Characterization of W and C surfaces exposed to low energy plasmas and ion beams

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overview

- **Part 1:**
  - Characterization of surface morphology and retention in tungsten materials exposed to high fluxes of D ions.

- **Part 2:**
  - The impact of specific surface area on the retention of D in carbon fiber composites.

- **Part 3:**
  - Low energy ion scattering measurements of W surfaces.

- **Part 4:**
  - Testing of tritium permeation barriers.
**Motivation:** W is known to blister when exposed to low energy H plasmas.

- Tritium can precipitate in blister cavities and other voids beneath the surface, affecting transport into the material.
- Melting of blister caps is possible during transient high heat loads, providing a contamination mechanism for the core plasma.

**Experiment:** Tungsten samples were exposed to a high flux, low energy deuterium plasma in the Tritium Plasma Experiment (TPE) over a range of temperatures \(147 \degree C \leq T_{\text{surf.}} \leq 704 \degree C\).

**Surface characterization:**

- Vertical scanning interferometry
- SEM
- AES (depth profiling)
- XRD

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surface profilometry results

Exposure conditions: $E=70$ eV, $\Phi=1.1\times10^{22}$ m$^{-2}$s$^{-1}$, $F=8.7\times10^{25}$ m$^{-2}$

Sample material: Warm rolled PLANSEE W, annealed for 1 hr at 1000 °C, 1 mm thick

Note: Each panel above represents a 500 μm × 500 μm area.
SEM images

- SEM results provide insight into the size of blisters relative to the grain boundaries.
- Blisters found in this study (PLANSEE W) are much larger than those observed under similar exposure conditions with re-crystallized W.
- Small fissures visible in blister caps located at grain boundaries, suggesting release of D is possible.
Auger depth profiling

- AES depth profiles obtained using 500 eV Ar\(^+\) ions to sputter the target material; etch rate is 10 Å/min.
- For 385 °C ≤ \(T_{\text{surface}}\) ≤ 561 °C, a carbide layer was formed up to depths of 30-40 nm deep into the material (corresponds to more highly blistered cases.)
- Samples exposed outside of this temperature range showed no carbide formation.
- XRD confirms carbide layer exists prior to AES depth profiling (i.e. carbide not created by Ar beam.)
- Due to T contamination concerns, it was not possible to analyze sample until after TDS.
- Further work in this area is needed to determine root cause of carbide formation.
Motivation: Internal porosity of CFC materials can affect retention of hydrogen isotopes in carbon fiber composites. Our objective is to determine the effect of specific surface area on retention directly.

Experiment:
- Performed specific surface area measurements for CFC N11, and Hitco and K-Karb composites.
- Samples exposed to a low energy (130 eV), high flux (2×10^{22} m^{-2}s^{-1}) plasma in PISCES-A (UCSD) at a sample temperature of 200 °C.

Test Matrix: SEM images showing the fiber structure of the plasma exposed surfaces of the CFC tiles: (a) Hitco CC139C (b) Hitco CC389L (c) K-Karb (d) N11, showing side view of fiber bundle (e) N11, showing end view of fiber bundle. The 100 μm scale applies to images (a)-(d), and the 20 μm scale applies to image (e).

The Brunauer-Emmett-Teller (BET) gas adsorption technique was used to determine the specific surface area of the samples.

Experimental Analysis:
- Measurements obtained with a Micromeritics ASAP 2000 instrument with Kr gas serving as the adsorptive.
- Adsorption isotherms for Hitco and K-Karb composites show a marked increase in the volume of gas adsorbed \( V_a \) at a pressure ratio \( P/P_0 \approx 0.3 \). (A non-porous material would be characterized by a linear increase in \( V_a \) until \( P/P_0 \approx 0.9 \).)
- Composite N11 shows a much more abrupt change in \( V_a \) at \( P/P_0 \approx 0.3 \).

**BET isotherms indicate each material contains a population of mesopores (>2 nm in diameter) in addition to a population of macropores (>50 nm in diameter).**

**BET Results:** BET surface areas for the materials described in this study ranged from 0.14-0.55 m²/g (CFC N11 had a BET surface area of 0.37 m²/g.)
CFC retention results

**Results:**
- A strong correlation is noted between retention and BET surface area.
- Results compared with exposure of N11 composite from a recent study by Roth [1] under nearly identical conditions in PISCES-A.
- Measurements show a factor of 5 reduction in retention may be achieved using a material with lower BET surface area.
- Further studies needed with the NB31 composite.

<table>
<thead>
<tr>
<th>CFC type</th>
<th>BET surface area (m²/g)</th>
<th>Fluence (m²)</th>
<th>Retention (m²)</th>
<th>Retained Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Karb</td>
<td>0.14</td>
<td>5×10²⁵</td>
<td>5.6×10²⁰</td>
<td>1.1×10⁻⁵</td>
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<tr>
<td>Hitco CC139C</td>
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<td>3.0×10²⁰</td>
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<td>2.0×10⁻⁵</td>
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<td>1×10²⁶</td>
<td>2.5×10²¹</td>
<td>2.5×10⁻⁵</td>
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<td>CFC N11</td>
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<td>Hitco CC389L</td>
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<td>2.6×10²¹</td>
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</tbody>
</table>

part 3: low energy ion scattering measurements

- Low energy ion scattering (LEIS) measurements of W surfaces
  - Low energy ion scattering is one of the only techniques capable of detecting H on surfaces.
  - Can provide detailed information regarding H recoil processes from surfaces, adsorbate binding sites, and binding energies.

Local atomic structure derived from shadowing effects.

- Incident ions are deflected around target atoms.
- A shadow cone represents a region behind the scattering center where incident ions can not reach.
- Beam angle of incidence $\alpha$ can be related to an intersection distance on the target surface $d$.
- Scattering intensity enhanced when shadow cone envelope intersects neighboring atoms.
H recoil maps for W(100)

(a) Dosed with molecular hydrogen
(b) Residual hydrogen

Which H binding site is preferred?
**shadowing mechanisms**

Structure associated with bridge site more prominent when the sample is dosed with H$_2$(g).

Pattern sensitive to height of H above surface.

$h_{bridge} = 1.25$ Å

$h_{4\text{-fold}} = 0.4$ Å
MARLOWE simulations reproduce the experimental recoil maps if binding in both four-fold hollow and bridge sites are assumed.

The differences between the recoil patterns from the two sites is striking.
Tritium Permeation Barriers are Needed for ITER and DEMO

Gas driven permeation of various materials is being studied
Current system: $T \leq 500 \, ^\circ\text{C}$ and deuterium gas ($< 1 \, \text{atm}$)
Example: $\text{ZrO}_2$ on Zircaloy-4 used in current fission reactors

Newly designed system under construction for studying SiC (SBIR with Ultramet)
$T \leq 1000 \, ^\circ\text{C}$
Improved sensitivity (mass discrimination)
Oxidation control
Concluding remarks / future work

• Part 1: Surface morphology and retention of D in W
  – Blister formation on W showed a strong temperature dependence, with largest defects approximately 10 μm high.
  – More analysis needed to determine the cause of carbide formation.

• Part 2: The impact of specific surface area on CFC retention
  – Test matrix included four different CFC materials, including the N11 composite used in Tore Supra.
  – BET measurements indicate surface connected porosity consisting of populations of mesopores (>2 nm dia.) and macropores (>50 nm dia.)
  – Strong dependence of retention on BET surface area.
  – For better comparison with NB31 data of Roth, we need to consider lower flux / lower fluence measurements.

• Part 3: Low energy ion scattering measurements of the W surface
  – Determined height and binding site of H adsorbed on W(100).
  – Further work will include monitoring surface concentration with temperature to determine the binding energy.
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