Thermal conductivity of boron carbide under fast neutron irradiation

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Abstract: Due to the complex products and irradiation-induced defects, it is hard to understand and even predict the thermal conductivity variation of materials under fast neutron irradiation, such as the abrupt degradation of thermal conductivity of boron carbide (B_4C) at the very beginning of the irradiation process. In this work, the contributions of various irradiation-induced defects in B_4C primarily consisting of the substitutional defects, Frenkel defect pairs, and helium bubbles were re-evaluated separately and quantitatively in terms of the phonon scattering theory. A theoretical model with an overall consideration of the contributions of all these irradiation-induced defects was proposed without any adjustable parameters, and validated to predict the thermal conductivity variation under irradiation based on the experimental data of the unirradiated, irradiated, and annealed B_4C samples. The predicted thermal conductivities by this model show a good agreement with the experimental data after irradiation. The calculation results and theoretical analysis in light of the experimental data demonstrate that the substitutional defects of boron atoms by lithium atoms, and the Frenkel defect pairs due to the collisions with the fast neutrons, rather than the helium bubbles with strain fields surrounding them, play determining roles in the abrupt degradation of thermal conductivity with burnup.

Keywords: boron carbide (B_4C); thermal conductivity; fast neutron irradiation

1 Introduction

Boron carbide (B_4C) is a promising neutron absorbing material which is extensively used as control rod and shielding material in nuclear reactor due to its high neutron absorption cross section accompanying low neutron induced radioactivity [1,2]. Especially in the fast reactor, it is the most preferred neutron absorbing material of the control rod [2]. The excellent neutron

absorption capability of boron carbide is attributed to the ^{10}B isotopes which can capture neutrons through (n, α) reaction. During the (n, α) reaction, a certain amount of heat is released and accumulated in boron carbide pellets. So high thermal conductivity is necessary for boron carbide pellets to transfer the heat into the surrounding coolant. Thermal conductivity is therefore one of the most concerned properties of boron carbide in the fast reactor application.

The unirradiated boron carbide ceramic possesses a relatively high thermal conductivity, about 28 W/(m·K) at room temperature [3]. However, Mahagin *et al.* [4] observed that under fast neutron irradiation, the boron

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carbide pellets suffer a significant reduction in the thermal conductivity which is saturated rapidly at the burnup of $\sim 5 \times 10^{26}$ cap/m³. Maruyama *et al.* [3] demonstrated that the thermal conductivity of boron carbide decreases rapidly to 1/3 of the unirradiated value as early as the burnup of $\sim 5 \times 10^{26}$ cap/m³, and then further decreases gradually to 1/10 at about 35×10^{26} cap/m³. Some other neutron irradiation investigations have also verified the abrupt degradation of thermal conductivity of boron carbide at the very beginning of the irradiation process [5–7].

It can be deduced simply that 5×10^{26} cap/m³ of neutron captures can only produce 0.455 at% ¹⁰B burnup of the total boron in a fully dense boron carbide pellet, which implies that the boron carbide pellet would endure an extremely high thermal gradient during most of its service life due to the thermal conductivity degradation. The high thermal gradient will result in a large thermal stress in pellets, and thus lead to an extensive cracking [7,8].

Until now, the mechanism of the abrupt degradation of thermal conductivity is still unclear. Mahagin *et al.* [4] inferred that the point defects induced by fast neutron irradiation as well as the plate-like pores/micro-cracks could serve as phonon scattering centers, while the crystal structure modifications may also enhance the phonon–phonon scattering (Umklapp processes), both of which degrade the thermal conductivity significantly. They also assessed the contributions of the defect scattering and Umklapp processes to the degradation, and came to a conclusion that the contribution of the former, especially the point defects, was remarkably higher than that of the latter. However, Gosset *et al.* [7] assumed that the helium bubbles as well as the high micro-strains induced, rather than the irradiation defects, might serve as phonon scattering centers. In our previous work [9], we tried to quantitatively estimate the effect of irradiation-induced point defects on the thermal conductivity of boron carbide by a classical phonon scattering model. The model predicted the degradation of thermal conductivity at the initial stage of irradiation. However, compared with the experimental data after irradiation reported by Refs. [3,4], it seems that the model underestimated the degradation, which may be due to the fact that the influence of irradiation-induced point defects was simplified by only taking the substitution of boron atoms by locally generated lithium atoms into the consideration in the model.

In the present work, all the factors that affect the thermal conductivity of boron carbide during the irradiation process were re-evaluated. The contributions of irradiation-induced point defects involving the substitution and Frenkel defects were re-calculated in terms of the phonon scattering theory. In addition, the contribution of the helium bubbles to the thermal conductivity was also assessed. A theoretical model with an overall consideration of various factors was proposed and validated to predict the thermal conductivity variation of boron carbide under fast neutron irradiation.

2 Theoretical models

As we know, the performance degradation of boron carbide under fast neutron irradiation stems from the following neutron capture reaction [2]:

It is believed that the lithium atoms generated by this reaction are most likely to substitute for the ¹⁰B atoms which have been removed from the lattice [10]. The substitution of boron atoms by locally generated lithium atoms has been considered to be one of the most important types of point defects to strongly scatter the phonons and significantly reduce the thermal conductivity, as discussed in our previous work [9]. On the other hand, the helium atoms associated with lithium atoms are virtually insoluble in the lattice of boron carbide [11]. Hence they will initially diffuse out through grain boundaries at very low burnup, and then nucleate and accumulate to form lenticular bubbles after a burnup threshold [10–12]. These helium bubbles lead to the macroscopic swelling, and microscopic intergranular and/or intragranular microcracking of boron carbide pellet. In addition, the interactions between fast neutrons and boron carbide without neutron captures can generate Frenkel defect pairs on both the carbon and boron sub-lattices [10]. All these defects, along with the resulting crystal structure modifications, contribute to the degradation of thermal conductivity, which dramatically reduce the conduction of the reaction heat. The continuously generated heat due to neutron captures will accumulate inside the pellet and increase remarkably the central temperature (with a maximum temperature even over 1600 °C under fast neutron irradiation as estimated), which gives rise to an extremely high thermal gradient and consequently ultrahigh thermal stress. The thermal

stress as well as the swelling-gradient stress is responsible for the cracking and fragmentation of boron carbide pellets [8]. Moreover, the increase of internal temperature due to the degradation of thermal conductivity conversely affects the swelling and also the thermal conductivity itself.

The influence of irradiation defects on thermal conductivity of boron carbide is usually interpreted as the scattering of the phonons [13,14]. Boron carbide is actually a classical semiconductor, in which the charge carrier can also be a carrier of heat; however, it is believed that the contribution of carriers on thermal conductivity is negligible for boron carbide [14]. So only the contribution of phonon scattering was considered in this work, as in most of the previous studies.

In terms of Debye's phonon gas theory, the thermal conductivity k of a ceramic material can be expressed in the form [15,16]:

$$k = \frac{1}{3} C_V \cdot \bar{v} \cdot l \quad (2)$$

where C_V is the heat capacity per unit volume, $\bar{v}$ is the average speed of sound, and l is the phonon mean free path. Since some physical properties such as heat capacity and sound speed are not sensitive to the irradiation within certain range of burnup, the phonon mean free path l predominates in determining the variation of thermal conductivity. On the other hand, the phonon mean free path l is chiefly determined by the phonon scattering process involving phonon–phonon (Umklapp) scattering, defect scattering, and grain boundary scattering, and can be expressed as

$$\frac{1}{l} = \frac{1}{l_i} + \frac{1}{l_d} + \frac{1}{l_b} \quad (3)$$

where l_i , l_d , and l_b are the phonon mean free paths corresponding to Umklapp scattering, defect scattering, and grain boundary scattering, respectively. As the grain size of the ceramic sample is several orders of magnitude larger than the phonon mean free path [16], the contribution of grain boundary scattering is usually ignored.

For the unirradiated samples free of defects, the intrinsic phonon mean free path due to Umklapp scattering l_i can be given by [16,17]:

$$l_i(\omega) = \frac{\mu \Omega v_t \omega_D}{2\gamma^2 k_B N^{1/3} T \omega^2} \quad (4)$$

where μ is the shear modulus, Ω is the average atomic volume, v_t is the transverse wave speed, ω_D is the

Debye frequency, γ is the Grüneisen anharmonicity parameter, k_B is the Boltzmann constant, N is the number of atoms per molecule, T is the absolute temperature, and ω is the frequency of phonon. The intrinsic thermal conductivity k_i can be then derived from Eqs. (2) and (4) as [16,17]:

$$k_i = \frac{3\mu v_t^2}{2\gamma^2 N^{2/3} \omega_D} \cdot \frac{1}{T} = \frac{A}{T} \quad (5)$$

It is the classical $1/T$ variation of thermal conductivity for the materials free of defects. However, most of ceramics, such as the unirradiated B_4C , show a less pronounced temperature dependence of thermal conductivity. Roufosse and Klemens [18] restricted the minimum of phonon mean free path, and the intrinsic thermal conductivity k_i can be represented as

$$k_i = \frac{A}{T} \left(\frac{2}{3} \sqrt{\frac{T_1}{T}} + \frac{T}{3T_1} \right) \quad (6)$$

where A is the same as in Eq. (5), and T_1 is the critical temperature at which the phonon at maximum frequency reaches the minimum phonon mean free path $l_{\min}$.

For the irradiated samples, the irradiation defects will scatter phonons in addition to Umklapp scattering, and further reduce the thermal conductivity. The phonon mean free path due to defect scattering l_d can be given by [19–21]:

$$l_d(\omega) = \frac{4\pi v_t^4}{\Omega \Gamma} \cdot \omega^{-4} \quad (7)$$

where Γ is the imperfection scattering parameter which represents the strength of defect scattering.

Klemens [19] proposed a model for the materials with lattice defects by defining a frequency ω_0 at which $l_i(\omega_0) = l_d(\omega_0)$, and the thermal conductivity can be derived as

$$k = k_i \cdot \frac{\omega_0}{\omega_m} \cdot \arctan\left(\frac{\omega_m}{\omega_0}\right) \quad (8)$$

and

$$\left(\frac{\omega_0}{\omega_m}\right)^2 = \frac{4\gamma^2 k_B N T}{3\pi \mu \Omega \Gamma} \quad (9)$$

where ω_m is the maximum phonon frequency. The generalized expression of the imperfection scattering parameter Γ proposed by Klemens [22] can be given as

$$\Gamma = \sum_i c_i S_i^2 \quad (10)$$

$$S_i^2 = \left(\frac{\Delta M_i}{M} \right)^2 + 2 \left(\frac{\Delta G_i}{G} - 2Q\gamma \frac{\Delta R_i}{R} \right)^2 \quad (11)$$

where c_i is the fractional concentration of a certain defect i , and S_i represents the scattering strength of the defect i involving the mass and bonding force differences as well as the elastic field around the defect. The average mass, stiffness constant, and radius of impurity and host atoms are labeled as M_i , G_i , R_i and M , G , R , respectively. $\Delta M_i = M_i - M$, $\Delta G_i = G_i - G$, $\Delta R_i = R_i - R$, and Q is the distortion parameter of the lattice in the vicinity of the defect which takes the value of 4.2 if the nearest linkages have the same anharmonicity as all other links, otherwise takes 3.2 if the anharmonicity of the nearest linkages is excluded.

Abeles [21] developed the model in terms of the elastic continuum “sphere-in-hole” model, and the imperfection scattering parameter Γ can be represented as

$$\Gamma = \sum_i c_i \left[\left(\frac{\Delta M_i}{M} \right)^2 + \psi \left(\frac{R'_i - R}{R} \right)^2 \right] \quad (12)$$

where R'_i is the radius of impurity in its own lattice, and ψ is the strain field parameter which is usually regarded as an adjustable parameter. Wan *et al.* [23] simplified the strain field parameter on the physical basis instead of fitting in the case of substitution:

$$\psi = \frac{2}{9} \left(6.4\gamma \frac{1+\sigma}{1-\sigma} \right)^2 \quad (13)$$

where σ is the Poisson ratio of the matrix.

Similar to the case of materials free of defects, the model will take a more complex form if considering the restricted minimum of phonon mean free path [24]:

$$k = \frac{A}{T} \cdot \frac{\omega_0}{\omega_m} \arctan \left(\frac{\omega_l}{\omega_0} \right) + \frac{A}{3T} \cdot \frac{1}{1 + \left(\frac{\omega_l}{\omega_0} \right)^2} \cdot \left[\left(\frac{\omega_m}{\omega_l} \right)^2 - \frac{\omega_l}{\omega_m} \right] \quad (14)$$

where ω_l is the critical frequency above which the free path of phonon reaches the low limit $l_{\min}$. For the sake of simplicity, it can be simplified as a first approximation to be the following expression [25]:

$$k = \frac{A}{T} \left(\frac{2}{3} \sqrt{\frac{T_l}{T}} + \frac{T}{3T_l} \right) \cdot \frac{\omega_0}{\omega_m} \cdot \arctan \left(\frac{\omega_m}{\omega_0} \right) \quad (15)$$

Eq. (15) can be applied to predict the thermal conductivity of the irradiated B₄C sample from the experimental thermal conductivity of the unirradiated

sample which shows a less pronounced temperature dependence than $1/T$.

3 Results and discussion

3.1 Significance assessment of various irradiation defects

The primary issue to confirm the mechanism of the degradation of thermal conductivity is evaluating the contributions of various irradiation-induced defects. As analyzed above, the irradiation-induced defects influencing the thermal conductivity of boron carbide generally consist of three types of defects: (1) the substitutional defects of boron atoms by lithium atoms; (2) the Frenkel defect pairs of boron and carbon atoms owing to the collisions with the fast neutrons; (3) the helium bubbles as well as the strain fields surrounding them [26,27] and the accompanying microcracking. All these defects can scatter the phonons, and reduce the mean free paths and consequently the thermal conductivity.

The controversy [4,7,9] with regard to the determining factor in the degradation of thermal conductivity stems from the lack of quantitative assessment on the contribution of various irradiation-induced defects. So we attempted to re-evaluate the contributions of the three types of primary defects throughout the irradiation process.

The first thing we need to know is that not all the defects contribute simultaneously to the degradation of thermal conductivity, such as the helium bubbles which do not exist initially. It has been observed that there is a period at the initial stage of irradiation during which nearly all the generated helium atoms release from the pellet to the plenum [11,28]. The burnup threshold of this period is about 10×10^{26} cap/m³, namely, ~ 0.910 at% burnup of the total boron, which is considered as the nucleation threshold of helium bubbles [11]. It implies that the abrupt degradation of thermal conductivity at around 5×10^{26} cap/m³ should not be attributed to the helium bubbles and the surrounding strain fields, which is contrary to the assumption of Gosset *et al.* [7]. After this period, the helium atoms aggregate and nucleate to form the lenticular bubbles with a nearly full retention of helium up to a higher burnup threshold. The bubbles will then scatter the phonons and contribute to the further decrease of thermal conductivity, though the degradation of which has saturated with burnup above 10×10^{26} cap/m³.

On the contrary, the formation of Frenkel defect

pairs is usually considered to coincide with the neutron captures. Zuppiroli *et al.* [12] estimated that the production of one helium atom was accompanied by 3000 vacancy-interstitial pairs. Gosset *et al.* [29] re-calculated the number of displaced atoms per produced helium by considering the energy spectra of both the primary knocked-on atoms and atoms created by the capture reactions, and obtained a much smaller estimation value of about 305. In the light of Eq. (1), the production rate of lithium atoms is the same as that of helium atoms. As noted, the generated lithium atoms are assumed to substitute for the removed ^{10}B atoms. So the concentration of the substitutional defects of boron atoms by lithium atoms should be closely related to that of Frenkel defect pairs, both of which can be expected to increase linearly with the burnup. These two types of point defects affect the thermal conductivity simultaneously from the start.

Morohashi *et al.* [6] carried out an annealing measurement of thermal conductivities of the irradiated $^{10}\text{B}_4\text{C}$ sample in contrast with the case of the irradiated $^{11}\text{B}_4\text{C}$ sample. It was demonstrated that after 1400 °C annealing, the thermal conductivity of the irradiated $^{11}\text{B}_4\text{C}$ is almost completely recovered, whereas the recovery of the thermal conductivity of the irradiated $^{10}\text{B}_4\text{C}$ is quite limited. Owing to the absence of ^{10}B in the $^{11}\text{B}_4\text{C}$ sample, the neutron captures cannot take place during the irradiation. Frenkel defect pairs due to the elastic collisions with neutrons are believed to be the only irradiation-induced defects in the $^{11}\text{B}_4\text{C}$ sample, which may be annihilated during the annealing. On the other hand, the limited recovery of the thermal conductivity of the $^{10}\text{B}_4\text{C}$ sample should be attributed to the residual substitutional defects of boron atoms by lithium atoms with the relevant Frenkel defect pairs annihilated. This may offer an opportunity to evaluate the contributions of Frenkel defect pairs and the substitutional defects separately. In our previous work [9], it was natural to assume that the contribution of Frenkel defect pairs was negligible due to the limited recovery. However, it probably underestimated the degradation of thermal conductivity, because the influence of point defects on phonon scattering and thermal conductivity is nonlinear. So the contribution of Frenkel defect pairs should be re-evaluated in comparison with that of the substitutional defects.

Moreover, a similar post-irradiation annealing at 1400 °C was performed by Jostsons *et al.* [26], and the results revealed that the strain fields surrounding

the helium bubbles have been eliminated. The limited recovery of the thermal conductivity under the same annealing condition adds to further evidence that the strain fields surrounding the helium bubbles are not the primary cause of the degradation of thermal conductivity. The higher recovery of the thermal conductivity in Gosset *et al.*'s work [7] could be attributed to the lower burnup and the much higher annealing temperature (2200 °C) than the irradiation temperature and even the brittle-to-ductile temperature threshold.

Based on the analysis above, the contributions of various irradiation-induced defects on the degradation of thermal conductivity were further assessed separately and quantitatively, and discussed in details in the following text.

3.2 Contribution of the substitutional defects

It has been demonstrated by some previous authors [10,30] that there is no visible precipitation of lithium observed even up to very high burnup while the Li/C ratio increases at the same rate as that of the decrease of the B/C ratio. Since the ^{10}B atoms are continually removed from the lattice due to the neutron captures, the resulting boron vacancies appear most feasible to accommodate the locally generated lithium atoms. These substitutional defects of boron atoms by lithium atoms were considered to be the primary factor leading to the degradation of thermal conductivity in our previous work [9]. In the present work, the contribution of these substitutional defects on the thermal conductivity was re-evaluated in terms of the phonon scattering theory. The most comprehensive experimental data obtained by Maruyama *et al.* [3] including the thermal conductivities of the irradiated boron carbide pellets as well as the unirradiated ones were used to validate the calculation results. The calculation details were quite similar to that in our previous work [9] with some parameters being revised, which are described briefly below.

The thermal conductivity of the unirradiated boron carbide from Maruyama *et al.* [3] was adopted as the intrinsic thermal conductivity k_i in this work. However, it shows a less pronounced temperature dependence than $1/T$ variation, which could be attributed to the initial defects introduced during the process of material synthesis and preparation. As shown in Fig. 1, neither the $1/T$ model from Eq. (5) nor the minimum mean free path model from Eq. (6) really fits the experimental data well. In order to obtain accurately the fundamental

Fig. 1 Thermal conductivities of the unirradiated B₄C pellets [3] fitted by different models. 1/T model refers to the classical intrinsic thermal conductivity model represented by Eq. (5), while the minimum mean free path model corresponds to Eq. (6).

data for calculation, a simple model based on the statistical analysis of the regression [4] was then used to fit the data:

$$k'_i = \frac{1}{aT + b} \quad (16)$$

where a and b are the fitting parameters. A satisfactory fit can be achieved with an adjusted R^2 of 0.998 when $a = 3.767 \times 10^{-5}$ m/W and $b = 2.429 \times 10^{-2}$ m·K/W.

The contribution of the substitutional defects on the thermal conductivity can be evaluated using Eq. (8) in which the intrinsic thermal conductivity k_i can be replaced by the k'_i in Eq. (16) (Model 1):

$$k = k'_i \cdot \frac{\omega_0}{\omega_m} \cdot \arctan\left(\frac{\omega_m}{\omega_0}\right) \quad (17)$$

On the other hand, the imperfection scattering parameter Γ in Eq. (12) can be re-expressed as the weighted sum of the scattering strengths of defects on each sub-lattice in the case of B₄C [21,23,31]:

$$\Gamma = \frac{4}{5} \left(\frac{M_B}{M} \right)^2 \Gamma_B + \frac{1}{5} \left(\frac{M_C}{M} \right)^2 \Gamma_C \quad (18)$$

where M , M_B , and M_C are the average mass of the atoms in the unit cell, and on the sub-lattices of boron and carbon atoms, respectively. Γ_B and Γ_C represent the individual scattering strength associated with defects on those two sub-lattice sites. Supposing all the substitutions take place at boron sites, Γ_C should be zero, and the overall scattering strength depends on the scattering strength of defects on the boron sub-lattice:

$$\Gamma = \frac{4}{5} \left(\frac{M_B}{M} \right)^2 \Gamma_B \quad (19)$$

In the case of the substitution of boron atoms by lithium atoms on the boron sub-lattice, Γ_B can be expressed in the form [9,21,23]:

$$\Gamma_B = x(1-x) \left[\left(\frac{M_{Li} - M_B}{\bar{M}} \right)^2 + \psi \left(\frac{R_{Li} - R_B}{\bar{R}} \right)^2 \right] \quad (20)$$

where $\bar{M} = xM_{Li} + (1-x)M_B$, $\bar{R} = xR_{Li} + (1-x)R_B$, and x corresponds to the c_i in Eq. (12) which equals to the fractional burnup of the total boron. M_{Li} , M_B and R_{Li} , R_B represent the mass and radius of the foreign Li atoms and the host B atoms, respectively.

To apply Eqs. (17), (9), (19), (20), and (13) to the case of the substitutional defects in the B₄C lattice, we can evaluate the contribution of these substitutional defects on the thermal conductivity. Some physical parameters used in the present work were revised in light of the irradiated samples in the work of Maruyama *et al.* [3], which were hot-pressed B₄C pellets with the ¹⁰B enrichment of 92 at%. In this case, the average mass of B₄C unit cell M and boron sites M_B should be 10.476 and 10.093, respectively. The theoretical density of sample can be estimated to be 2.389 g/cm³, and the average atomic volume Ω is 7.282×10^{-30} m³.

The Grüneisen anharmonicity parameter γ can be estimated by the equation [23]:

$$\gamma = \frac{3\alpha_1 K}{C_p \rho} \quad (21)$$

where α_1 is the linear coefficient of thermal expansion, K is the bulk modulus, C_p is the heat capacity at constant pressure, and ρ is the density. It has been demonstrated that the variation of α_1 with temperature is consistent with that of C_p above certain temperature [23]. The data of these two parameters at 600 K ($\alpha_1 = 4.323 \times 10^{-6}$ K⁻¹, $C_p = 1.761$ J/(g·K)) [2] were used. The experimental bulk modulus K and shear modulus μ are 245 GPa and 200 GPa for B₄C [2]. Substituting into Eq. (21), the Grüneisen parameter γ can be estimated to be 0.755. Since the Poisson ratio σ is 0.18 [2], the strain field parameter ψ is calculated to be 10.748 by Eq. (13).

Moreover, the covalent radii of the boron and lithium atoms are 0.85 and 1.33 Å respectively, and the mass of lithium atoms M_{Li} is 6.941. As the atomic density of the total boron is about 1.099×10^{29} atoms/m³, the burnup can be easily converted from the absolute value in the form of the capture density (cap/m³) to the relative value as the proportion of the consumed ¹⁰B atoms to the initial number of total boron atoms (x).

Figure 2 shows the calculated results compared with the experimental data obtained by Maruyama *et al.* [3]. It can be seen clearly from the figure that the model only considering the contribution of the substitutional defects underestimates the degradation of the thermal conductivity, which suggests that the contributions of some other factors should be determined to predict more accurately the thermal conductivity of boron carbide under irradiation. In addition, it can also be seen from the comparison of the cases at different burnups that the deviation of the predicted values from the experimental data at the burnup of 4×10^{26} cap/m³ is much greater than those at higher burnup, which coincides with the abrupt degradation of thermal conductivity. The predicted value at room temperature is about 60% of the corresponding unirradiated one, with comparison to the actual degradation to about 1/3.

Moreover, the predicted temperature dependence of thermal conductivity is getting more and more insignificant gradually with increasing burnup. The curve at 35×10^{26} (also 36×10^{26}) cap/m³ shows an almost temperature-independent thermal conductivity, which is consistent with the actual variation of the thermal conductivity at

this burnup. The distinct difference in temperature dependence of thermal conductivity with burnup indicates that the defect scattering, instead of the Umklapp scattering, is becoming the primary factor to influence the thermal conductivity with increasing burnup.

3.3 Contribution of Frenkel defect pairs

Now that the prediction above underestimates the degradation of the thermal conductivity, the contribution of Frenkel defect pairs should be considered in addition to that of the substitutional defects. Theoretically, the contribution of Frenkel defect pairs can be evaluated with a similar model to the case of the substitutional defects. However, some inevitable problems were encountered when calculating with the equations in last section.

Firstly, it is hard to accurately determine the fractional concentration of the Frenkel defect pairs due to the continuing recombination of the interstitials and vacancies under fast neutron irradiation, although the number of displaced atoms per produced helium atom has been estimated by many researchers [12,29]. On

Fig. 2 Predicted thermal conductivities at different burnups by the model only considering the contribution of the substitutional defects (Model 1) with comparison to the experimental data of the samples before and after irradiation by Maruyama *et al.* [3].

the other hand, it is also very difficult to estimate the strength of defect scattering by the Frenkel defect pairs. Till now, no available literature has discussed the influence of the interstitial atoms on the thermal conductivity of materials. Additionally, the migration and annihilation of Frenkel defect pairs will lead to various secondary lattice defects, such as the antisite defects. Furthermore, the interaction and association between lattice defects due to the clustering of Frenkel defect pairs cannot be estimated either.

Fortunately, the post-irradiation annealing may provide an effective way to separate out the contribution of Frenkel defect pairs from that of the substitutional defects on thermal conductivity. The almost complete recovery of the thermal conductivity of the irradiated $^{11}\text{B}_4\text{C}$ sample [6] implies that Frenkel defect pairs due to the collisions with neutrons can be annihilated by high temperature annealing. In contrast, the substitutional defects of boron atoms by locally generated lithium atoms cannot be eliminated, and are believed to be retained in the lattice. The residual damage of thermal conductivity of the irradiated $^{10}\text{B}_4\text{C}$ sample could be attributed to the contribution of the substitutional defects, whereas the recovered proportion owes to the contribution of Frenkel defect pairs. On the basis of the thermal conductivity data of the irradiated $^{10}\text{B}_4\text{C}$ samples before and after annealing [6], the proportion of the contribution of Frenkel defect pairs to that of the substitutional defects can be evaluated.

Prior to the calculation, we firstly assumed that: (1) the concentration of Frenkel defect pairs retained in the lattice varies linearly with the increasing burnup and the related substitutional defects within a certain irradiation dose; (2) most of the physical properties of the irradiated samples, such as heat capacity and sound speed, vary little within a certain irradiation dose. For clarity, suppose the initial value, annealed value, and irradiated value of the thermal conductivity and the phonon mean free path of B_4C are k_0 , k_1 , k_2 and l_0 , l_1 , l_2 , respectively. The thermal conductivities of samples under three conditions can be then re-expressed in terms of Eq. (2):

$$\begin{cases} k_0 = \frac{1}{3} C_V \cdot \bar{v} \cdot l_0 \\ k_1 = \frac{1}{3} C_V \cdot \bar{v} \cdot l_1 \\ k_2 = \frac{1}{3} C_V \cdot \bar{v} \cdot l_2 \end{cases} \quad (22)$$

On the other hand, it can be easily derived from Eqs. (3), (7), and (10) that the effective value of the reciprocal of phonon mean free path can be given by the sum of the corresponding reciprocal for each process involving various defects scattering:

$$\frac{1}{l_1} = \frac{1}{l_0} + \frac{1}{l_S} = \frac{1}{l_0} + B \cdot c_S \cdot S_S^2 \quad (23)$$

$$\frac{1}{l_2} = \frac{1}{l_0} + \frac{1}{l_S} + \frac{1}{l_F} = \frac{1}{l_0} + B \cdot (c_S \cdot S_S^2 + c_F \cdot S_F^2) \quad (24)$$

where l_S and l_F are the phonon mean free paths corresponding to the substitutional defects and Frenkel defect pairs respectively, c_S and c_F are the fractional concentrations of these two types of defects, S_S and S_F are the corresponding scattering strengths, and B is a constant related to the physical properties of material in Eq. (7). Substituting Eqs. (23) and (24) into Eq. (22), we derived a formula as follows:

$$\frac{\frac{1}{k_2} - \frac{1}{k_1}}{\frac{1}{k_1} - \frac{1}{k_0}} = \frac{\frac{1}{l_2} - \frac{1}{l_1}}{\frac{1}{l_1} - \frac{1}{l_0}} = \frac{c_F \cdot S_F^2}{c_S \cdot S_S^2} \approx \text{constant} \quad (25)$$

In light of the assumption (1) above, c_F varies linearly with c_S . In addition, S_S and S_F depend on the species of defects, which can be considered as fixed values. So the formula above approximately equals to a constant. It can be obtained from the work of Morohashi *et al.* [6] that the initial value k_0 at room temperature is about 28.15 W/(m·K), the value after annealing k_1 is about 6.11 W/(m·K), and the irradiated value k_2 is about 2.77 W/(m·K). Substituting into Eq. (25), the constant is estimated to be about 1.54. The thermal conductivity of the irradiated B_4C sample can be predicted considering both the contributions of the substitutional defects and Frenkel defect pairs in the form (Model 2):

$$k_2 = \frac{1}{1.54 \left(\frac{1}{k_1} - \frac{1}{k_0} \right) + \frac{1}{k_1}} = \frac{k_1}{1.54 \left(1 - \frac{k_1}{k_0} \right) + 1} \quad (26)$$

where k_0 can be replaced by the experimental thermal conductivity of the unirradiated B_4C that is the k'_i in Eq. (16), and k_1 can be substituted by the predicted thermal conductivity k in Eq. (17) which only considers the contribution of the substitutional defects.

The calculated results of the improved model (Model 2) are shown in Fig. 3. Compared with the predicted values by Model 1 in Fig. 2, a much better agreement with the experimental data [3] has been achieved,

Fig. 3 Predicted thermal conductivities at different burnups by the model considering both the contributions of the substitutional defects and Frenkel defect pairs (Model 2) with comparison to the experimental data of the samples before and after irradiation by Maruyama *et al.* [3].

though the contribution of the helium bubbles is still not considered. Interestingly, the degree of the agreement with the experimental data varies with the burnup. The best consistency appears at the burnup of $14 \times 10^{26} \text{ cap/m}^3$, whereas the degradation of the thermal conductivity is slightly underestimated at a higher or lower burnup. It may be attributed to the lack of the contribution of the helium atoms from the neutron capture reaction. At a lower burnup than $10 \times 10^{26} \text{ cap/m}^3$, the helium atoms diffuse from the lattice to the grain boundaries, a small portion of which could be retained in the lattice as helium interstitials, and possibly contribute to the degradation of the thermal conductivity. On the other hand, at a higher burnup, the helium atoms nucleate to form helium bubbles with strain fields surrounding them. The helium bubbles and the surrounding strain fields may also contribute to the degradation of the thermal conductivity, which will be evaluated hereafter.

3.4 Re-assessment of the significances

The calculations above demonstrate that the phonon mean free path l dominates the variation of thermal

conductivity, which can be used to evaluate the significances of various irradiation defects. So a quantitative reassessment was performed prior to evaluating the contribution of the helium bubbles.

It can be derived from Eq. (2) as well as the relation $C_V = C_p \cdot \rho$ that the phonon mean free path l can be expressed as

$$l = \frac{3k}{C_p \cdot \rho \cdot \bar{v}} \quad (27)$$

The heat capacity C_p of B_4C at room temperature is about $0.950 \text{ J/(g}\cdot\text{K)}$ [2], and the average speed of sound $\bar{v}$ can be calculated from the values of the bulk modulus K and shear modulus μ mentioned above:

$$\bar{v} = 3^{1/3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right)^{-1/3} \quad (28)$$

$$v_l^2 \cdot \rho = K + \frac{4}{3} \mu \quad (29)$$

$$v_t^2 \cdot \rho = \mu \quad (30)$$

where v_l and v_t are the longitudinal and transverse acoustic speeds of materials, respectively. The average

speed of sound in B_4C is estimated to be 10,079.048 m/s. Then the phonon mean free paths at different burnups were calculated from the thermal conductivity data at room temperature measured by Maruyama *et al.* [3], which is shown in Table 1.

The phonon mean free path of the unirradiated sample at room temperature is estimated to be about 37.24 Å, which is consistent with the previous result (~36 Å) [6]. With the increase of burnup, it decreases rapidly as what happens in thermal conductivity.

It can be seen from Eq. (3) that the effective value of the phonon mean free path is chiefly determined by the minimum among all the component ones corresponding to various scattering processes. Generally, the possible lower limit of the phonon mean free path associated with a certain defect is restricted by the average distance between the defects. For instance, the grain size of the ceramic samples is generally above several micrometers, which is about several orders of magnitude larger than the phonon mean free path. So the contribution of grain boundary scattering to the thermal conductivity is usually ignored for most of the ceramic materials.

In the case of the irradiated B_4C sample, we can also give a rough estimate of the contributions of various irradiation-induced defects by their average distances though which do not necessarily equal to the corresponding phonon mean free path. The average distance between the possible substitutional defects can be easily estimated from the burnup in the form of the capture density, as shown in Table 1. Obviously, the estimated average distances of these defects are very close to the phonon mean free paths, especially at low burnups. As the fractional concentration of the Frenkel defect pairs is hard to be determined accurately, it is impossible to estimate their average distance directly. However, it can be deduced from the estimated fractional concentration

of the recovered point defects after annealing [6] that their average distance may be on the same order of magnitude as the corresponding value of the substitutional defects. As a contrast, the observed distance between the helium bubbles is much greater than the estimate values above of the substitutional defects and the Frenkel defect pairs. In the TEM observations [7,10,26, 27,30], the average distance between the helium bubbles is more than a few tens of nanometers with an estimated value about 736.81 Å at the burnup of $\sim 5 \times 10^{26}$ cap/m³ from the average density of 2.5×10^{21} m⁻³ [30]. It is approximately two orders of magnitude larger than the phonon mean free paths in Table 1.

Thus, it may be concluded that the substitutional defects as well as the Frenkel defect pairs are believed to play primary roles in the abrupt degradation of thermal conductivity with burnup, whereas the helium bubbles with strain fields surrounding them contribute slightly to the thermal conductivity, especially at low burnups.

Furthermore, we can also estimate the corresponding phonon mean free paths of the substitutional defects and the Frenkel defect pairs from Eqs. (22)–(24) as well as the experimental thermal conductivity data after irradiation and annealing [6]. The phonon mean free path corresponding to the substitutional defects l_s is calculated to be about 10.23 Å, while that of Frenkel defect pairs l_f is estimated to be about 6.65 Å. It is surprising to see that the latter is even lower than the former, which suggests that the contribution of Frenkel defect pairs to the degradation of thermal conductivity may be greater than that of the substitutional defects. It demonstrates that it is wrong in our previous work [9] to assume that the contribution of Frenkel defect pairs is negligible, although a very limited recovery of the thermal conductivity was observed after high temperature annealing [6].

3.5 Contribution of the helium bubbles

Owing to the slight contribution to the degradation of thermal conductivity, the helium bubbles can be treated as pores in the sample, which are generally considered to affect the thermal conductivity in an empirical linear relation [5,16,23]:

$$k = k_f \cdot (1 - C\phi) \quad (31)$$

where k_f is the initial value of the thermal conductivity which is usually the thermal conductivity of the fully dense sample in the unirradiated case and can be

Table 1 Phonon mean free paths estimated from the experimental thermal conductivities [3] at room temperature in comparison with the average distance between the substitutional defects at different burnups

Burnup (10^{26} cap/m ³)	Thermal conductivity (W/(m·K)) [3]	Phonon mean free path (Å)	Average distance between the substitutional defects (Å)
0	28.40	37.24	—
4	8.99	11.78	13.57
14	6.38	8.37	8.94
35	2.18	2.86	6.59
36	2.35	3.08	6.52

replaced by the k_2 in Model 2 in our case, C is an empirical parameter that is 3/2 [16] or 4/3 [23] for the unirradiated samples and is much larger as 3.6 ± 0.6 for the irradiated samples, and ϕ is the porosity.

The initial value of the intrinsic thermal conductivity used in our work, that is the k'_i in Eq. (16), originates from a hot-pressed B₄C pellet with a relative density of 95% [3]. So, when considering the contribution of the helium bubbles, it is necessary to extrapolate firstly the thermal conductivity to that of the fully dense sample, and then to calculate the ultimate thermal conductivity with the overall porosity after irradiation. The thermal conductivity can be predicted with the contribution of the helium bubbles in addition to those of the substitutional defects and the Frenkel defect pairs (Model 3):

$$k = k_2 \cdot \frac{1 - C\phi_1}{1 - C\phi_0} \quad (32)$$

where k_2 is the same one as in Eq. (26), ϕ_0 is the initial porosity, and ϕ_1 is the porosity after irradiation. The porosity before and after irradiation can be expressed as

$$\phi_0 = 1 - \frac{\rho_0}{\rho_t} \quad (33)$$

$$\phi_1 = 1 - \frac{\rho_1}{\rho_t} = 1 - \frac{\rho_0}{\rho_t \cdot \left(1 + \frac{\Delta V}{V}\right)} = \frac{\phi_0 + \zeta}{1 + \zeta} \quad (34)$$

where ρ_t is the theoretical density, ρ_1 is the density after irradiation, and ζ is the fractional swelling which is $\Delta V/V$. As mentioned above, there is a burnup threshold N_α^0 at the initial stage of irradiation before which nearly all the generated helium atoms release with no helium bubbles in the samples [11,28]. So the

fractional swelling can be expressed in piecewise [12]:

$$\zeta = \frac{\Delta V}{V} = \begin{cases} 0, & N_\alpha \leq N_\alpha^0 \\ D(N_\alpha - N_\alpha^0), & N_\alpha > N_\alpha^0 \end{cases} \quad (35)$$

where N_α is the burnup, N_α^0 is the burnup threshold exceeding which the helium bubbles form with an estimated value of 10×10^{26} cap/m³ [11,12], D is the covolume term in the van der Waals equation with a value of 1.5×10^{-29} m³ [12,30].

The calculated results of the model (Model 3) considering all the contributions of three types of irradiation-induced defects are shown in Fig. 4. Since the burnup of 4×10^{26} cap/m³ is lower than the burnup threshold, N_α^0 ($\sim 10 \times 10^{26}$ cap/m³) in Eq. (35), Model 3 gives the same result as Model 2 does, which is not shown in Fig. 4. The result corresponding to the burnup of 35×10^{26} cap/m³ which is quite similar to that of 36×10^{26} cap/m³ is not shown here for clarity either. It can be seen from Fig. 4 that the degradation of thermal conductivity induced by the helium bubbles is quite limited compared with the contributions of the substitutional defects and the Frenkel defect pairs in Figs. 2 and 3. The predicted values by Model 3 at the burnup of 14×10^{26} cap/m³ show a very slight difference from the corresponding values by Model 2, which may be attributed to the low swelling at this burnup close to the threshold. Meanwhile, a better agreement has been achieved for the predicted values at the burnups of 35×10^{26} and 36×10^{26} cap/m³. Moreover, as mentioned above, the slight mismatch at the burnup of 4×10^{26} cap/m³ is assumed to result from the helium atoms retained in the lattice, although the experimental error could be one of the possible reasons. However, the state of the helium atoms below the nucleation

Fig. 4 Predicted thermal conductivities at different burnups by the model considering all the three types of irradiation-induced defects (Model 3) with comparison to the experimental data of the samples before and after irradiation by Maruyama *et al.* [3].

threshold is still unclear. Further work should be performed to improve the prediction of the degradation of thermal conductivity below the nucleation threshold of the helium bubbles.

3.6 Degradation of thermal conductivity with burnup

With an overall consideration of the contributions of various irradiation-induced defects, we proposed a theoretical model (Model 3) to predict the degradation of thermal conductivity of boron carbide under fast neutron irradiation. Based on the experimental thermal conductivity data of the unirradiated, irradiated, and annealed B₄C samples, Model 3, without any adjustable parameters, shows a good agreement with the experimental data after irradiation. The degradation of thermal conductivity with burnup was also predicted using all the three models in this work, as shown in Fig. 5.

It can be seen more clearly from Fig. 5 that Model 1 proposed in our previous work [9] underestimates the degradation of the thermal conductivity in the whole range of burnup, especially at low burnup. The models (Models 2 and 3) considering the contribution of the Frenkel defect pairs successfully predict the abrupt degradation of thermal conductivity at low burnup, which indicates that the Frenkel defect pairs in addition to the substitutional defects play primary roles in the degradation, as discussed in Section 3.4. A slight difference between Models 2 and 3 appears only when a high burnup is reached, which indicates the much smaller contribution of the helium bubbles than those of the other two irradiation-induced defects.

Compared with the three sets of experimental data by Maruyama *et al.* [3], the calculated results of our

models (Models 2 and 3) are quite consistent with those of AMIR. It seems that the degradation of thermal conductivity was still underestimated for the other two sets of experimental data, especially at a lower burnup than the threshold. Besides the lack of the possible contribution of the helium atoms, some other reasons should also be considered. For the case of MK-I, the highly dispersed data may be responsible for the distinct deviation at low burnup, whereas a good agreement has been achieved at relative high burnup. On the other hand, the deviation with the data of MK-II may be attributed to the relatively lower density of the irradiated samples (~90%).

4 Conclusions

In this work, the contributions of various irradiation-induced defects in B₄C primarily consisting of the substitutional defects, Frenkel defect pairs, and the helium bubbles were re-evaluated quantitatively in terms of the phonon scattering theory. The post-irradiation annealing data were used to separate out the contribution of Frenkel defect pairs from that of the substitutional defects to thermal conductivity. A theoretical model (Model 3) with an overall consideration of the contributions of all these irradiation-induced defects was proposed without any adjustable parameters, and validated to predict the thermal conductivity variation based on the experimental data of the unirradiated, irradiated, and annealed B₄C samples. The results show that Model 3 successfully predicts the degradation of thermal conductivity of boron carbide under fast neutron irradiation. The predicted thermal conductivities and the analysis of phonon mean free paths as well as the irradiation effects demonstrate that the contribution of Frenkel defect pairs may be slightly greater than that of the substitutional defects, both of which are believed to play determining roles in the abrupt degradation of thermal conductivity with burnup, whereas the helium bubbles with strain fields surrounding them contribute slightly to the thermal conductivity, especially at low burnups.

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Fig. 5 Burnup dependence of the thermal conductivities predicted by all the models in this work with comparison to the experimental data by Maruyama *et al.* [3] which are labeled by the facilities where the samples were irradiated.

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