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Helium release and diffusion mechanism in SiC containing B_4C

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Abstract

Helium release measurement have been carried out in the temperature range of 750–1260 °C for neutron-irradiated α-SiC powder. The powders were obtained from SiC ceramics containing B_4C with varying contents of ^{10}B, i.e., 4.2×10^{16}, 1.13×10^{17} and 1.84×10^{17} atom/mg. Neutron irradiation was conducted up to a fluence of 2.8×10^{24} n/m^2 ($E > 0.1$ MeV) at ~300 °C. The diffusion coefficients were calculated for the temperature region of 750–1060 °C and for time intervals 0–10, 10–60 min and 1–6 h at each temperature. The diffusion coefficient of He for SiC was affected by the original ^{10}B concentration. Both helium diffusion coefficient and apparent activation energy were smaller for higher concentrations of ^{10}B.

1. Introduction

Silicon carbide (SiC) or SiC fiber-reinforced SiC composite is one of the candidate materials for use in structure and blanket materials of advanced fusion reactors. Many ceramics will experience significant gas productions due to nuclear transmutations under high-energy neutron irradiation [1]. In particular production of helium (He) in SiC, is anticipated to have a high impact on its properties. For this reason, studying the effects of neutron-irradiation on SiC ceramics is very important [2,3]. The limited diffusion of helium in SiC may cause significant volume swelling and mechanical stress in SiC-based materials [1].

The release of helium from neutron-irradiated SiC induced via the $^{10}B(n,\alpha)^7Li$ reaction has been studied by several authors [4,5]. Sasaki et al. [6,7] investigated helium release rates and microstructure of neutron-irradiated SiC which was sintered with B. Temperature dependence of helium release from powder and bulk specimens was reported. The present authors examined helium release behavior and change in physical properties of neutron-irradiated SiC ceramics containing B_4C of different ^{10}B concentrations [8], and investigated their microstructures by transmission electron microscopy (TEM) after annealing at several temperatures [9].

Recently, the diffusion coefficient of helium in neutron-irradiated SiC containing B_4C with natural ^{10}B concentration was measured in the temperature range of 750–1260 °C using post-irradiation isothermal annealing [10]. The effects of varying ratios of helium concentration to neutron fluence on the diffusion coefficient have not yet been reported. In the present paper, therefore, the diffusion coefficients of helium in neutron-irradiated SiC ceramics with various concentrations of ^{10}B were measured in the temperature range of 750–1260 °C.

2. Experimental procedure

2.1. Specimen

Specimens were sintered α-SiC ceramics containing B_4C with different ^{10}B concentrations, the same specimens as previously reported [8]. For helium release measurement, samples were prepared containing 0.4 wt% B_4C with different ^{10}B concentrations, i.e., 19.6% and 91.6% ^{10}B, named natural and enriched B_4C, respectively. In addition, a ceramics containing a

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mixture of the two B_4C was prepared (56.8% of ^{10}B), which is named mixed B_4C.

These samples, of size 2 mm × 5 mm × 20 mm, were neutron-irradiated in the Japan Materials Testing Reactor up to a fluence of 2.8×10^{24} n/m^2 ($E > 0.1$ MeV) at ~300 °C in an He-filled capsule. By this neutron fluence, 25.5% of the ^{10}B is burned up and transmuted into He and Li. The calculated helium production amounts after neutron-irradiation of the natural, mixed and enriched B_4C were 360, 1030 and 1690 appm, corresponding to He concentrations of 1.05×10^{16}, 2.84×10^{16} and 4.62×10^{16} atom/mg, respectively [9]. After the neutron-irradiation, the specimens were crushed into powder.

2.2. Diffusion equation

We consider the diffusion calculation method for spherical particles using Booth's equation [10–12], where the cumulative fractional release, f, is given as

$$f = [6(Dt/a^2)^{0.5}/(\pi^{0.5})] - 3(Dt/a^2), \quad (1)$$

where D is the diffusion coefficient, a the sphere radius, and t is time. The fractional release $f(t)$ is defined as the amount of helium released until time t divided by the total released helium up to 1920 °C [8]. The formula is valid if π^2Dt/a^2 is less than 1 [11,12], and according to Ref. [13] the error is small if $f < 0.7$. Only the first term of Eq. (1) can be used as an approximation of Booth's model, if $f < 0.2 \sim 0.3$ [10],

$$f = 6(Dt/a^2)^{0.5}/(\pi^{0.5}). \quad (2)$$

In this case, the error is less than 10% for 30% release ($f < 0.3$). According to this equation, by plotting f against the square root of time, an effective diffusion coefficient D can be obtained from the slope.

Effects of point defects, defect clusters, bubbles and dislocation are all included in the diffusion coefficient of the equivalent sphere model (Eq. (1)). The only assumption we make is approximating actual granular shapes by spheres. The temperature dependence of the diffusion coefficient is given by

$$D = D_0 \exp(-Q_A/kT), \quad (3)$$

where D_0 is a constant for a given diffusion system and Q_A is the activation energy for the diffusion process [14]. From the slope of $\log D$ plotted against $1/T$ (T = absolute temperature) the apparent activation energy of the diffusion process is obtained [11–14].

2.3. Diffusion experiments

The post-irradiation helium release experiment was conducted in the temperature range of 750–1260 °C. The procedure was reported previously [10]. The isothermal annealing duration was about 6 h at each temperature, after temperature increase by ~80 °C/min. A high temperature vacuum furnace (Tokyo Vacuum) and a helium leak detector were used (Shimadzu Corp., MSE-110). At each isothermal annealing step, a part of the as-irradiated specimen without additional annealing was used. The sphere radius of particles was estimated from size measurements of about 1000 particles by scanning electron microscopy. The equivalent sphere radii of the as-irradiated SiC with natural, mixed and enriched B_4C were 0.66, 0.70 and 0.43 μm, respectively, which are less than the grain size in the sintered material. During and after heating to the selected temperature, the release of helium increased quickly, and after the first few minutes at temperature a steady state of release was reached. D was calculated from the steady state period of a plot of f against square root of t using Eq. (2). The resulting D was then used as an input value for the next calculation using Eq. (1) which has a higher accuracy and can be used up to $f < 0.7$. Iteration fitting was conducted by changing D step wise until the difference between the new f-value obtained from Eq. (1) and the observed f-value was less than 1×10^{-6}. The resulting values of D at various annealing temperatures were used to derive D_0 and Q_A from Arrhenius plots.

3. Results and discussion

3.1. Effect of temperature and time

Our helium release measurements after neutron irradiation showed that fractional release generally increased with increasing annealing temperature up to ~1100 °C for all ^{10}B concentrations and was highest between 1060 and 1160 °C. After long annealing time, the fractional helium release at annealing temperature range 750–850 °C for all sample, and 1260 °C from the SiC with mixed/enriched B_4C were $f < 0.3$, whereas f was >0.3 for other measurement temperatures. Consequently, the calculation for all data was done using firstly Eq. (2) and then Eq. (1) by the method mentioned above.

Based on the Eq. (1), fractional helium release pattern should reveal a parabolic dependence as a function of $\sqrt{t}$. This was not observed, however, for all three concentrations of ^{10}B. Therefore, it is supposed that the diffusion coefficient varies with time.

In order to compare the time dependences of the diffusion coefficient, the measurement period was considered in three segments, i.e., 0–10 min, 10–60 min and 1–6 h. Within each segment, straight lines were fitted to the $f(\sqrt{t})$.

The temperature dependences of the diffusion coefficient for the three time segments are given in Fig. 1(a)–(c), respectively. As mentioned above, diffusion

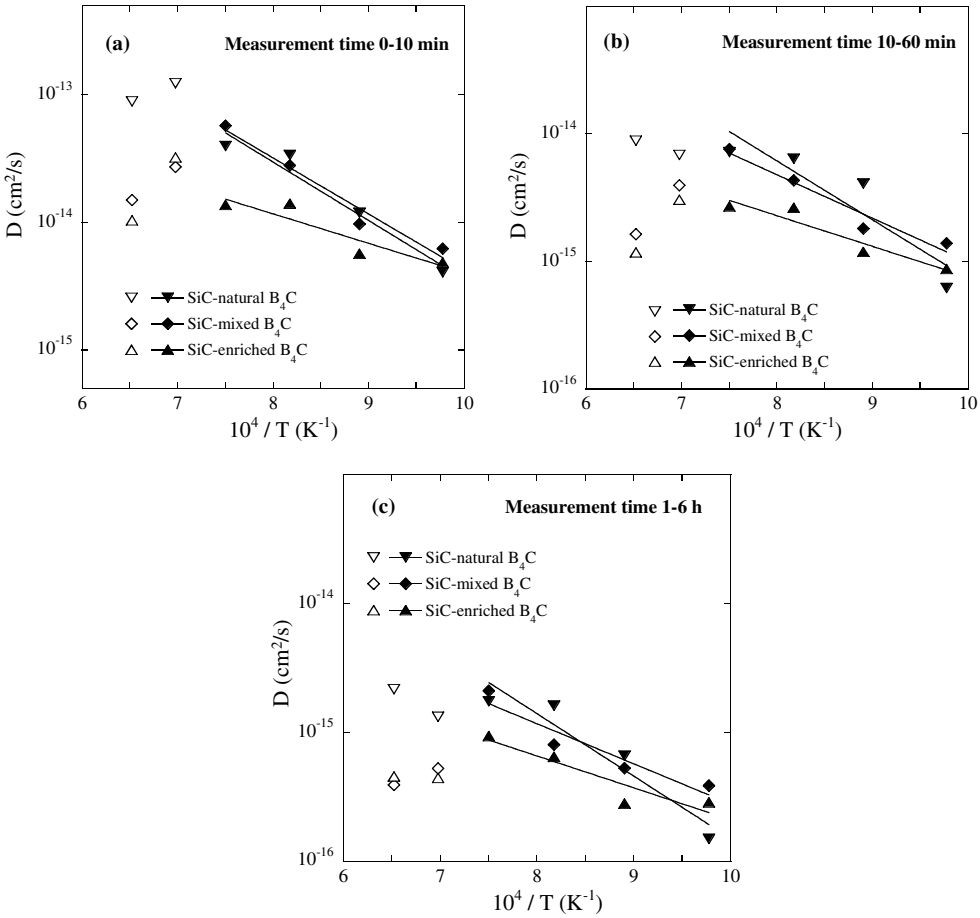

Fig. 1. Temperature dependence of the diffusion coefficient of helium from the neutron-irradiated SiC containing B_4C of different ^{10}B concentrations, as determined in the time segments (a) 0–10 min, (b) 10–60 min, and (c) 1–6 h. Straight lines have been fitted to each data set between 750 and 1060 °C (closed symbols), while data points with open symbols (for 1160 and 1260 °C) were not included in the fit.

coefficient graphs at each time segment show a maximum at 1060–1160 °C. Activation energies of diffusion were calculated from the slopes of data between 750 and 1060 °C. The values of diffusion constant, D_0 and activation energy, Q_A are also shown in Fig. 2. All D_0 values decreased with increasing measurement time range and were the lower the higher ^{10}B concentration. Also Q_A values decreased with increasing ^{10}B content, but were only slightly dependent on the time range. Helium release profiles during continuous heating from the same powders used in the present study as reported in Ref. [8,9] are shown in Fig. 3. Within the covered temperature range of 100–1900 °C, a broad peak was revealed extending from 600 to 1400 °C and the height of which increased with increasing ^{10}B concentration. Helium release rates indicated that the diffusion of helium is accelerated with increasing temperature up to ~1100 °C. Above ~1200 °C, helium release rate gradually decreased.

The diffusion coefficients of SiC containing natural, mixed and enriched B_4C show no significantly different characteristics. One of the most appropriate diffusion mechanisms of helium in neutron-irradiated SiC was shown to be the dissociative and interstitial diffusion mechanism [10]. Decrease of the helium release rate at temperatures above ~1100 °C may correlate to the vacancy migration process [15,16], where trapped helium atoms migrate to the surface of particles or to grain boundaries. In the latter case they form bubbles predominantly at grain boundaries [7–9].

Comparison between Figs. 1 and 2 reveals that in the temperature range of 750–1060 °C the diffusion coefficient apparently decreases with time, while it increases with temperature. With regard to usual diffusion mech-

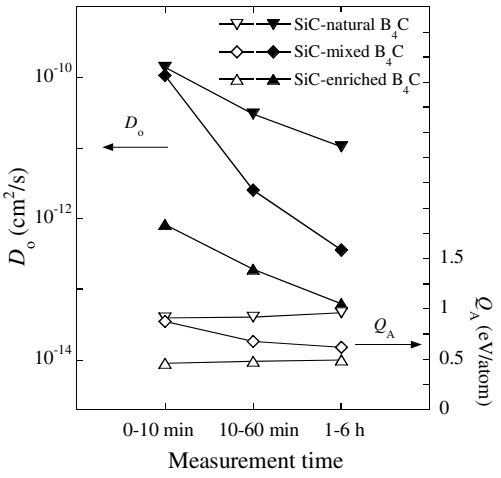

Fig. 2. Diffusion constant (closed symbols) and activation energy of helium diffusion (open symbols) in neutron-irradiated SiC containing B_4C of different ^{10}B concentrations, at 750–1060 °C.

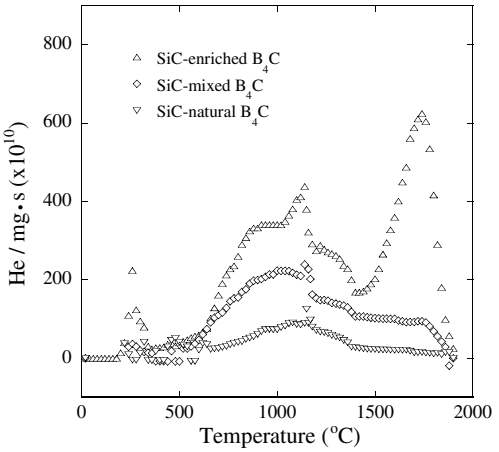

Fig. 3. Helium release rates during continuous heating, from 1 mg of irradiated SiC powder containing natural B_4C, mixed B_4C, and enriched B_4C. The figure is originally from Ref. [8,9].

anisms this is a discrepancy which we need still to resolve by performing further experiments and consider alternative diffusion mechanisms.

3.2. Effect of ^{10}B concentration

The diffusion coefficients in the temperature range of 750–1060 °C and for helium release times between 0 and 6 h did not vary significantly with ^{10}B concentration, although higher ^{10}B concentration specimen gave a slightly lower D value. It was reported that black-dot defects were formed at around 600–700 °C [9]. Further TEM observations of the specimen after annealing at 800 °C for 1 h showed that the quantity of the black-dots was larger than that after annealing at the lower temperatures and was larger with higher ^{10}B concentrations. As a consequence helium may not easily diffuse through SiC lattice containing enriched B_4C, due to large amount of Frenkel defects, black-dot type clusters, or other defects induced by the neutron-irradiation and subsequent recoil of α-particles and Li atoms.

When the annealing temperature was raised to 750–1060 °C, the helium release rate increased with increasing ^{10}B concentration, not accompanied, however, by an increase of the diffusion coefficient. An increased number of defects in SiC containing higher ^{10}B concentration is thought to cause the lower rate of helium diffusion due to increased helium trapping.

The excess helium retention in SiC containing enriched B_4C could be the reason for the helium release at ~1750 °C, as shown in Fig. 3. This was supported by TEM investigations after annealing at 1800 °C for 1 h of neutron-irradiated SiC containing enriched B_4C, where intragranular bubble formation was revealed. It is concluded that defects such as Frenkel defects and black-dot type clusters trap helium atoms in SiC crystals. The peak at ~1750 °C did not occur in SiC containing natural and mixed B_4C.

4. Conclusion

Helium diffusion in neutron-irradiated SiC was measured in the temperature range of 750–1260 °C. The SiC specimens were sintered with B_4C additives with various ^{10}B concentrations. They were neutron-irradiated in JMTR up to a fluence of 2.8×10^{24} n/m^2 ($E > 0.1$ MeV) at ~300 °C. The conclusions are summarized as follows:

(1) The diffusion coefficient of helium at a temperature range of 750–1060 °C for neutron-irradiated SiC containing B_4C with higher ^{10}B concentration was lower than that with natural ^{10}B concentration. The helium diffusion is supposed to depend on the defects induced by neutron-irradiation.

(2) For a measurement time range of 0–10 min, the diffusion coefficients of helium in SiC were,
- D (cm^2/s) $= 1.38\times10^{-10}$ exp(-0.91 ± 0.07 eV/kT) for SiC with natural B_4C;
- D (cm^2/s) $= 1.06\times10^{-10}$ exp(-0.87 ± 0.04 eV/kT) for SiC with mixed B_4C;
- D (cm^2/s) $= 8.27\times10^{-13}$ exp(-0.46 ± 0.05 eV/kT) for SiC with enriched B_4C.

For 10–60 min,
- D (cm^2/s) $= 3.04\times10^{-11}$ exp(-0.92 ± 0.06 eV/kT) for SiC with natural B_4C;
- D (cm^2/s) $= 2.54\times10^{-12}$ exp(-0.68 ± 0.02 eV/kT) for SiC with mixed B_4C;

- D (cm^2/s) $= 1.93\times10^{-13}$ exp(-0.48 ± 0.04 eV/kT) for SiC with enriched B_4C.

For 1–6 h,

- D (cm^2/s) $= 1.05\times10^{-11}$ exp(-0.96 ± 0.05 eV/kT) for SiC with natural B_4C;
- D (cm^2/s) $= 3.60\times10^{-13}$ exp(-0.62 ± 0.04 eV/kT) for SiC with mixed B_4C;
- D (cm^2/s) $= 6.25\times10^{-14}$ exp(-0.49 ± 0.04 eV/kT) for SiC with enriched B_4C.

(3) The apparent activation energy of helium diffusion for SiC containing natural B_4C and enriched B_4C is $\sim$0.95 and $\sim$0.5 eV/atom, respectively, mostly independent of measurement time. An intermediate value was obtained for mixed B_4C.

(4) The excessive helium retention at $\sim$1750 °C in SiC with the high ^{10}B concentration indicates trapping of helium atom at defects introduced by neutron-irradiation.

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