Cavity Formation in SiC/SiC Composites during Multi-ion-beam Irradiation at Elevated Temperatures

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ITER conceptual design is using stainless steels as the first wall and blanket structures.

SiC/SiC is one of the major candidate materials for future fusion power reactors as the first wall and blanket structures. $(T>1000^\circ \text{C}, \eta_{\text{th}} = 70\%)$

Also can be used for hydrogen production from water.

http://www-fusion-magnetique.cea.fr/iter/iter_coupe01.jpg
Background

- SiC/SiC composites are the major candidates as the advanced structural materials for fusion reactors due to its low induced radioactivity, high specific strength, high thermal conductivity and high temperature strength.

- In a fusion reactor, the first wall and blanket will receive not only high level of radiation damage from the high energy neutrons but also contains large amount of deuterium and helium atoms. The stability of the microstructures of the SiC/SiC composites under the fusion environments is a major interest.

- We are using triple-ion-beam irradiation facility to simulate the fusion environments to study the microstructural evolution of the SiC/SiC composites.
The relationship of damage level (dpa) to the amount of He and H gas atoms (appm)

He = 150 appm/dpa
H = 60 appm/dpa

Irradiation facility

Turbo Pump  Viewing port

Faraday cups

Ion gauge  Viewing port
500 keV Ion-Implanter
NEC 9SDH-2 3MV Tandem Accelerator
KN 3 MV van der Graaff Accelerator
Specimen Holders
Irradiation angles between the beams
Materials

- Uni-directional SiC/SiC composites with Tyranno-SA fibers and the matrix was fabricated using CVI method.
- Uni-directional SiC/SiC composites with Hi-Nicalon Type-S fibers and the matrix was also fabricated using CVI method.
Experiments

unirradiated

Unirradiated microstructures

Annealed at 1000 °C for 67 hours

Si\(^{3+}\)+He\(^{+}\), 600 °C and 800 °C, 10 dpa/1500 appm

Si\(^{3+}\)+He\(^{+}\), 800 °C and 1000 °C, 100 dpa/15000 appm

H\(^{+}\)+He\(^{+}\), 800 °C and 1000 °C, 6000 appm/15000 appm

Dual-beam irradiations

Triple-beam irradiation → He\(^{+}\)+H\(^{+}\)+Si\(^{3+}\), 800 °C/1500 appm/600 appm/10 dpa
The SiC matrix was manufactured by chemical vapor infiltration (CVI).
The holes between the layers in the SiC matrix
Grains size of the fiber is between 50\(\sim\)100 nm

Tyranno-SA Fiber
Interface and Carbon layer

![Image of interface and Carbon layer with labels]

- **Tyranno-SA Fiber**
- **Matrix**
- **940 nm**
- **1.0 um**
- **Magnification 0025K**
3C $\beta$-SiC nano-grain
<table>
<thead>
<tr>
<th></th>
<th>2H-SiC</th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>α-phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>structure</strong></td>
<td>Hexagonal structure (Wurtzite)</td>
<td>Cubic (Zincblende)</td>
<td>Hexagonal structure (Wurtzite)</td>
<td>Hexagonal structure (Wurtzite)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2H-SiC</strong></td>
<td>$a=5.8125$ Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3C-SiC</strong></td>
<td>$a=4.3596$ Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>4H-SiC</strong></td>
<td>$a = 3.0730$ Å</td>
<td>$b = 10.053$ Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>6H-SiC</strong></td>
<td>$a = 3.0730$ Å</td>
<td>$b = 10.053$ Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2H, 4H, 6H intermixing microstructures
Si/He Dual-beam Irradiation

Schematics of the Triple-beam Irradiation Facility

Turbo Pump

Faraday Cups

Ion gauge

Viewing port

Implantor

9SDH

$\text{Si}^{3+}$

22$^\circ$

25$^\circ$

$6\text{MeV Si}^{3+}$

$1.13\text{MeV He}^+$

$\kappa_N$

Specimen holder
Si-He Dual-beam irradiation calculated by TRIM98 Code
Dual beams implant (Si\textsuperscript{3+} and He\textsuperscript{+})
@600°C, 10dpa/1500appm
Dual beams implant ($\text{Si}^{3+}$ and $\text{He}^+$) @800°C, 10dpa/1500appm

Matrix  Fiber
Dual beams implant (Si^{3+} and He^{+})
@800°C, 100dpa/15000appm
Dual beams implant (Si$^{3+}$ and He$^+$) @1000°C, 100dpa/15000appm
H/He Dual-beam Irradiation

Schematics of the Triple-beam Irradiation Facility

- Turbo Pump
- Viewing port
- Faraday Cups
- Ion gauge
- 280keV H⁺
- 800keV He⁺
- Implantor
- 9SDH
- $K_N$
- Specimen holder

[Diagram showing the layout of the facility with various components and beams.]
He/H Dual-beam Irradiation calculated by SRIM

At 1.56 μm depth the He/H ratio is 15000/6000 appm
Dual beams implant (H\textsuperscript{+} and He\textsuperscript{+})
@800\textdegree C, 6000/15000appm
Dual beams implant ($\text{H}^+$ and $\text{He}^+$) @1000°C, 6000/15000appm
Si/He/H Triple-beam Irradiation

Schematics of the Triple-beam Irradiation Facility
Si/He/H Triple-beam Irradiation Calculated by SRIM Code

At 1.56 μm depth we get 10dpa/1500appm/600appm
Triple beams implant (Si$^{3+}$, H$^+$ and He$^+$) @800°C, 10dpa/6000appm/15000appm

Matrix

Fiber

Bubbles

Magnification 0800K
After 67 hours annealing @1000°C
Bubble formation mechanism in dual-beam irradiation conditions

He atoms in the lattice → At high temperatures vacancies can move which assist He atoms migrate to grain boundaries → He bubbles form at grain boundaries.
Temperature Effects

Comparison between temperatures

\[
\begin{align*}
600^\circ C \text{ and } 800^\circ C \ (Si^{3+/He^+} = 10\text{dpa/1500appm}) \\
800^\circ C \text{ and } 1000^\circ C \ (Si^{3+/He^+} = 100\text{dpa/15000appm}) \\
800^\circ C \text{ and } 1000^\circ C \ (H^+/He^+ = 6000\text{appm/15000appm})
\end{align*}
\]
Comparison between 600°C and 800°C Dual-beam (Si$^{3+}$/He$^+$= 10dpa/1500appm)

There is no bubbles found in the SiC matrix or fibers in 600° C dual-beam irradiated specimens.

We found bubbles in the SiC matrix but not in the Tyranno-SA fibers in 800° C irradiated specimens.
Comparison between 800 °C and 1000 °C Dual-beam (Si³⁺/He⁺= 100dpa/15000appm)

<table>
<thead>
<tr>
<th></th>
<th>800 °C</th>
<th></th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si/He = 100dpa/15000 appm</td>
<td></td>
<td>Si/He= 100dpa/15000 appm</td>
</tr>
<tr>
<td>Matrix</td>
<td>10nm</td>
<td>Matrix</td>
<td>40nm</td>
</tr>
<tr>
<td>Fiber</td>
<td>5nm</td>
<td>Fiber</td>
<td>15nm</td>
</tr>
<tr>
<td>Density (#/m³)</td>
<td>2.6 x10²¹</td>
<td>Density (#/m³)</td>
<td>1.4 x10²¹</td>
</tr>
<tr>
<td></td>
<td>4.5 x10²¹</td>
<td></td>
<td>2.7 x10²¹</td>
</tr>
</tbody>
</table>

Higher temperature gives larger in bubble size but fewer in number density.

Smaller bubbles and higher density found in Tyranno-SA SiC fibers than in the SiC matrix.
Comparison between 800 °C and 1000 °C Dual-beam (H⁺/He⁺= 6000appm/15000appm)

<table>
<thead>
<tr>
<th></th>
<th>800 °C</th>
<th>1000 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H/He= 6000/15000appm</td>
<td>H/He= 6000/15000appm</td>
</tr>
<tr>
<td>Matrix</td>
<td>2~3 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>Fiber</td>
<td>1 nm</td>
<td>2 nm</td>
</tr>
<tr>
<td>Density (#/m³)</td>
<td>3.4 x10²²</td>
<td>0.9 x10²²</td>
</tr>
<tr>
<td></td>
<td>5.6 x10²²</td>
<td>2.7 x10²²</td>
</tr>
</tbody>
</table>

Higher temperature gives larger in bubble size and fewer in number density.

Fibers contain higher density but smaller diameter of bubbles than in the matrix.
Higher dose effects

800 °C dual-beam irradiation

\[
\begin{align*}
\text{(Si}^{3+}/\text{He}^+ &= 100 \text{dpa/15000 appm)} \\
\text{(Si}^{3+}/\text{He}^+ &= 10 \text{dpa/1500 appm)}
\end{align*}
\]

<table>
<thead>
<tr>
<th>800 °C</th>
<th>Si/He= 10 dpa/1500 appm</th>
<th>Si/He= 100 dpa/15000 appm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>matrix</td>
<td>matrix</td>
</tr>
<tr>
<td>bubble size</td>
<td>1.2 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>density (#/m³)</td>
<td>0.85x10^{22}</td>
<td>2.6x10^{21}</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>4.5x10^{21}</td>
</tr>
<tr>
<td>fiber</td>
<td></td>
<td>5 nm</td>
</tr>
</tbody>
</table>
Hydrogen plays a role to enhance the bubble nucleation in the Tyranno-SA fiber and also increase the number density in the matrix.
The role of He and H atoms in the bubble nucleation

- More gas atoms to the bubble to grow
- Bubble embryo
- Gas stabilizes the embryo to form bubble nucleous
- More gas atoms to the bubble to grow
Unirradiated Microstructures of CVI SiC Matrix with Hi-Nicalon Type-S Fibers
Hi-Nicalon Type-S fibers (grain size 10-50 nm)
1000 °C He/Si dual-beam irradiation (15000 appm/100 dpa)

Fiber: 1.5 nm, 9.9 × 10^{21}/m^3

Matrix: 30 nm, 5.7 × 10^{21}/m^3
<table>
<thead>
<tr>
<th>Irradiation Conditions</th>
<th>600°C He/Si 1500appm/10dpa</th>
<th>800°C He/Si 1500appm/10dpa</th>
<th>800°C He/Si 15000appm/100dpa</th>
<th>1000°C He/Si 15000appm/100dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nicalon Type-S SiC Fiber</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>1.5nm 9.9×10^{21}/m^3</td>
</tr>
<tr>
<td>CVI SiC Matrix</td>
<td>none</td>
<td>2.5nm 7.6×10^{21}/m^3</td>
<td>8.5nm 6.2×10^{21}/m^3</td>
<td>30nm 5.7×10^{21}/m^3</td>
</tr>
</tbody>
</table>
Comparison among single-, dual- and triple-beam irradiations at 800°C to 10 dpa

<table>
<thead>
<tr>
<th>Irradiation Conditions</th>
<th>800°C Si, 10dpa</th>
<th>800°C He/Si 1500appm/10dpa</th>
<th>800°C He/H/Si 1500appm/600appm/10dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nicalon Type-S Sic Fiber</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>CVI SiC Matrix</td>
<td>none</td>
<td>2.5nm 7.6×10^{21}/m^3</td>
<td>1.8nm 3.1×10^{22}/m^3</td>
</tr>
</tbody>
</table>

## Comparison between Hi-Nicalon Type-S and Tyranno-SA Fibers

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Si/He 10dpa/1500 appm</th>
<th>Si/He/H 10dpa/1500/600 appm</th>
<th>Si/He 100dpa/15000 appm</th>
<th>H/He 6000/15000 appm</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td>HNS</td>
<td>TSA</td>
<td>HNS</td>
<td>TSA</td>
</tr>
<tr>
<td>Bubble size</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
<td>&lt;1nm</td>
</tr>
<tr>
<td>Density (number/m³)</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
<td>3*10²²</td>
</tr>
<tr>
<td>1000 °C</td>
<td>Si/He 100dpa/15000 appm</td>
<td>H/He 6000/15000 appm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bubble size</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
</tr>
<tr>
<td>Density (number/m³)</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
<td>Non</td>
</tr>
</tbody>
</table>
Hi-Nicalon Type-S fiber has better resistance to bubble formation is probably due to its smaller grain size (10-50 nm) than that of Tyranno-SA fiber (50-100 nm) which in turn diverse the segregation of He atoms to delay the formation of He bubbles.

However, when it does form He bubbles, due to its higher grain boundary area which induces more nucleation sites that let the Hi-Nicalon Type-S fiber shows higher number density and smaller bubble size.

Hi-Nicalon Type-S fiber does have a better irradiation stability in terms of bubble formation than that of Tyranno-SA fiber.
Hi-Nicalon Type-S fiber shows a better irradiation stability in terms of bubble formation than that of Tyranno-SA fiber. The main reason for this is due to the smaller grain size.

Hydrogen plays some role in bubble nucleation which increases the number density of bubble formed both in the matrix and in the fibers.

We will perform more triple-beam irradiation experiments to higher temperature and higher dose levels to further study the mechanism of bubble formation.

We will also focus on the other microstructural evolution during irradiation (such as: dislocation loops, stacking fault tetrahedron, ..etc) in **Hi-Nicalon Type-S fiber SiC/SiC composites**.
Acknowledgement

- This work is financially supported by the National Science Council of TAIWAN, R.O.C.
- The SiC/SiC composite material is offered by Dr. Y. Katoh (ORNL, USA) and Prof. Kohyama (Kyoto Univ., JAPAN).
- Ion-irradiation was performed in the Accelerator Group of the Nuclear Science and Technology Development Center in the National Tsing Hua University.
Amorphous carbon interlayer and SiC matrix
3C, 2H, 4H, 6H intermixing microstructures
Annealed at 1000 °C for 67 hours
Si-He Dual-beam irradiation calculated by TRIM98 Code

He

2.4 μm
depth (μm)
600 ℃ He/Si dual-beam irradiation
(1500appm/10dpa)
800 °C He/Si dual-beam irradiation
(1500appm/10dpa)

母材氦气泡平均2.5nm；密度7.6×10^{21}/m^{3}
800 °C He/Si dual-beam irradiation (15000 appm/100 dpa)

母材氦气泡平均8.5nm；密度6.2×10^{21}/m^3
1000°C He/Si dual-beam irradiation (15000appm/100dpa)

纖維氣泡平均1.5nm；密度9.9×10^{21}/m^3

母材氦氣泡平均30nm；密度5.7×10^{21}/m^3
<table>
<thead>
<tr>
<th>Irradiation Conditions</th>
<th>600°C He/Si 1500appm/10dpa</th>
<th>800°C He/Si 1500appm/10dpa</th>
<th>800°C He/Si 15000appm/100dpa</th>
<th>1000°C He/Si 15000appm/100dpa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nicalon Type-S SiC Fiber</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>1.5nm 9.9×10^{21}/m^3</td>
</tr>
<tr>
<td>CVI SiC Matrix</td>
<td>none</td>
<td>2.5nm 7.6×10^{21}/m^3</td>
<td>8.5nm 6.2×10^{21}/m^3</td>
<td>30nm 5.7×10^{21}/m^3</td>
</tr>
</tbody>
</table>
• P. Jung has proved that the diffusivity of He atoms in amorphous carbon is 30 times faster than in SiC so that the thicker carbon interlayer offers a fast diffusion channel for He atoms to diffuse out. P. Jung, J. Nucl. Mater. 191–194 (1992) 377.

• Smaller grain size gives much higher grain boundary area which in turn diverse the segregation of He atoms to delay the formation of He bubbles.

• Higher dose and higher temperature irradiation enhances bubble coarsening which increases the bubble size but reduces the number density.
He/H Dual-beam Irradiation calculated by SRIM

At 1.56 μm depth the He/H ratio is 15000/6000 appm
appm

depth from surface $\mu$m

1.0 $\mu$m
800°C He/H dual-beam irradiation 15000/6000appm

纖維氣泡平均1nm；密度

母材氣泡平均2nm；密度$6.8 \times 10^{22}/m^3$
1000°C He/H dual-beam irradiation

纖維氣泡平均1.6nm；密度$2.4 \times 10^{22}$/m$^3$

母材氣泡平均7nm；密度$1.8 \times 10^{21}$/m$^3$
<table>
<thead>
<tr>
<th>Irradiation Conditions</th>
<th>800°C He/H 15000appm/6000appm</th>
<th>1000°C He/H 15000appm/6000appm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-Nicalon Type-S Sic Fiber</td>
<td>1nm 9.6×10^{22}/m^3</td>
<td>1.6nm 2.4×10^{22}/m^3</td>
</tr>
<tr>
<td>CVI SiC Matrix</td>
<td>2nm 6.8×10^{22}/m^3</td>
<td>7nm 1.8×10^{21}/m^3</td>
</tr>
</tbody>
</table>
在800°C以上氦氢原子、过饱和空孔、氦-空孔、氢-空孔，皆能扩散移动到晶界聚集成气泡，但因为氢氦会个别稳定化空孔的关系，使气泡成核点变多，所以800°C实验的中，气泡小又多可由此解释

1000°C氦氢原子与过饱和空孔在晶界聚集更多，加上更高温的扩散，因此非常容易被群聚成为大气泡而造成气泡体积变大数目变少
Si/Ho/H triple beam irradiation
Calculated by SRIM Code

At 1.56 μm depth we get 10dpa/1500appm/600appm
800 °C He/H/Si triple-beam irradiation (1500appm/600appm/10dpa)

纖維中沒發現氣泡，或許是劑量不足之緣故

母材氣泡平均1.8nm；密度3.1×10^{22}/m^3
Comparison among single-, dual- and triple-beam irradiations at 800 °C to 10 dpa

<table>
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<tr>
<th>Irradiation Conditions</th>
<th>800°C Si, 10dpa</th>
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<tbody>
<tr>
<td>Hi-Nicalon Type-S Sic Fiber</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>CVI SiC Matrix</td>
<td>none</td>
<td>2.5nm $7.6 \times 10^{21}/m^3$</td>
<td>1.8nm $3.1 \times 10^{22}/m^3$</td>
</tr>
</tbody>
</table>

氦氫矽三射束比較

比較本實驗中三射束和雙射束，發現三射束的氣泡密度多，但體積稍微變小，應該是氫氦分散掉過飽和空孔以至於氣泡成核數目多體積變小之緣故


但是本實驗結果和T.Taguchi等人(Journal of Nuclear Materials 335 (2004)508–514)，大致符合