Nuclear Graphite - Fission Reactor
Brief Outline of Experience and Understanding

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Overview

- Nuclear Graphite – Use, Manufacture, Microstructure
- Irradiation Damage to Crystal Structure
- Radiolytic Oxidation
- Physical Changes – to Polycrystalline Graphite due to Fast Neutron Damage and Radiolytic Oxidation
- Irradiation Creep
Use of Graphite in the Nuclear Industry

- **Moderator**
  - Slow down neutrons by scattering
  - High scatter cross-section
  - Low absorption cross-section

- **Reflector**
  - Reflects neutrons back into the core
  - Protect surrounding supports structure and pressure vessel

- **Major Structural Component**
  - Provided channels for control rods and coolant gas

- **Neutron Shield**
  - Boronated graphite

- **Thermal columns in research reactors**

- **Moulds for casting uranium fuel**
Type of Graphite Moderated Reactors

- **Air-cooled**
  - Chicago Pile, GLEEP, BEPO, Windscale Piles, G1-France

- **Light Water-cooled Graphite Moderated**
  - Hanford, Russian-PPR, RBMK

- **Carbon Dioxide Cooled**
  - UK and French Magnox reactors, AGR

- **Helium Cooled**
  - Dragon, Peach Bottom, Fort St. Vrain, THTR, AVR
  - HTR, HTR-10 China, HTTR Japan, PBMR South Africa
  - Generation IV - VHTR

Chicago Pile 1
Typical Graphite Components

Torness Core – During Construction

HTR-10 During Construction in China
RAW PETROLEUM OR PITCH COKE

CALCINED AT 1300°C

CALCINED COKE

CRUSHED, GROUND & BLENDED

BLENDED PARTICLES

PITCH

MIXED

EXTRUDED OR MOULDED

COOLED

GREEN ARTICLE

BAKED AT ~1000°C

BAKED ARTICLE

IMPREGNATED WITH PITCH

FURTHER IMPREGNATION AND BAKING AS REQUIRED

GRAPHITISED AT ~2800°C

GRAPHITE
Final Product

• Either anisotropic or semi-isotropic product
  – Modern reactors use graphite with semi-isotropic properties
• Significant porosity ~20%
  – ~10% open porosity, ~10% closed porosity
  – Density 1.72 – 1.8g/cm³ compared to 2.26g/cm³ for perfect graphite crystal
• High purity – impurities measured in parts per million (ppm)
• Nuclear designer requires
  – Semi-isotropic 1.1 Defined by Coefficient of Thermal expansion (CTE) in orthogonal directions
  – High density
  – Optimum material properties
  – High thermal conductivity
  – High purity (neutronic and waste point of view)
  – Dimensional stability under irradiation, associated with high CTE $\sim 4 \times 10^{-6} \text{K}^{-1}$ (20-120°C)
Pile Grade A Microstructure – Anisotropic

Binder phase

~0.5 mm

Needle coke filler particle

More spherical porosity in binder phase

Longitudinal porosity within filler particles
<table>
<thead>
<tr>
<th>Grade</th>
<th>ZXF-5Q</th>
<th>AXF-5Q</th>
<th>Gilscarbon</th>
<th>IG-430</th>
<th>IG-110</th>
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</thead>
<tbody>
<tr>
<td>Comment</td>
<td>candidate</td>
<td>similar to AXF-8Q1 (US historical experience)</td>
<td>UK AGR experience</td>
<td>Japanese &amp; EU experience</td>
<td>Japanese &amp; EU experience</td>
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<tr>
<td>Particle size (µm)</td>
<td>1</td>
<td>5</td>
<td>500</td>
<td>10</td>
<td>20</td>
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<tr>
<td>Pore size (µm)</td>
<td>0.3</td>
<td>0.8</td>
<td>42</td>
<td>-</td>
<td>16</td>
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<tr>
<td>Density (g/cm³)</td>
<td>1.78</td>
<td>1.78</td>
<td>1.81</td>
<td>1.82</td>
<td>1.77</td>
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<tr>
<td>Comp. strength (MN/m²)</td>
<td>175</td>
<td>138</td>
<td>70</td>
<td>97</td>
<td>79</td>
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<tr>
<td>Flex. strength (MN/m²)</td>
<td>112</td>
<td>86</td>
<td>23</td>
<td>52</td>
<td>40</td>
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<tr>
<td>Tensile strength (MN/m²)</td>
<td>79</td>
<td>62</td>
<td>18</td>
<td>38</td>
<td>27</td>
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<tr>
<td>Modulus (GN/m²)</td>
<td>14.5</td>
<td>11.0</td>
<td>10.8</td>
<td>10.8</td>
<td>9.7</td>
</tr>
<tr>
<td>CTE (10⁻⁶ K⁻¹)</td>
<td>8.1</td>
<td>7.9</td>
<td>4.3</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Thermal conduct. (W/m K)</td>
<td>70</td>
<td>95</td>
<td>131</td>
<td>143</td>
<td>135</td>
</tr>
</tbody>
</table>
Computed X-ray tomography images of various grades of graphite
Crystal structure

- lattice spacing
  - $a = 2.4612 \times 10^{-10} \text{ m}$
  - $c = 6.7079 \times 10^{-10} \text{ m}$
- alternately stacked planes
  - $335 \times 10^{-12} \text{ m}$
- density
  - $2.66 \text{ g/cm}^3$
- CTE
  - $\alpha_a = -1.25 \times 10^{-6} \text{ K}^{-1} (20-120^\circ \text{C})$
  - $\alpha_c = 26 \times 10^{-6} \text{ K}^{-1} (20-120^\circ \text{C})$
Irradiation damage to graphite Crystallites

- Damage leads to crystal changes:
  - Stored energy (Significant below irradiation temperatures 150°C, insignificant above 350°C)
  - Dimensional changes
  - Thermal conductivity changes
  - Modulus changes
  - Strength changes?
  - No Coefficient of Thermal Expansion (CTE) changes above ~300°C
  - Irradiation creep (when under stress)
Fast Neutron Damage

- Thermal reactor neutron energies up to 10MeV, average 2MeV
- About 60eV to permanently displace a carbon atom from the lattice
- Most damage due to fast neutron energies > 0.1 MeV
- Cascade caused by primary and secondary knock-ons
- Interstitial and vacancy loops are formed
- Size of loops depends on irradiation annealing
- Change in crystallite behaviour at an irradiation temperature of about 250°C
- A measure of damage is irradiation “dose” of “fluence” units:
  - displacements per atom “dpa”
  - \( \text{n/cm}^2 \) - Equivalent DIDO Dose (EDND)
  - \( \text{n/cm}^2 \) – with energies greater than 0.18MeV (\( \text{En}>0.18\text{MeV} \))
  - nvt – neutron velocity time
Formation of interstitial and vacancy loops

Cascade

Interstitial defects

(a) Interstitial defects
(b) Interstitial loops

Sub-microscopic cluster of interstitials

Layer planes

(1) Single vacancy
(2) $D_1$-vacancy

Increase in dose

Interstitial loop
Interstitial diffusing to loop

(3) Vacancy line (Schematic)

(4) Vacancy loop
(Circular or hexagonal in-plane)

Vacancy loops
Irradiation defects in graphite crystals (HOPG) (x 20,000)

200°C, 1.5 x 10^{20} (nvt)

350°C, 2.1 x 10^{20} (nvt)

650°C, 1.7 x 10^{20} (nvt)
Significant change in rate between 200 and 250°C

Crystal Dimensional Changes measured in HOPG with increasing Dose

Perpendicular to the Basal Plane

Parallel to the Basal Plane
Upon heating, a gradual closure of cracks was observed because of the thermal expansion of the graphite crystallites surrounding the cracks.
Closure of a crack in Gilsocarbon after In-situ electron irradiation. The feature with bright contrast does not disappear completely. Note a small part of crack (indicated by arrow), which was covered by the electron beam has not closed completely.
Radiolytic Oxidation

- Two types of oxidation can occur in CO₂.
  - Thermal oxidation is a purely chemical reaction between graphite and CO₂.
  - Reaction is endothermic, is negligible below about 625°C and is not important up to 675°C.
  - Only an issue for HTRs

- Radiolytic oxidation occurs when CO₂ is decomposed by fast neutron and gamma radiation (radiolysis) to form CO and an active oxidising species which attacks the graphite porous structure.
  - Radiolytic oxidation occurs predominantly within the graphite pores.
  - Overall component geometry stays essentially the same
Radiolytic Oxidation

- The mechanism of radiolytic oxidation is:
  - Gas Phase
    \[ \text{CO}_2 \xrightarrow{\text{radiation}} \text{CO} + \text{O}^* \]
    \[ \text{CO} + \text{O}^* \rightarrow \text{CO}_2 \]
  - Graphite Pore Surface
    \[ \text{O}^* + \text{C} \rightarrow \text{CO} \]
- Definition
  - \( G_c \) is the number of carbon atoms gasified by the oxidising species produced by the absorption of 100eV of energy in the \( \text{CO}_2 \) contained within the graphite pores.
Irradiation Damage in Polycrystalline Graphite

- Crystal changes modify polycrystalline dimensions and properties through the microstructure
  - Stored Energy – Only significant below 150°C, negligible at 350°C
  - Dimensional changes
  - CTE
  - Young’s modulus
  - Strength
  - Thermal conductivity
  - Irradiation creep (when under stress)
- Radiolytic oxidation further modifies these properties
- Semi-isotropic graphite is considered in the next section
Graphite Irradiation Behaviour – Isotropic Gilsocarbon irradiated at 550°C

Coefficient of Thermal Expansion change (Red)

Volume change (Blue)

Young’s modulus change (Green)

Thermal Resistivity change (Yellow)
Shrinkage of CSF Graphite Irradiated at 800°C to various Irradiation Doses
Gilsocarbon Dimensional Changes

Gilsocarbon Dimensional change

Higher temperature

GCMB and IM1-24 data

Mrozowski cracks

Figure 5.8: Dimensional changes of pyrolytic graphite.
Unirradiated Gilsocarbon Specimens
7mm long by 5mm dia.

285 x 10^{20} \text{ n/cm}^2
EDND

+0.9\% \Delta V/V_0

Swelling Gilsocarbon particles

Swelling Gilsocarbon particles
Gilsocarbon irradiated to $271 \times 10^{20}$ n/cm$^2$
EDND 33% $\Delta V/V_o$
Gilsocarbon Coefficient of Thermal Expansion

![Graph showing the relationship between dose and CTE at different temperatures.](image)

- **Increasing Temperature**
  - At R.T.
  - At 800°C
  - At 940°C & 1240°C
  - At 600°C
  - At 430°C

Mrozowski crack closure
Gilsocarbon Thermal Resistivity

High dose secondary increase due to microstructural damage

GCMB Data

430°C
600°C
940°C
1240°C
Gilsocarbon Change Young’s Modulus

Gilsocarbon Young’s Modulus

Pinning

Structure

Rapid reduction at high dose

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>E/E₀ - 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td></td>
</tr>
<tr>
<td>940</td>
<td></td>
</tr>
<tr>
<td>1240</td>
<td></td>
</tr>
<tr>
<td>1430</td>
<td></td>
</tr>
</tbody>
</table>
Reduction in properties due to radiolytic oxidation

• The black symbols are drilled specimens indicating the loss of section is a major factor
Irradiation Creep in Graphite

- Due to fast neutron irradiation
- Significantly reduces stresses in nuclear graphite components
- Definition
  - The difference in dimensions between a stressed sample and a sample having the same properties as that sample when unstressed
Dimensional Change Under Load
Example ATR-2E Graphite

- Under compressive load shrinkage is increased
  - Upper right
- Under tensile load shrinkage is decreased
  - Lower right
- There is also a lateral (Poisson's) effect
  - Below
Irradiation Creep Curves

Example ATR-2E (500°C)

- Irradiation creep curve can be simply obtained by subtraction of the unloaded dimensional change curve from the crept dimensional change curve.

- However, for assessments this would require data for a range of temperatures and fast neutron fluence covering all the expected conditions.

- In addition changes to the Coefficient of Thermal Expansion (CTE) and Young’s modulus have been observed.
Issues to consider

• Properties
  – thermal conductivity
  – thermal shock resistance
  – modulus of elasticity
  – tensile strength
  – CTE
  – dimensional change & irradiation creep
    • initial compressive stress

• Protons versus neutrons
  – dose rate effect (pulsed versus continuous)
  – helium production

• POCO
  – historical experience