Original Article

Effects of helium irradiation on fine grained β-SiC synthesized by spark plasma sintering


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ABSTRACT

Silicon carbide has a high resistance to irradiation making it a material of choice for use in the nuclear reactors. In this work, we focus on experiments involving implantation of 30 keV 3He ions at room temperature (RT) in sintered β-SiC. Helium is produced in large quantities in fission and fusion reactors, and its accumulation in materials can lead to the formation of bubbles. The irradiation induces structural modifications within the material that can be coupled with changes in composition, especially at high fluence. Three ion fluencies are used here: 5 × 10¹⁵, 1 × 10¹⁷ and 1 × 10¹⁸ at. cm⁻². Structural damages are studied by electron microscopy and helium profiles are measured by nuclear reaction analysis (NRA). At 1 × 10¹⁸ at. cm⁻², helium bubbles are formed in the implanted zone, which also undergoes strong oxidation. Surface blisters are also observed and helium concentration threshold for bubble formation is estimated to about 4 at. % by correlating the MET observations with the results obtained by ion beam analysis. For the highest fluence, a residual concentration of 3.6 × 10¹⁷ at. cm⁻² was measured just after implantation (instead of 1 × 10¹⁸ at. cm⁻²), which indicates a significant release of helium by the material during the process. The link between the microstructural evolution of the material, its progressive oxidation under beam and the release of helium is discussed. The very likely role played by the porosity on the oxidation of the material under irradiation at RT is underlined. Finally, the results obtained here on silicon carbide are compared with those obtained on another ceramic (TiC) which does not amorphize in similar conditions.

1. Introduction

Nuclear industry is looking to develop new materials able to withstand increasingly hostile environments. Because of its remarkable properties (creep and oxidation resistance [1–3], radiation tolerance [4–8]), silicon carbide is under investigation as cladding with enhanced tolerance for light water reactors [9–16] as well as cladding for GenIV nuclear plants [9–11, 17, 18]. For nuclear fusion [9,10] the addition of SiC in the form of a thin layer on the metallic structures (W [19] or Eurofer [20], i.e. Reduced Activation Ferritic Martensitic steel), should enable better control of the tritium inventory (diffusion barrier limiting tritium losses). It should also improve corrosion resistance in the case of SiC inserts in tritium blankets where the liquid metal, PbLi, circulates [20]. For all the above-mentioned nuclear applications, the (n, α) nuclear transmutation reaction inevitably introduces numerous atomic helium atoms in the SiC. The He/dpa production rate in SiC is reported to be 2.5 appm/dpa for typical fission neutron spectra [21,22]. In a fusion reactor, SiC will be exposed not only to a high irradiation dose (up to 200 dpa), but also high helium generation rates, i.e. 70 appm/dpa in the reactor, 130 appm/dpa for the first wall [3,23–25], and about 16,000 appm/yr at 10 MW/m² [26]. A rapid calculation leads to typical helium concentrations of the order of 0.05 at. % for fuel components in fission reactors and about 2.5 at. % (and even greater) for structural materials in fusion reactors.

Línez et al. [27] have shown experimentally that helium preferentially occupies tetrahedral interstitial sites after implantation at room temperature in 6H-SiC. After annealing at 400 °C, a migration of helium to the silicon vacancies and silicon and carbon bi-vacancies is observed. Due to the low solubility of He atoms in SiC, a certain concentration of He atoms that are trapped in the matrix in the form of helium-vacancy clusters would form bubbles upon annealing [28,29]. These bubbles can cause degradation of the material properties
after irradiation with a 1MeV He+ ion beam at room temperature. This bubble formation in 3C-SiC (β-SiC) at a concentration of about 4 at. % between 1.7–8.0 at. %.

As an illustration, Zinkle et al. [30] observed a threshold for helium bubble formation at room temperature has been observed to lead to amorphization and chemical disordering, as well as drive the production and accumulation of defects due to the implantation of noble gases. This can result in a well-known helium concentration profile. Secondly, the evolution of the sample surface morphology was followed by TEM observations: Bright field, Selected Area electron diffraction (SAED) and Scanning TEM (STEM) with a High Angle Annular Dark Field detector (HAADF), coupled with EDX analysis (elemental mapping).

Note that this threshold can vary according to irradiation ion species, irradiation temperature and microstructure [44].

After implantation, the helium content was determined using the 3He (d, p) 4He nuclear reaction characterized by a wide resonance centered on Ed = 450 keV [45]. The incident deuteron energy was set at 350 keV with a current density of 0.25 μA.cm⁻². Forward scattered or recoiled particles, except protons and α particles from the 3He (d, p) α reaction. The incident deuteron beam impinges on the sample surface at an angle of 20° (Fig. 2), and a mylar foil with a thickness of 23 μm is placed in front of a Si detector to block the forward scattered or recoiled particles, except protons and α particles from the 3He (d, p) α reaction. The incident deuteron energy was set at 600 keV in order to reach 0.45 MeV around the maximum theoretical helium concentration.

The evolution of the sample surface morphology was followed by SEM (FEG Quanta 250 FEG ESEM). Cross-sections prepared by FIB were observed by TEM (Jeol® 2100F). Three modes were used for these observations: Bright field, Selected Area electron diffraction (SAED) and Scanning TEM (STEM) with a High Angle Annular Dark Field detector (HAADF), coupled with EDX analysis (elemental mapping).
3. Results

3.1. Surface morphology and structure

The surface of the SiC pellets was observed by SEM after ion implantation (Fig. 3). No visible modification occurred after irradiation at Φ₁ and Φ₂, and the images of the surface shown in Fig. 3a and b are very similar to those obtained before irradiation. For Φ₃, blisters of <1 μm formed on the surface (Fig. 3c). 3D analysis of the Φ₃ sample is shown in Fig. 3d (Zeiss® 3DSM software). An Rₐ value of 50 nm was found after irradiation (about 10 nm before implantation). Thin sections of these samples were prepared by FIB and then observed by TEM (Fig. 4).

In the case of Φ₁, grain boundaries are clearly visible in the implanted area and no gas bubbles were formed near Rp(He) (Fig. 4a). SAED analysis (insert in Fig. 4a) confirmed that the material is still crystalline after implantation. Nevertheless, some crystalline disorder is observed in SAED pattern n°1 up to a depth of 265 nm ± 25 nm (white line). For Φ₂ (Fig. 4b), nanometric bubbles are visible near the Rp (see also Fig. 10). Smallest bubbles (~1 nm) need a slight defocus to be better observed. These appear light in underfocus and dark in overfocus and we assume these are full of helium and not voids. The irradiated area is completely amorphous up to a depth of 265 nm ± 25 nm (dashed line in Fig. 4b), as indicated by the SAED pattern in Fig. 4b. Gas bubbles are also visible on Fig. 4c (Φ₃) and their sizes vary from a few nm on both sides of the implantation profile, to a maximum of ~100 nm in the area of maximum concentration. The bubble-containing band within the dotted lines is located at a depth of between 50–370 nm (see Fig. 3).
also Fig. 6), and the center of gravity of the largest bubbles is at a depth greater than the theoretical $R_p$ calculated by SRIM, i.e. about 160 nm. The formation of large bubbles is responsible for surface swelling as shown on the TEM micrograph in Fig. 5, taken near the boundary between the irradiated and nonirradiated zones. The shift of implanted surface due to swelling with respect to the position of the non-implanted surface can reach 100 nm and this value gives a good indication of the height of the surface blisters observed in Fig. 3c.

An attempt to segment the image using ImageJ software [46] was done based on the TEM micrograph of Fig. 6a. The corresponding binary image is given in Fig. 6b. Measurement of bubble size as well as its eccentricity is difficult in this case because of the significant superposition of bubbles in the thickness of the FIB cross-section (about 100 nm). From this segmentation, bubbles have an average size of $9.2 \pm 2.5$ nm with a standard deviation of 9.3 nm. The latter reflects the large variety of bubble size. In addition, the low image contrast makes it difficult to take into account bubbles smaller than 1 or 2 nm. The average bubble size is therefore certainly overestimated here. Furthermore, no reliable eccentricity value can be given, but from Fig. 6a, it appears that the bubbles appear to be relatively spherical. Therefore, both the superposition of the bubbles on the thickness of the cross-section and the relative sphericity of those are better visualized on Fig. 7a-c, obtained by electronic tomography.
3.2. Implanted area composition

STEM-EDX analysis of the implanted area was performed. No noticeable changes in composition were observed for $\Phi_1$ (not shown) and the resulting elemental mapping for $\Phi_2$ and $\Phi_3$ is shown in Figs. 8 and 9, respectively.

As can be seen from Figs. 8 and 9 the irradiation at $\Phi_2$ and $\Phi_3$ resulted in O-enrichment of the implanted area to a depth that also corresponds to the end of the band containing visible bubbles. This band extends from 120 to 210 nm for $\Phi_2$ and from 50 to 330 nm for $\Phi_3$. However, some areas co-enriched in silicon and carbon and O-depleted still remain in the irradiated area (white circles in Fig. 9).

The theoretical helium profile at $\Phi_2$ is superimposed on the STEM image in Fig. 10. The threshold of the helium concentration above which bubbles are formed can be estimated. It is found to be close to 4.0 at. % ± 1 at. %.

4. Helium profiles

Nuclear reaction analysis spectra obtained for each fluence are given in Fig. 11. Fig. 11b and c show the zoomed in areas. The signal corresponding to the $^3$He (d, p) $^4$He reaction (zoom 1) was integrated for the three fluences. The experimental ratios $\Phi_{\text{exp2}}/\Phi_{\text{exp1}}$ and $\Phi_{\text{exp3}}/\Phi_{\text{exp1}}$ were found to be 20 ± 5 and 73 ± 5, respectively ($\Phi_{\text{th2}}/\Phi_{\text{th1}} = 20$ and $\Phi_{\text{th3}}/\Phi_{\text{th1}} = 200$). In the region of the (d, $\alpha$) peak a signal associated with (d, p) reactions on oxygen is observed (Zoom 2). Indeed, the oxidation that was already visible on the STEM-EDX elemental mapping is confirmed here for the highest fluences. The (d, $\alpha$) peak was integrated and the experimental ratios were found to be very close to the ones deduced previously from the $^3$He (d, p) $^4$He reaction i.e. 20 ± 5 and 69 ± 8 for $\Phi_{\text{exp2}}/\Phi_{\text{exp1}}$ and $\Phi_{\text{exp3}}/\Phi_{\text{exp1}}$, respectively. If one considers that the intensity of the (d, p) signal at $\Phi_1$ is associated with the theoretical fluence of $5 \times 10^{15}$ at. cm$^{-2}$ (no helium release expected at this fluence [47]), then $\Phi_{\text{exp2}}$ is close to $1 \times 10^{17}$ at. cm$^{-2}$ whereas a value of $3.64 \times 10^{17}$ at. cm$^{-2}$ is found for $\Phi_{\text{exp3}}$, i.e. nearly 36.4% of the theoretical fluence $\Phi_{\text{th3}}$ ($1 \times 10^{18}$ at. cm$^{-2}$).

5. Discussion

Helium irradiation at low fluence ($\Phi_1$) does not cause material amorphization even at the dpa profile maximum which places the

![Fig. 5. TEM image of He gas bubbles and surface swelling after irradiation at $\Phi_1$.](image1)

![Fig. 6. a) TEM image of SiC after helium RT-implantation $\Phi_3$ and b) the corresponding binary image calculated using ImageJ software.](image2)
threshold of amorphization above 0.16 dpa in our experimental conditions. A certain degree of disorder is nevertheless created within the host matrix, symbolized by the visible halo on the diffractogram in Fig. 4a. At higher doses ($\Phi_2$ and $\Phi_3$), there is total amorphization of the material over a large band as expected for such dpa levels (see Fig. 1). The critical dose for amorphization in SiC at room temperature has been reported to be $\sim 0.3$ dpa for 1.5 MeV Xe ions [48] (concordant with an earlier study [39]), and $\sim 1.1$–1.5 dpa for 20–70 keV He ions [43,49]. The trend for the increase in dpa dose required with decreasing incident projectile mass, which has been reported previously by Snead et al. [50] is due to the decrease in residual chemical disorder per ion impact. Thus, more displacement damage is required to produce amorphization with lighter projectiles.

Irradiation at room temperature and at high fluence leads to a considerable oxidation of the material. This phenomenon may seem enigmatic since the irradiation is conducted under a controlled secondary vacuum. Oxygen uptake increases with the irradiation fluence as it was also observed on samples irradiated by xenon at room temperature in a previous study [39]. Quantitative NRA analysis of irradiated surfaces confirmed the link between ion fluence and the uptake of oxygen by the material (Table 1).

The question of the source of oxygen at the origin of this chemical evolution is worth asking. Two main hypotheses can be formulated according to whether one considers an “under beam” or “out of beam” oxidation. Oxygen incorporation in 4H-SiC during hydrogen implantation was already underlined by Barcz et al. [52]. These

Fig. 7. a–c): 2D projections at different angles of electron tomography analysis after implantation at $\Phi_3$. 

S. Gavarini, et al. 
Journal of the European Ceramic Society 40 (2020) 1–11
authors have shown that a cavity band near the end of range of hydrogen (or deuterium) tends to getter oxygen. They concluded that the oxygen most likely penetrates from the ambient (gaseous $\text{O}_2$ and $\text{H}_2\text{O}$ molecules) by migrating from the sample edges along the heavily damaged and partially porous zone of damage produced by hydrogen implantation. In our case, the entire implanted area is oxidized and not only the area with helium cavities. It can be stipulated that the initial porosity of the material promotes the penetration of oxygen species that could come from the secondary vacuum in the irradiation chamber, the latter can never be considered perfect. This oxygen can also come partly from the oxide layer inevitably formed on the surface of SiC before irradiation. Another possibility is that oxidation occurs just after irradiation when the sample is vented. Indeed, the atmosphere then provides an abundant source of oxygen. A comprehensive study with a systematic parametric approach would be required to highlight the mechanics and key parameters involved in this process.

Up to a fluence of $1 \times 10^{17}$ at.cm$^{-2}$, no helium release was
measured. However, a significant release of helium (about 70%) was measured at the highest fluence $\Phi_3$. The remaining fluence of $3.64 \times 10^{17}$ at. cm$^{-2}$ could correspond to the saturation yield in our experimental conditions. Moreover, at this fluence, blisters form on the surface (around 100 nm in size) due to the presence of large bubbles beneath the surface. A threshold concentration of 4.0 at. % ± 1 at. % for the formation of helium bubbles was determined based on TEM observations. This value is in good agreement with the value reported by Zinkle et al. [30]. On the other hand, Harrison et al. [43], did not observed any He bubbles nucleation up to 5 dpa in the case of in situ experiments carried out on thin cross sections (~100 nm thick) in a TEM with 20 keV He at RT. In the latter case, however, the very specific experimental conditions perhaps explain such an apparent discrepancy. It is not clear whether oxidation, material amorphization and bubble formation are correlated phenomena or not in the present study. However, an instructive comparison can be done with another carbide (TiC) irradiated in similar conditions [40]. In this case, helium irradiation at $\Phi_3$ result in the formation of micro- or nano-cracks beneath the surface near the projected range (Fig. 12). As indicated by the SAED pattern, no amorphization occurred during ion implantation even if

Fig. 9. Elemental mapping of the implanted area obtained by STEM-EDX after helium irradiation at $\Phi_3$.

Fig. 10. Superposition of the STEM micrograph and theoretical SRIM data at $\Phi_2$. 

S. Gavarini, et al.  
Journal of the European Ceramic Society 40 (2020) 1–11
some disorder was present (insert in Fig. 12b). The accumulation of defect and gas at depth induces here a fracturing of the material rather than the formation of round bubbles. Almost no oxidation was measured in the irradiated TiC whatever the fluence. A possible conclusion could thus be that material amorphization favors oxygen incorporation in the case of SiC but this assumption may be confirmed by additional experiments (see next step below).

In Fig. 12a, a grain boundary is present which appears to be decorated with bubbles outside the implanted He region by several tens of nanometers. Such segregation suggests enhanced He mobility in the grain boundary compared to the crystalline matrix and these could play a role in the release path for the implanted gas. Indeed, about 80% of helium is released from TiC after RT implantation at $\Phi_3$. This loss is higher than for SiC implanted in similar conditions (about 70%). Note that the mechanism at the origin of helium release is still unclear in the case of SiC. In Fig. 4c, most bubbles are located at a depth comprised between 100–340 nm. Almost no bubbles are observed in the first 100 nm and the surface blisters are closed for the most part which prevents the formation of visible outlets for the release of the gas. Bubble emptying is thus suspected, possibly including helium re-dissolution and a diffusion step through the amorphous SiC layer.

The next step of this work will consist in using different thermal treatments during implantation. Irradiation experiments at temperatures between 300–1000 °C (to preserve SiC crystallinity) will be performed as a follow-up to this study. A similar protocol will be applied at RT and at high temperature on CVD deposits. Indeed, the advantage of CVD technique (epitaxial growth) over HP or SPS sintering is that it allows a reproducible deposition of very fine microstructures (grain size $< 100$ nm and down to a few nanometers) without classical manufacturing bias: very high densification rate, no porosity and composition/quasi-perfect stoichiometry.

6. Conclusion

$\beta$-SiC sintered bodies were implanted with 30 keV $^3$He ions at room temperature and up to an ion fluence of $1 \times 10^{16}$ at. cm$^{-2}$. Nanometric bubbles are formed after irradiation at $10^{17}$ at. cm$^{-2}$ and the threshold concentration for their formation is estimated at $\sim 4.0$ at. %. Virtually no helium release is measured below $10^{17}$ at. cm$^{-2}$ by NRA technique. For the highest fluence, the maximum size of bubbles reaches a hundred nanometers and surface blistering is observed. Approximately 70% of the helium is released during implantation and the irradiated zone also undergoes significant oxidation. The link between the microstructural evolution of the material, its progressive oxidation under beam and the release of helium is discussed. The very likely role played by the porosity on the oxidation of the material under irradiation at RT is underlined. Finally, a penetration of oxygen by migrating from the porosities through the heavily damaged area seems to be the most likely hypothesis.

<table>
<thead>
<tr>
<th>Theoretical fluence</th>
<th>$Dp_{max}$</th>
<th>Experimental helium fluence</th>
<th>Experimental oxygen fluence*</th>
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</thead>
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<tr>
<td>$\Phi_{1}^{16}$ = 5 $\times 10^{15}$ at. cm$^{-2}$</td>
<td>0.16</td>
<td>$5 \times 10^{14}$ at. cm$^{-2}$</td>
<td>$&lt; 3.40 \times 10^{14}$ at. cm$^{-2}$</td>
</tr>
<tr>
<td>$\Phi_{2}^{16}$ = 1 $\times 10^{17}$ at. cm$^{-2}$</td>
<td>3.26</td>
<td>$1 \times 10^{16}$ at. cm$^{-2}$</td>
<td>$1.89 \times 10^{17}$ at. cm$^{-2}$</td>
</tr>
<tr>
<td>$\Phi_{3}^{16}$ = 1 $\times 10^{18}$ at. cm$^{-2}$</td>
<td>32.6</td>
<td>$3.64 \times 10^{17}$ at. cm$^{-2}$</td>
<td>$2.97 \times 10^{17}$ at. cm$^{-2}$</td>
</tr>
</tbody>
</table>

* NRA, Non-Rutherford cross-section [51].
Fig. 12. TEM images of the TiC cross-section obtained by FIB after He RT-irradiation at a fluence of $\Phi = 1 \times 10^{18}$ at cm$^{-2}$.

Acknowledgments

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References


