Effects of Thermal Annealing on the Macroscopic Dimension and Lattice Parameter of Heavily Neutron-Irradiated Silicon Carbide

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Reaction-sintered \( \beta \)-SiC specimens were neutron-irradiated in fast breeder reactors to fluences from \( 3.0 \times 10^{24} \) to \( 1.7 \times 10^{26} \) n/m\(^2\) (\( E > 0.1 \) MeV) at temperatures from 370 to 620°C. Irradiation to fluences above \( 4.8 \times 10^{26} \) n/m\(^2\) caused swelling (growth) that was significantly greater in respect of macroscopic dimension than of lattice parameter. These highly irradiated specimens also showed significant broadening of their X-ray line profiles, accompanied by generation of interstitial dislocation loops. Upon annealing, all specimens, irrespectively of the fluence to which they had been irradiated, tended toward recovery of their swelled macroscopic dimension and lattice parameter. This tendency was initiated when the annealing temperature exceeded that of irradiation, with the percentage of residual swelling lowering roughly in proportion to annealing temperature. The more highly irradiated specimens, in which the macroscopic dimension had swelled significantly more than the lattice parameter, lowered their percentages of residual swelling while maintaining a constant difference between them, as the annealing temperature was raised from that of irradiation to 1,200°C. In a certain range of higher annealing temperatures, the lattice parameter fell below the pre-irradiation level. In the range below 1,200°C, the broadened X-ray line profile indicated no tendency to recover. Microstructural observations have indicated that the size and the number density of dislocation loops remain unchanged up to 1,000°C. The recovery of swelled macroscopic dimension and lattice parameter by annealing is discussed in terms of the recombination of point defects, which occurs even in the specimens irradiated to \( 1.7 \times 10^{27} \) n/m\(^2\) fluence.

KEYWORDS: silicon carbide, neutron irradiation, radiation doses, point defects, dislocation loop, lattice parameter, macroscopic dimension, X-ray diffraction, X-ray line broadening, thermal annealing, irradiation temperature

I. INTRODUCTION

Silicon carbide (SiC) is counted among promising materials for use in the components of fusion reactors first-wall, on account of the many attractive properties presented by this compound, including high strength at elevated temperatures, good thermal conductivity, low induced radioactivity and low plasma impurity contamination by low-Z elements\(^{(1)}\).

The effect of neutron irradiation on SiC has been the subject of a number of reports\(^{(2)}\)~\(^{(6)}\), which have shown that SiC undergoes isotropic expansion at irradiation temperatures below 1,000°C. The amount of expansion increases in keeping with the fast neutron fluence up to about \( 3 \times 10^{24} \) n/m\(^2\), where it approaches a saturation value that lowers with increasing irradiation temperature. The swell-
ing—or growth—of the macroscopic dimension is accompanied by a similar swelling of the lattice parameter\(^{(6)}\). The swelled macroscopic dimension and lattice parameter recover toward their original values possessed prior to irradiation, when the irradiated SiC is annealed. Upon isochronal annealing for 1 h, recovery shrinkage starts around the irradiation temperature and progresses roughly linearly with increasing temperature until it is completed at around 1,400°C. This approximate correspondence of temperature between that of annealing shrinkage onset and that of irradiation, which characterizes the behavior of SiC, is utilized for passive temperature monitoring in irradiation experiments\(^{(4)(5)}\).

The basic mechanism of the irradiation-induced swelling of SiC is the generation of an equal number of interstitials \(I\) and vacancies \(V\). Most of these defects are annihilated through \(V-I\) recombination and a part of those that remain aggregate into point defect clusters and dislocation loops during the irradiation. What would still remain after irradiation to fluences not exceeding \(5 \times 10^{25} \text{n/m}^2\) are considered to consist mainly of Frenkel defects and/or small clusters of interstitials\(^{(10)}\).

Upon irradiation to higher fluences (say above \(10^{26} \text{n/m}^2\)), swelling of the macroscopic dimension becomes greater than that of the lattice parameter, accompanied by marked broadening of the X-ray line profile\(^{(10)}\). In a previous work, the present authors have suggested that the swelled macroscopic dimension should show a similar behavior of recovery, whether following high or low fluence irradiation\(^{(5)(11)}\). No data are available on changes in the lattice parameter of highly irradiated SiC during annealing, due to the difficulty of determining X-ray profiles affected by appreciable broadening.

The present paper covers measurements made on the swelling of both macroscopic dimension and lattice parameter occurring in SiC upon high neutron irradiation up to \(1.7 \times 10^{27} \text{n/m}^2\), and on the subsequent recovery of the swelled values upon post-irradiation annealing. The changes observed in X-ray line broadening are also quantitatively observed. Based on these results and on earlier work covering microstructural changes\(^{(12)(13)}\), a discussion is presented concerning the cause of irradiation-induced swelling and its recovery upon annealing.

### II. EXPERIMENTAL PROCEDURE

The specimens used were reaction-sintered \(\beta\)-SiC rods, 10~15 mm in length and 2~3 mm in diameter, of around 80% theoretical density. No evidence of excess silicon or carbon was revealed by X-ray diffractometry.

The specimens were neutron-irradiated in the fast breeder reactors “JOYO”, “Phenix” and “Rapsodie” to neutron fluences from \(3.0 \times 10^{24}\) to \(1.7 \times 10^{27} \text{n/m}^2\) \((E>0.1 \text{ MeV})\), at temperatures from 370 to 620°C. After irradiation, each specimen was cut into two pieces—one each for macroscopic dimension measurement and for X-ray measurement.

The macroscopic dimension of the rods was measured using a regular point-type micrometer. The accuracy of measurement was about 1 μm. X-ray diffraction measurements were made with a Philips PW-1700 diffractometer using copper Kα radiation, to obtain the traces of \((400), (331), (420), (422)\) and \((333)/(511)\) reflections. The profiles were corrected for the \(a_1-a_2\) doublet. Silicon was used as internal standard for correcting the diffraction angle.

At fluences above \(4.8 \times 10^{24} \text{n/m}^2\), all the reflections were affected by considerable broadening, which made it difficult to determine the lattice parameters precisely. For this reason, the profiles were corrected to account for Lorentz-polarization effects and for the \(\alpha_1-\alpha_5\) doublet. On a profile thus corrected, the positions of its peak was estimated by fitting the Gaussian function to the top part of the profile and measuring its centroid.

The specimens were vacuum-annealed for 1 h at temperatures between 100 and 1,800°C. The annealing furnace was loaded with both halves of specimens from the same batch—the rods for macroscopic dimension measurements and the other halves for X-ray measurement, which were ground into powder and mounted on SiO\(_2\) glass holder. Annealing of
each batch was followed by measurements performed at 25±2°C on macroscopic dimension and lattice parameter. Annealing at higher temperatures—above 1,400°C—was performed solely on the rod specimens. For X-ray measurement on these specimens, the rod remaining from length measurement had a small piece cut out and pulverized for the purpose.

### III. RESULTS AND DISCUSSION

#### 1. Radiation-induced Changes in Macroscopic Dimension and Lattice Parameter

The SiC specimens irradiated to $3.0 \times 10^{24}$ n/m² and to $1.7 \times 10^{27}$ n/m² presented X-ray line profiles of the (333)/(511) reflection as shown in Fig. 1, where the corresponding profile of unirradiated SiC is also indicated for comparison. Compared with the unirradiated specimen, the specimen irradiated to $3.0 \times 10^{24}$ n/m² is seen to have shifted its reflection to a smaller angle, accompanied by a lowering of peak intensity. On the other hand, the specimen irradiated to $1.7 \times 10^{27}$ n/m² has seen its reflection recover roughly to the position it occupied before irradiation, while its line profile has broadened to a very large full-width at half-maximum (FWHM) and to a considerably lowered peak intensity.

#### Table 1 Changes observed in macroscopic dimension, lattice parameter and X-ray line broadening of irradiated SiC

<table>
<thead>
<tr>
<th>Neutron fluence (n/m²)</th>
<th>Irradiation temperature (°C)</th>
<th>Macroscopic growth (%)</th>
<th>Lattice growth (%)</th>
<th>FWHM (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3.0 \times 10^{24}$</td>
<td>470</td>
<td>0.45</td>
<td>0.46</td>
<td>0.35</td>
</tr>
<tr>
<td>$1.5 \times 10^{26}$</td>
<td>370</td>
<td>0.44</td>
<td>0.50</td>
<td>0.52</td>
</tr>
<tr>
<td>$4.8 \times 10^{26}$</td>
<td>620</td>
<td>0.23</td>
<td>0.11</td>
<td>1.75</td>
</tr>
<tr>
<td>$1.7 \times 10^{27}$</td>
<td>480</td>
<td>0.28</td>
<td>0.01</td>
<td>1.76</td>
</tr>
</tbody>
</table>

It is known that macroscopic dimension and lattice parameter are changed to equal extent by single point defects and small point defect clusters \(^{14}\). This would suggest the presence of such isolated defects in the specimens irradiated to lower fluences not exceeding $1.5 \times 10^{24}$ n/m², where fairly good correspondence was noted above between the changes in macroscopic dimension and in lattice parameter. A similar behavior was

* Irradiation-induced changes in macroscopic dimension: Derived on the assumption that the recovery was completed upon 1 h annealing at 1,400°C. It has been reported that, with specimens irradiated to fluences below $10^{24}$ n/m², full recovery of irradiation-induced defects is obtained upon annealing at 1,300~1,400°C \(^{15,10}\). When irradiated to higher fluences, the specimens may retain some stable defects after annealing at 1,400°C. In such cases, the swelling of macroscopic dimension may actually be larger than estimated.
observed also in a previous study, at fluences below \(5 \times 10^{23} \text{ n/m}^2\) \((7)\). Transmission electron microscopic observation on the present specimens irradiated below \(1.0 \times 10^{24} \text{ n/m}^2\) \((13)\) revealed no definite presence of dislocation loops, whereas small 'black dot' defects not exceeding \(2\~3\) nm have been observed by Price in specimens irradiated to around \(1 \times 10^{25} \text{ n/m}^2\) \((15)\). This discrepancy in the observed state of specimen between the two studies can be attributed to difference in the irradiation temperature, which was higher in the case of Price's specimens.

Specimens irradiated to fluences above \(4.8 \times 10^{26} \text{ n/m}^2\), noted earlier in this chapter to be characterized by X-ray line broadening and by marked difference in growth between the macroscopic dimension and lattice parameter, have previously been found to contain relatively large interstitial dislocation loops of sizes up to \(10\~30\) nm\((12)\~(13)\).

Lattice growth \(g_1\) is made up of the terms \(\sum c_n d_n\), where \(c_n\) and \(d_n\) are respectively the concentration of the \(n\)-th type of defects and the fractional change in atomic volume associated with them. Some defects (e.g. interstitials) give rise to lattice expansion, whereas others (e.g. vacancies) cause lattice contraction. In what follows, it is assumed for the sake of example that the relevant defects consist of single interstitials and single vacancies, and that, after neutron irradiation, \(c_i = c_v\) (subscripts \(i\) and \(v\) indicate the contributions of interstitials and vacancies, respectively). Further, the data from specimens irradiated to the lowest fluence—believed to contain solely single vacancies and single interstitials—show \(g_i > 0\), so that \(d_i > d_v\). As already mentioned, \(g_i = g_m\) (\(g_m\): growth in macroscopic dimension) from theoretical consideration\((14)\). This is the case where the irradiation fluence is below \(1.5 \times 10^{26} \text{ n/m}^2\). With increasing fluence, interstitials condense into interstitial loops, to lower \(c_i\) in comparison with \(c_v\). Hence, in contrast to the case of \(c_i = c_v\), the lattice parameter diminishes, to result in \(g_i < g_m\).

The X-ray line broadening is probably related to the presence of dense interstitial loops, but further study is required for deriving a conclusive judgment.

### 2. Mechanism of Irradiation Effect

#### Recovery by Thermal Annealing

(1) Specimens Irradiated to Fluences below \(1.5 \times 10^{26} \text{ n/m}^2\)

Upon annealing the specimen irradiated to \(3.0 \times 10^{24} \text{ n/m}^2\) at various temperatures, the swelled macroscopic dimension and lattice parameter recovered hand in hand, as plotted in Fig. 2 against annealing temperature. The plots reveal that the recovery commenced in the vicinity of the irradiation temperature of 470°C (see Table 1) and continued to progress linearly with increasing annealing temperature up to around 1,400°C, by which time the values of residual swelling percentage had almost completely regained their pre-irradiation level. The specimen irradiated to \(1.5 \times 10^{26} \text{ n/m}^2\) proved to behave in much the same manner, showing similarly good agreement of residual swelling percentage between macroscopic dimension and lattice parameter.

![Residual swelling percentages of macroscopic dimension and lattice parameter plotted against annealing temperature—SiC irradiated to \(3.0 \times 10^{24} \text{ n/m}^2\) at 470°C](image)

The corresponding plots of the FWHM of X-ray line profile are presented in Fig. 3, which reveals that this value has remained practically unchanged, in contrast to the distinct dependence on annealing temperature shown in the preceding case by the residual changes of the macroscopic dimension and lattice parameter.

It has already been mentioned that no dislocation loops were detected by transmission
electron microscopy in specimens annealed at temperatures below 1,400°C, whereas a slight increase in the diameter of loops has been reported by Price in SiC irradiated to $1.4 \times 10^{26} \text{n/m}^2$ upon annealing at 1,500°C\(^{(15)}\).

In Fig. 4, the variation with annealing temperature shown by the lattice parameter is plotted against that of the macroscopic dimension. The open plots representing the specimens irradiated to $3.0 \times 10^{24}$ and $1.5 \times 10^{26} \text{n/m}^2$ rise with a slope close to unity, indicating a similar rate of change in macroscopic dimension and in lattice parameter. It can thus be concluded that the recovery of defects in the specimens irradiated to fluences below $1.5 \times 10^{26} \text{n/m}^2$ proceeds by mutual recombination of interstitials and vacancies, as reported by Thorne \textit{et al.}\(^{(17)}\) and by Suzuki \textit{et al.}\(^{(11)}\).

(2) Specimens Irradiated to Fluences above $4.8 \times 10^{24} \text{n/m}^2$

The X-ray line profiles from the specimen irradiated to $1.7 \times 10^{27} \text{n/m}^2$ obtained as irradiated and upon subsequent annealing at 1,200 and 1,800°C are shown in Fig. 5, together with the profile from unirradiated SiC. The as-irradiated specimen is seen to have markedly broadened its profile, accompanied by a slight shift of the position of peak toward smaller angle. Annealing at 1,200°C has caused the peak to shift instead toward larger angle, without much altering the profile's FWHM. Annealing at temperatures above 1,400°C has tended to resharpen the peak, until at 1,800°C the FWHM is seen in Fig. 3 to have recovered almost to its pre-irradiation level.

From the same specimen as above, the residual percentage changes of macroscopic dimension and lattice parameter are plotted in Fig. 6 against annealing temperature. As in the case of the specimen irradiated to $3.0 \times 10^{24} \text{n/m}^2$ described in the preceding section, recovery of the two values is seen to have commenced in the vicinity of the irradiation temperature (480°C), to progress linearly with increasing annealing temperature. Up to around 1,200°C, the plots for macroscopic dimension and for lattice parameter are seen to maintain a constant difference between
them. A particularity to be noted in Fig. 6 is that, beyond about 700°C, the lattice parameter plots fall below zero, to rise again beyond about 1,200°C, and regain zero around 1,800°C. Through this interval of annealing temperature, the macroscopic dimension has maintained its decreasing trend, to gradually narrow the gap between it and the lattice parameter. An identical behavior has been noted with irradiated SiC and MgO.

The plots of Fig. 7 reveal that a similar relation between macroscopic dimension and lattice parameter characterized also the specimen irradiated to a lower fluence of $4.8 \times 10^{26}$ n/m$^2$, though with a smaller distance separating the plots for macroscopic dimension and lattice parameter in the range below 1,200°C.

It is to be noted that in both Figs. 6 and 7, the two lines of plots change their relationship at a point around 1,200°C, up to which they run roughly parallel to each other, meaning that, in this range of annealing temperature, while differing in absolute level, the values share a common rate of variation with change in annealing temperature.

The range of parallel progress of the two series of plots in Figs. 6 and 7 corresponds to that in Fig. 4, where the closed plots fall along straight lines. These lines run roughly parallel to the open plots, which represent the specimens irradiated to lower fluences of $1.5 \times 10^{26}$ n/m$^2$ and below. Thus, in the range of annealing temperatures below 1,200°C, the mechanism of recovery can be considered to be the same between lightly and heavily irradiated SiC, i.e. both are caused by the recombination of point defects.

A similar upper limit of annealing temperature around 1,200°C is noted in Fig. 3 for the change in recovery behavior shown by the FWHM of X-ray profiles for specimens irradiated above $4.8 \times 10^{26}$ n/m$^2$. This behavior is paralleled by microstructural observations, which have indicated that, below 1,000°C, both the number density and the size of the interstitial loops formed in heavily irradiated SiC remain unchanged.

The particular recovery behavior of the lattice parameter noted in Fig. 6—to fall below pre-irradiation level in a certain range of annealing temperature—can be explained as follows. In specimens irradiated to fluences above $4.8 \times 10^{26}$ n/m$^2$, dense interstitial dislocation loops are generated, which would bring about a situation where $c_i < c_v$ in as-irradiated condition. Upon annealing at temperatures below 1,200°C, $c_i$ should further decrease along with $c_v$ at the same rate through V-I recombination caused mainly by interstitial migration. When annealed at higher temperature, $c_i$ would eventually drop to a very low level below $c_v$, such that $c_i < c_v$, and hence $\Sigma c_i d_{i} < 0$, which means that the lattice parameter has dropped below the pre-irradiated value.

Beyond 1,200°C annealing temperature, it
has been noted that the recovery behavior changed radically; the lattice parameter that had fallen below pre-irradiation level reversed its trend, to begin rising again with increasing annealing temperature, while in the same temperature interval the macroscopic dimension maintained its downward course, to result in a narrowing gap between it and the lattice parameter. The corresponding behavior of the X-ray profile was to retract its swelled FWHM with rising annealing temperature (Fig. 3). Microstructural observations made in the previous study have indicated that the number density of dislocation loops present in the specimen was smaller when annealed at 1,400°C than at 1,000°C, while their size was larger \(^{(13)}\).

When irradiated at room temperature, the recovery of macroscopic dimension and of thermal diffusivity commences around the same temperature, which suggests that the interstitials have relatively high mobility even at room temperature. On the other hand, from the following observations it is indicated that vacancies begin migrating with significant mobility only above \(\sim 1,200°C\). Price has noted that voids were formed only upon irradiation at temperatures above \(\sim 1,250°C\) \(^{(14)}\). Sasaki et al. have reported that He-trapped vacancies migrated toward grain boundaries or toward surface, to create prominent peaks in the range of 1,200~1,300°C \(^{(15)}\).

Thus, in the range of annealing temperature above 1,200°C, there occurs migration of vacancies, letting \(c_v\) decrease further: through the recombination of the vacancies with interstitials originally trapped at the interstitial loops. This is what causes the lattice parameter to reverse its trend and start increasing, and the density of dislocation loops to diminish. This reduction in dislocation loop density would appear to be related to an increase in the crystallinity of the specimen. Actually, other factors may also come into play, since defects exist in a variety of forms. The foregoing explanation should, however, still be valid in its general form.

3. Temperature Monitor Using Heavily Irradiated SiC

It has been reported that SiC became amorphous when irradiated to fluences above \(10^{24} n/m^2\) \(^{(19)}\), and hence unsuitable for lattice parameter determination, so that, for temperature monitoring in high-fluence irradiation experiments, it should be preferable to adopt macroscopic dimension measurement. The results obtained in the present study indicate, however, that even with specimens irradiated to \(1.7\times10^{27} n/m^2\), recovery of the swelled lattice parameter actually commences at the irradiation temperature, and continues roughly linearly with increasing annealing temperature up to 1,000°C at least. It can thus be suggested that the X-ray method should be applicable to determining the irradiation temperatures of highly irradiated specimens up to \(1.7\times10^{27} n/m^2\) at temperatures up to say 500°C, provided that the lattice parameter is measured with adequate accuracy.

IV. CONCLUSION

Reaction-sintered \(\beta\)-SiC specimens were neutron-irradiated in fast breeder reactors at temperatures from 370 to 620°C to fluences from \(3.0\times10^{24}\) to \(1.7\times10^{27} n/m^2\) \((E>0.1\,\text{MeV})\). The changes brought by the irradiation and by subsequent annealing at various temperatures were observed in respect of macroscopic dimension, lattice parameter and X-ray line broadening, and the results are discussed in terms of microstructural changes. The results obtained from this study can be summarized as follows:

1. Irradiation to fluences below \(1.5\times10^{24} n/m^2\) brought about swelling of macroscopic dimension and of lattice parameter to roughly equal extent, whereas with fluences above \(4.8\times10^{24} n/m^2\), a significantly larger swelling was seen of the macroscopic dimension than of the lattice parameter, and this was accompanied by conspicuous flattening and broadening of the X-ray line profiles.

2. Upon annealing of specimens irradiated beyond \(4.8\times10^{24} n/m^2\), the macroscopic dimension and lattice parameter—swelled
by the irradiation—commenced recovering toward their pre-irradiation level when the annealing temperature exceeded that of irradiation, and the residual percentages of the swelled values plotted against annealing temperature roughly followed straight lines parallel to each other throughout the interval from irradiation temperature to around 1,200°C, indicating a constant difference between the residual percentages of swelling shown by the two values. The X-ray line profile, on the other hand, remained broadened even after annealing at temperatures up to 1,200°C.

(3) A particular behavior noted of the specimens irradiated above 4.8x10^{26} n/m^2 was that the lattice parameter fell below the pre-irradiation value upon annealing at relatively high temperature, but reversed its trend around 1,200°C, to rise again and regain the pre-irradiation value at yet higher annealing temperature. Consequently, beyond 1,200°C annealing temperature, the residual percentages of macroscopic dimension and of lattice parameter departed from their trend of constant difference between them, to enter a converging phase. In the same phase, the X-ray line profiles recovered toward their pre-irradiation form of high and sharp peaking.

(4) The foregoing behavior of highly-irradiated specimens regarding the difference in residual swelling between macroscopic dimension and lattice parameter shown in response to changing conditions of irradiation and annealing is explained in terms of the effect of differences in these conditions of irradiation and annealing on the number of isolated interstitials and vacancies present in as-irradiated specimens, and on the mobility of these defects.

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