Fabrication of Br-doped Glow Discharge Polymer (GDP) Capsules

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OUTLINE

- Purpose of Br-doped capsules
- Br loss and diffusion
- Unexpected Br-Si interaction
- Reducing Br trapped in the Si-doped layers
Bromine-doped GDP capsules are desired for mix and burn physics experiments

- To understand charged-particle transport and plasma stopping powers in NIF cryo shots
- Reaction $^{79}$Br(d,2n)$^{79}$Kr:

$$^{35}_{35} \text{Br} + ^{1}_{1} \text{H} \rightarrow ^{36}_{36} \text{Kr} + 2^{1}_{0}n$$

(deuteron)

(1) $^{79}$Kr is measured by RAGS (Radiochemical Analysis of Gaseous Samples apparatus)

(2) RIF (Reaction-in-Flight) neutrons are produced in cold fuel and measured by neutron foil activation

- Both RAGS $^{79}$Kr and RIFs measure production and transport of knock-on deuteron

### Ignition capsule design

Wall 175µm (cryo)

<table>
<thead>
<tr>
<th>Layers</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dopants (at.%)</td>
<td>Br</td>
<td>Si</td>
<td>Si</td>
<td>Si</td>
<td>Un-doped</td>
</tr>
<tr>
<td>0.25%</td>
<td>1%</td>
<td>2%</td>
<td>1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>6</td>
<td>6</td>
<td>35</td>
<td>10</td>
<td>118</td>
</tr>
</tbody>
</table>

2x$10^{16}$ Br atoms on inner surface

IR=935  OR=1110
Capsule fabrication steps

- Bromine loss during pyrolysis - starting Br at. %?

<table>
<thead>
<tr>
<th>Layer 1</th>
<th>Layers 2-4</th>
<th>Layer 5</th>
<th>Pyrolysis and Polishing</th>
<th>Drilling CFTA hole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-GDP</td>
<td>Si-GDP</td>
<td>un-doped CH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br at%</td>
<td></td>
<td></td>
<td>Br retention?</td>
<td></td>
</tr>
<tr>
<td>Smoothness</td>
<td></td>
<td>Surface quality</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>On PAMS mandrel</th>
<th>Pyrolysis in N₂ To remove PAMS</th>
</tr>
</thead>
</table>


Bromine loss and diffusion during pyrolysis is a major challenge in Br-doped capsule fabrication

- Aimed for high at.% of Br to counter loss
  - Ethylbromide (C₂H₅Br) as the Br source
  - Coating parameters: H₂, T₂B, C₂H₅Br, RF power (5W)
- To start Br at ~3 at.%, post-pyro 0.2-0.3 at.%

Low H₂ flow for high Br at%:

~9% Br remaining post pyro
Br profile is studied with two-layered “test capsules” with thick un-doped outer layer

- Br diffuses into the un-doped region before pyrolysis — by CR and EDS
- Pyrolysis removed diffused Br region – No problem for two-layered capsule
- Br diffuses out as CH$_3$Br

2-layered

<table>
<thead>
<tr>
<th>Inside</th>
<th>Thickness (µm)</th>
<th>outside</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br migrated during coating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-GDP 6.9 at%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Undoped GDP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br migrated region</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pre pyro Diffused Br

Post pyro No diffused Br

Mass spec

<table>
<thead>
<tr>
<th>Mass spec</th>
</tr>
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<tbody>
<tr>
<td>CH$_3$-Br+ 94/96</td>
</tr>
<tr>
<td>Br+ 79/81</td>
</tr>
</tbody>
</table>

280°C

170°C

Relative intensity

m/z
An unexpected Br-Si interaction trapped Br in the third layer (2 at.% Si) in the 5-layered “real capsule”

- Capsule retained Br >> than the expected 9% after pyrolysis
- Profile verified by EDS, Edge, CR

First layer retained $3 \times 10^{16}$ Br atoms

Unwanted Br atoms in the 3rd layer 2% Si

Si profile

Br profile

1.7x10$^{17}$ unwanted Br atoms

8.5X
Three methods to reduce unwanted Br in 2 at.% Si layer

1. Block Si-Br bonds formation
2. Provide additional Br escaping path
3. Reduce Br in the 1st layer by partial pyrolysis
Method 1: Block Si-Br bonds formation with stable Si-OH bonds

- Bond enthalpies evaluation

<table>
<thead>
<tr>
<th>Single Bonds</th>
<th>Bond Dissociation enthalpies (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-OH</td>
<td>911</td>
</tr>
<tr>
<td>Si-O</td>
<td>798</td>
</tr>
<tr>
<td>CH₃-H</td>
<td>431</td>
</tr>
<tr>
<td>CH₃-OH</td>
<td>377</td>
</tr>
<tr>
<td>H-Br</td>
<td>366</td>
</tr>
<tr>
<td>Si-Br</td>
<td>343</td>
</tr>
<tr>
<td>Si-H</td>
<td>318</td>
</tr>
<tr>
<td>CH₃-Br</td>
<td>284</td>
</tr>
</tbody>
</table>

- Stored capsule 1 day in air and 2 days in O₂ to form Si-OH bonds

- CR and EDS

Oxygen profile

\[
\begin{align*}
\text{Si-H} + \text{CH₃-Br} & \rightarrow \text{Si-Br} + \text{CH₃-H} \\
602 + 774 & = 1376
\end{align*}
\]

\[
\begin{align*}
\text{Si-OH} + \text{CH₃-Br} & \rightarrow \text{Si-Br} + \text{CH₃-OH} \\
1195 + 720 & = 1915
\end{align*}
\]
Si-OH (no drill hole) reduced Br retention in 2 at.% Si layer but delaminated after pyrolysis and laser drilling

- Unwanted Br is reduced from $1.7 \times 10^{17}$ to $4.3 \times 10^{16}$ atoms (25%)

- Br layer delaminated
  - Stress-induced?

Br profile

Post-pyro of oxygen-stored 5-layered capsule

Delaminated in CFTA drilling

Before
Method 2: Laser drilling a CFTA hole before pyrolysis allowed ~40% more Br to escape during pyro:

- Standard process uses pyro then drill – now drill first
- Use CFTA hole as an additional escape path

**Br profiles with and without laser hole**

- **Drill CFTA hole first**
- **Pyro**

**Br in the 2 at% Si layer**
- \(9 \times 10^{16}\) of Br
- Repeat pyro not much change
  - \(~15 \pm 5\%\) more Br loss
- **Not good enough**
Method 3: Partial pyrolysis to limit Br in the 1st layer that can diffuse outward

- A new Br-GDP batch and two-step pyrolysis
  - Partial Pyro 240°C<
  - coat and drill
  - Full pyro 302°C

Br-layer only, PAMS stay reduce Br

- Wrinkling of 6µm Br-GDP is a major concern
  - No pyro
  - 220°C 10hr
  - Partial pyro to reduce Br amount

0.53 at% (19%)
Method 3 produced Br in the first layer within spec, but some Br is still trapped in the 2 at% Si layer

- Br atoms whole shell $4.2 \times 10^{16}$ compared to $2 \times 10^{16}$ spec
  - No Br reduction in 2nd pyro but Br migrated

No delamination after drilling and pyrolysis
Fabrication of Br-doped GDP Capsules for RAGS $^{79}$Kr and RIF experiments involves controlling Br migration

- **Br-GDP fabrication has challenges**
  - High Br loss
  - Br-Si reaction trapped Br in 2 at.% Si layer
  - Delamination
    - Tensile stress in Br-GDP
- **Two-step pyrolysis reduces Br in 2 at.% Si layer**
  - Partial pyro reduces Br
  - Reduces tensile stress
    - no delamination
- **Produced Br-doped capsules for mix and burn study**

<table>
<thead>
<tr>
<th>Methods</th>
<th>Br atom in layer 1</th>
<th>Br atom in layer 3 (2 at.% Si layer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular pyro</td>
<td>$3 \times 10^{16}$</td>
<td>$1.7 \times 10^{17}$</td>
</tr>
<tr>
<td>O$_2$ pre-soak</td>
<td>$3.7 \times 10^{16}$</td>
<td>$4.3 \times 10^{16}$</td>
</tr>
<tr>
<td>Pre-drilled</td>
<td>$4.0 \times 10^{16}$</td>
<td>$9 \times 10^{16}$</td>
</tr>
<tr>
<td>2-step pyro</td>
<td>$2.3 \times 10^{16}$</td>
<td>$1.9 \times 10^{16}$</td>
</tr>
</tbody>
</table>