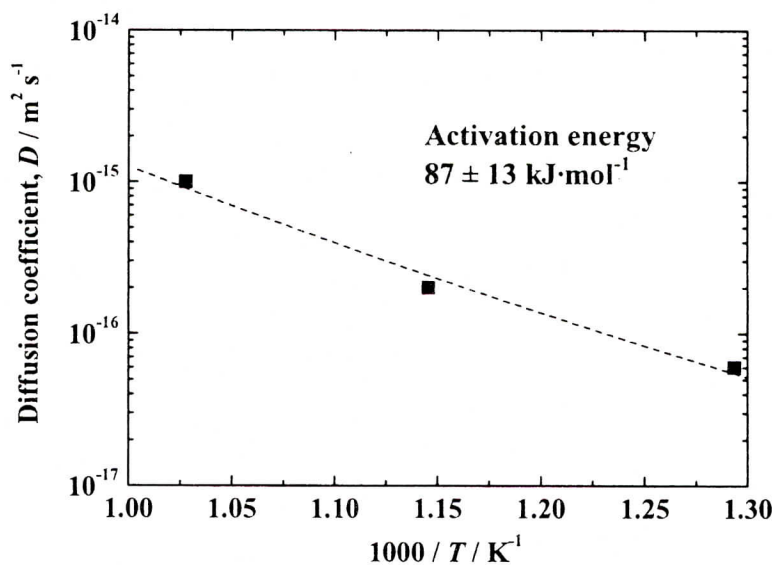
Fig. 6   Arrhenius plot of diffusion coefficient of hydrogen in TiC.

hydrogen diffusion in TiH$_2$. These authors believed that the activation energy of

hydrogen diffusion in TiC is comparable to that in TiH_2 because the arrangements of Ti atoms in these materials are similar to each other. In TiH_2, hydrogen occupies *tetrahedral* sites of fcc structure formed by Ti atoms. On the other hand, carbon in TiC occupies *octahedral* sites. It is known that stoichiometric TiC does not react with hydrogen [1,9-11]: the presence of carbon vacancies is essential for dissolution of hydrogen in TiC. Results of neutron-diffraction analysis on Ti carbohydrides [12] and combination study of X-ray and neutron diffraction methods on $TiC_{0.48}D_{0.60}$ [13] showed that majority of hydrogen isotopes in TiC_{1-x} occupied *octahedral* sites (carbon vacancy) and only minor portion was found in *tetrahedral* sites. Hence, the activation energy of hydrogen diffusion in TiC could be significantly different from that in TiH_2. In our opinion, the possibility of diffusion-limited absorption could not be ruled out in their study [8]; the difference between the present value of activation energy of diffusion (87 ± 13 $kJ\cdot mol^{-1}$) and their apparent activation energy (114 $kJ\cdot mol^{-1}$) is not very large.

If majority of hydrogen forms cluster with carbon vacancy (occupation of octahedral site itself or that of tetrahedral site adjacent to the vacancy), the concentration of hydrogen possible to be accommodated in TiC should have an upper limit determined by the concentration of carbon vacancy. Indeed, the equilibrium

concentration of hydrogen in the present TiC specimen showed very weak dependence on H_2 pressure ([H]/[TiC] $\propto P^{1/4} - P^{1/5}$). Namely, the increase of [H]/[TiC] with P tended to cease at the value around 1×10^{-2}. This value of [H]/[TiC] is comparable to but slightly higher than the concentration of carbon vacancy evaluated by the chemical analysis ($2\text{-}4 \times 10^{-3}$). The concentrations of oxygen and nitrogen may be overestimated due to pick up of these impurities during the transportation of specimen in air. The mechanism underlying this discrepancy, however, has not been fully understood. The details of pressure dependence will be reported as a separate paper.

The activation energy for the self-diffusion of carbon in TiC has been reported to be $208 - 460$ kJ·mol^{-1}[14]. Namely, the presently obtained value of activation energy for hydrogen diffusion is radically smaller than that of carbon. This clear difference indicates that hydrogen does not migrate as a cluster with carbon vacancy. The experiments for the specimen with larger extent of carbon deficiency (i.e. large x in TiC$_{1-x}$) is currently under preparation to get better understanding of the mechanism of hydrogen diffusion.

4. Conclusions

The diffusion coefficient of hydrogen in commercially supplied TiC powder was measured at 773, 873 and 973 K. The value obtained was expressed as

$10^{-11} \times \exp(-87 \pm 13 \text{ kJ} \cdot \text{mol}^{-1}/RT)$ [$\text{m}^2 \cdot \text{s}^{-1}$]. Although carbon vacancies appeared to play a key role in hydrogen accommodation in TiC, the presently obtained value of activation energy for hydrogen diffusion was radically smaller than that of carbon in TiC.

Acknowledgements

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