Radiation Damage in Nuclear Graphite

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Sponsors:
Content

• Introducing graphite as a neutron moderator
• What happens to graphite in a nuclear reactor?
• Radiation damage through the length scales
  • Nanoscale – dislocations
  • Microscale – cracks and pores
• Future of graphite moderated reactors
• Summary
Graphite moderated reactors

- > 80% current UK nuclear reactors
- Graphite:
  - Moderates neutron energy
  - Accommodates fuel and control rods
  - Cooled by CO$_2$ coolant
  - Low atomic weight
  - Low thermal neutron absorption cross section
  - High scattering cross section
  - High thermal conductivity
  - Low thermal expansion coefficient
Graphite moderated reactors

Other important properties:
- Can be machined into intricate shapes
- Very high melting point (4027 °C)
- Very resistant to thermal shock
- Provide large heat sink in case of thermal transients

Challenges
- Irradiation induced dimensional change (up to 8%)
- High anisotropy
- Radiolytic and thermal oxidation (in air/CO₂ coolant/T>500°C)
- Longer lifetime for new reactors
Graphite moderated reactors

Nuclear reactor

Fuel rods
Control rods
Coolant channel
Graphite core

(002) planes

Changes in strength, porosity, dimension etc.

Neutrons bombard the graphite moderator and transfer energy

High energy neutrons released from fission events

Uranium fission
High energy neutrons
Energy demand vs. reactor closure

- EDF Energy: 4 new EPRs (6.4GW) at Hinkley Point in Somerset and Sizewell in Suffolk.
- Hitachi Ltd: 2 or 3 new nuclear reactors at Wylfa on Anglesey and the same at Oldbury.
- NuGeneration: up to 3.6GW of new nuclear capacity at Moorside, near Sellafield.

It is increasingly recognised that existing “mechanistic” models do not fully explain the observed behaviour of graphite in these reactors. There are substantial gaps in understanding, which have become apparent.

The consortium investigated irradiation induced dimensional change, creep, and other property changes using various complementary characterisation techniques.
• Nanoscale (0.1 to 100 nm)
  • TEM, EELS, FIB, SEM, SPM, SANS, Raman, XRD
  • DFT, MD, kMC, Ab initio modelling

• Microstructure (100nm-10micron)
  • XRD, Raman, EELS, tomography
  • Dislocation theory

• Crystallite scale (10μm to mm)
  • XRD, EELS,
  • DFT, FE modelling

• Macroscopic (Component) modelling: (mm to m)
  • FE modelling
Manufacture

Removes volatiles HCs

Extrusion:
Alignment of filler particles

Shrinkage

Crystal growth, diffusion and annealing

“Filler”

“Binder”

2.3 mm
Manufacture

1. Filler
2. Binder
3. Voids

Voids arise during manufacture and operation.
(T / F gradients, CTE anisotropy, internal stresses)
Atomistic model of neutron damage

NANOSCALE: BONDING AND DENSITY ANALYSIS

A 1 MeV neutron produces ca. 500 atomic displacements

\[ \Delta E = \frac{4A}{(A + 1)^2} E_n \]

\[ \Delta E = 0.28E_n \]

PKA = primary knock on atom
SDG = secondary displacement group

vacancy
interstitial

The cascade model

PKA
SDG
Atomistic model of neutron damage
NANOSCALE: BONDING AND DENSITY ANALYSIS

Problems:

- Assumes flat graphite layers
- No quantitative fit with experiment for dimensional change
- First principles calculations show that interstitial is much less mobile than thought
Multiple basal plane dislocations
Single vacancies and interstitials
Di-vacancies and interstitials
Prismatic dislocation loops
Basal/edge dislocation
Stone-Wales defect
Screw dislocation
Stacking faults
Ruck and tuck
Voids

Heggie et al. J. Nuc Mat 413(3) (2011)
Quantification of radiation damage
NANOSCALE: BONDING, DENSITY AND DISLOCATION ANALYSIS

Transmission Electron Microscopy

Selected Area Electron Diffraction

In-situ TEM

Electron energy loss spectroscopy
High voltage

Accelerated electrons

High energy electrons

Small wavelength

High resolution

\[ n\lambda = 2ds\sin\theta \]

\( \lambda \text{(light)} \quad 400 – 750 \text{ nm} \)

\( \lambda \text{(e\textsuperscript{-})} \quad 1 – 4 \text{ pm} \)

TEM facility at Leeds

Image from the Super-STEM facility, UK
Quantification of radiation damage
TRANSMISSION ELECTRON MICROSCOPY

1.3 x 10^{20} \text{ e}^{-}\text{cm}^{-2}

5.1 x 10^{20} \text{ e}^{-}\text{cm}^{-2}

3.3 x 10^{21} \text{ e}^{-}\text{cm}^{-2}

(002) Graphite planes

200 \text{ kV}
5 \text{ nm}

(002) Graphite planes

200 \text{ kV}
5 \text{ nm}

(002) Graphite planes

200 \text{ kV}
5 \text{ nm}

(002) Graphite planes

80 \text{ kV}
5 \text{ nm}

(002) Graphite planes

80 \text{ kV}
5 \text{ nm}

(002) Graphite planes

80 \text{ kV}
5 \text{ nm}
Quantification of radiation damage

2D image analysis and 3D image reconstruction and modelling of Pyrocarbons
Transmission electron microscopy
NANOSCALE: 002 FRINGE ANALYSIS

Mironov & Freeman. Carbon 83 106 – 117(2015) / Image analysis software courtesy of 'PyroMaN' research group – University of Bordeaux
Transmission electron microscopy

NANOSCALE: 002 FRINGE ANALYSIS

Electron diffraction → Young’s double-slit experiment
Selected area electron diffraction
NANOSCALE: 002 FRINGE ANALYSIS

Software courtesy of Anne Campbell, Oak Ridge National Lab, USA
Transmission electron microscopy
NANOSCALE: 002 FRINGE ANALYSIS – INSITU HEATING

Images courtesy of University of York in-situ TEM facilities

Literature* quotes the migration energy of a single vacancy is 1.2 eV, i.e. mobile at temperatures above 100-200 °C

Transmission electron microscopy
NANOSCALE: 002 FRINGE ANALYSIS – IN SITU HEATING

Change in d-spacing over time at 100 °C and 200 kV

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<th>d-spacing (nm)</th>
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Change in fringe length over time at 100 °C and 200 kV

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<th>Time (minutes)</th>
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<td>10</td>
<td>15</td>
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<td>10</td>
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</tbody>
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0.001 dpa /s

Images:
- t = 0
- t = 14 min
Electron Energy Loss Spectroscopy
NANOSCALE: BONDING AND DENSITY ANALYSIS

“finger print of local bonding”
1. Valence electron density (N)
2. Planar sp² content
3. C-C bond length

\[ E_p = \frac{\hbar}{2\pi} \left( \frac{N e^2}{m_0 \epsilon_0} \right)^{0.5} \]

**C-K core loss**

**Low loss**

- Zero Loss Peak (ZLP)
- Bulk plasmon peak

Electron irradiation damage series

- D = 0.267 dpa
- D = 0.209 dpa
- D = 0.113 dpa
- D = 0 dpa

Multiple Scattering Resonance
1. Valence electron density (N)
2. **Planar sp² content**
3. C-C bond length

\[ \text{sp}^2 \text{ content} \propto \frac{\text{Integration 1}}{\text{Integration 2}} \]

**Integration 1**  **Integration 2**

**C-K core loss**

- D = 0.267 dpa
- D = 0.209 dpa
- D = 0.113 dpa
- D = 0 dpa

**Multiple Scattering Resonance**

Energy Loss (eV)

265 285 305 325 345

Electron irradiation damage series
1. Valence electron density ($N$)
2. Planar sp$^2$ content
3. C-C bond length

\[
E_{MSR} = \frac{K_{MSR}}{R_{MSR}^2}
\]

**C-K core loss**

- $D = 0.267$ dpa
- $D = 0.209$ dpa
- $D = 0.113$ dpa
- $D = 0$ dpa

Electron irradiation damage series

- Excited carbon atom
- Carbon atom
- 1$^{\text{st}}$ shell
- 2$^{\text{nd}}$ shell

Energy Loss (eV)

270 290 310 330 350

Electron irradiation damage series
Electron Energy Loss Spectroscopy

NANOSCALE: BONDING AND DENSITY ANALYSIS

Variation in plasmon peak energy

\[ E_p \propto \sqrt{N_{e^-}} \propto \sqrt{N_{bulk}} \]

Variation in C-C bond length

\[ E_{MSR} \propto \frac{1}{(L_{C-C})^2} \]

Variation in \( sp^2 \) content

\[ sp^2 \propto \frac{I_{\pi^*}}{I_{\pi^*+\sigma^*}} \]

Quantification of radiation damage
NANOSCALE: BONDING, DENSITY AND DISLOCATION ANALYSIS

Transmission Electron Microscopy
- 002 graphite planes
- Reduction in fringe length and increase in tortuosity

Selected Area Electron Diffraction
- Increase in d-spacing

In-situ TEM
- 400 °C (002) Graphite planes
- Temperature dependent damage threshold

Electron energy loss spectroscopy
- Reduction in sp2 content, increase in C-C bond length, slight reduction in density
• Voids
  • Closed porosity (OLM) in filler
  • Open porosity (FLM) in binder
Porosity related property changes

Matsuo J. Nuc. Mat 89(1) (1980) (Effect of oxidation at 1000°C)


(a) BEPO1 was farthest from the core and received 0.4 dpa (displacements per atom)
(b) BEPO16 was in the middle of the channel and received 1.27 dpa
(c) BEPO20 was closest to the core and received 1.44 dpa

5 - 200 nm x < 10μm
Examples of EDX spectra over a microcrack in BEPO1

negligible Ga content (0.12%)

significant Ga content (5.85%)
Void and Crack Analysis
MICROSCALE: ENERGY FILTERED TEM

Energy Filtered TEM

magnetic prism → path of the electrons will vary depending on their energy.

loss of energy and a change in momentum
Void and Crack Analysis
MICROSCALE: ENERGY FILTERED TEM

Contrast in TEM image from:
- Thickness and graphitic nature of material

Contrast in EFTEM image from
- Graphitic nature of material only

Dark = disordered (or hole)
Light = graphitic

Intensity calibration from Daniels et al. Ultramicroscopy 96(3) 547-58 (2003)
Energy ($E_p$) $\propto$ density ($N$)

$$E_p = \frac{h}{2\pi} \left( \frac{Ne^2}{m_0\varepsilon_0} \right)^{0.5}$$
Changes in Crystallite Size
MICROSCALE: X-RAY DIFFRACTION

XRD spectrum for virgin graphite (PCEA grade)

**L\textsubscript{c}** value (crystallite dimension)

L\textsubscript{c} value (crystallite dimension)

Damaged material is evident through changes in:

1. Peak position
2. Peak width (FWHM) by the Scherrer equation

\[ \tau = \frac{K\lambda}{\beta\cos\theta} \]

\( \tau \) = mean size of the crystallite
\( K \) = shape factor
\( \lambda \) = X-ray wavelength
\( \beta \) = broadening at FWHM
\( \theta \) = Bragg angle
Changes in Crystallite Size
MICROSCALE: X-RAY DIFFRACTION

virgin
1.5 dpa
350 °C

4.0 dpa
535 °C

6.8 dpa
670 °C

Work of Brindusa Mironov pmbem@leeds.ac.uk | Samples provided by Will Windes INL
Changes in Crystallite Size
MICROSCALE: X-RAY DIFFRACTION

- <1 % ↑ c spacing
- < 1% ↓ a spacing
- Decrease in both $L_a$ and $L_c$ with irradiation dose and temperature by up to 50%.
- i.e. crystals are breaking up and getting smaller but are experiencing *intra-crystalline* dimensional change
Results Summary

- Neutron radiation induces chemical and physical property changes
  - Atomic displacements $\rightarrow$ expansion of graphite planes (in $c$-direction) $\rightarrow$ contraction of graphite planes (in $a$-direction) $\rightarrow$ increased tortuosity and length of graphite planes $\rightarrow$ change in bonding
  - Breaking up of crystallites
  - Formation of cracks and closure of cracks with swelling (at turnaround)
Future of Nuclear Graphite

Gen IV Very High Temp Reactor

- Cogeneration of electricity and hydrogen
- Outlet temperature 1000°C
- TRISO coated particle fuel

Collaborations/Acknowledgments

Anne Campbell
Oakridge National Lab
Diffraction pattern analysis software (‘GAAP’)

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SuperSTEM Daresbury
HRTEM, EELS analysis

Will Windes
Idaho National Lab
Radioactive sample provision

Kazu Suenaga
National Institute of Advanced Industrial Science and Technology (AIST)
TEM graphene specialist

PyroMaN research group
University of Bordeaux
EELS and TEM analysis, sample preparation

+ Universities of Leeds, York, Huddersfield, Manchester & Surrey
Nuclear Summer School

- To respond to the nuclear skills gap
- Studying the whole nuclear fuel cycle, nuclear materials, waste/storage, nuclear policy
- A mix of lecture and laboratory sessions
- Introduction to university life at Leeds

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