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Microstructure of heavily neutron-irradiated SiC after annealing up to 1500 °C

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ABSTRACT

β-SiC specimens were irradiated by fast neutrons up to 28 – 42 dpa at 480, 585, 730 and 735 °C. Post-irradiation annealing was carried out up to 1500 °C. Changes in macroscopic length and lattice parameter were measured. The swelling of macroscopic length was not recovered completely in the specimens irradiated above 585 °C (~40 dpa) after annealing at 1500 °C. After annealing, lattice parameters of the specimens irradiated above 585 °C (~40 dpa) were slightly shrunk compared to the unirradiated value. Microscopic defects were observed by transmission electron microscopy. Void formation was confirmed along grain boundaries in the shrunk specimens after annealing up to 1500 °.

1. Introduction

Blanket materials of a fusion reactor are irradiated by high energy neutrons. They are required for heat removal, radiation shielding and generating nuclear fusion fuel. Therefore, blanket structural materials are used under the most sever environment in a fusion reactor. Physical properties of importance for the blanket structural materials include resistance to high neutron fluence, high-temperature strength, resistance to high heat flux, low activation and good chemical stability.

Besides its low activation and quick decay of activity, silicon carbide (SiC) has excellent behavior such as an low atomic number material, good thermal conductivity, excellent high-temperature properties and corrosion resistance [1–5]. Recently, a high-crystalline and stoichiometric SiC fiber and an advanced fabrication method have led to great improvement in SiC/SiC composites [6–8], based on the same hot-press technique previously reported by the present authors [9–12]. Consequently, SiC based materials are positioned as an advanced candidate material of fusion reactors. Whereas relatively many researches have been reported on neutron irradiation effects of SiC [13–15,17–19], it is still important to clarify the neutron induced defects, particularly, formed after high dose at high-temperature irradiation.

We reported physical property change of heavily neutron-irradiated β-SiC by thermal annealing [20]. Post-irradiated isochronal annealing up to 1500 °C was conducted for the specimens which were irradiated in two different irradiation conditions, and recovery behavior of macroscopic length were measured. Large part of macroscopic length of the specimen irradiated at lower temperature (480 °C) was recovered by annealing up to 1500 °C. On the other hand, macroscopic length of the specimen irradiated at higher temperature (730 °C) shrank up to 1200 °C and it was showed almost constant length up to 1500 °C.

In this work, change in macroscopic length and lattice parameter of another two β-SiC sintered specimens irradiated with the different conditions were measured after irradiation and after post-irradiation isochronal annealing up to 1500 °C. They were irradiated up to fluencies of 3.9×10^{26} n/m^2 (E > 0.1 MeV) at 585 °C and 3.7×10^{26} n/m^2 at 735 °C. Furthermore, microscopic defect structures in these specimens (including previously reported [20] specimens) were observed by electron microscopy. The difference of recovery process among them was discussed based on the present and previous results.

2. Experimental procedures

High-purity β-SiC sintered specimens were irradiated with fast neutrons in the JOYO fast experimental reactor in Japan. The SiC specimens (Type C101, Nippon Steel, Japan) contained >99 wt% SiC and <1 wt% Al_2O_3 as an additive. They were hot-pressed and were cut into $1.2 \times 1.2 \times 15$ mm^3 bars for length measurement. Bulk density was 3.20 g/cm^3. All specimens were irradiated in helium-filled capsules up to fluences 2.8 – 4.2×10^{26} n/m^2 (E > 0.1 MeV) at 480, 585, 730 and 735 °C. The specimens in the capsules received roughly from 28 to 42 dpa – SiC [21,22]. The temperature of specimens during irradiation was estimated based on TED temperature monitors, flux distribution and position of specimen in the irradiated rig. Macroscopic length was measured by a micrometer at room temperature before irradiation, after irradiation, and after each isochronal annealing. The length before irradiation was set as a standard. Changes in macroscopic length due

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to isochronal annealing were obtained successively with increased annealing temperature on the same irradiated specimens. The isochronal annealing was carried out in a vacuum (up to 1000 °C: $\sim10^{-1}$ Pa and 1050 – 1500 °C: $\sim6\times10^{-4}$ Pa). After the temperature of the specimens had been raised from room temperature to 200 °C, the temperature was raised at a rate of 30 °C/min until the designated temperature was reached. The designated temperature was then maintained for 1 h.

To determine the lattice parameter of SiC, X-ray diffraction with a CuKα source (40 kV, 40 mA) was used on a Philips PW-1700 diffractometer equipped with a graphite monochromator at room temperature (26 ± 1 °C). For the X-ray measurement, an Si internal standard (a_0 = 0.53408 nm at 26 °C) was stuck on the SiC specimen surface with glue. The lattice parameter of 3 C – SiC in the reference [16] set as a standard. The SiC specimen was placed in the center of an aluminum holder and the step scan was taken over the range of 2θ angles from 85 ° to 140 ° in steps of 0.02 ° (2θ). The diffraction profiles of peak with indices (331), (420), (422) and (333)/(511) of β-SiC were precisely measured using the internal standard.

Microstructure was observed by a transmission electron microscope (TEM). The bar specimens were cut and thin foils for TEM observation were prepared by dimpling and ion-milling technique. The TEM used in the present study was a Hitachi H-9000 microscope, which was operated with an accelerating voltage of 300 kV and point resolution of 0.1 nm.

3. Results and discussion

Changes in macroscopic length and lattice parameter of SiC due to the present neutron irradiation are listed in Table 1. The changes in macroscopic length and lattice parameter of SiC irradiated up to a fluence of 3.9×10^{26} n/m^2 at 585 °C and 3.7×10^{26} n/m^2 at 735 °C were similar to those of the specimen irradiated up to 4.2×10^{26} n/m^2 at 730 °C. The changes in macroscopic length were larger than these in lattice parameter.

The changes in macroscopic length of the specimens irradiated at 585, 760 and 735 °C by isochronal annealing up to 1400 °C are shown in Fig. 1, with the previous data irradiated at 480 °C and 730 °C [20]. The macroscopic length of the specimen irradiated at 585 °C decreased gradually for annealing temperatures from $\sim$600 °C until around 1300 °C, and it showed almost constant or slightly increase tendency after further heating up to 1400 °C. The recovery started near the irradiation temperature (585 °C). Macroscopic swelling of 0.13% was remained after the isochronal annealing at 1400 °C. The macroscopic length of the specimen irradiated at 735 °C decreased gradually for annealing temperatures from 500 – 600 °C until around 1300 °C. Macroscopic swelling of 0.18% was remained up to 1400 °C. After annealing at 1400 °C, the larger macroscopic swelling was remained in the specimen irradiated at higher temperature except for the specimen irradiated at 735 °C. Although the irradiation condition of 37 dpa at 735 °C was similar condition of 42 dpa at 730 °C, the length change of the specimen irradiated at 735 °C was similar to that of the specimen irradiated not at 730 °C but at 585 °C. There is a possibility that the real irradiation temperature of the 37 dpa specimen was lower than the nominal irradiation temperature of 735 °C.

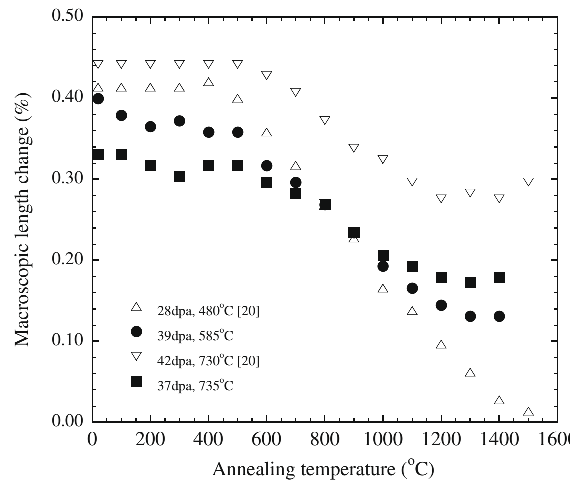

Fig. 1. Change in macroscopic length of irradiated SiC specimens by isochronal annealing for 1 h up to 1500 °C, measured at room temperature.

The changes in lattice parameter of the specimens irradiated at 585 °C and 735 °C by isochronal annealing up to 1500 °C are shown in Fig. 2, with the previous data irradiated at 480 °C and 730 °C [20]. The lattice parameter of the specimen irradiated at 585 °C started to decrease at 500 – 600 °C. Above 1250 °C the lattice parameter showed almost constant value which was slightly negative in change compared with the unirradiated standard. It shows that excess vacancy-type point defects existed after isochronal annealing [18]. The lattice parameter of the specimen irradiated at 735 °C started to decrease at 500 – 600 °C. Above 1250 °C the lattice parameter showed almost constant value which was slightly negative in change, as same as the specimen irradiated at 585 °C. Therefore, it is supposed that interstitial-type point defects were almost annihilated by annealing up to 1250 °C. Defects are annealed during the irradiation when the irradiation temperature is avobe their recovery stages. Fig. 2 shows that the swelling of the lattice parameter was smaller in the specimen irradiated higher temperature before the annealing. It also supports that the 735 °C specimen was irradiated at between 585 and 730 °C.

Based on the microstructure observation, the formation of voids was not revealed in the specimens irradiated at 585 °C and 735 °C before annealing. The specimens irradiated at 480 °C and 730 °C also reported that they included no voids before annealing [20]. The irradiation temperature of these specimens should be lower than a temperature where vacancies are mobile and form small voids during irradiation. It is reported that significant diffusion of vacancies in SiC was started at 800 – 900 °C under silicon ion irradiation [23,24]. Void formation during neutron irradiation was reported for the specimen irradiated at 1250 °C or 1130 °C

Table 1
Irradiation condition and changes in macroscopic length and lattice parameter of SiC.

Fluence (E > 0.1 MeV) (n/m^2)	Estimated dpa* (dpa)	Irradiation temperature (°C)	Macroscopic length change (%)	Lattice parameter change (%)	Remark
2.8×10^{26}	28	480	0.42	0.43	[20]
3.9×10^{26}	39	585	0.40	0.18	This work
4.2×10^{26}	42	730	0.44	0.09	[20]
3.7×10^{26}	37	735	0.33	0.12	This work

* dpa based on ref [21,22].

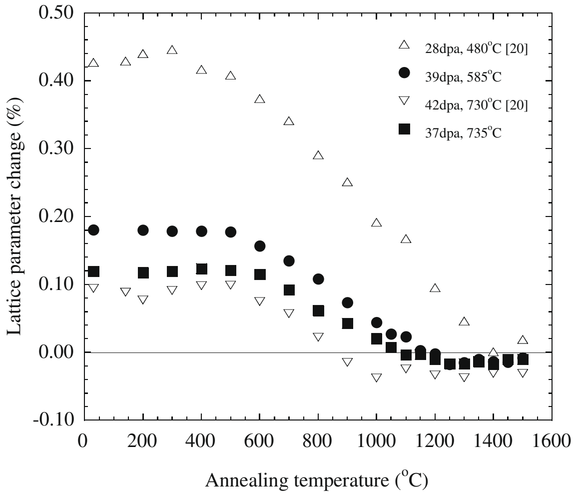

Fig. 2. Changes in lattice parameter of irradiated SiC specimens by isochronal annealing for 1 h up to 1500 °C, measured at room temperature.

[13,25]. On the other hand, Senor et al. [26] reported that voids were not observed after neutron irradiation at 1100 °C.

Microstructure of irradiated SiC specimens annealed at 1500 °C is shown in Fig. 3. High density'black dots' were remained in grains of all specimens. Voids were partially appeared along grain boundaries in the specimens irradiated at 585 °C and 730 °C after annealing at 1500 °C. Void size was 30 – 50 nm. Voids at triple junctions and extended voids along grain boundaries were observed in the specimen irradiated at 735 °C after annealing at 1500 °C. Extended voids terminated at triple junctions. It suggests that vacancies accumulated in grain boundaries and coalesced into voids, large voids at triple junctions and finally developed extended voids along grain boundaries at the annealing temperature above the vacancy migration temperature. However, voids were not observed inside grains of all specimens. Vacancies were not mobile during the neutron irradiation and vacancy clusters were considered to not grow sufficiently to form voids inside grains by annealing. Voids, large voids at triple junctions or extended voids along grain boundaries were not detected in the specimen irradiated at 480 °C after annealing at 1500 °C. Most vacancies in this specimen were considered to be recombined with interstitial atoms by annealing.

Recent theoretical studies have provided the annealing mechanisms on recovery stages in irradiated SiC. The first stages are related to the recombination of Frenkel pairs and to the migration of interstitials with activation energies 0.2 – 1.6 eV [27–31]. The second stages are associated with the complex defects and the vacancy diffusion. Bockstedte et al. have calculated that silicon vacanceis transform into vacancy-antisite complex $V_{Si} \rightarrow V_C - C_{Si}$ from 1.9 eV to 2.7 eV and the barrier of the transformation $V_C - C_{Si} \rightarrow V_{Si}$ lies between 2.4 and 6.1 eV [29,30]. The diffusion of silicon and carbon vacancies require energies of 3.2 – 3.6 eV and 3.5 – 5.2 eV, respectively, which depends on the charge state [29,30]. Figs. 1 and 2 show two recovery stages in the specimens irradiated at 585, 730, 735 °C. The fiest stage appeared when the annealing temperature was above the irradiation temperature (500 – 600 °C) and the second recovery stage was reached above 1000 – 1200 °C, leading to the formation of voids through the migration of vacancy like defects. The theoretical studies describes that the first stage was the recombination of interstitials with almost immobile vacancies. At the second stage, due to its high migration

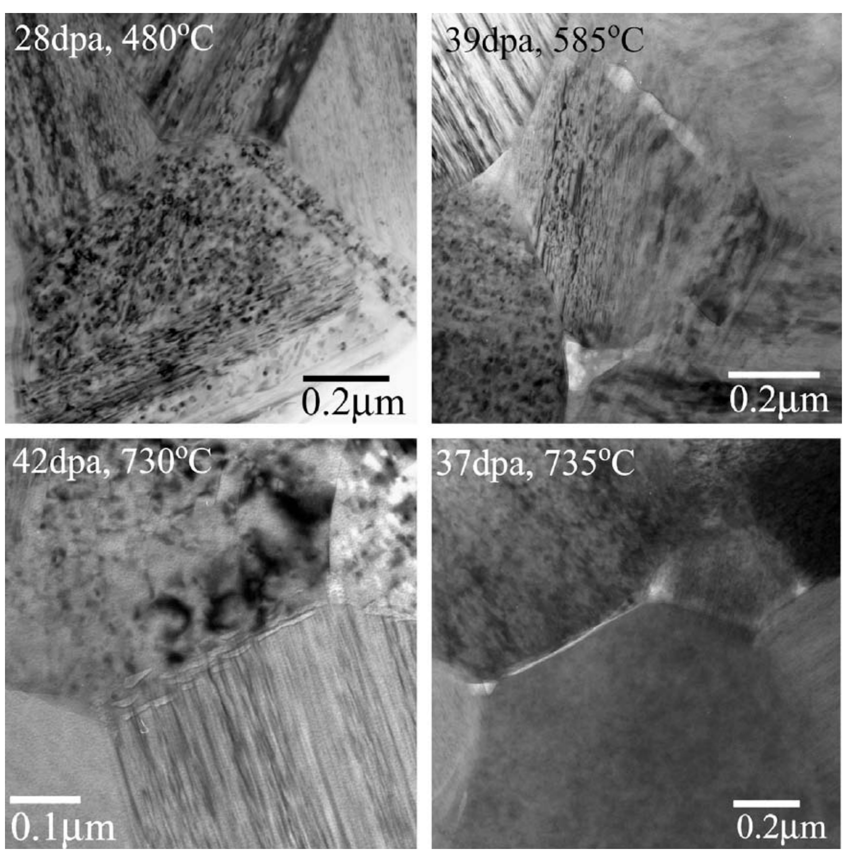

Fig. 3. Microstructure of irradiated SiC specimens annealed at 1500 °C for 1 h.

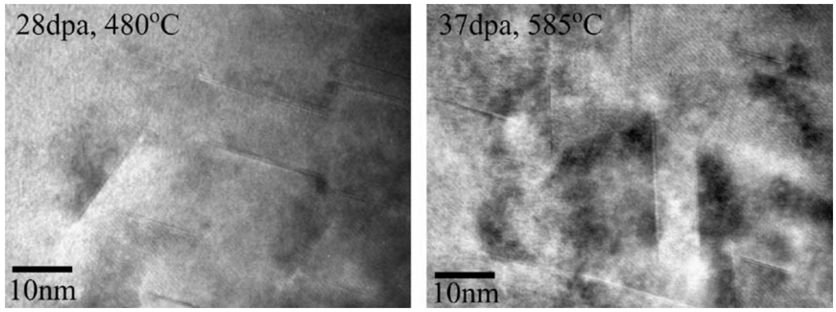

Fig. 4. Microstructure of as-irradiated SiC specimens.

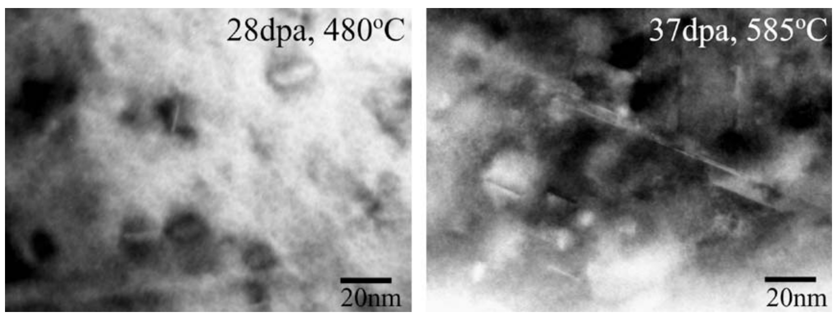

Fig. 5. Microstructure of irradiated SiC specimens subjected to a post-irradiated annealing at 1500 °C for 1 h.

energy the diffution of silicon vacancy should be possible but probably through indirect diffution mechanisms involving the formation of complex with antisite.

Microstructures of the as-irradiated specimens irradiated at 480 °C and 585 °C were observed (Fig. 4). Dislocation loops were found on the {1 1 1} planes of both specimens after the neutron irradiation, as previously reported [32]. Length of the dislocation loops were around 10 – 20 nm. Fig. 5 is the microstructures of these specimens annealed at 1500 °C. The dislocation loops in the specimen irradiated at 480 °C did not grow after annealing. In the annealed specimen irradiated at 585 °C, some grown dislocation loops were found with unchanged dislocation loops, as reported previously for heavily neutron-irradiated SiC [18].

Interstitial dislocation loops were remained in grains of all specimens after annealing at 1500 °C, and the lattice parameters of all specimens were almost recovered. The dislocation loops did not affect to change in lattice parameter from these results. The lattice parameter of the specimens would expand due to interstitial atoms induced by neutron – irradiation, and Fig. 2 explains the following. There were less interstitial atoms in the specimen irradiated at higher temperature before annealing and they were almost annihilated by vacancy-interstitial recombination up to 1250 °C. The atomic arrangement of inside dislocation loops in SiC was similar as a perfect crystalline arrangement and inserted layers are the same tetrahedral arrangement with normal lattice [32]. Therefore, if size of dislocation loop is large, presence of interstitial dislocations basically dose not influence on the lattice parameter, except for around their edges (dislocation core). On the other hand, dislocation loops generate new layers in grains and they should increase a volume of grains, so that the gap between macroscopic length change and lattice parameter change of each as-irradiated specimen is considered to give a rough estimate of macroscopic swelling caused by dislocation loops (Figs. 1 and 2). Number of single vacancies increase with area of interstitial dislocation loops as a counterpart of Frenkel defect. Our results explain that development of dislocation loops remained single vacancies distributed in lattice which were not mobile during irradiation. These single vacancies are partly annihilated with single interstitial atoms during annealing corresponding to the amount of single interstitials. Excess un-annihilated vacancies should migrate to grain boundaries and formed into voids during annealing. Consequently, macroscopic swelling of the specimens irradiated at 585, 730, 735 °C was remained after annealing, whereas lattice parameter mostly recovered. Slight compaction in lattice parameter after annealing may indicates presence of un-annihilated vacancies.

Saturation and slightly increasing tendency of shrinkage in macroscopic length of higher irradiation temperature specimens by annealing above 1200 ° (Fig. 1) can be attributed as a result of void swelling.

4. Conclusion

β-SiC specimens were heavily neutron-irradiated under four conditions. Changes in macroscopic length of three specimens, which were irradiated at 585, 730 and 735 °C, were not recovered completely by isochronal annealing up to 1500 °C. The amounts of residual macroscopic swellings after annealing were arranged according to high to low irradiation temperature. Rounded and extended voids were revealed along grain boundaries and triple junctions in them after annealing at 1500 °C. Growth of some interstitial dislocation loops was also confirmed. On the other hand, voids were not observed in the specimen irradiated at the lowest temperature of 480 °C. Length of the dislocation loops in the annealed specimen irradiated at 480 °C was almost the same as those before annealing. It suggests that in the specimens irradiated at 585, 730 and 735 °C, dislocation loops were developed by absorption of independent interstitial atoms and the number of single interstitial atoms was far less than that of vacancies and more vacancies were remained as point defects or very small clusters during irradiation. Interstitial atoms as point defects can migrate to annihilate with vacancies over the irradiation temperature during annealing, but excess single vacancies accumulated in the grain boundaries to form voids.

Changes in lattice parameter of all specimens were almost recovered after annealing, and many dislocation loops, as black dots, were confirmed inside grains of them before and after annealing. Thus, lattice parameter was changed by not dislocation loops but interstitial atoms and vacancies. In the specimen irradiated at 480 °C, interstitial atoms and vacancies were almost recombined by annealing. On the other hand, vacancies were slightly remained in the other annealed specimens because the lattice parameters of them were slightly shrunk for the annealed specimens above 1250 °C compared to the unirradiated specimens.

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