The Temperature Dependence of Defect Evolution in Irradiated Graphite

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Initially, a decrease in volume is observed, followed by the "turnaround" point. With prolonged neutron dose, volume then increases, reaching "Crossover" where the graphite component is expanding beyond its original dimensions. "Crossover" marks the lifetime of the graphite component. For high-temperature irradiation, turnaround/crossover occurs at a relatively low dose.
‘General’ Accepted Atomic Mechanism for $c$-axis Expansion

Dark field TEM image showing dislocation loops found in neutron irradiated natural graphite.

Ex-Situ Observations of Dislocation Loops

As-prepared natural graphite showing many defects exist intrinsically
In-Situ TEM

- Electrons may be used as a substitute for fast neutrons
- ROIs may be observed prior to irradiation experiments
- Allows monitoring of the atomic response ‘live time’ as irradiation damage is accumulated
- In-situ heating of specimens
- Models the environment found in nuclear reactors
Diffraction Techniques With Single Crystal Natural Graphite

- Use diffraction techniques for observation of dislocation loops
- Irradiate single crystal natural graphite with a large field of view
• The mechanism contributing to the “mottled contrast” remains unclear
• Preliminary \( g \cdot b \) analysis shows no significant change in contrast
• Defect domains are believed to be too small for diffraction analysis
HRTEM Studies on Polycrystalline IG-110

• Image specimens perpendicular to the c-axis

• Observe the dynamic evolution of defects ‘live time’ with video recordings of in-situ electron-irradiation

[HRTEM micrograph of IG-110 imaged perpendicular to the c-axis.]
In-Situ Electron-Irradiation at Room Temperature

• Defects are created and annihilated rapidly

• However, no stable dislocation loops have been observed via in situ electron-irradiation at room temperature studies

• No clear consensus on atomic mechanisms controlling irradiation induced defect evolution at room temperature

IG-110 irradiated at room temperature with a 200kV electron beam for approximately 30s (2X Normal speed).
Curling and closure via solely thermal annealing (800°C)

At RT no curling, closure or reconstruction of basal planes.

At 800°C and ~0 dpa, curling and closure of basal planes resulting in localized swelling.

Curling and closure of basal planes within disordered regions of microstructure and interstitially.

Self Organization of Carbon Species Due to Irradiation - Fullerene Transformation

- Significant amount of In-situ electron irradiation experiments at elevated temperatures (not specific to NG)

- Almost all graphitic precursors such as soot particles, or any disordered graphitic filaments, will show fullerene transformations when irradiated with an electron beam of sufficient intensity

Simulated TEM images of the transformation of a graphene sheet into a fullerene when subjected to electron irradiation. A. Chuvilin et al., Nat. Chem. 2 (2010), p.450

Bright-field TEM micrographs of IG-110. (a) the termination of a filler particle and (b) a QI particle
High-Temperature Electron-Irradiation

- In situ electron irradiation conducted on IG-110 at 800°C (8X normal speed)

- Formation of carbon onions

High-Temperature Electron-Irradiation

• In situ electron irradiation conducted at 800°C

• Formation of fullerene like structures

• Curling and closure of basal planes (observed by thermal annealing alone)
IG-110 nuclear graphite irradiated at 800°C showing the formation of an interstitial carbon nanostructure. S. Johns et al., Carbon 143 (2019), p.908.
High temperature electron irradiation does not show evidence of additional basal planes

In situ analysis show interstitially formed carbon nanostructures resulting in 51% expansion along the \( c \) – axis of the crystallite

Are Electrons Comparable to Fast Neutrons?

- For electron-irradiation, the dose rate is generally observed to be $10^{-4} - 10^{-3}$ dpa/s
- That of typical neutron-irradiation is $10^{-7}$ dpa/s
- Electrons (200keV) do not cause cascade damage (isolated point defects)
- Given the high operating temperatures of nuclear reactors, cascade damage is believed to partially anneal (approximated net effect of isolated point defects)
- Electron-irradiation must be compared to neutron-irradiation at similar dose and temperature
Neutron Irradiated IG-110 – Irradiated at ~815°C to 3.56 dpa

• HRTEM studies of neutron irradiated IG-110

• Formation of fullerene like structures occurring within a Mrozowski crack
Temperature Dependent Mechanism

NBG-18
Neutron irradiated at $678^\circ\text{C}$ to a dose of $6.78\text{ dpa}$

IG-110
Neutron irradiated at $815^\circ\text{C}$ to a dose of $3.56\text{ dpa}$
Neutron Irradiated IG-110 – Irradiated at ~815°C to 3.56 dpa
Neutron Irradiated IG-110 – Irradiated at ~815°C to 3.56 dpa
Macroscopic Theory for Volumetric Change

• Initial volumetric shrinkage is accommodated by pore closure

• However, high-temperature HRTEM studies suggest the accommodating Mrozowski cracks may be ‘filled’ by fullerene-like defects

• Potentially, prior to significant $c$-axis expansion, some of the porosity may no longer accommodate $c$-axis expansion (early turnaround)

c-axis expansion in high-temperature irradiated graphite

Schematic of the Buckle, ruck and tuck model proposed by M.I. Heggie et al., Journal of Nuclear Materials 413 (2011), p.150
Neutron Irradiated IG-110 - 3.56 dpa at ~815°C
Neutron Irradiated IG-110 - 3.56 dpa at ~815°C
Conclusions

• High-temperature electron-irradiation does not show evidence of the formation of additional basal planes (HRTEM or diffraction techniques)
• Given disordered regions of the graphite microstructure, high-temperature electron-irradiation shows the formation of fullerene-like defects will occur at low a relatively low dose ~2dpa
• Preliminary results from neutron irradiated IG-110 (3.56 dpa at ~815°C) suggest accommodating Mrozowski cracks may be ‘filled’ by fullerene-like defects (carbon onions or other)
• The formation of such defects could potentially be a mechanism contributing to early turnaround behavior in high-temperature irradiated nuclear graphite
• First experimental evidence supporting “Buckle, ruck and tuck”
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EELS Analysis of Irradiated Natural Graphite

• EELS analysis of the C K-edge at elevated irradiation temperatures suggesting the graphite structure is retained

• Natural graphite irradiated at 25°C shows the most amount of change in bonding character

• Qualitatively, irradiation 25°C shows the only increase in a residual peak
The plasmon energy is given as a function of valence electron density \( n_e \)

\[
E_p = \hbar \left( \frac{n_e e^2}{\varepsilon_0 m^*} \right)^{1/2}
\]

**Theoretical** \( \rho = 2.26 \text{g/cm}^3 \)

As-prepared, 800°C and 400°C \( \rho = 2.18 \text{g/cm}^3 \)

25°C \( \rho = 2.08 \text{g/cm}^3 \)
(a) Irradiated to 0.06 dpa at 25°C
(b) Irradiated to 0.94 dpa at 400°C