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Hydrogen solubility in boron carbide

Yoshirou Shirasu, Shinsuke Yamanaka and Masanobu Miyake
Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565 (Japan)

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Abstract

Solubility measurements have been performed for hydrogen in B_4C in the temperature range 700–1000 °C at a hydrogen pressure below 10^5 Pa. The solubility data closely obeyed Sieverts' law. A negative enthalpy of solution was obtained. A dilute solution model was proposed for the hydrogen solubility in B_4C on the assumption that hydrogen atoms are dissolved in interstitial sites in B_4C. The partial molar enthalpy and entropy of hydrogen in B_4C were estimated from the thermodynamic analysis.

1. Introduction

Boron carbide is used as a neutron absorber in the control rods of nuclear fission reactors because of the high neutron absorption cross-section of ^{10}B. A considerable amount of tritium is produced in neutron-irradiated boron carbide via $^{10}B(n, 2\alpha)^3T$ [1, 2]. Boron carbide is suitable for use in a nuclear fusion reactor because of its low atomic number and high thermal shock resistance. Boron carbide will be exposed to tritium gas as well as to energetic tritium ions and atoms. The hydrogen behaviour in boron carbide is therefore one of the important issues for use of this material in both fission and fusion reactors. Several studies on the interaction of hydrogen isotope gas and ions with boron carbide have been conducted, relating to tritium diffusion [1, 2], chemical erosion [3], hydrogen retention [4] and thermal desorption [5].

For a clear understanding of the interaction, equilibrium data for hydrogen isotope gas in boron carbide are one of the significant parameters. No information is available for the thermodynamics of hydrogen in boron carbide. In the present study, hydrogen solubility in boron carbide has therefore been measured, and the results obtained are discussed.

2. Experimental details

The sample used in the present study was a B_4C crystal (6.5 mm in diameter and 3 mm high). The composition of the B_4C sample by means of chemical analysis indicated that the boron-to-carbon ratio was 4.05. The crystal structure of the sample was identified by the X-ray diffraction technique. Prior to solubility measurement, the sample was degassed at 1000 °C for 5 h in a vacuum below 10^{-6} Pa.

The solubility of hydrogen was measured by thermal desorption spectroscopy (TDS) in the solubility measurement apparatus schematically shown in Fig. 1. The experimental apparatus consisted of a gas exposure system and a hydrogen-analysing system. Each system was isolated by a gate valve. The apparatus was constructed mainly of stainless steel. The gas exposure system was evacuated to 10^{-6} Pa with an oil diffusion pump possessing a liquid-nitrogen trap. Pressures were measured with a Baratron capacitance manometer

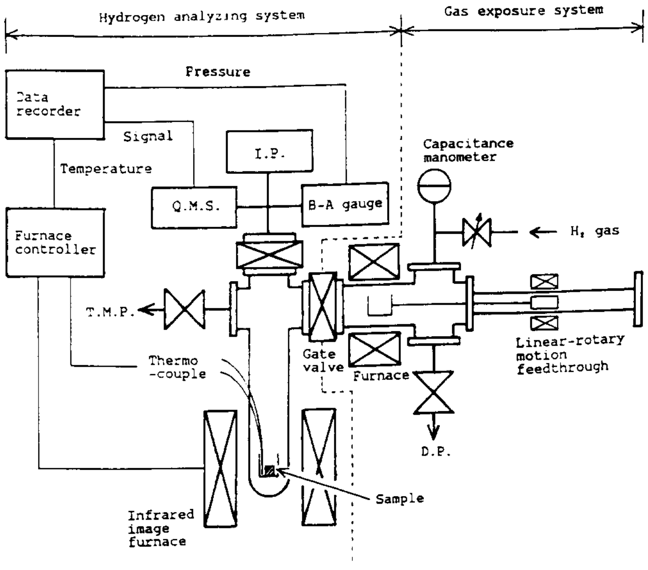

Fig. 1. Schematic diagram of the experimental apparatus: I.P., ion pump; Q.M.S., quadrupole mass spectrometer; Bayard-Alpert gauge; T.M.P., turbomolecular pump; D.P., diffusion pump.

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(MKS instruments, Inc.) which covered the pressure range 13.3–1.33 × 10^5 Pa. The sample temperature was measured with a PR thermocouple and controlled within ±3 °C. The hydrogen-analysing system was evacuated to 10^{-7} Pa with a sputter ion pump and a turbomolecular pump. The sample was heated with an IR furnace and hydrogen gas released from the sample was detected with a quadrupole mass spectrometer. The temperature of the sample was measured with a PR thermocouple.

The B_4C crystal was exposed to hydrogen gas (purity, 99.999%) in the temperature range 700–1000 °C at pressures below 10^5 Pa for 20 h. After the exposure, the sample was quenched to room temperature in the gas exposure system. The sample was transferred to the hydrogen-analysing system in a vacuum below 10^{-6} Pa. The total amount of hydrogen gas dissolved in the sample was analysed by TDS at a heating rate of 20 °C min^{-1} up to 1000 °C. The hydrogen solubility in the B_4C sample was determined from the total amount of hydrogen gas released.

3. Results

The solubility data for hydrogen in B_4C closely obeyed Sieverts' law, which states that the solubility of a diatomic gaseous element in a material is proportional to the square root of the pressure:

$$C_H = K_H P_{H_2}{}^{1/2} \qquad (1)$$

where C_H is the hydrogen content in hydrogen atoms per B_4C molecule, P_{H_2} is the equilibrium hydrogen pressure in pascals and K_H is Sieverts' constant. The linear relation between the square root of the equilibrium pressure and the hydrogen content is shown in Fig. 2. As indicated in this figure, the solubility of hydrogen in B_4C at a fixed pressure decreases with increasing temperature. Since Sieverts' law can be applied to hydrogen dissolution in B_4C, hydrogen gas is dissolved in B_4C as atomic hydrogen. In other words, hydrogen cannot be absorbed into B_4C as diatomic molecules. Moreover, the contribution of the H-H interaction in B_4C appears to be insignificant.

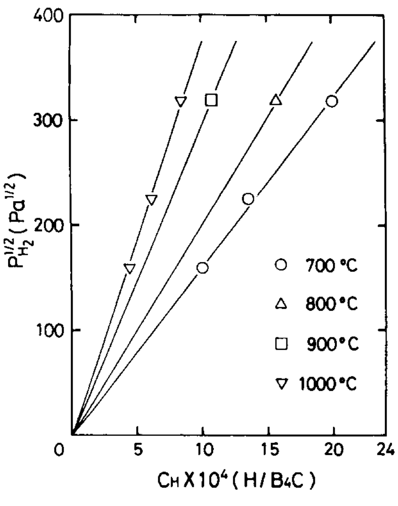

Fig. 2. Sieverts' plots for B_4C at 700–1000 °C.

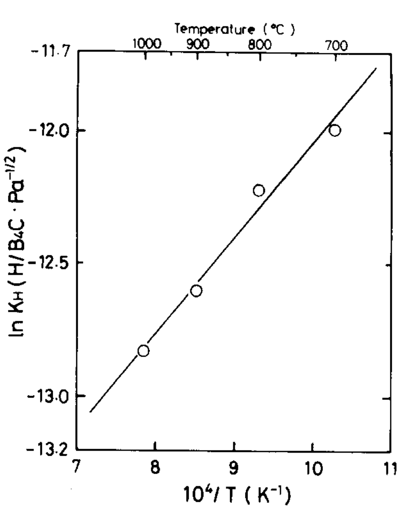

Fig. 3. Temperature dependence of Sieverts' constant K_H for B_4C.

The temperature dependence of Sieverts' constant K_H is illustrated in Fig. 3. It is obvious from this figure that the following relationship holds:

$$\ln K_H = A + \frac{B}{T} \qquad (2)$$

where A and B are constants and T is the sample temperature in kelvins. The values of A and B were estimated to be −15.6 and 3570 respectively. The enthalpy ΔH of a solution of hydrogen in B_4C derived from the B value was −29.7 kJ mol^{-1}. The negative enthalpy of solution suggests that B_4C should exothermically dissolve hydrogen.

4. Discussion

The crystal structure of boron carbide is rhombohedral (or hexagonal) with the space group D^5_{3d} ($R\bar{3}m$). According to Thévenot [6] and Gosset and Colin [7], the rhombohedral unit cell (Fig. 4) contains 15 atoms corresponding to $B_{12}C_3$. The boron carbide consists of 12-atom icosahedral clusters at the corners of the rhombohedral unit cell with a three-atom intericosahedral chain along the diagonal. The boron carbide exists as a single phase with carbon concentrations from about 8.8 to 20 at.%. The most widely accepted structural model for B_4C has $B_{11}C$ icosahedra with C–B–C intericosahedral chains. The more recent description for the other compositions of boron carbides is $B_{11}C$ (C–B–B

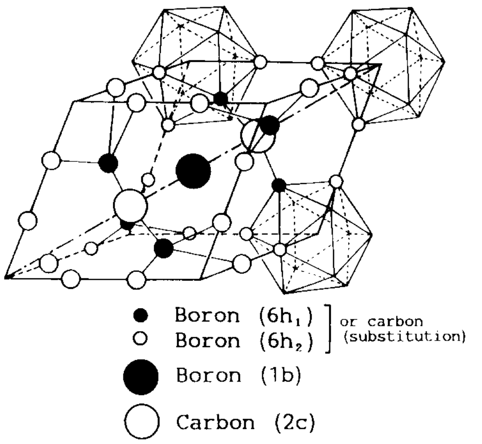

Fig. 4. Rhombohedral crystalline structure of boron carbide.

chains) for $B_{13}C_2$ and $B_{11+x}C_{1-x}$ (C–B–B chains) for $B_{10}C$. The C–B–C chains are, however, slightly replaced with C–C–C chains for the B_4C composition. The hexagonal lattice parameters of the B_4C sample ($a_H = 5.608$ Å and $C_H = 12.088$ Å) are in good agreement with the data published on B_4C [8]. The rhombohedral framework of boron carbide encloses two holes per unit cell, each large enough to accommodate an extra atom. They are located on the threefold axis just above and below the central chain [9]. These holes in the rhombohedral lattice of boron carbide appear to serve as interstitial sites for hydrogen.

On the assumption that hydrogen atoms occupy the interstitial sites in boron carbide, the present result on hydrogen solubility in B_4C was analysed by a dilute solution model [10, 11].

The chemical potential μ_H^s of hydrogen in the solid solution is written

$$\mu_H^s = \bar{H}_H - T(\bar{S}_H + \bar{S}_H^c) \qquad (3)$$

where $\bar{H}_H$ and $\bar{S}_H$ are the partial molar enthalpy and the partial molar excess entropy of hydrogen which are referred to the standard state of hydrogen atoms at rest in a vacuum.

$\bar{S}_H^c$ in eqn. (3) is the partial molar configurational entropy of hydrogen. If we denote the ratio of the number of dissolved hydrogen atoms to the total number of carbon and boron atoms in B_4C by θ_H, $\bar{S}_H^c$ can be estimated as follows:

$$\bar{S}_H^c = -k \ln\left(\frac{\theta_H}{\beta - \theta_H}\right) \qquad (4)$$

In this equation, k is Boltzmann's constant and β is the ratio of the number of interstitial sites to the number of lattice atoms in the rhombohedral unit cell: $\beta = \frac{2}{15}$. The value of θ_H is equal to one fifth of C_H in eqn. (1).

The chemical potential of atomic hydrogen in the gas phase is represented as

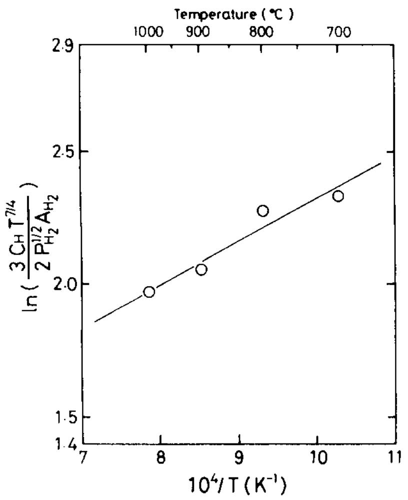

Fig. 5. Thermodynamic analysis of hydrogen solubility in B_4C.

$$\mu_H^g = kT \ln P_{H_2}^{1/2} + kT \ln(A_{H_2} T^{-7/4}) + E_{H_2}^d \qquad (5)$$

where $E_{H_2}^d$ is half the dissociation energy of the hydrogen molecule at 0 K. A_{H_2} refers to the partition functions of hydrogen gas, the value of which can be evaluated from spectroscopic data for hydrogen gas [12, 13].

At equilibrium, $\mu_H^s = \mu_H^g$. Hence, the following solubility equation was obtained for a dilute B_4 C–H solid solution:

$$\ln\left(\frac{3C_H T^{7/4}}{2P_{H_2}^{1/2}A_{H_2}}\right) = \frac{-(\bar{H}_H - E_{H_2}^d)}{kT} + \frac{\bar{S}_H}{k} \qquad (6)$$

Equation (6) was applied to the solubility data for hydrogen in B_4C. Plots of $\ln(3C_H T^{7/4}/2P_{H_2}^{1/2}A_{H_2})$ vs. $1/T$ are shown in Fig. 5, indicating a good straight line. The values of the slope and intercept give $-(\bar{H}_H - E_{H_2}^d)/k$ and $\bar{S}_H/k$. For B_4C, the enthalpy term $\bar{H}_H - E_{H_2}^d$ and the entropy term $\bar{S}_H$ were −13.4 kJ mol^{-1} and 5.9 J mol^{-1} K^{-1} respectively. The partial molar enthalpy $\bar{H}_H$ was estimated to be −229.5 kJ mol^{-1}, the value of which is slightly smaller than that for graphite reported in our previous paper [14].

5. Conclusions

The hydrogen solubility in B_4C has been measured in the temperature range 700–1000 °C at a hydrogen pressure below 10^5 Pa. The solubility data obtained in the present study closely obeyed Sieverts' law. A negative enthalpy of solution was derived by a relationship between Sieverts' constant and the reciprocal temperature.

A dilute solution model was developed for the hydrogen solubility in B_4C on the assumption that hydrogen atoms have access to interstitial sites in B_4C. The thermodynamic analysis based on the model provided the partial molar enthalpy and entropy of hydrogen in B_4C.

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