Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 329–333 (2004) 1022–1028
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Relationship between dimensional changes and the thermal conductivity of neutron-irradiated SiC

Tadashi Maruyama [a,*], Masaaki Harayama [b]

[a] The Wakasa Wan Energy Research Center, Tsuruga, Fukui 914-0192, Japan
[b] Industrial Science and Technology Policy and Environment Bureau, Ministry of Economy Trade and Industry, Tokyo 100-8901, Japan

Abstract

Three kinds of commercially available SiC ceramics, hot-pressed, pressureless-sintered and reaction-bonded SiC were neutron irradiated at temperatures of 300 and 650 °C and fluences 8.0×10^{23} and 4.3×10^{24} n/m^2 ($E > 0.18$ MeV), respectively. The thermal conductivity and dimensional change were measured by isochronal annealing experiment up to 1700 °C. The change in thermal conductivity was analyzed in terms of phonon scattering by point defects. The defect concentration calculated from the thermal conductivity agreed well with that calculated from the dimensional change of the same specimen. We obtained quite good agreement between changes of thermal conductivity and swelling. Therefore, it is confirmed that the same kind of irradiation induced defects are involved in the degradation of thermal conductivity and swelling of SiC.

1. Introduction

SiC is a candidate for use as the plasma facing materials (PFM) of fusion reactors. One of the serious consideration as to application of SiC to the PFM is exposure of material to fast neutrons of 14 MeV at high temperatures. Therefore, it is important to determine the effect of neutron irradiation on the material properties, particularly on swelling and thermal conductivity [1,2].

When SiC is irradiated by high energy neutrons, displacement damage occurs in the material. Since, the lattice dilatation associated with a Frenkel pair is positive, their presence results in expansion [3]. Simultaneously, point defects such as vacancy and strain fields around the point defects scatters phonons thereby degradation in thermal conductivity occurs.

It is well known that when SiC is irradiated at temperatures below 1000 °C, swelling linearly increases with increasing fluence up to about 5×10^{21} n/cm^2 ($E > 0.18$ MeV), and then saturates [4,5]. The saturation level depends on the irradiation temperature. It is also well known that if SiC is subjected to post-irradiation annealing, macroscopic dimensional change and lattice parameters begin to linearly recover at temperature around the irradiation temperature. This phenomenon is used to determine irradiation temperature of nuclear reactors [6].

Studies of thermal conductivity of neutron irradiate SiC have been carried out by many investigators. Price [7] measured the thermal conductivity of pyrolytic β-SiC which was irradiated to fluences from 2.7×10^{21} to 7.7×10^{21} n/cm^2 ($E > 0.18$ MeV) at 550–1100 °C. The thermal conductivity decreased to 1/9 of the value for unirradiated materials irradiated at 550 °C and to 1/3 at 1100 °C. He also showed that temperature variation became small. Lee et al. [8] studied the effect of boron addition on the thermal conductivity of neutron-irradiated reaction-bonded SiC which contains boron. They report that effect of ^{10}B(n,α)^{7}Li is not substantial and the change in specific heat is less than 2%.

* Corresponding author. Present address: Japan Nuclear Cycle Development Institute, International Cooperation and Technology Development Center, Shiraki 1, Tsuruga, Fukui 919-1279, Japan. Tel.: +81-0770 39 1031; fax: +81-0770 39 9226.

E-mail address: maruyama.tadashi@jnc.go.jp (T. Maruyama).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.04.128

As described above, swelling and degradation in thermal conductivity are important material properties that must be well characterized for use of SiC in a nuclear environment. The present investigation evaluated the relationship between dimensional changes and the thermal conductivity of neutron-irradiated SiC. The effect of point defects on the thermal conductivity degradation and dimensional change was quantitatively evaluated.

2. Experimental

2.1. Specimen and irradiation conditions

Specimens used in the present investigation are three kinds of SiC ceramics. They are pressure-less sintered SiC (SC-201, Kyocera Co.), reaction-bonded SiC (SE-10, Shin-etsu Chemical Co.) and hot-pressed SiC (SC-101, Hitachi Co.). The pressure-less sintered SiC (PLS-SiC) contains B and free C at 1 mass% respectively and the hot pressed SiC (HP-SiC) contains 1 mass% of BeO. Reaction-bonded SiC (RB-SiC) contains free Si at about 10 mass%. The specimens were machined into rectangular bars $2\times4\times25$ mm^3 in size and circular plates 10 mm in diameter and 1 mm in thickness. The rectangular bars were used for dimensional measurement and the circular plates for the thermal conductivity measurement.

Neutron irradiation was carried out in the Japan Materials Testing Reactor (JMTR) to fluences from 4.3×10^{24} n/m^2 ($E > 1$ MeV) at 650 °C and 8.0×10^{23} n/m^2 at 300 °C. The irradiation temperature was monitored with thermocouples during irradiation.

2.2. Measurement

The dimensional change was obtained by measuring the specimen length before and after neutron irradiation using a conventional micrometer with and accuracy of ±1 μm. The thermal conductivity was measured from room temperature to 1200 °C by the laser flash method. The surface of a specimen was heated by a laser pulse and the temperature rise curve at the back surface was measured by an infrared thermometer. The thermal diffusivity was obtained from the following relation:

$$\alpha = 0.1388\frac{L^2}{t_{1/2}}, \tag{1}$$

where L is the thickness of specimen and $t_{1/2}$ the time at which temperature reaches half of the saturated value after laser irradiation. The thermal conductivity k was then calculated by multiplying the thermal diffusivity with density ρ and specific heat capacity C_v as

$$k = \rho C_v \alpha. \tag{2}$$

The value of heat capacity of SiC was taken from the literature [9]. It was assumed that the effect of neutron irradiation on the heat capacity and density of SiC was negligibly small [8]. In the measurement of thermal diffusivity for unirradiated specimens, the correction for the pulse width effect proposed by Heckman [10] was made on the diffusivity data because unirradiated SiC specimens possessed very high values of thermal conductivity.

A post-irradiation annealing experiment for irradiated specimens was undertaken for the thermal conductivity and dimensional changes using an infrared furnace and a carbon resistance vacuum furnace. The annealing temperature ranged from room temperature to 1700 °C with heating rate 160–180 °C/min. After holding for 30 min at each temperature, the specimens were quickly cooled to room temperature and the thermal conductivity and dimensions were measured. In the reaction-bonded SiC, extensive evaporation of free Si occurred above 1400 °C. Therefore, annealing treatment was made below 1300 °C.

3. Results

3.1. Temperature dependence of thermal conductivity

Fig. 1 shows the neutron irradiation effect on the thermal conductivity of SiC. Before neutron irradiation, room temperature thermal conductivity of hot-pressed SiC (HP-SiC), reaction-bonded SiC (RB-SiC) and pressureless sintered SiC (PLS-SiC) were about 280, 180, and 100 W/(m K), respectively. It is noted that the HP-SiC had particularly high thermal conductivity at room temperature. The thermal conductivity of RB-SiC is relatively high because free Si of about 10 mass% and fine grained β-SiC particles filled the pores of the α-SiC matrix which makes the porosity of RB-SiC low. The thermal conductivity of all the samples rapidly decreased with increasing temperature and reached almost the same value of about 40 W/(m K) at 1200 °C. When SiC samples were neutron irradiated to 4.3×10^{24} n/m^2 at 650 °C, a substantial decrease in the thermal conductivity occurred as shown in Fig. 1. The thermal conductivity of all the SiC samples ranged from 12 to 20 W/(m K) up to 1200 °C with little temperature dependence.

Fig. 2 show the temperature dependence of thermal conductivity of SiC samples irradiated to 8.0×10^{23} n/m^2 at 300 °C and 4.3×10^{24} n/m^2 at 650 °C. Although the neutron fluence is low, the decease in thermal conductivity is larger for specimens irradiated at 300 °C than that irradiated at 650 °C. It is also noted that the thermal conductivity of irradiated samples tended to increase at high temperatures because of recovery effects at high temperatures.

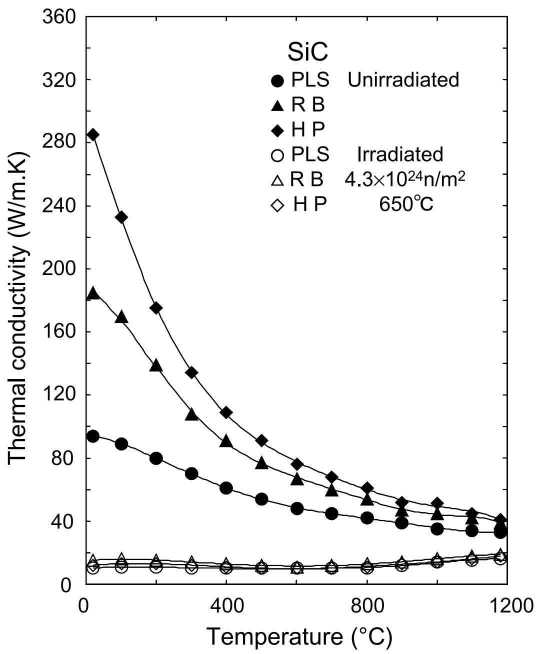

Fig. 1. Neutron irradiation effects on the thermal conductivity of SiC.

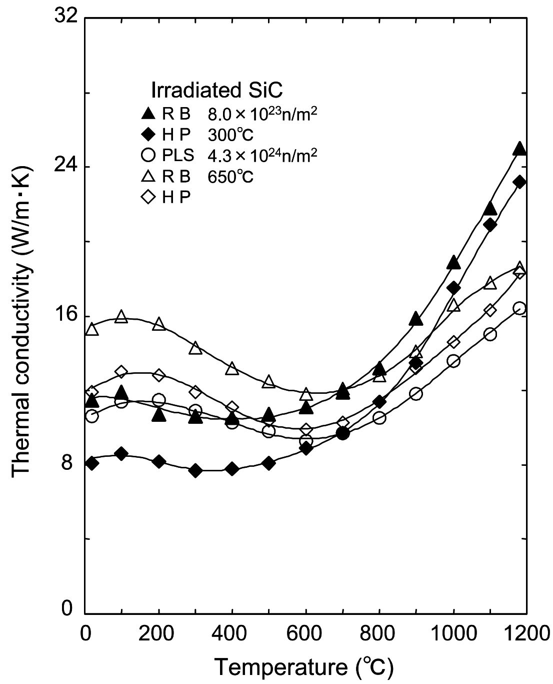

Fig. 2. Temperature dependence of the thermal conductivity of neutron-irradiated SiC.

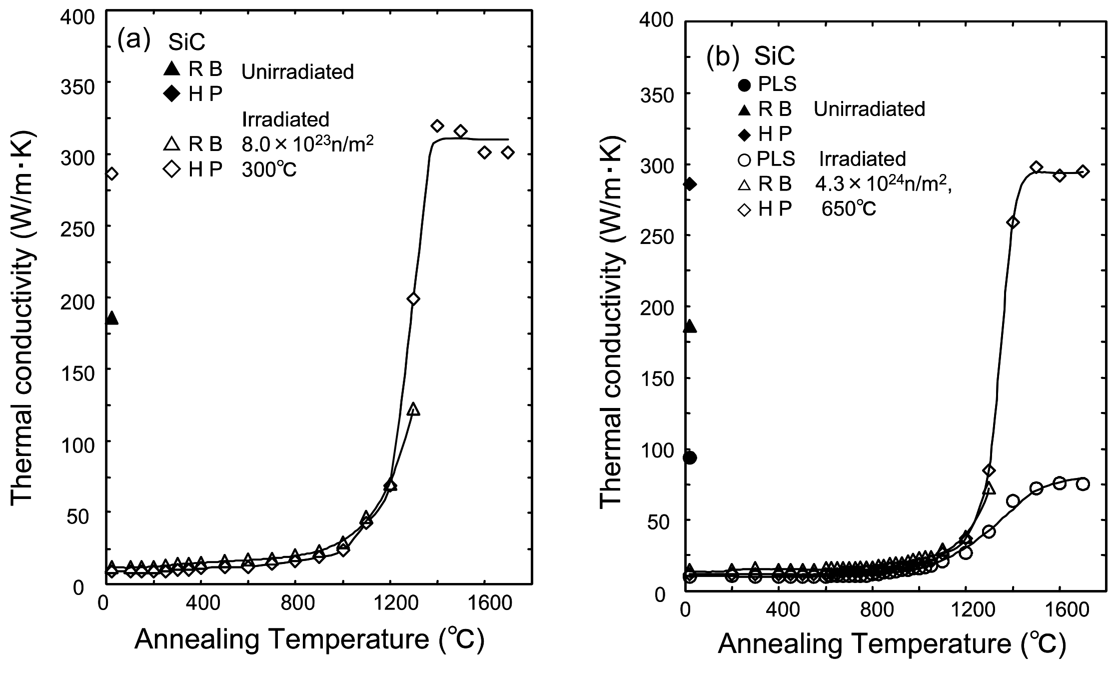

Fig. 3. Isochronal annealing of the room temperature thermal conductivity of neutron-irradiated SiC. Irradiation conditions: (a) 8.0×10^{23} n/m^2, 300 °C, (b) 4.3×10^{24} n/m^2, 650 °C.

3.2. Post-irradiation annealing experiments on thermal conductivity

Results of post-irradiation annealing experiments on thermal conductivity of irradiated SiC specimens are shown in Fig. 3. The room temperature thermal conductivity of irradiated samples gradually increased with increasing annealing temperature up to about 1000 °C and then rapidly increased to saturate at about 1400 °C, at which the thermal conductivity almost recovered to the unirradiated value.

4. Discussion

4.1. Phonon mean free path and the defect concentration

The results of the present investigation indicated that neutron irradiation reduced the thermal conductivity of all type of SiC to similar levels irrespective of the original values. The change in thermal conductivity of irradiated SiC samples is interpreted as follows. In SiC ceramics, phonons are carriers of heat and the thermal conductivity k is expressed as

$$k = \frac{1}{3}\rho C_v v l, \tag{3}$$

where ρ is density, C_v the lattice specific heat, v the velocity of phonons and l the phonon mean free path. The change in l is the main cause of irradiation induced degradation of thermal conductivity of SiC, since the changes in other factors are not very large.

The phonon mean free path (mfp) l of irradiated materials can be generally expressed as

$$\frac{1}{l} = \frac{1}{l_0} + \frac{1}{l_\mathrm{d}}, \tag{4}$$

where l_0 is the mfp of unirradiated material and l_d the mfp associated with the irradiation induced defects. If the mfp l_d is very small compared with l_0, the mfp l in Eq. (4) is virtually equal to l_d and the thermal conductivity of irradiated material is mainly determined by the irradiation induced defects.

We assume that degradation of thermal conductivity is caused by the scattering of phonons by vacancies and that swelling is caused by the lattice dilatation associated with Frenkel pairs. Then we can calculate the defect concentration as follows.

If we apply phonon scattering theory developed by Klemens [11], we obtain the mfp l_d for the phonons with frequency ω as follows:

$$\frac{1}{l_\mathrm{d}} = 3S^2 C_\mathrm{d}\frac{a^3\omega^4}{\pi v^4}, \tag{5}$$

$$S^2 = S_1^2 + (S_2 + S_3)^2, \tag{6}$$

$$S_1 = \frac{\Delta M}{M}\frac{1}{2\sqrt{3}}, \quad S_2 = \frac{\mathrm{d}(v^2)}{v^2}\frac{1}{\sqrt{6}},$$
$$S_3 = -Q\gamma\frac{\Delta R}{R}\sqrt{2/3}, \tag{7}$$

where C_d is the point defect concentration, a^3 the atomic volume, and ω the phonon frequency.

S_1 represents scattering of phonons by substitutional atom with different mass, S_2 scattering by atoms with different coupling force, and S_3 scattering by strain field around point defects. $\Delta M/M$ is the mass difference of substitutional atoms ($\Delta M/M = -1$ for vacancy) and v is the phonon velocity ($\Delta(v^2)/v^2 = -1$ for vacancy). Q represents anharmonicity factor and the value is given as $Q = 3.2$ [11]. γ is the Grüneisen parameter ($\gamma \sim 1.5$ for SiC). R is the atomic distance and ΔR is the change in atomic distance.

According to the Debye model, the phonon frequency distribution function is given as

$$G_\mathrm{D}(\omega) = 9N(\omega^2/\omega_\mathrm{D}^3), \tag{8}$$

where N is the number of atoms and ω_D the Debye frequency. Taking the average phonon frequency, we get

$$si^4 = \frac{\int_0^{\omega_\mathrm{D}}\omega^4 G_\mathrm{D}(\omega)\,\mathrm{d}\omega}{\int_0^{\omega_\mathrm{D}} G_\mathrm{D}(\omega)\,\mathrm{d}\omega} = \frac{3}{7}\omega_\mathrm{D}^4. \tag{9}$$

Substituting ϖ^4 into ω^4 of Eq. (5), we obtain an expression for the defect concentration as

$$C_\mathrm{d} = \frac{7\pi}{9S^2}\frac{v^4}{a^3\omega_\mathrm{D}^4}\frac{1}{l_\mathrm{d}}. \tag{10}$$

Now we can calculate the defect concentration C_d from materials parameters and the thermal conductivity of irradiated and unirradiated SiC. The Debye frequency ω_D is given as

$$\omega_\mathrm{D} = 2\pi v\left(\frac{3N_0}{4\pi}\right)^{1/3}, \tag{11}$$

where N_0 is the number of atoms per unit volume and v the average velocity of phonons. The average velocity of phonons is given as

$$\frac{1}{v^3} = \frac{1}{3}\left(\frac{1}{v_\mathrm{l}^3} + \frac{2}{v_\mathrm{t}^3}\right), \tag{12}$$

where v_l is the sound velocity of longitudinal wave and v_t is the sound velocity of transverse wave.

The Young's modulus E, shear modulus G and Poisson's ratio v of SiC ceramics are given as $E = 450$ GPa, $G = 193$ GPa, $v = 0.16$, respectively. From these parameters, we get velocity of sound as follows, $v_\mathrm{l} = 12\,000$ m/s, $v_\mathrm{t} = 7800$ m/s and the average value of velocity of phonons $v = 8500$ m/s. Other parameters for SiC are given as follows: The density $\rho = 3.2$ g/cm^3,

Table 1
Defect concentration C_d of neutron-irradiated SiC calculated from the thermal conductivity and swelling data

Specimen	Irradiation condition	Thermal conductivity		Swelling data	
		l_d (nm)	C_d (%)	$\Delta V/V$ (%)	C_d (%)
RB-SiC	8.0×10^{23}, 300 °C	2.2	0.94	1.6	2.3
HP-SiC	”	1.5	1.5	1.9	2.8
PLS-SiC	4.3×10^{24}, 650 °C	2.2	1.2	1.1	1.6
RB-SiC	”	3.0	0.82	1.0	1.4
HP-SiC	”	2.1	1.2	1.2	1.7

The parameter $\Delta R/R$ was assumed to be $\Delta R/R = -0.12$.

$N_0 = 9.4 \times 10^{28}$ atoms/m^3, $a^3 = 1.0 \times 10^{-29}$ m^3, and the Debye frequency $\omega_D = 1.5 \times 10^{14}$ Hz.

The change in atomic distance ΔR is obtained from the volume change $\Delta\Omega/\Omega$ associated with a vacancy. The relationship between R and Ω is expressed as

$$1 + \Delta\Omega/\Omega = (1 + \Delta R/R)^3. \quad (13)$$

The volume change $\Delta\Omega/\Omega$ for SiC is not certain, however it is given as −0.61 for Si and −0.31 for diamond [12]. Therefore, from Eq. (13) we obtained the value $\Delta R/R = -0.12$ for diamond and −0.27 for Si. We consider that the value of $\Delta R/R$ for SiC would be closer to that of diamond.

The results of calculation of phonon mfp l_d and the corresponding defect concentration C_d of irradiated SiC using Eq. (10) are shown in Table 1, where the parameter $\Delta R/R$ was assumed to be $\Delta R/R = -0.12$, the value for diamond.

The defect concentration was also calculated from swelling data as follows. Assuming that a single interstitial atom creates volume expansion by one atomic volume, we obtain relationship between volume change (swelling) $\Delta V/V$ and the defect concentration C_D (number of Frenkel pair per unit volume) as

$$C_D = \frac{\Delta V}{V} \bigg/ \left(1 + \frac{\Delta\Omega}{\Omega}\right). \quad (14)$$

The defect concentration C_d calculated from swelling data are also shown in Table 1, where the volume change $\Delta\Omega/\Omega$ was assumed to be −0.31 which is the value for

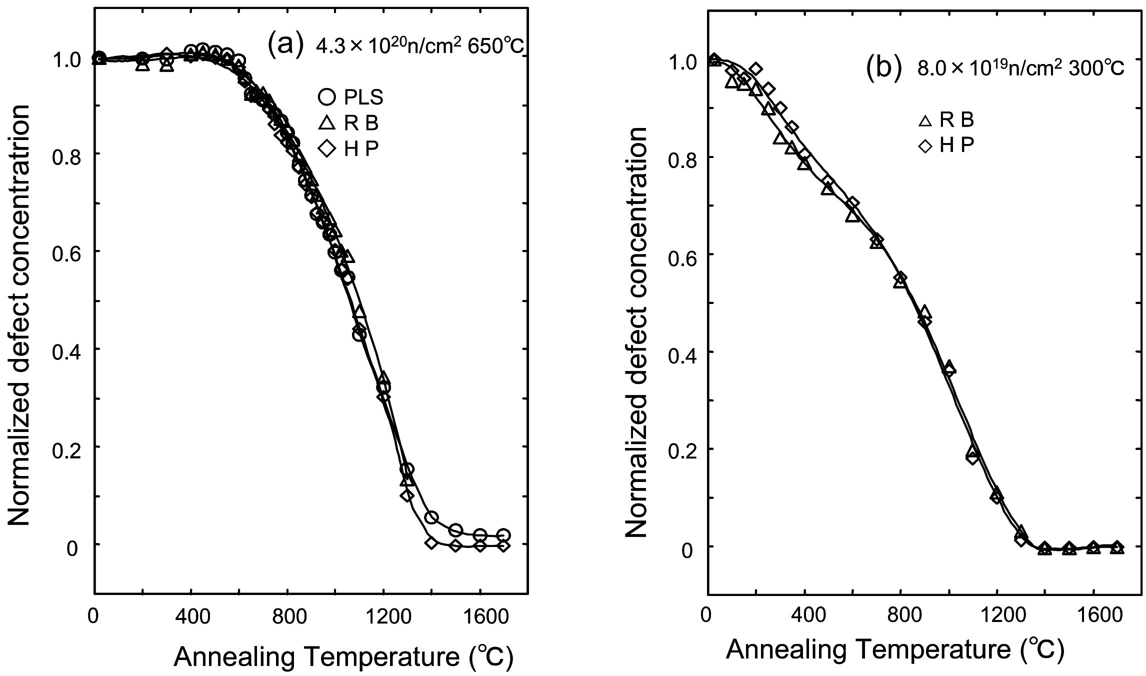

Fig. 4. Annealing temperature and the normalized defect concentration calculated from the thermal conductivity of neutron-irradiated SiC. Irradiation conditions: (a) 4.3×10^{24} n/m^2, 650 °C, (b) 8.0×10^{23} n/m^2, 300 °C.

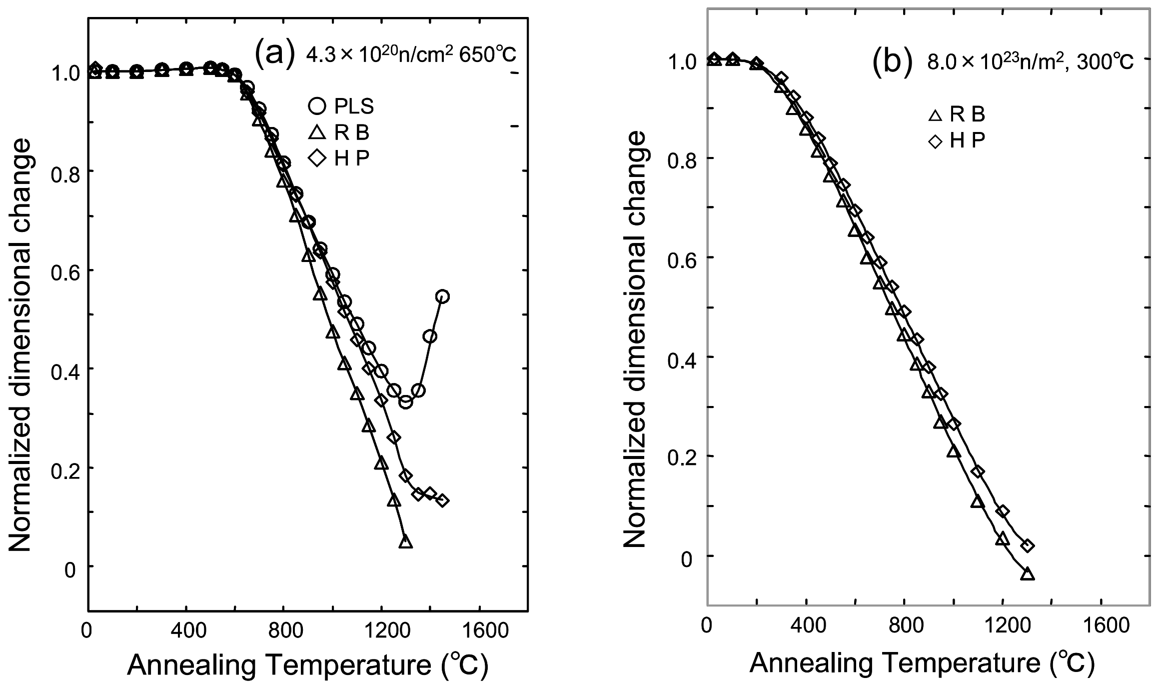

Fig. 5. Annealing temperature vs. the normalized dimensional change of neutron-irradiated SiC. Irradiation conditions: (a) 4.3×10^{24} n/m^2, 650 °C, (b) 8.0×10^{23} n/m^2, 300 °C.

diamond. As shown in Table 1, a fair agreement was obtained between the defect concentration calculated from the thermal conductivity and swelling data.

4.2. Recovery behavior of thermal conductivity and dimensional changes

The relationship between thermal conductivity and dimensional changes was studied by comparing the temperature dependence of defect concentrations calculated from the annealing data. Fig. 4 shows the change of defect concentration calculated from the annealing data of thermal conductivity of SiC, where the values of defect concentration were normalized to those of as-irradiated material so that they are easily compared with swelling data. It is noted that in the SiC irradiated at 650 °C to 4.3×10^{24} n/m^2, the defect concentration began to decrease from the irradiation temperature and linearly decreased to vanish at around 1400 °C, as shown in Fig. 4(a). The similar temperature dependence was generally observed for the defect concentration of SiC irradiated to 8.0×10^{23} n/m^2, at 300 °C, as shown in Fig. 5(b).

Fig. 5 shows the recovery behavior of neutron-irradiated SiC. The values of dimensional change were normalized to those of as-irradiated materials. As shown in Fig. 5, the swelling began to recover at each irradiation temperature and linearly decreased with increasing annealing temperature. It is well known that the onset of recovery of dimensional change of SiC coincides well with the irradiation temperature. Thus SiC is often used as a passive temperature monitor of nuclear reactors [6]. It is also observed that the dimension of PLS-SiC began to increase at temperatures above 1300 °C. This is caused by the formation and growth of He bubbles since PLS-SiC contains boron atoms which produce He through the $^{10}B(n,\alpha)^{7}Li$ reaction [13,14].

Comparing the annealing behavior of defect concentrations calculated from the thermal conductivities with that of dimensional changes, similar temperature dependences are observed as shown in Figs. 4 and 5. We obtained quite good agreement between changes of thermal conductivity and swelling. Therefore, it is confirmed that the same kind of irradiation induced defects are involved in the degradation of thermal conductivity and swelling of SiC. In the present paper, we showed that the scattering of phonons by vacancies is the main cause of thermal conductivity degradation. The coincidence between recovery process of thermal conductivity and dimensional changes shown in Figs. 4 and 5 would also support the validity of this assumption.

5. Conclusions

We carried out measurement of neutron irradiation effect on the thermal conductivity of SiC. Studies were made of relationship between dimensional changes and the thermal conductivity and the following conclusions were obtained.

(1) Neutron irradiation at temperatures of 300 and 650 °C and fluences 8.0×10^{23} and 4.3×10^{24} n/m^2 markedly reduced the thermal conductivity of SiC to similar levels and yielded similar temperature dependence irrespective of original unirradiated values.
(2) The onset of recovery in thermal conductivity began at temperature near the irradiation temperature and was complete at about 1400 °C.
(3) Assuming scattering of phonons by vacancies is the main cause of thermal conductivity degradation, the point defect concentration was calculated and compared with that obtained from swelling data. A fair agreement was obtained between them.
(4) The defect concentrations showed similar annealing behavior determined from either thermal conductivity or swelling. The result shows that the same irradiation induced defects are involved in the degradation of thermal conductivity and swelling of SiC.

Acknowledgements

The experimental work of present investigation was carried out at the Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology The author is grateful to Mr S. Yoshida for his help in carrying out the measurements.

References

[1] L.H. Rovner, G.R. Hopkins, Nucl. Technol. 29 (1976) 274.
[2] F. Clinard Jr., in: K. Kawamura, T. Iseki, A. Miyahara, F.W. Clinard Jr., (Eds.), Proceedings of the 1st Japan–US Workshop on Advanced Ceramics for Fusion Application (p115), Resarch Laboratory for Nuclear Reactors, T.I.T., Japan, 1988, p. 5.
[3] F.W. Clinard Jr., L.W. Hobbs, Radiation Effects in Non-Metals, in: R.A. Johinson, A.N. Orlov (Eds.), Physics of Radiation Effects in Crystals, Elsevier Science Publishers BV, 1986, p. 387.
[4] R.J. Price, J. Nucl. Mater. 33 (1969) 17.
[5] R.J. Price, Nucl. Technol. 35 (1977) 320.
[6] R.P. Thorne, V.C. Howard, B. Hope, Proc. Brite. Ceram. Soc. 7 (1967) 449.
[7] R.J. Price, J. Nucl. Mater. 46 (1973) 268.s.
[8] C.W. Lee, F.J. Pineau, J.C. Corelli, J. Nucl. Mater. 108&109 (1982) 678.
[9] Y.S. Touloukian, C.Y. Ho (Eds.), Thermophysical Properties of Matter, Vol. 5, Purdue Reserch Foundation, 1970, p. 448.
[10] R.C. Heckman, J. Appl. Phys. 44 (1973) 1455.
[11] P.G. Klemence, Proc. Phys. Soc., A 68 (1955) 1113.
[12] A.M. Stoneham, Theory of Defects in Solids, Clarendon, Oxford, 1975, p. 880.
[13] T. Yano, K. Sasaki, T. Maruyama, T. Iseki, M. Ito, S. Onose, Nucl. Technol. 93 (1991) 412.
[14] K. Sasaki, T. Yano, T. Maruyama, T. Iseki, J. Nucl. Mater. 179–181 (1991) 407.