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Physical property change of heavily neutron-irradiated Si_3N_4 and SiC by thermal annealing

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Abstract

Changes in macroscopic length, lattice parameter and thermal diffusivity of neutron-irradiated Si_3N_4 and SiC ceramics up to a fluence of 4.2×10^{26} n/m^2 were measured. Macroscopic length increase of Si_3N_4 was almost one half of that of SiC. Thermal diffusivity of both ceramics was reduced severely by the irradiation at 390–540°C. Slight increase in the *a*-axis and slight decrease in the *c*-axis lattice parameter were detected for Si_3N_4. The amount of lattice parameter change of Si_3N_4 was very small compared with the macroscopic length change. Changes in these properties due to post-irradiation thermal annealing up to 1500°C were measured. Large part of thermal diffusivity of Si_3N_4 was recovered by annealing, with small step at ~1100°C, but macroscopic length did not significantly change by annealing. Change in lattice parameter showed a complicated trend. It is supposed that formation of interstitial loops on the planes parallel to the *c*-axis, formation of voids during annealing or difficulty of recovery of points defects/loops, or solid solution formation due to glassy grain boundary phase may influence the recovery behavior of Si_3N_4 ceramics. Changes in macroscopic length, lattice parameter or thermal diffusivity of SiC by annealing coincided with the results of previous works. The critical irradiation conditions for loop formation/XRD line broadening for SiC is discussed based on the present and previous results.

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1. Introduction

Thermo-nuclear fusion reactors, which are proposed as an ultimate power generator for the 21st century, require many non-metal materials. Radiation-induced changes in the physical properties of ceramics will have a significant influence on the design of fusion reactors. Physical properties of importance for fusion ceramics include dimensional stability, thermal conductivity, electrical conductivity, dielectric breakdown strength and loss tangent at high frequencies. These properties are strongly influenced by high-energy neutron irradiation. Furthermore, the use of low-activation components as structural material for fusion power reactors seems essential in terms of safety.

Besides its low activation and quick decay of activity, SiC has excellent behavior such as low atomic number material, good thermal conductivity, excellent high-temperature properties and corrosion resistance [1–6]. Furthermore, SiC shows good resistance to high-energy neutron irradiation until very high doses [7–12]. So far, SiC has been used as the structural material of the DREAM [13] and the ARIES IV [14] conceptual reactor designs. Whereas relatively many researches have been reported on neutron irradiation effects of SiC, it is still important to clarify the neutron-induced defects, particularly, formed after very high dose irradiation.

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On the other hand, another important commercial engineering ceramic is Si_3N_4, which exhibits excellent strength, toughness and thermal shock resistance and has been highly developed for structural applications such as gas turbine components and automobile engine parts such as turbo-charger rotor. Thus, it has a potential usefulness for fusion reactor applications [15]. It is very strange that only limited number of researches on neutron irradiation effects on Si_3N_4 have been reported up to the present [15–22]. Particularly, no recovery data of neutron-induced defects have been reported.

In this work, silicon carbide and silicon nitride ceramics were irradiated concurrently in the neutron fluence range 0.4–4.2 $\times 10^{26}$ n/m^2 and the macroscopic length, lattice parameter and thermal diffusivity changes were measured. Post-irradiation isochronal annealing up to 1500°C was conducted for these specimens, and recovery behavior of macroscopic length, thermal diffusivity and lattice parameter were measured. The difference in irradiation response of both ceramics was discussed based on the result of microstructure observation.

2. Experimental procedures

High-purity SiC(Type C101, >99 wt% SiC, sintering additive: <1 wt% Al_2O_3, density 3.20 g/cm^3, Nippon Steel) and Si_3N_4(Type NS101, >88 wt% Si_3N_4, sintering additives: <10 wt% Y_2O_3, <2 wt% $ZrSi_2$, Nippon Steel) ceramics were irradiated concurrently with fast neutrons in the JOYO fast experimental reactor in Japan up to fluences of 0.4–4.2 $\times 10^{26}$ n/m^2($E > 0.1$ MeV) at 390–730°C. The irradiation conditions are listed in Table 1. The temperature of specimens during irradiation was estimated based on TED temperature monitors. The specimens irradiated were 1.2 $\times$ 1.2 $\times$ 15 mm^3 for length measurement; 10 mm in diameter and 2 mm in thickness for thermal diffusivity measurement; and 3 mm in diameter and 0.5 mm in thickness for transmission electron microscopy (TEM). All specimens were irradiated in helium-filled capsules.

Macroscopic length was measured by micrometer at room temperature. The accuracy of length measurement was <0.01% (1 μm). Thermal diffusivity was measured using the laser-flash method (RIGAKU, LF/TCM-FA8510B) at room temperature in vacuum (2×10^{-3} Pa). The experimental uncertainty of thermal diffusivity was less than 1%. To determine the lattice parameter of SiC and Si_3N_4, X-ray diffraction with a CuKα source was used on a Philips PW-1700 diffractometer equipped with a graphite monochrometer. The diffraction profiles of peaks with indices (4 0 0), (3 3 1), (4 2 0), (4 2 2), (4 0 4), and (3 3 3) /(5 1 1) of β-SiC, and (3 0 1), (2 2 1), (3 1 1), (3 2 0), (4 1 1), (4 1 2), (5 0 2), and (3 0 3) of β-Si_3N_4 were precisely measured using an internal standard of Si at 26°C ($a_0 = 0.534088$ nm). For the X-ray measurement, the bulk was carefully crushed into powder using a mortar. The experimental error of the measurement was less than 0.01% for the specimen with broadened peaks.

Microstructure was observed by TEM. Thin foils for electron microscopy were prepared by dimpling and ion-milling technique. The transmission electron microscope used in the present study was a Hitachi H-9000 microscope which was operated with an accelerating voltage of 300 kV.

Changes in macroscopic length, thermal diffusivity and lattice parameter due to isochronal annealing were obtained successively with increasing annealing temperature on the same irradiated specimens. Thermal annealing was carried out in vacuum (up to 1000°C: $\sim 10^{-1}$ Pa and 1100–1500°C: $\sim 6 \times 10^{-4}$ Pa). Temperature of the specimens was raised at a rate of 30°C/min, except for a very low temperature up to 200°C, from room temperature to the designated temperature, and it was held at the annealing temperature for 1 h.

3. Results

3.1. Physical property change due to irradiation

The changes in macroscopic length, lattice parameter and thermal diffusivity of SiC and Si_3N_4 due to the

Table 1
Irradiation condition and changes in macroscopic length, lattice parameter and thermal diffusivity of SiC and Si_3N_4[a]

Fluence ($E > 0.1$ MeV) (n/m^2)	Irradiation temperature (°C)	Macroscopic length change (%)		Lattice parameter change (%)			Thermal diffusivity change (%)	
		SiC	Si_3N_4	SiC	Si_3N_4		SiC	Si_3N_4
				a-axis	*a*-axis	*c*-axis		
0.4 $\times 10^{26}$	540	–	–	–	–	–	−87	−71
1.4 $\times 10^{26}$	390	–	–	–	–	–	−88	−81
2.8 $\times 10^{26}$	480	+0.42	+0.19	+0.43	+0.06	−0.03	–	–
4.2 $\times 10^{26}$	730	+0.44	+0.21	+0.09	+0.02	−0.06	–	–

[a] Thermal diffusivities of unirradiated SiC and Si_3N_4 are 0.410 and 0.266 cm^2/s, respectively.

neutron irradiation are summarized in Table 1. Changes in macroscopic length and lattice parameter of SiC were of similar magnitude (~0.42%) after irradiation to the fluence of 2.8×10^{26} n/m^2 at 480°C, but these amounts showed large discrepancy in the specimen irradiated to a fluence of 4.2×10^{26} n/m^2 at 730°C. The change in lattice parameter of the 730°C SiC specimen was very small (0.09%). Profile of XRD peaks of this specimen was significantly broadened after the irradiation, whereas that of the 480°C specimen kept the separation of $K\alpha_1$ and $K\alpha_2$ and was not so significantly broadened. Reduction of thermal diffusivity of SiC after two different irradiation conditions (390°C and 540°C) was almost by the same amount (~87%).

Macroscopic length increase of Si_3N_4 was less than one half of that of SiC after the same irradiation condition. On the other hand, it is interesting to note that change in lattice parameter of Si_3N_4 was very small and anisotropic, i.e., slight expansion of the *a*-axis and slight contraction in the *c*-axis were observed in both irradiation conditions. Profiles of XRD peaks were broadened, but were not so significant after both irradiation conditions. Almost no shift in the position of peaks was observed. Reduction of thermal diffusivity of Si_3N_4 after two different irradiation conditions was different with a smaller reduction observed in the lower fluence and higher irradiation temperature specimen. The amount of reduction in thermal diffusivity in Si_3N_4 was smaller than that of SiC.

3.2. Change in physical properties of Si_3N_4 by isochronal annealing

The changes in macroscopic length and *a*- and *c*-axes lattice parameter of Si_3N_4 irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C during isochronal annealing up to 1400°C are shown in Fig. 1. Macroscopic length decreased gradually from ~500°C until around 1100°C, and a slight increase was observed between 1200–1300°C. Finally it shows a slight decrease at 1400°C. A slight decrease in length at 1400°C was observed for the unirradiated control specimen, probably due to sintering phenomena. It is noted that a large amount of macroscopic swelling is not recovered by thermal annealing up to 1400°C. A similar trend of macroscopic length change during annealing in the specimen irradiated to a fluence of 4.2×10^{26} n/m^2 at 730°C was observed, and is shown in Fig. 2. In this specimen, the decrease in macroscopic length started around 600°C. Another trend was very similar to that of the lower fluence specimen.

Change in lattice parameter of Si_3N_4 irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C and 4.2×10^{26} n/m^2 at 730°C is very complicated, as shown in Figs. 1 and 2, respectively. It should be noted that the *a*-axis and *c*-axis parameters were not independently determined in the lattice parameter determination procedures. In the 480°C specimen, change in the *a*-axis length kept positive values but gradually decreased up to around 1000°C, whereas the *c*-axis length kept negative values up to about 1000°C. The *c*-axis parameter increased following 900–1100°C annealing. At 1200°C, both the *a*- and *c*-axes length returned to the original value of the unirradiated specimen and anisotropy of lattice growth was diminished. In the specimen irradiated up to 4.2×10^{26} n/m^2 at 730°C, the change in lattice parameter is more complicated. No systematic change was observed, but the *c*-axis parameter change was slightly negative up to ~1200°C and that of the *a*-axis was almost ~0 at all annealing temperatures. Following 1400°C annealing, the *c*-axis parameter of 480 and 730°C specimens showed small negative values.

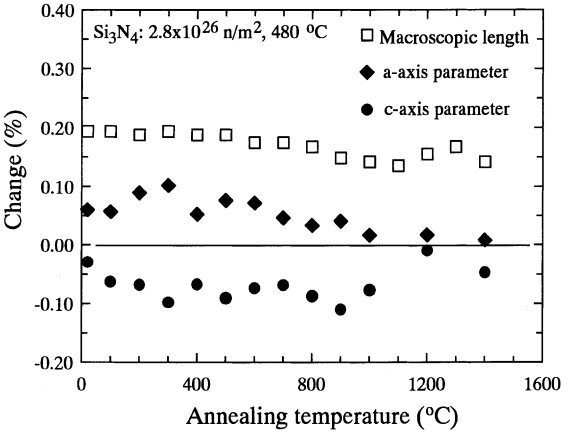

Fig. 1. Changes in macroscopic length and *a*- and *c*-axes lattice parameter at room temperature of Si_3N_4 irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C by isochronal annealing up to 1400°C.

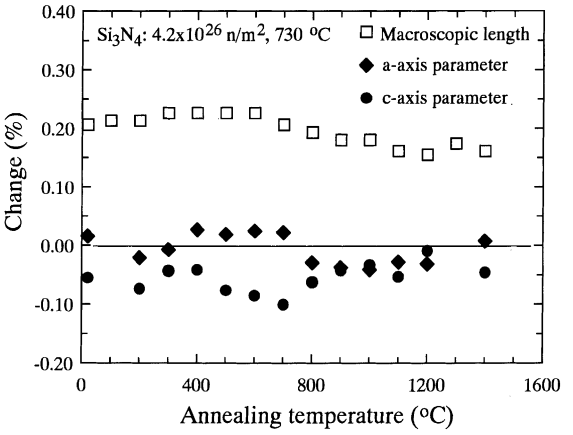

Fig. 2. Changes in macroscopic length and *a*- and *c*-axes lattice parameter at room temperature of Si_3N_4 irradiated up to a fluence of 4.2×10^{26} n/m^2 at 730°C by isochronal annealing up to 1400°C.

Thermal diffusivity of Si_3N_4 recovered gradually during annealing above the irradiation temperatures in both specimens irradiated up to a fluence of 0.4×10^{26} n/m^2 at 540°C and 1.4×10^{26} n/m^2 at 390°C, as shown in Fig. 3. The thermal diffusivity of the unirradiated Si_3N_4 is 0.266 cm^2/s. During the recovery of thermal diffusivity, there is a small step at around 1100°C. After isochronal annealing at 1500°C, thermal diffusivity of the lower or higher fluence specimens was recovered to be 71% or 45% of the original value. This indicates that the recovery of the thermal diffusivity is not completed even after annealing at 1500°C.

3.3. Change in physical properties of SiC by isochronal annealing

The changes in macroscopic length and lattice parameter of SiC irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C and 4.2×10^{26} n/m^2 at 730°C by isochronal annealing up to 1500°C are shown in Figs. 4 and 5, respectively. The room temperature macroscopic length of the 480°C specimen decreased gradually for annealing temperatures from ~500°C until around 1400°C, and returned almost completely to the pre-irradiation length. A slight decrease at 1500°C can be attributed to sintering or evaporation of specimen, which was also observed in the unirradiated specimen. On the other hand, macroscopic length of the 730°C, higher fluence specimen showed different behaviors compared to the lower fluence specimen. It started to decrease at around 600°C, and gradually shrunk up to around 1200°C, and then it showed almost constant length up to 1500°C. It is noted that a large amount of macroscopic swelling of this specimen was not recovered by thermal annealing up to 1500°C.

Change in lattice parameter of SiC irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C and 4.2×10^{26} n/m^2 at 730°C showed different behaviors, as shown in Figs. 4 and 5, respectively. In the 480°C specimen, recovery behavior of lattice parameter is very similar both in the trend and the quantitative amount with those of macroscopic length in full range of the present annealing experiment. In the specimen irradiated up to a fluence of 4.2×10^{26} n/m^2 at 730°C, the trend of change in lattice parameter due to annealing was close to the change in macroscopic length, but the amount of values shifted almost in a parallel manner toward very small values. The lattice parameter started to decrease at 500–600°C, and reached a constant value above 1000°C. Further-

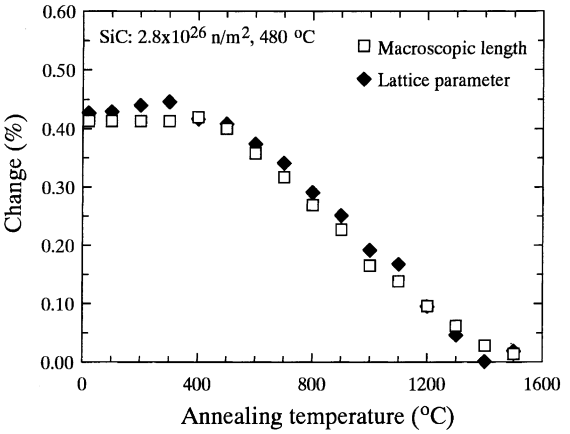

Fig. 4. Changes in macroscopic length and lattice parameter at room temperature of SiC irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C by isochronal annealing up to 1500°C.

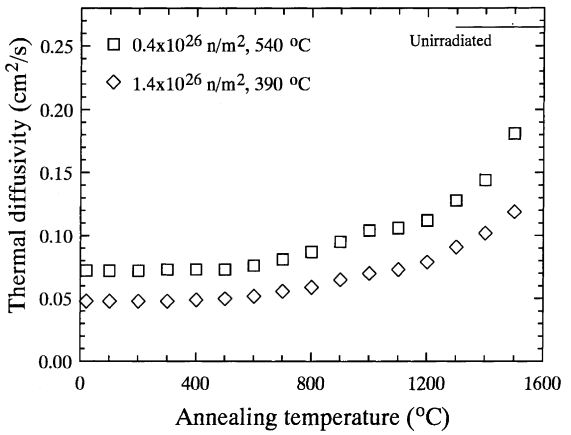

Fig. 3. Room temperature thermal diffusivity of Si_3N_4 irradiated up to a fluence of 0.4×10^{26} n/m^2 at 540°C and 1.4×10^{26} n/m^2 at 390°C. Thermal diffusivity of the unirradiated Si_3N_4 is 0.266 cm^2/s.

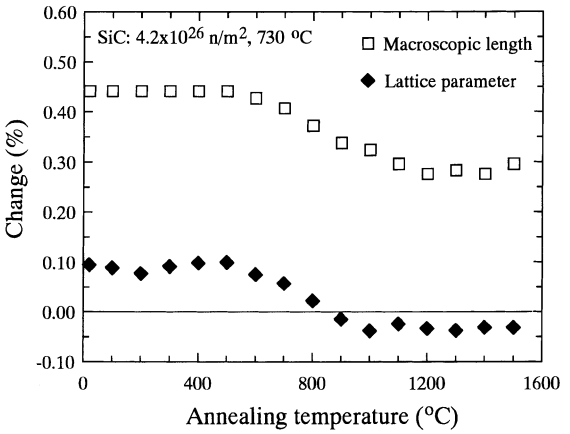

Fig. 5. Changes in macroscopic length lattice parameter at room temperature of SiC irradiated up to a fluence of 4.2×10^{26} n/m^2 at 730°C by isochronal annealing up to 1500°C.

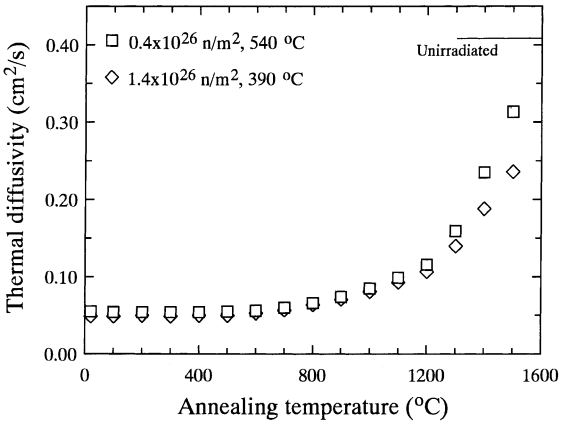

Fig. 6. Room temperature thermal diffusivity of SiC irradiated up to a fluence of 0.4×10^{26} n/m^2 at 540°C and 1.4×10^{26} n/m^2 at 390°C. Thermal diffusivity of the unirradiated SiC is 0.410 cm^2/s.

more, the saturated value was slightly negative (−0.03%); it means contraction of lattice from the pre-irradiated value.

Thermal diffusivity of SiC recovered gradually during annealing above the irradiation temperatures in both specimens irradiated up to a fluence of 0.4×10^{26} n/m^2 at 540°C and 1.4×10^{26} n/m^2 at 390°C, as shown in Fig. 6. Thermal diffusivity of the unirradiated SiC is 0.410 cm^2/s. It is interesting that there is no difference in absolute diffusivity in both specimens after annealing from room temperature to ~1100°C. At higher annealing temperatures, with the increase in diffusivity of the 540°C, lower fluence specimen is more rapid than in the 390°C, higher fluence specimen. After isochronal annealing at 1500°C, thermal diffusivity of the lower or higher fluence specimens was recovered to be 76% or 58% of the original value. This indicates that the recovery of the thermal diffusivity is not completed even after annealing at 1500°C. Compared to the thermal diffusivity recovery of Si_3N_4 (Fig. 3), there is no discontinuity in the diffusivity recovery of SiC.

4. Microstructure observation and discussion

4.1. Si_3N_4

Volume swelling and thermal diffusivity reduction of Si_3N_4 were reported to be 0.3–0.4% and 52–53%, respectively, after neutron irradiation to a fluence of 3×10^{25} n/m^2 at 740°C [18]. Volume swelling of about 1% was also reported after irradiation to a fluence of 2.2×10^{26} n/m^2 at a wide range of irradiation temperatures between 410°C and 825°C [15,20]. Regarding the lattice parameter change of Si_3N_4, only data of very slight increase in both the *a*- and the *c*-axes in Norton NC-132, larger contraction in the *a*-axis and no change in the *c*-axis in Ceradyne Si_3N_4 after neutron irradiation to a fluence of 3×10^{25} n/m^2 at 740°C were reported [21]. The latter Si_3N_4 contained a relatively large amount of MgO. Present result of linear swelling corresponds with ~0.6% volume swelling for both conditions. It is a slightly smaller value compared with the previous study at a comparable fluence (2.2×10^{26} n/m^2). From the present study, no irradiation temperature effect was observed on macroscopic length change. This phenomenon is in agreement with the previous report mentioned above [15,20]. Lattice parameter change observed in the present study indicates slight expansion in the *a*-axis and a slight contraction in the *c*-axis, which was not observed by Hurley and Cocks' [21]. The change is very small in both studies, and because of the difficulty to obtain data due to peak broadening, further research should be necessary to obtain conclusive result on lattice parameter change in heavily irradiated Si_3N_4. The reduction of thermal diffusivity observed in this study was larger than the previous study [18].

HREM photographs of the as-irradiated Si_3N_4 up to a fluence of 2.8×10^{26} n/m^2 at 520°C are presented in Fig. 7(a), which was observed along the [0 0 0 1] direction. It is clear that there are many line contrasts. Most of these lines are straight along $\langle 1\,0\,\bar{1}\,0 \rangle$ directions, but some are bent or slightly curved. The detailed discussion on these defects is given elsewhere [22], but these are interstitial-type dislocation loops. These loops are mostly located on the $\{1\,0\,\bar{1}\,0\}$ planes, i.e., parallel to the *c*-axis. Formation of these defects was first reported by Youngman and Mitchell [16]. The size (diameter) of loops was measured to be 10–20 nm. No void was observed along the grain boundary glassy phase. Fig. 7(b) shows the microstructure of the specimen annealed at 1500°C. The specimen was subjected to an irradiation of 2.8×10^{26} n/m^2 at 480°C, which is comparable with that of the specimen shown in Fig. 7(a). The dislocations observed in Fig. 7(b) are very similar with those of Fig. 7(a), in size and in nature (precise study is now ongoing). Whereas the dislocation distribution in grains is not significantly affected by the thermal annealing up to 1500°C, presence of relatively large voids at grain boundary was observed, as shown in Fig. 7(c).

Based on the microstructural observation mentioned above, the annealing behavior of physical properties of heavily irradiated Si_3N_4 can be deduced as follows. First of all, the anisotropic change in lattice parameter may be attributed partly to the formation of interstitial loops on the crystallographic planes parallel to the *c*-axis. As shown in Figs. 1 and 2, macroscopic length does not show a large recovery up to 1400°C. Only a slight decrease above the irradiation temperature was observed, and furthermore, a slight increase in length above ~1200°C also detected. Former change qualitatively

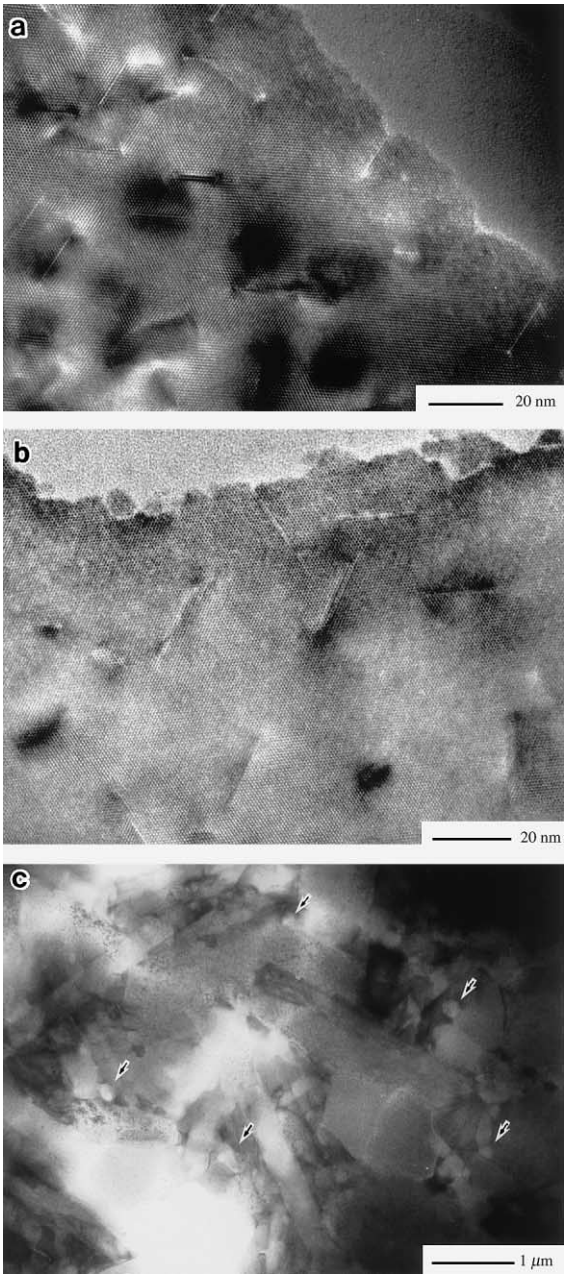

Fig. 7. TEM photographs of the as-irradiated Si_3N_4 irradiated up to a fluence of 2.8×10^{26} n/m^2 at 520°C (a), and irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C and annealed at 1500°C for 1 h (b) and (c).

corresponds with the decrease in the *a*-axis parameter and the increase in the *c*-axis parameter, indicating a decrease in point defects between the irradiation temperature and ~1200°C. The latter increase in length at around 1200°C may be the result of void formation along the grain boundary, as shown in Fig. 7(c). The slight step observed in the recovery of thermal diffusivity at ~1100°C probably corresponds with the formation of grain boundary voids.

Another reason should be attributed to the crystal-chemical nature of β-Si_3N_4. The structure of β-Si_3N_4 is based on the connection of SiN_4 tetrahedra. Each tetrahedron has a silicon atom at the center and a nitrogen atom at each corner (phenacite-type structure). The structure contains six-membered, corner-shared tetrahedral rings, with relatively large open channels at their centers. These rings are not isolated, but are connected along the *c*-axis. Sheets consisting of tetrahedral rings stack along the *c*-axis without any relative displacement, so that channels penetrate the (0 0 0 1) plane along the *c*-axis. From the viewpoint of crystal chemistry, this structure is less dense packing due to covalent bonding nature. Most prominent feature of the β-Si_3N_4 structure is the presence of a large open channel. As in the case of α-Sialon, it can contain extra ions such as Ca, Y, Mg. If β-Si_3N_4 changes into an α-phase, such as α-Si_3N_4 or α-Sialon, the *a*-axis length expands whereas the *c*-axis length shrinks (the *c*-axis length of β-Si_3N_4 corresponding to one half of that of the *c*-axis length in α-phases). It agrees, therefore, with the change in lattice parameter after irradiation of the present study. Then, it is seemed that self-interstitials caused by Frenkel pair formation may be located into interstitial positions in the structure such as large channels, and expand the lattice in the *a*-axis direction whereas shrink the *c*-axis direction, as in the case of α-Si_3N_4. These interstitial clusters seem to be relatively stable, and they do not migrate easily even at higher temperatures. Thus, these defects cannot completely recover during annealing up to 1400°C. The limited recovery of thermal diffusivity in the case of Si_3N_4 supports this estimation.

The other effect that we should mention concerns the grain boundary phases. Most of the grain boundary phase was glassy phase, and we could not observed an apparent irradiation effect. On the other hand, higher temperature annealing may progress sintering/densification in the case of liquid phase sintered Si_3N_4, such as in the present study. This effect was observed in the unirradiated specimen as a linear shrinkage after isochronal annealing above 1400°C. The promotion of solid solution with grain boundary phases means formation of β-Sialon or α-Sialon. This phase change also induces the lattice parameter change, therefore, more complicated phenomena may happen. Further research is necessary.

4.2. SiC

It has generally been accepted that SiC undergoes an isotropic expansion at irradiation temperature below 1000°C. As the neutron fluence increases up to about 3×10^{24} n/m^2, the expansion saturates at a level which depends strongly on the irradiation temperature. The

saturated level of the swelling decreased with increase of irradiation temperature up to around 1000°C [1,9]. The increase of lattice parameter is in good correspondence with the increase in macroscopic dimension. Lattice expansion, and consequently, macroscopic length expansion, originated mainly from points and point-like defects. Above 1200°C, expansion of macroscopic length increases due to formation of voids [23].

After high dose neutron irradiation, Price [24] reported that X-ray line broadening occurred in β-SiC irradiated to 5×10^{25} n/m^2 and found that the degree of broadening increased more after the irradiation of 1×10^{26}n/m^2 [9]. We also confirmed that the lattice parameter growth became smaller than the macroscopic length growth at fluences of 4.8×10^{26} and 1.7×10^{27} n/m^2, and significant broadening of X-ray diffraction peaks was observed [25]. From a precise analysis of the X-ray peak profiles, it was clarified that the broadening could be attributed mainly to the crystallite size effect at a fluence below 1.5×10^{26} n/m^2, but a strain contribution was significant above $2–3 \times 10^{26}$ n/m^2 at the irradiation temperature of ~500°C [12,26]. Severe line broadening and corresponding decrease in lattice parameter change of SiC have a good relation with the formation of fine interstitial dislocation loops on the {1 1 1} planes of β-SiC [12], which was observed using HREM [27,28].

From microstructural observation (HREM), the interstitial loops were found to form on the {1 1 1} planes of SiC irradiated up to a fluence of 2.8×10^{26} n/m^2 at 520°C and to a fluence of 4.2×10^{26} n/m^2 at 730°C. It is the same type of loop that was reported before by the present authors [12,27,28].

Recovery of the macroscopic length and lattice parameter of the specimen irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C indicates good correspondence of these values, as shown in Fig. 4. Previous reports indicate that both the specimens irradiated up to 2.0×10^{26} n/m^2 at 600°C or 3.2×10^{26} n/m^2 at 530°C showed severe XRD peak broadening and decrease in lattice parameter, indicating the formation of the interstitial loops [12]. Also the present HREM observation of the specimen irradiated up to a fluence of 2.8×10^{26} n/m^2 at 520°C showed the presence of the interstitial loops. It is estimated that the critical temperature for loop formation lies between 480°C and 520°C in the case of a fluence of 2.8×10^{26} n/m^2. Fig. 8 is a summary of loop formation/XRD line broadening conditions in SiC as a function of neutron fluence and irradiation temperature based on the present data and previous reports [9,12,24–26,28].

In the case of the specimen of the present study in the loop formation region, 4.2×10^{26} n/m^2 at 730°C, lattice parameter and macroscopic length started to shrink at around the irradiation temperature in an almost parallel manner. Then, the lattice parameter change went through the original value and was negative during recovery process, as shown in Fig. 5. This phenomenon was already observed and is discussed as follows [12]. Between irradiation temperature and ~1200°C, the macroscopic length and lattice parameter reduced concurrently and with the same rate. Up to ~1200°C, small interstitial clusters start to migrate above irradiation temperature and annihilate with vacancies, which cannot migrate significantly below ~1000°C. During this stage, therefore, reduction of interstitials and vacancies occur in equal numbers. If this recombination proceeds continuously, the number of residual vacancies becomes much greater than that of residual interstitials, since a large fraction of interstitial atoms are condensed into interstitial loops. The excess vacancy-type point-defects lead to contraction of the lattice.

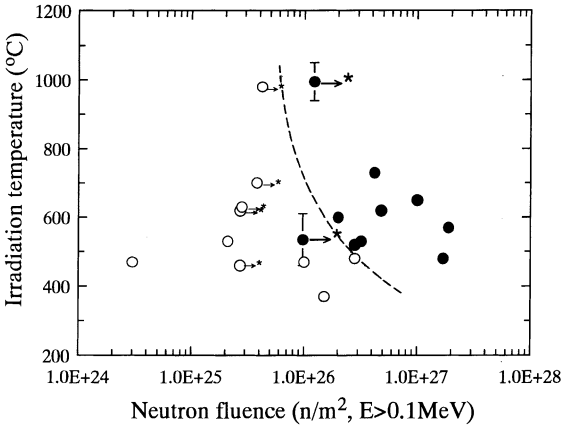

Fig. 8. A summary of loop formation/XRD line broadening conditions in SiC as a function of neutron fluence and irradiation temperature based on the present data and previous reports [9,12,24–26,28]. *Arrows indicate higher fluences (original data reported using $E > 0.18$ MeV [9,24]). Open circles indicate no severe XRD line broadening or no obvious loop formation. Closed circles indicate severe XRD line broadening or loop formation.

5. Conclusions

Changes in macroscopic length, lattice parameter and thermal diffusivity of heavily and concurrently neutron-irradiated Si_3N_4 and SiC ceramics up to a fluence of 4.2×10^{26} n/m^2 was measured. Furthermore, changes in these properties due to post-irradiation thermal annealing up to 1500°C were measured. The results are summarized as follows.

(1) Macroscopic length increase of Si_3N_4 was almost one half of that of SiC.

(2) Lattice parameter change of SiC irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C coincided with the macroscopic length change, but the change in lattice

parameter was significantly smaller compared with the length change for the specimen irradiated up to 4.2×10^{26} n/m^2 at 730°C. The critical irradiation conditions for loop formation/XRD line broadening were presented based on the present and previous results.

(4) Slight increase in the *a*-axis and slight decrease in the *c*-axis lattice parameter were detected for the Si_3N_4 specimens irradiated up to a fluence of 2.8×10^{26} n/m^2 at 480°C and 4.2×10^{26} n/m^2 at 730°C. The amount of change was very small compared with the macroscopic length change.

(5) Thermal diffusivity of Si_3N_4 and SiC was reduced severely by the irradiation up to a fluence of 4×10^{25} n/m^2 at 540°C.

(6) Changes in macroscopic length, lattice parameter and thermal diffusivity of irradiated Si_3N_4 by post-irradiation annealing were measured for the first time. Large part of thermal diffusivity was recovered by annealing, with small step at ~1100°C, but macroscopic length did not significantly change by annealing. Change in lattice parameter showed a complicated trend. It is supposed that formation of interstitial loops on the planes parallel to the *c*-axis, formation of voids during annealing or difficulty of recovery of points defects/loops, or solid solution formation due to glassy grain boundary phase may influence the recovery behavior of Si_3N_4 ceramics.

(7) Changes in macroscopic length, lattice parameter or thermal diffusivity of SiC by annealing coincided with the results of previous studies.

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References

[1] G.R. Hopkins, R.J. Price, Nucl. Eng. Design/Fus. 2 (1985) 111.
[2] R.H. Jones, C.H. Henager Jr., G.W. Hollenberg, J. Nucl. Mater. 191–194 (1992) 75.
[3] L.L. Snead, S.J. Zinkle, D. Steiner, J. Nucl. Mater. 191–194 (1992) 560.
[4] P. Fenici, H.W. Scholz, J. Nucl. Mater. 212–215 (1994) 60.
[5] H.W. Scholz, M. Zucchetti, K. Casteleyn, C. Adelhelm, J. Nucl. Mater. 212–215 (1994) 655.
[6] L.L. Snead, R.H. Jones, A. Kohyama, P. Fenici, J. Nucl. Mater. 233–237 (1996) 26.
[7] S.D. Harrison, J.C. Corelli, J. Nucl. Mater. 122–123 (1984) 833.
[8] J.C. Corelli, J. Hoole, J. Lazzaro, C.W. Lee, J. Am. Ceram. Soc. 66 (1983) 529.
[9] R.J. Price, Nucl. Tech. 35 (1977) 320.
[10] C.H. Wu, J.P. Bonal, B. Kryger, J. Nucl. Mater. 208 (1994) 1.
[11] T. Suzuki, T. Yano, T. Mori, H. Miyazaki, T. Iseki, Fus. Tech. 27 (1995) 314.
[12] T. Yano, H. Miyazaki, A. Akiyoshi, T. Iseki, J. Nucl. Mater. 253 (1998) 78.
[13] S. Ueda, S. Nishino, Y. Seki, R. Kurihara, J. Adachi, S. Yamazaki, J. Nucl. Mater. 258–263 (1998) 1589.
[14] F. Najmabadi, R.W. Conn, in: Proceedings of the 14th International Conference on Plasma Physics and Controlled Nuclear Fusion Research, Wurzberg, Germany, IAEA, Vienna, 1993.
[15] F.W. Clinard Jr., G.F. Hurley, R.W. Klaffky, Res. Mech. 8 (1983) 207.
[16] R.A. Youngman, T.E. Mitchell, Rad. Eff. 74 (1983) 267.
[17] F.W. Clinard Jr., L.W. Hobbs, in: R.A. Johnson, A.N. Orlov (Eds.), Physics of Radiation Effects in Crystals, Elsevier, Amsterdam, p. 425 (Chapter 7).
[18] G.F. Hurley, J.M. Bunch, Am. Ceram. Soc. Bull. 59 (1980) 456.
[19] L.W. Hobbs, J. Am. Ceram. Soc. 62 (1979) 267.
[20] F.W. Clinard Jr., G.F. Hurley, L.W. Hobbs, D.L. Rohr, R.A. Youngman, J. Nucl. Mater. 122–123 (1984) 1386.
[21] G.F. Hurley, F.H. Cocks, Ceram. Bull. 60 (1981) 1302.
[22] M. Akiyoshi, T. Yano, M.L. Jenkins, Phil. Mag. A, to be published.
[23] R.J. Price, J. Nucl. Mater. 48 (1973) 47.
[24] R.J. Price, J. Nucl. Mater. 33 (1969) 17.
[25] H. Miyazaki, T. Suzuki, T. Yano, T. Iseki, J. Nucl. Sci. Tech. 29 (1992) 656.
[26] T. Iseki, T. Yano, H. Miyazaki, J. Nucl. Mater. 191–194 (1992) 588.
[27] T. Yano, T. Iseki, Philos. Mag. A62 (1990) 421.
[28] T. Yano, T. Suzuki, T. Maruyama, T. Iseki, J. Nucl. Mater. 155–157 (1988) 311.
[29] T. Yano, Post-Irradiation Experiments on Physical, Thermal and Microstructural Properties of Neutron-Irradiated Ceramics, PNC TJ9607 98-002, 1998.