In-situ TEM of electron-beam damage process in next-generation nuclear graphite

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Background and motivation
Graphite will be used as a structural and moderator material in next-generation nuclear reactors. Under irradiation, graphite is known to undergo changes in its thermo-mechanical properties, especially via swelling and irradiation-induced creep, which affects the graphite's in-service life time. Developing an understanding of these life-limiting phenomena is very important for the development of new grades of nuclear graphite. The current understanding is that the ballistic displacement of carbon atoms caused by irradiation results in the accumulation of interstitial atoms between the basal planes, forming them apart. These interstitial clusters eventually rearrange to form new basal planes resulting in the expansion along the c-axis; however, this explanation has been disputed by several researchers whose electron microscopic studies did not show any evidence for the formation of interstitial basal planes and their existence at room temperature is contradictory to date. Our aim is to use in-situ transmission electron microscopy (TEM) to capture the irradiation induced changes in real-time and identify the swelling as well as creep mechanism. Furthermore, the historic nuclear grades of graphite no longer exist; therefore, it is imperative to characterize the microstructures of new grades of graphite and demonstrate that they exhibit acceptable properties in both the non-irradiated and irradiated state.

Objectives
- Microstructural characterization of various commercial grades of nuclear graphite before and after irradiation.
- Quantify the size and shapes of filler particles, micro-cracks, binder phase etc.
- Identify the mechanism behind the irradiation-induced swelling via in-situ TEM – Study the creation of vacancy and interstitial loops and their dynamics – validate/invalidate the interstitial clustering model.
- Identify the mechanism of irradiation-induced creep via in-situ TEM straining experiments as well as by studying the samples crest under neutron irradiation.

Microstructural Characterization
Filler, Binder, micro-cracks

- Nuclear graphite has a complex microstructure – several different phases
- Manufacturing: Coke particles (filler) mixed with pitch binder and sintered
- Gas evolution from binder results in highly porous microstructure
- Anisotropic thermal expansion results in delamination of basal planes and hence a high concentration of micro-cracks
- Quinoline-insoluble (QI) particles present in the binder graphite into rosette like structures
- A comparative microstructural characterization has been carried out identify these features in different grades of nuclear graphite – important to model the physical properties and identify a suitable grade

QI Particles

- Concentration of QI particles vary significantly: NBG-18 = highest

Chaotic structures

- PCEA
- NBG-18

In-situ electron-beam irradiation

- Swelling of graphite can be observed in-situ under TEM using electron-beam
- The above figure shows the closing of a micro-crack due to e-beam induced swelling
- Swelling rate controlled by the intensity of the incident electron-beam

Baseline planes lose their long-range order with irradiation
Breaking and bending of layers leads to randomization at higher doses
Increase in the average (0002) inter-planar spacing ~1.2% increase at 1 dpa (displacement per atom)
Navy images at higher scan rates – need processing

EELS was used to monitor the changes in the bonding environment as well as atomic density
Plasmon peaks in the low loss spectrum show a shift towards lower energies with increase in dpa.
A ~5% decrease in atomic density (after 1 dpa irradiation) was estimated from the plasmon shift which along with the increase (0002) spacing indicates an increased openness of the lattice.
Changes in core-loss spectrum indicate the formation of non-hexagonal (diamond-like ?) atomic rings with irradiation.

Interstitial loops

- Nucleation and growth of interstitial loops ~ 5 to 10 nm long
- Concentration of interstitial loops was very low and unstable – destroyed by further irradiation
- Unlikely cause for the swelling in graphite despite widespread belief

Summary and conclusions
- A comparative TEM study was carried out to characterize the different constituents such as filler, binder and micro-cracks which constitute the complex microstructure in various nuclear graphites.
- In-situ electron-beam irradiation studies were carried out to identify the mechanism behind the irradiation induced swelling.
- In-situ experiments provide a clear evidence for the formation of vacancy loops, interstitial loops, dislocation dipoles and associated buckling/breaking of basal planes.
- Dislocations were found to undergo positive climb resulting in the formation of new basal planes.
- Extra basal planes formed through climb along with the opening of the lattice induced by the breaking and buckling of basal planes, is believed to be responsible for the swelling.
- We found no evidence for the widely believed theory of interstitial clustering induced swelling.

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