HTGR Technology Course for the Nuclear Regulatory Commission

May 24 – 27, 2010

Module 9
Graphite

Outline

- Role in HTGRs
- Manufacturing processes
- Nuclear graphite for HTGRs
- Graphite and graphite testing standards
- Physical & mechanical properties and irradiation effects
- International graphite irradiation programs
- Graphite oxidation and other chemical reactions
- Wear of graphite – tribology
- Graphite performance modeling

Role of Graphite in a Nuclear Reactor

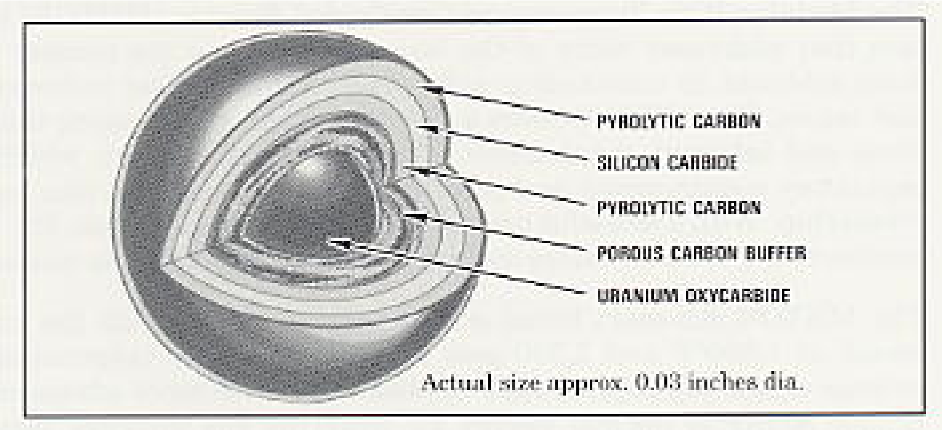
- **Neutron moderator (carbon & graphite)**
  - Thermalize fast neutrons to sufficiently low energies that they can efficiently fission ${}_{92}U^{235}$
- **Neutron reflector – returns neutrons to the active core**
- **Graphite (nuclear grade) has a low neutron capture cross section**
- **High temperature material**

Role of Graphite in a Nuclear Reactor

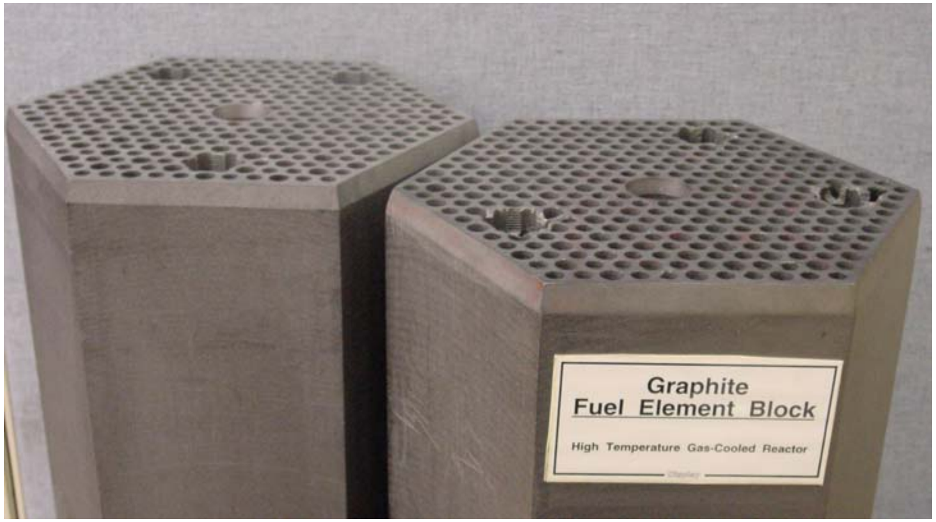
- Graphite is the reactor core structural material
- HTGR cores are constructed from graphite blocks
- In prismatic cores the graphite fuel elements retain the nuclear fuel
- In a pebble bed the graphite reflector structure retains the fuel pebbles
- The graphite reflector structure contains vertical penetrations for reactivity control
- Reactivity control channels are also contained in prismatic graphite fuel elements

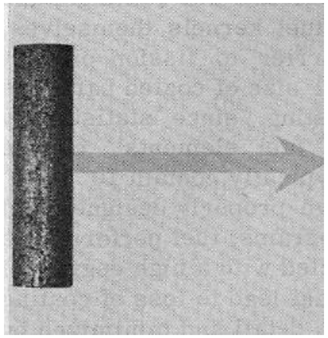
The GT-MHR Utilizes Ceramic Coated Particle Fuel

The TRISO fuel particles are formed into 12 mm diameter graphite (carbon) fuel sticks and inserted into graphite fuel blocks

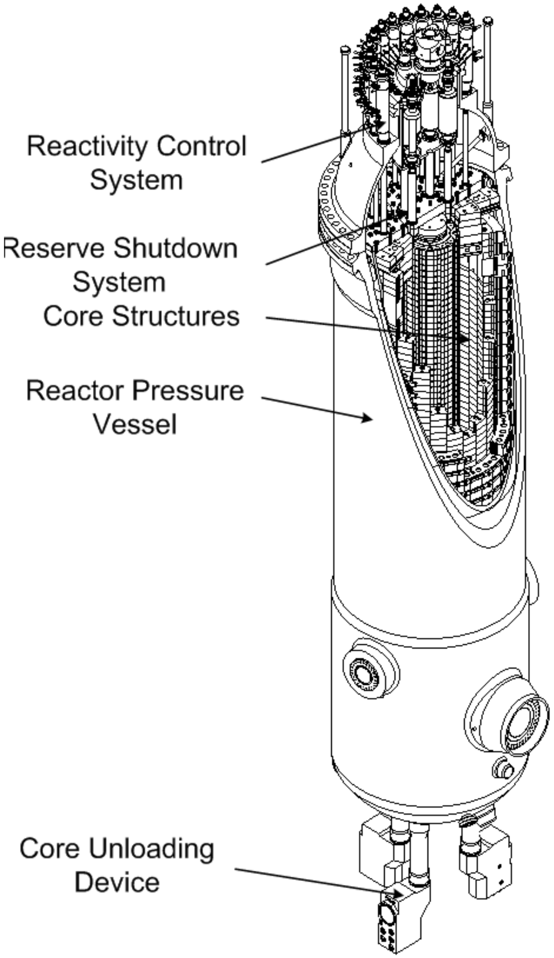


Actual size approx. 0.03 inches dia.



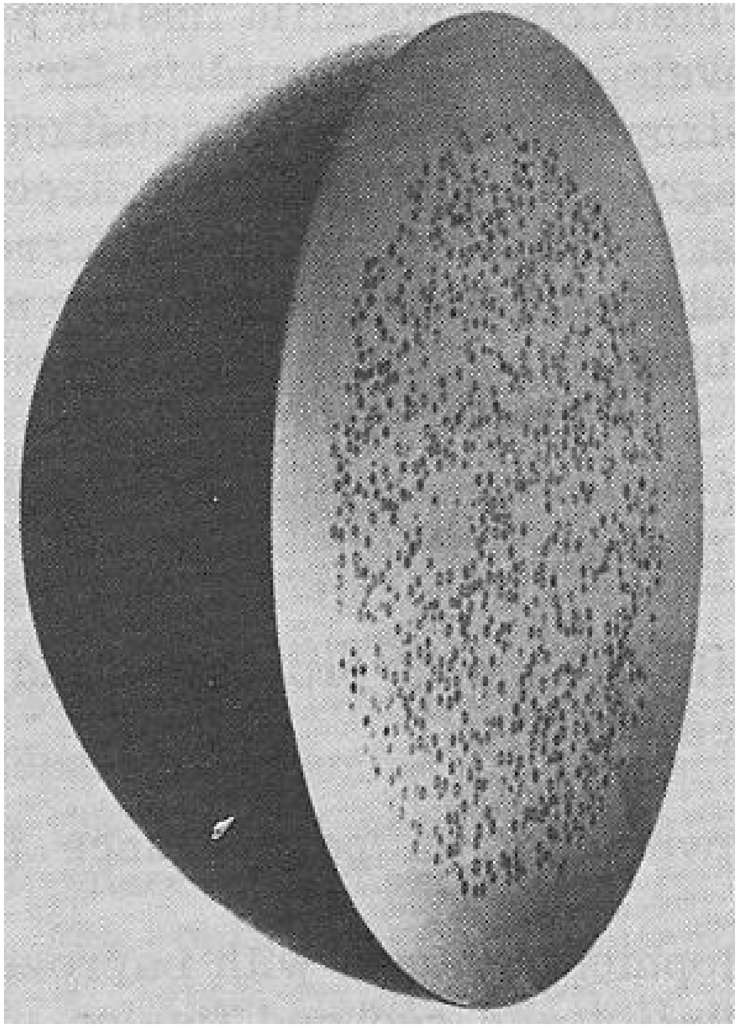


Graphite Core Components – Pebble Type HTGR (PBMR)

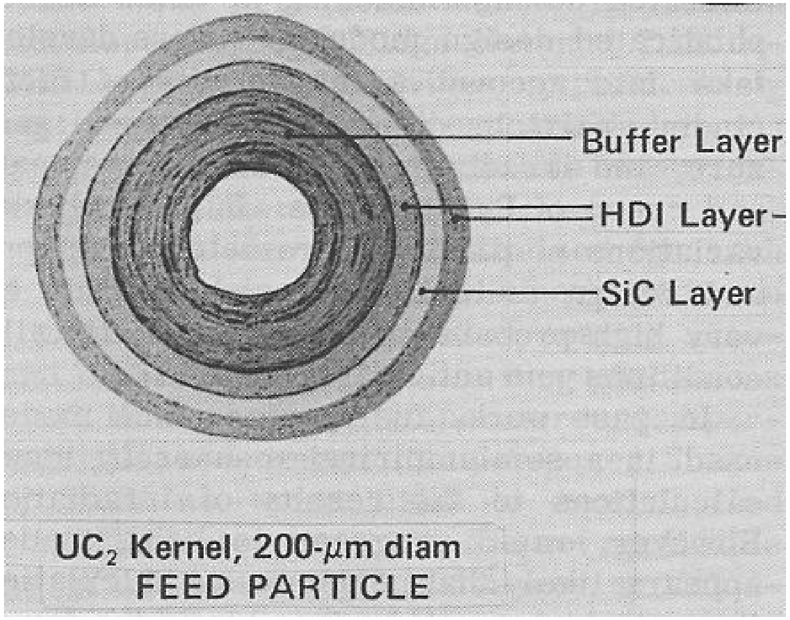


- NBG-18 Graphite blocks form the PBMR outer reflector
- Reflector penetrations are for the control rods and reserve shutdown system

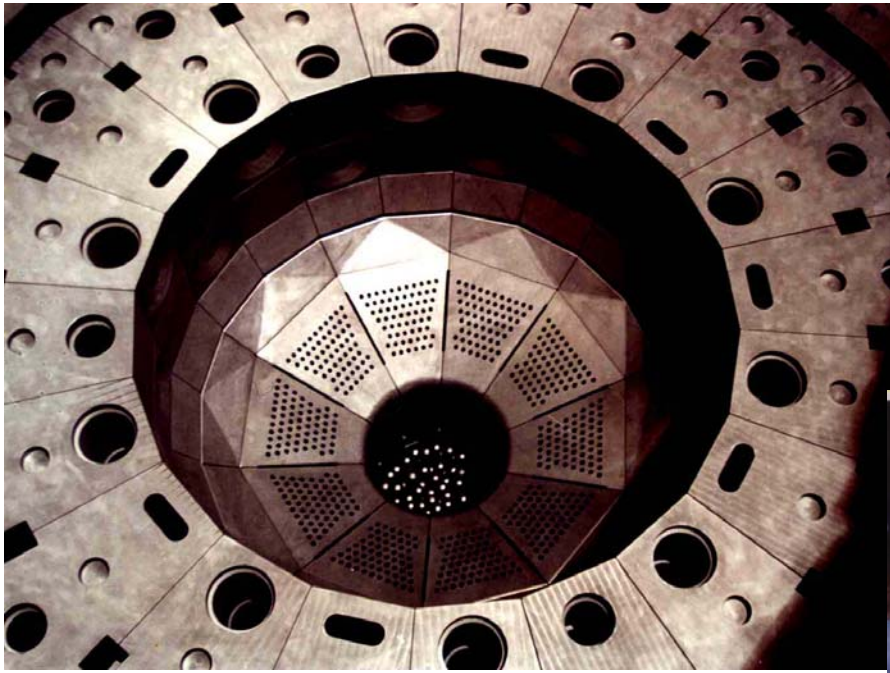
The Pebble Type HTGR Utilizes Ceramic Coated Particle Fuel



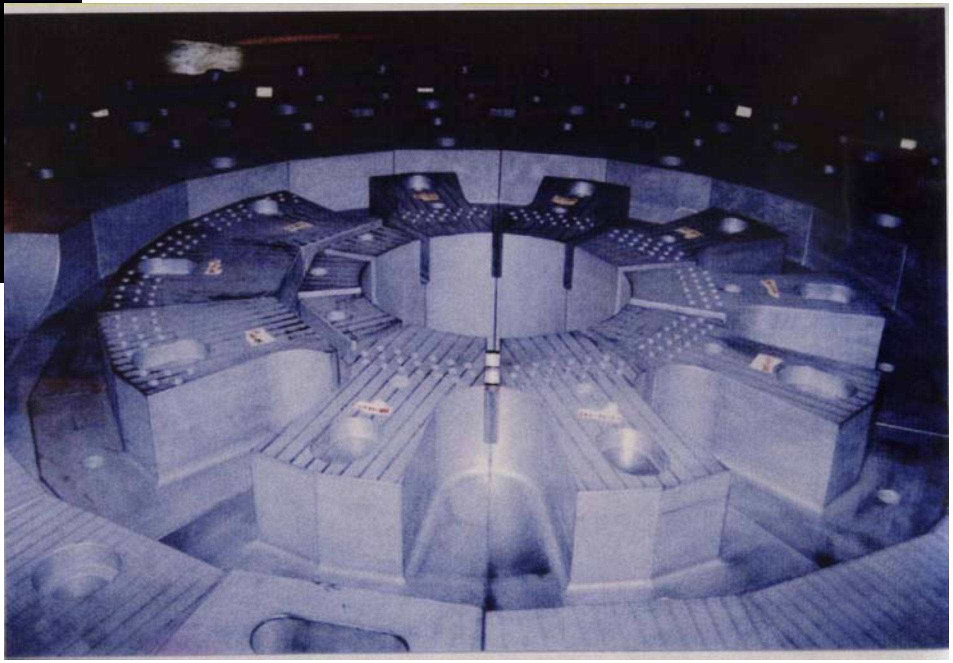
The TRISO fuel particles are combined into a graphite (carbon) fuel ball (pebble)
6 cm in diameter



HTR-10 Graphite Reactor Internal Structures (Grade IG-110)



Top of the graphite core of HTR-10



Core bottom of the HTR-10 showing the fuel pebble collection area

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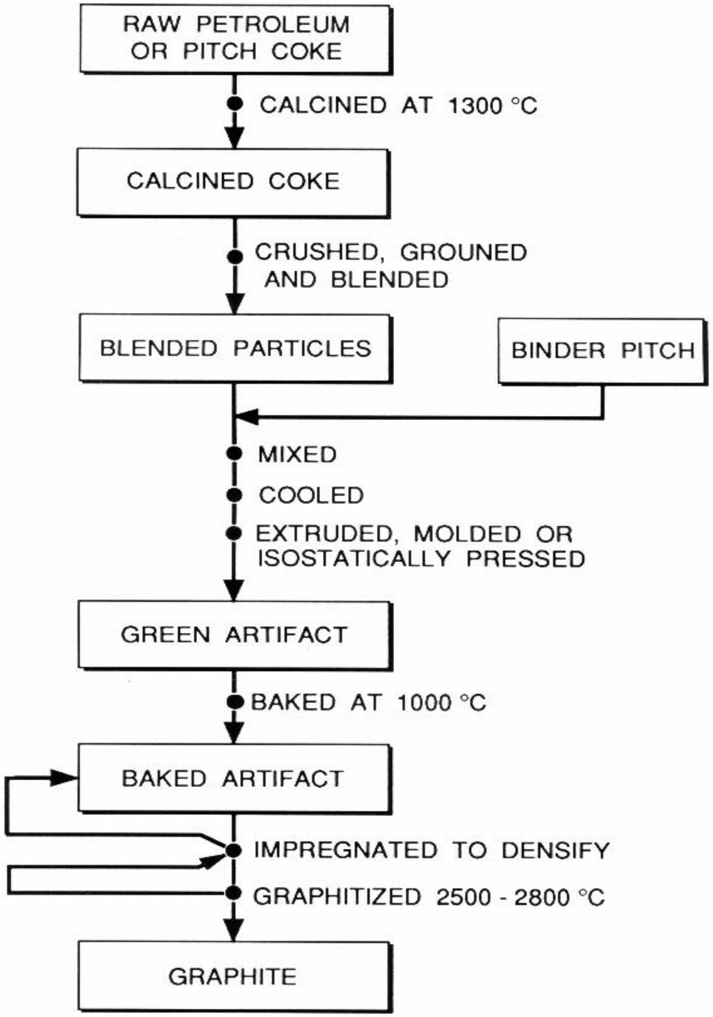
The Major Processing Steps in the Manufacture of Nuclear Graphite



RAW PETROLEUM OR PITCH COKE

CALCINED AT 1300 °C

CALCINED COKE

CRUSHED, GROUNED AND BLENDED

BLENDED PARTICLES

BINDER PITCH

MIXED

COOLED

EXTRUDED, MOLDED OR ISOSTATICALLY PRESSED

GREEN ARTIFACT

BAKED AT 1000 °C

BAKED ARTIFACT

IMPREGNATED TO DENSIFY

GRAPHITIZED 2500 - 2800 °C

GRAPHITE

- Typical manufacturing time for a nuclear graphite is 6 - 9 months
- Nuclear purity achieved through judicious selection of feedstock
- Chemical purification is achieved by additives to graphitization furnace or by halogen gas treatment
- Gas purification may occur as a post graphitization process
- The largest market for synthetic graphite is arc furnace electrodes (steel industry) – about 1,000,000 tons per year produced

Video Clip Showing Mixing and Extrusion

Video Clip Showing Baking

Video Clip Showing Impregnation

Video Clip Showing Rebaking

Video Clip Showing Graphitization

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Factors Controlling The Neutron Irradiation Damage Response Of Graphite

- **Crystallinity (degree of graphitization): More graphitic crystals retain less displacement damage. Crystallinity is a function of precursor (pitch/coke) and graphitization temperature.**
- **Small particle size promotes higher strength and retardation of pore generation.**
- **Structural isotropy (both coke isotropy and final product isotropy). Isotropic irradiation behavior is much preferred. Coefficient of Thermal Expansion (CTE) ratio is used as an indication of isotropy. Higher coke CTE preferred.**
- **Forming technique – structural and property anisotropy may be introduced by extrusion and molding. Isostatic molding produces an isotropic graphite.**

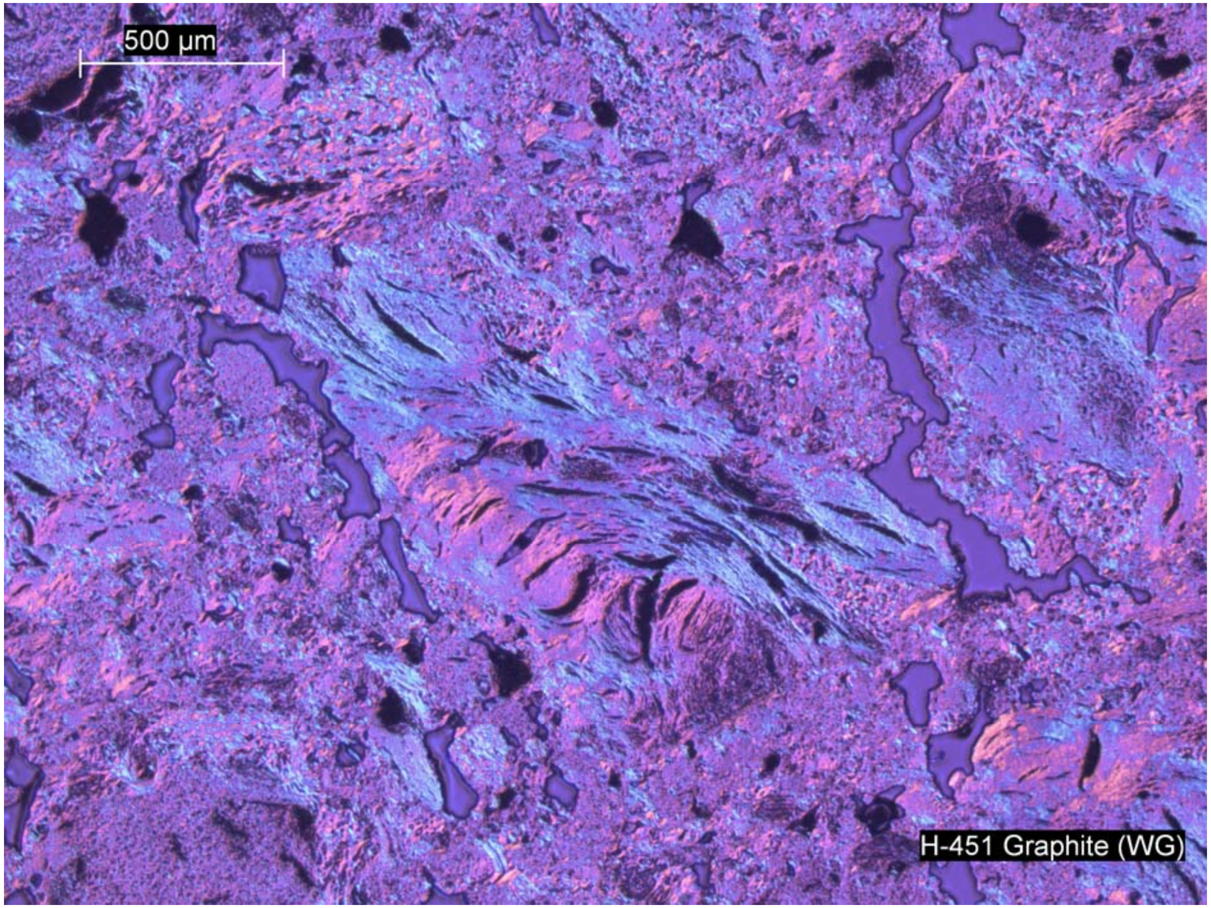
Developments in Nuclear Graphite – Process Improvements

- **Purity**
  - Advent of in-graphitization furnace purification
- **Crystallinity**
  - High crystallinity retains less radiation damage
- **Filler coke size**
  - Small size preferable (stronger) but larger block sizes requires coarser particles size
- **Forming method**
  - Isostatic pressing & vibrational molding yields less anisotropy than extrusion or molding
- **Higher strength graphites**
  - Resists pore generation
- **Near-isotropic (isotropic filler coke and graphite artifact)**
  - Minimizes internal dimensional change strains

What Was Learned Over The Years Flowed Down To Improved Graphites:-

- **Halogen purification (allowed alternate feedstock sources)**
- **Understanding of damage mechanism and role of graphite crystallite size**
- **Need for isotropic cokes - high CTE which yield isotropic properties in the final artifact**
- **Thus second generation graphites were born**
  - USA, H-451 – extruded, isotropic petroleum coke
  - UK, IM1-24 – molded, Gilsonite coke

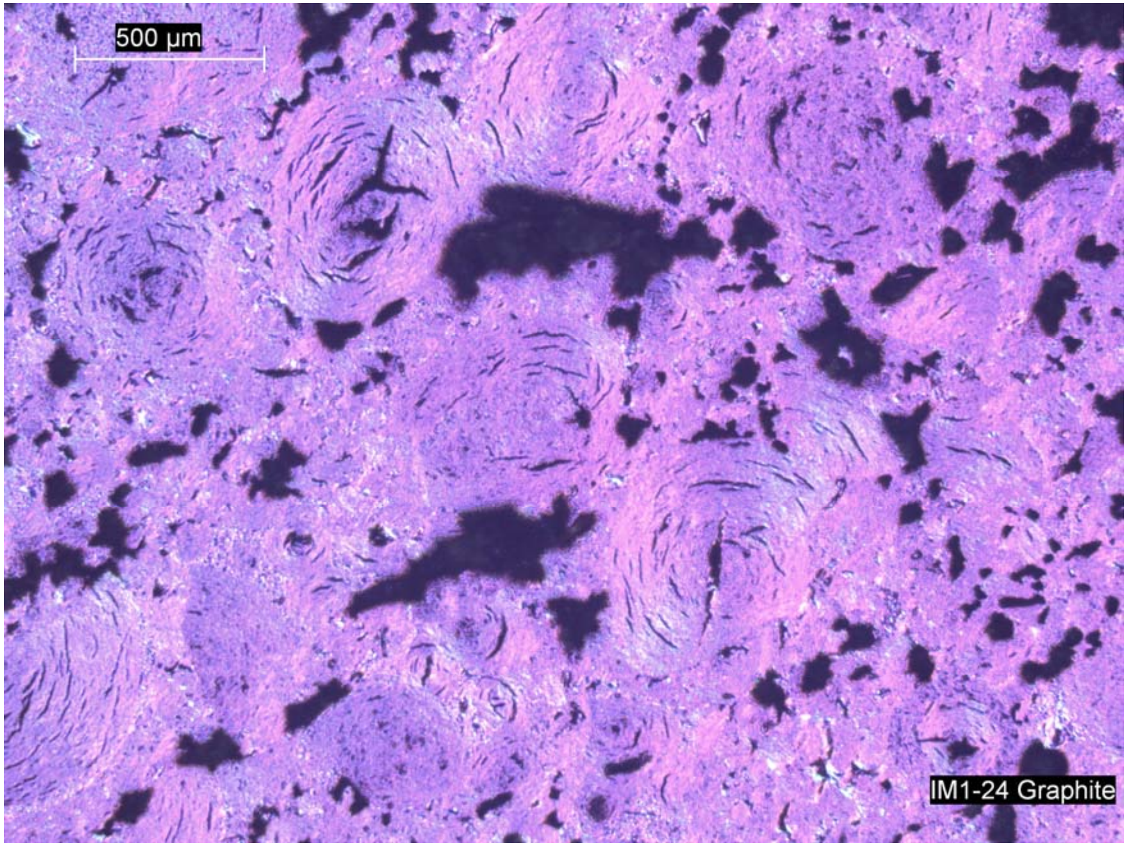
Near-isotropic Graphites – H-451



- Extruded, isotropic petroleum coke (NO LONGER AVAILABLE)
- 500 µm mean filler particle size
- Near-isotropic physical properties
- High CTE & reasonable strength
- Replaced H-327

Fuel elements & replaceable reflectors in the FSV HTGR (GA)

Near-isotropic Graphites – IM1-24 (UK)



- Molded, isotropic Gilsonite coke (NO LONGER AVAILABLE)
- ~500µm filler particle size
- Isotropic physical properties
- High CTE and reasonable strength
- Replaced Pile Grade A (Magnox)

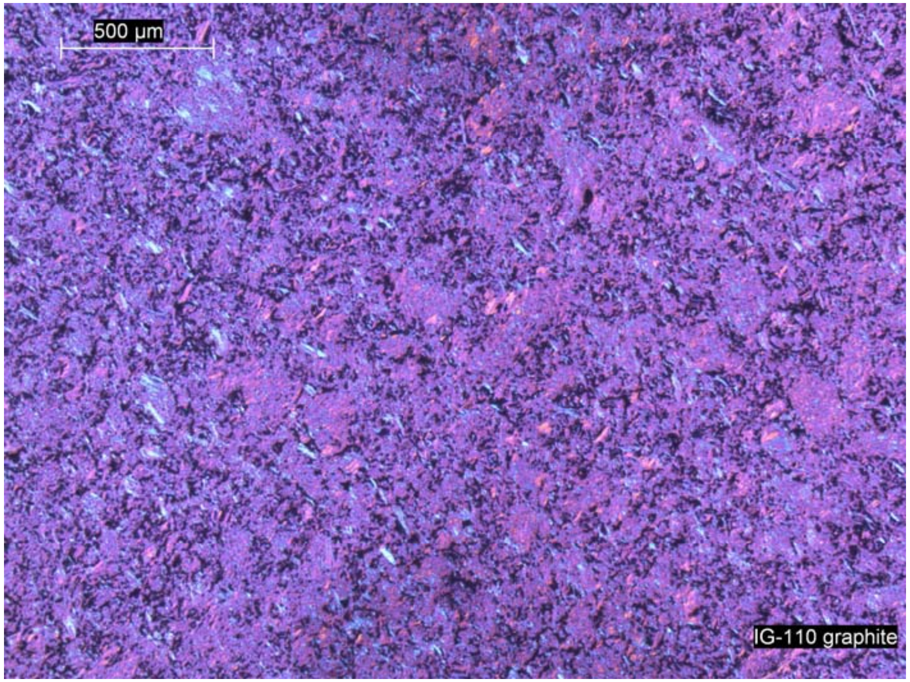
Advanced Gas-Cooled Reactor (CO_2 cooled) permanent core structure (lifetime component)

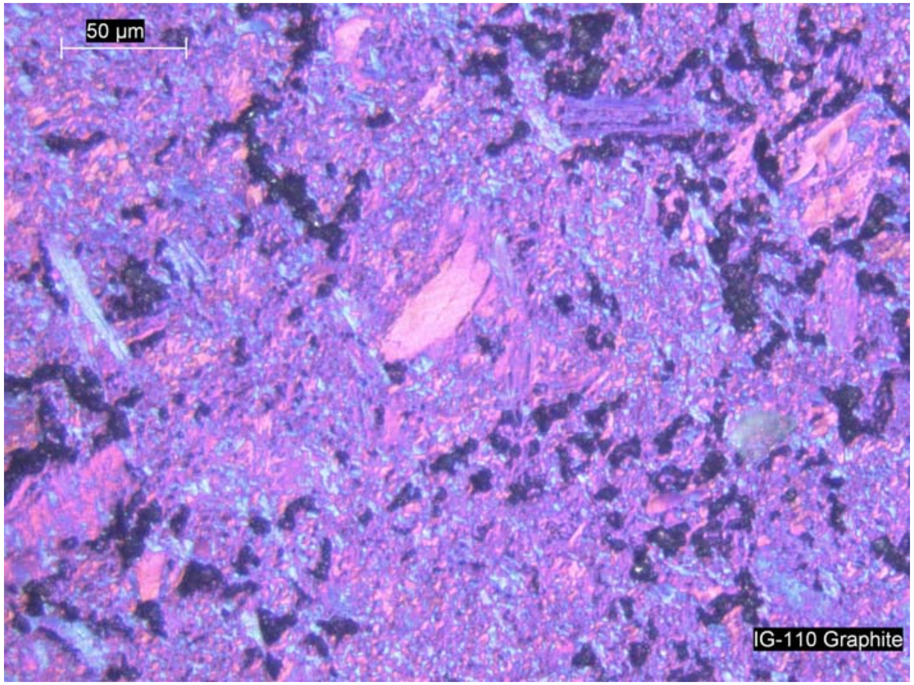
Developments In Nuclear Graphite- Near Isotropic Graphites

- **Crystallinity**
- **Smaller particle size**
- **Forming method (Isostatic molding)**
- **Green coke technology**
- **High strength**
- **Isotropic**
  - Properties
  - Irradiation induced dimensional change
- **Third generation graphites are born**

Developments in Nuclear Graphite - isotropic graphites - IG-110

- Fine grain (~20 µm)
- High CTE 4-5 x 10^{-6} $^{0}C^{-1}$
- High strength
- isotropic properties and irradiation response

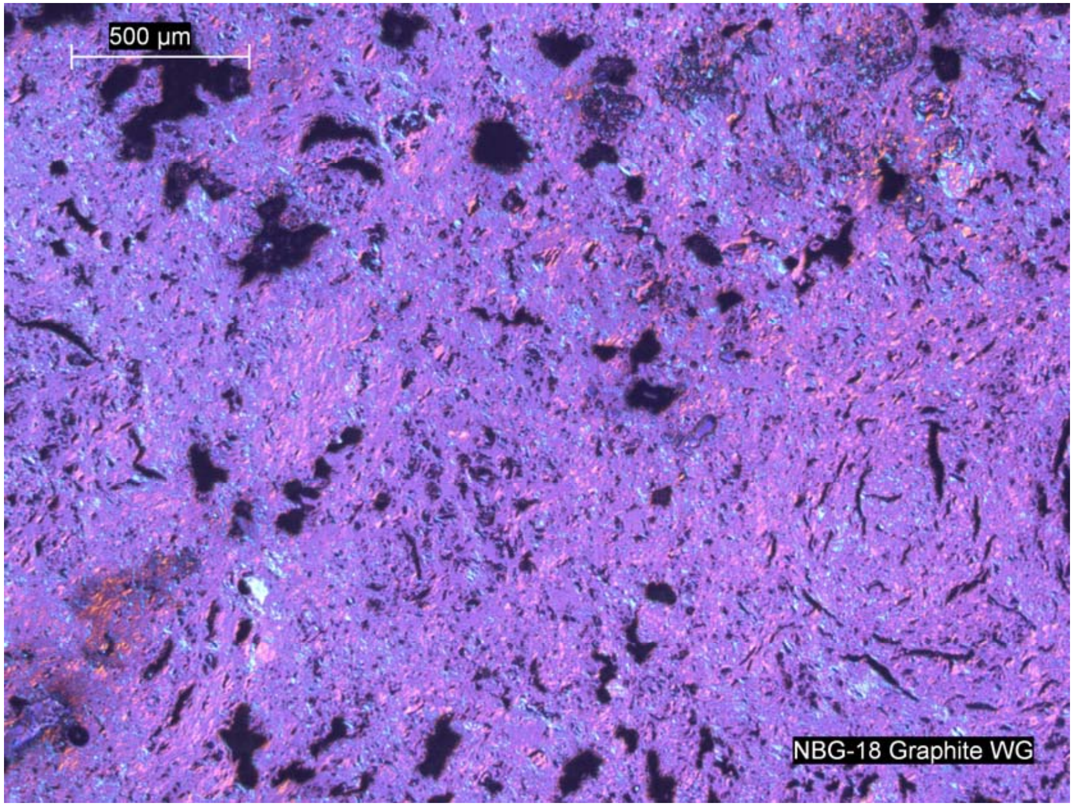




High Temperature Test Reactor (Japan), Fuel Blocks and Replaceable Reflector Blocks

HTR-10 & HTR-PM, Permanent Core Structure

Developments in Nuclear Graphite - isotropic graphites – NBG-18



- Vibrationally molded graphite
- Isotropic Pitch coke
- Medium grain (1.6 mm max)
- High CTE 5-5.5 x 10^{-6} $^{0}C^{-1}$
- isotropic properties and irradiation response

Permanent and replaceable core structures in the Pebble Bed Modular Reactor

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ASTM Standard Specifications

- **D7219-08 Standard Specification for Isotropic and Near-isotropic Nuclear graphites**

- **D7301-08 Standard Specification for Nuclear Graphite Suitable for Components Subjected to Low Neutron Irradiation Dose**

What is Specified by the ASTM Specifications?

- Coke type and isotropy (CTE)
- Method of determining coke CTE
- Maximum filler particle size
- Green mix recycle
- Graphitization temperature (2700°C)
- Method of determining graphitization temperature
- Isotropy ratio and chemical purity
- Properties: density, strength (tensile, compressive, flexural), CTE, E
- Marking and traceability
- Quality assurance (NQA-1)

ASTM Standard Practices

- C625 Reporting Irradiation Results on Graphite
- C781 Testing Graphite and Boronated Graphite Materials for High-Temperature Gas-Cooled Nuclear Reactor Components
- C783 Core Sampling of Graphite Electrodes
- C709 Standard Terminology Relating to Manufactured Carbon and Graphite

ASTM Standard Test Methods

- C559 Bulk Density by Physical Measurement of Manufactures Carbon and Graphite Articles
- C560 Chemical Analysis of Graphite
- C561 Ash in a Graphite Sample
- C562 Moisture in a Graphite Sample
- C565 Tension testing of Carbon and Graphite Mechanical Materials
- C611 Electrical Resistivity of Manufactured Carbon and Graphite Articles at Room Temperature

ASTM Standard Test Methods (continued)

- C651 Flexural Strength of Manufactured Carbon and Graphite Articles Using Four-Point Loading at Room Temperature
- C695 Compressive Strength of Carbon and Graphite
- C714 Thermal Diffusivity of Carbon and Graphite by Thermal Pulse Method
- C747 Moduli of Elasticity and Fundamental Frequencies of Carbon and Graphite by Sonic Resonance
- C748 Rockwell Hardness of Graphite Materials

ASTM Standard Test Methods (continued)

- C749 Tensile Stress Strain of Carbon and Graphite
- C769 Sonic Velocity in Manufactured Carbon and Graphite for Use in Obtaining Young's Modulus
- C816 Sulfur in Graphite by Combustion-Iodometric Titration Method
- C838 Bulk Density of As-Manufactured Carbon and Graphite Shapes
- C886 Scleroscope Hardness Testing of Carbon and Graphite Materials

ASTM Standard Test Methods (continued)

- **C1025 Modulus of Rupture in Bending of Electrode Graphite**
- **C1039 Apparent Porosity, Apparent Specific Gravity, and Bulk Density of Graphite Electrodes**
- **C1179 Oxidation Mass Loss of Manufactured Carbon and Graphite Materials in Air**
- **D7542 Air Oxidation of Carbon and Graphite in the Kinetic Regime**

New ASTM Test Methods Currently in Development

- **ASTM D02.F on manufactured carbons and graphites has several test methods in development**
  - Critical stress intensity factor, K_{Ic} (Fracture Toughness)
  - Shear modulus and Poisson's ratio from sonic velocity
  - Flexural strength by three point bend
  - Chemical purity by ICP- OES and GDMS
  - Small (irradiation) specimen best practice
  - Non-destructive test and evaluation
  - X-Ray diffraction analysis

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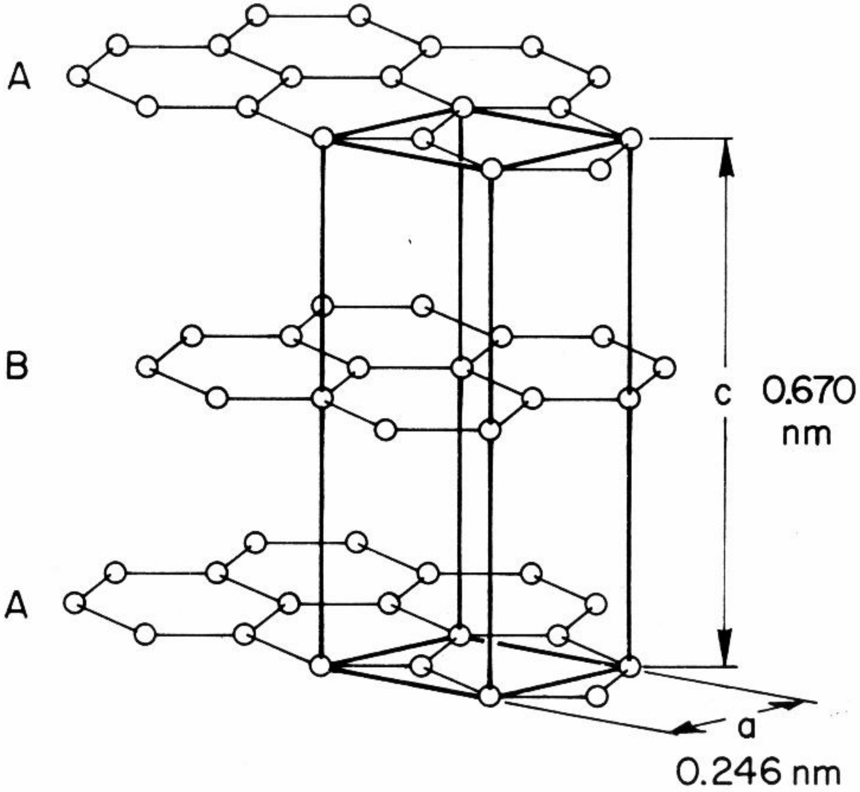
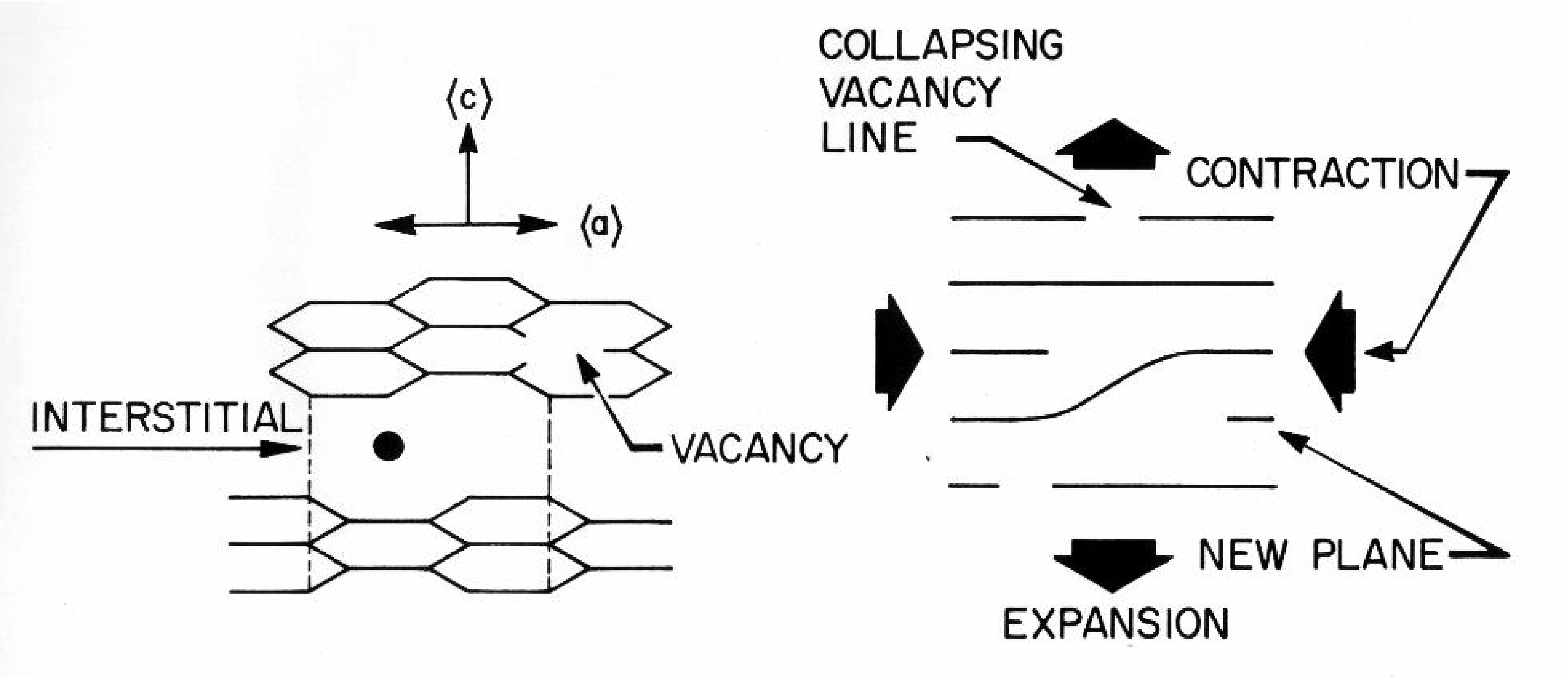
Neutron Irradiation Damage

- Neutron irradiation causes carbon atom displacement
- Dimensional and physical property changes result
- Damage mechanism well understood
- Key physical properties are: irradiation dimensional stability, strength, elastic moduli, thermal expansion coefficient, thermal conductivity, radiation creep behavior, fracture behavior, oxidation behavior.

GRAPHITE CRYSTAL STRUCTURE



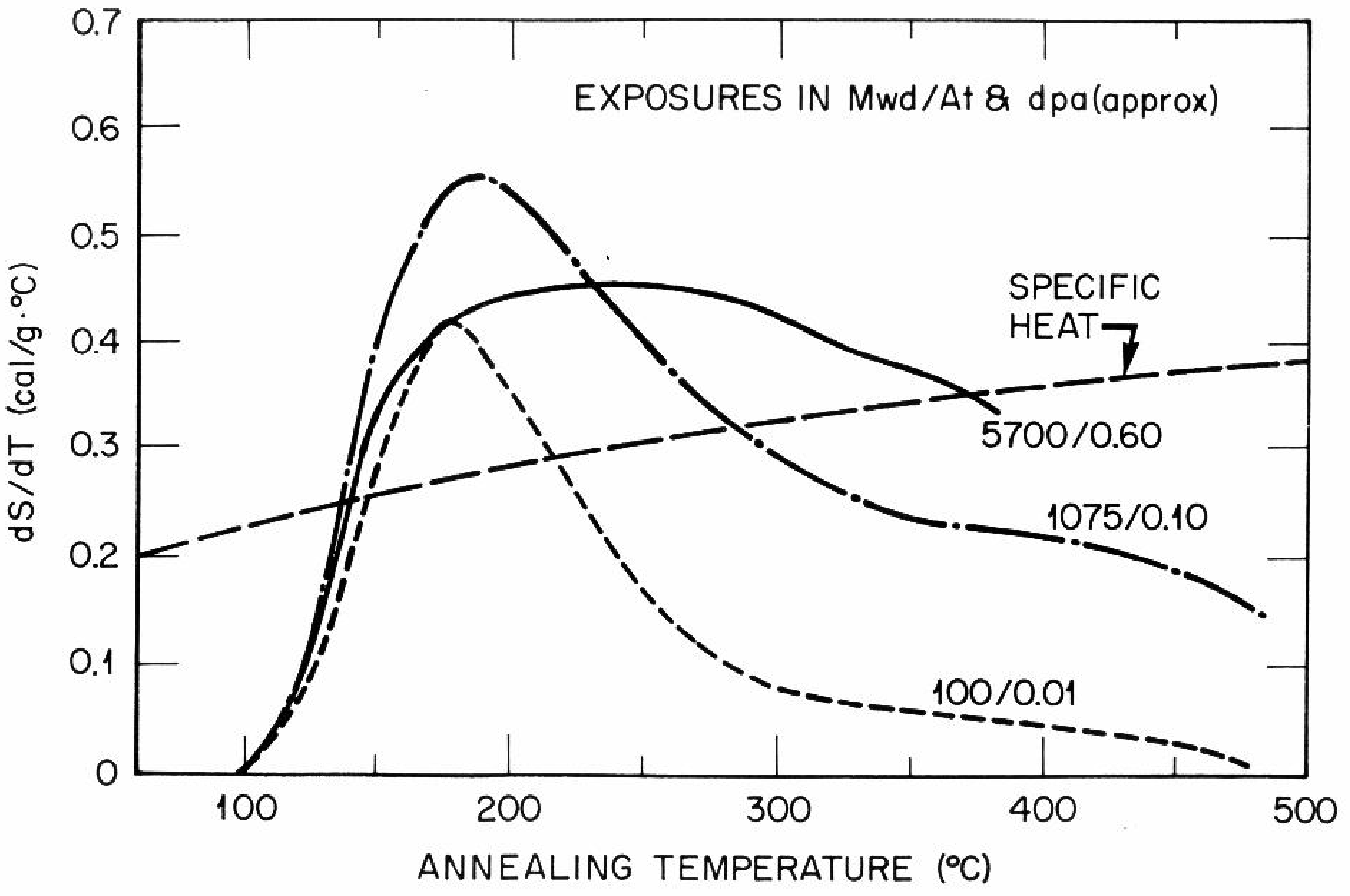
The Radiation Damage Mechanism In Graphite



CARBON ATOM BINDING ENERGY IN GRAPHITE LATTICE IS 7 eV

DISPLACEMENT ENERGY FOR CARBON ATOM IS APPROX. 30 eV

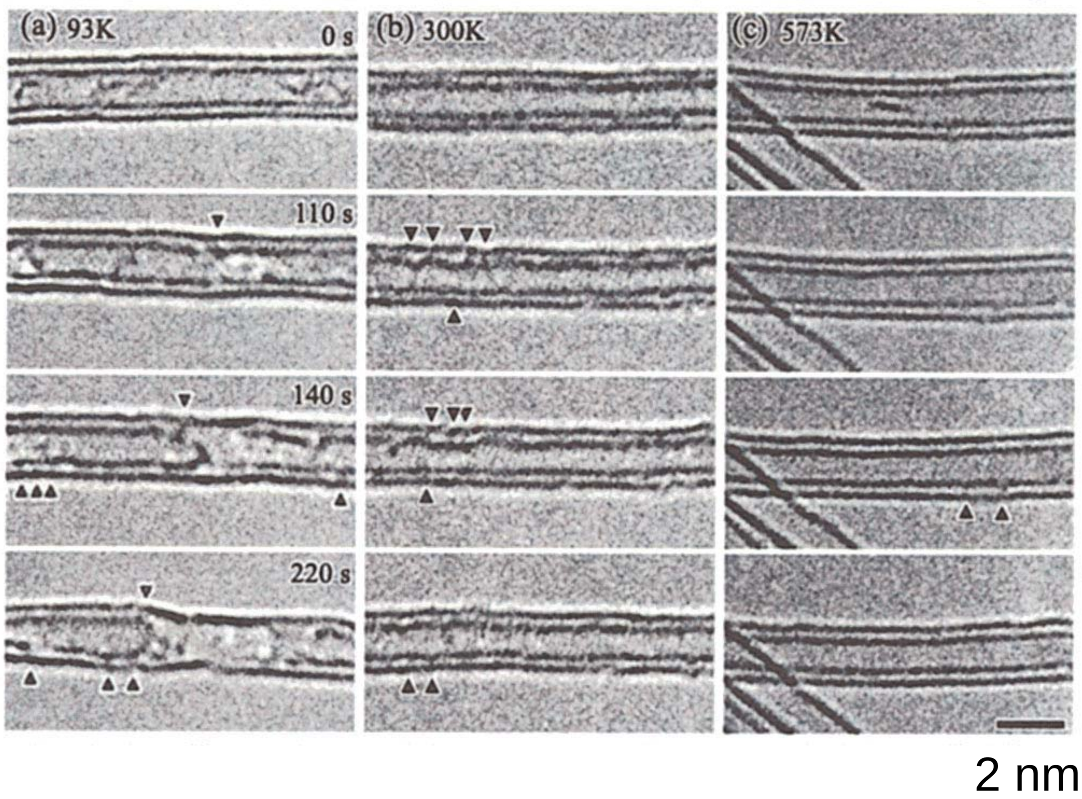
Low Temperature Stored Energy Release



- T_{irr} ~ 30°C
- Hanford K
- reactor test
- Data
- Traditionally associated with Frenkel pair recombination

Burchell T, Carbon Materials for Advanced Technologies, Chpt. 13 (1999) p. 429

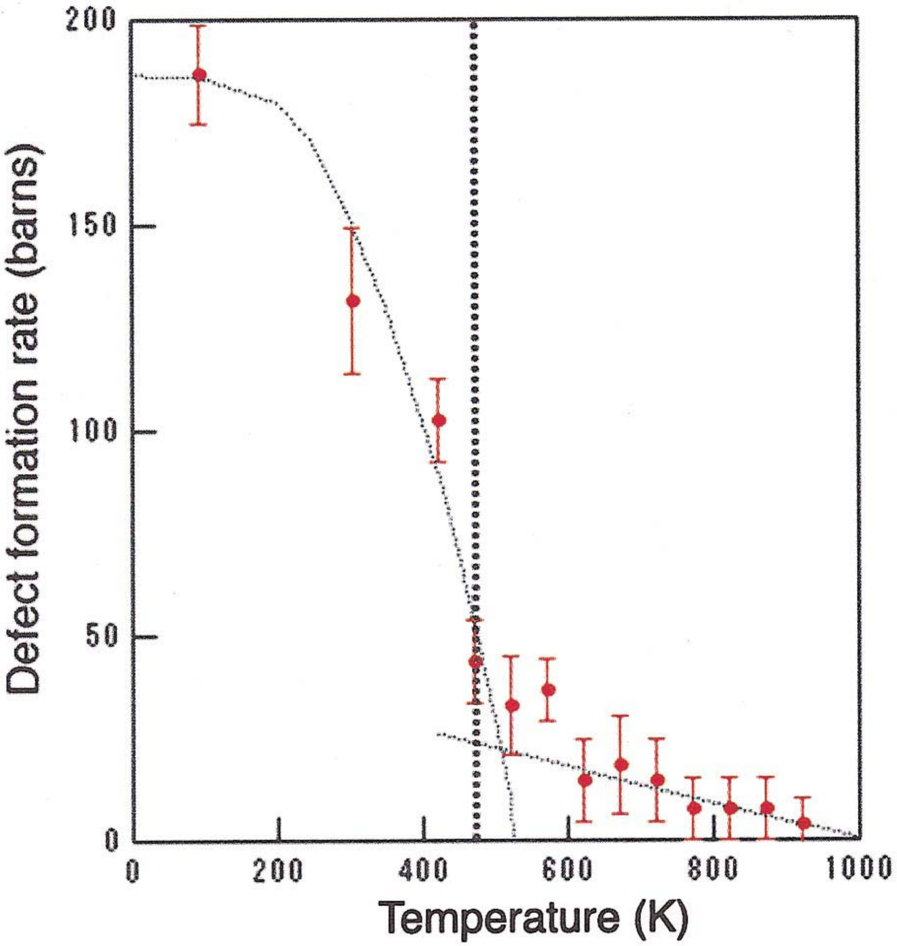
Displacement Damage in Layered Graphitic Structures



Urita, K.; Suenaga, K.; Sugai, T.; Shinohara, H.; Iijima, S. *Physical Review Letters* **2005**, 94, 155502.

- **Sequential high resolution transmission electron microscope images illustrating the formation rates of interlayer defects at different temperatures with the same electron irradiation flux & time scale (0 to 220 seconds). (a) 93K, (b) 300K, (c) 573K, in double-wall carbon nanotubes.**
- **The arrows indicate possible interlayer defects.**

Displacement Damage in Layered Graphitic Structures

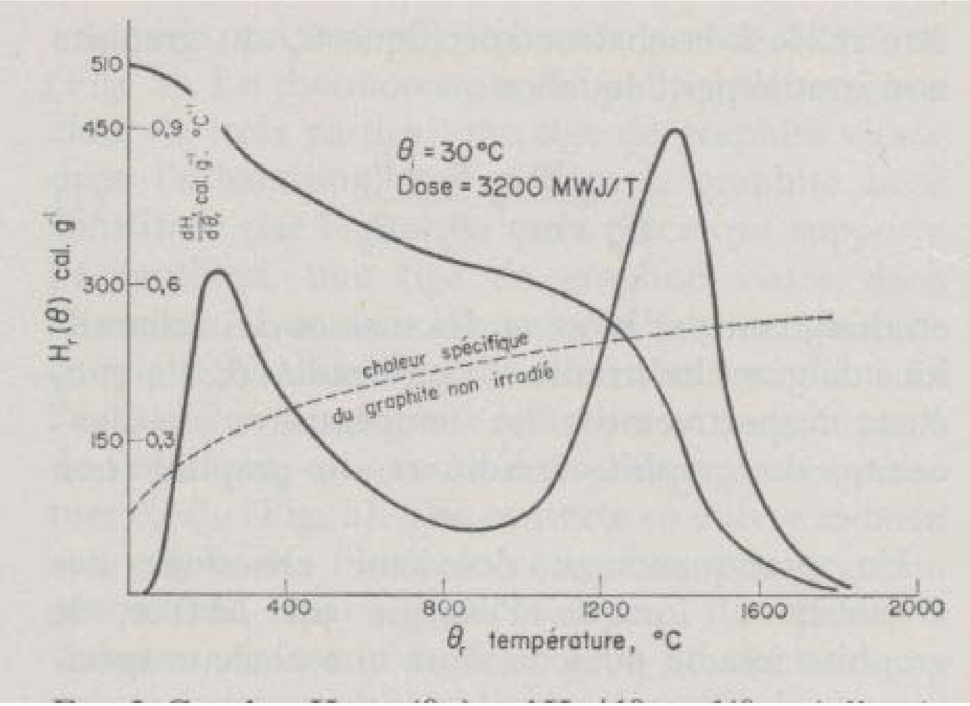


- **Normalized formation rate of the clusters of *I-V* pair defects per unit area of bilayer estimated in HRTEM images recorded at different temperatures**
- **The dotted line shows the known temperature for Wigner-energy release (~473 K)**

Urita, K.; Suenaga, K.; Sugai, T.; Shinohara, H.; Iijima, S. *Physical Review Letters* **2005**, 94, 155502.

High Temperature Stored Energy Release

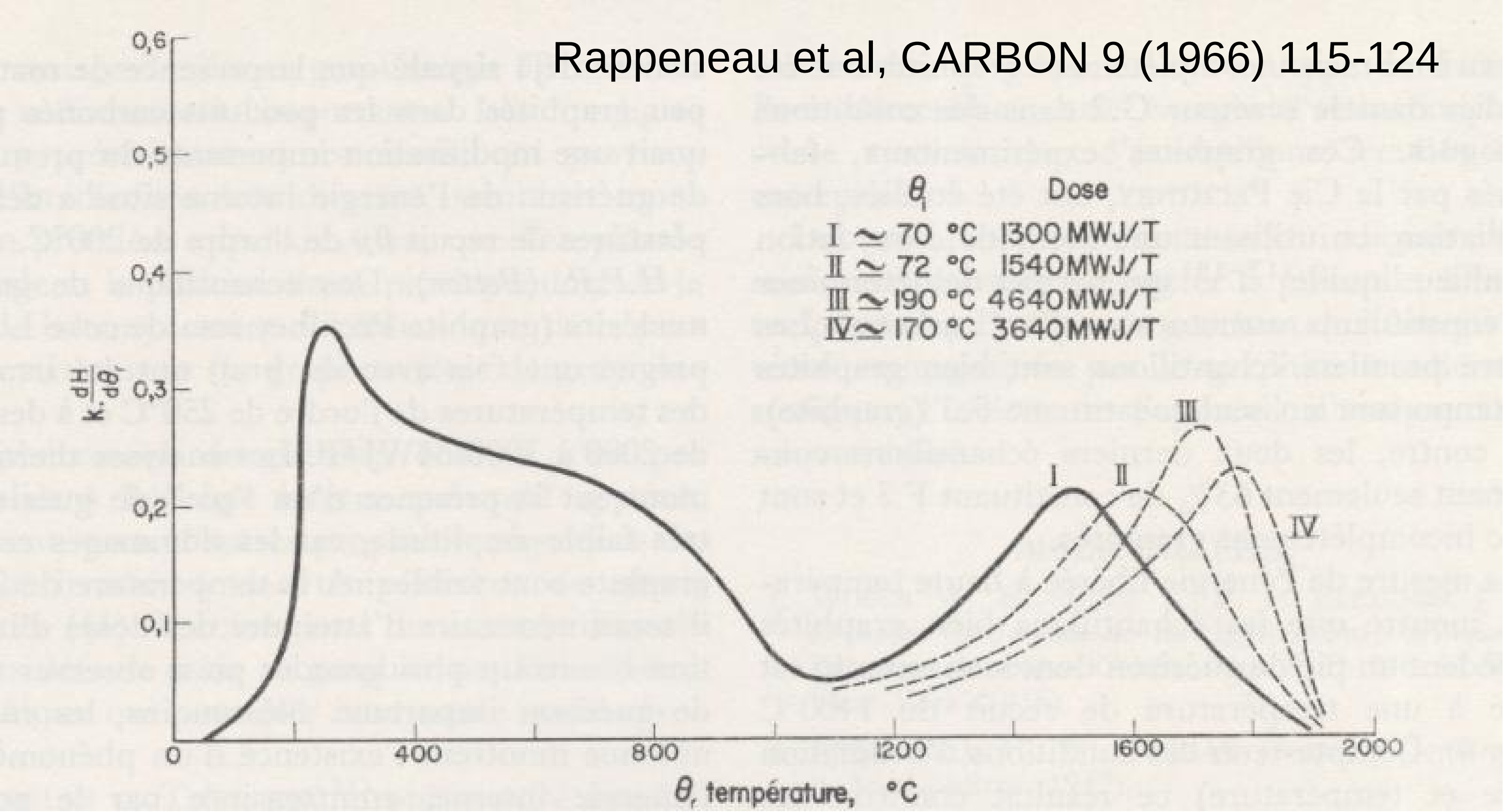
Stored Energy Release Curve for Graphite Irradiated at 30°C Compared with Unirradiated Graphite Cp Curve



Rappeneau et al, CARBON 9 (1966) 115-124

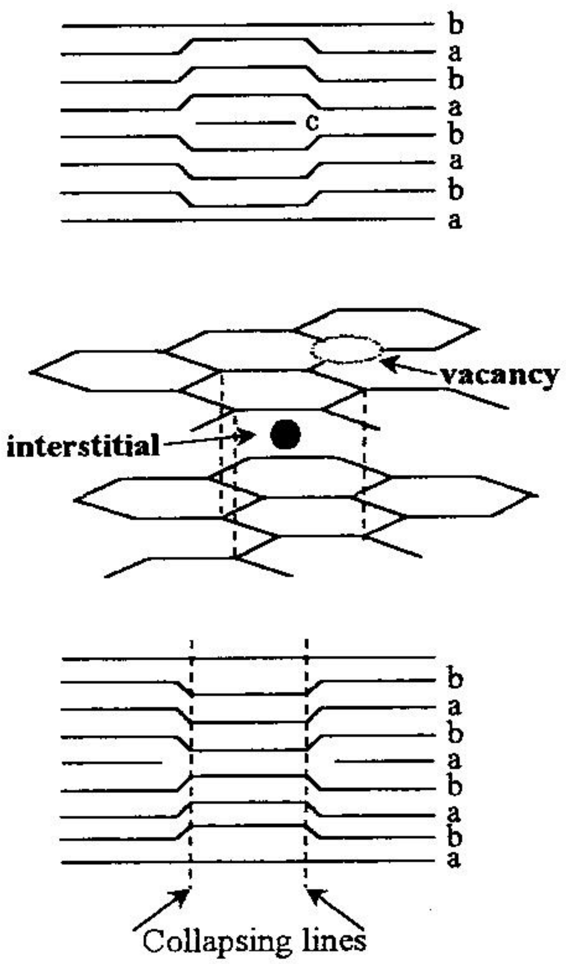
- A second release peak is observed at ~1400°C in graphite irradiated at LOW temperatures
- Associated with annealing of small interstitial clusters
- Immobile vacancies can coalesce at high temperature
- Release rates > Cp NOT seen in graphite irradiated at higher temperatures

High Temperature Stored Energy Release


Rappeneau et al, CARBON 9 (1966) 115-124

- **High temperature release is due to a separate mechanism (confirmatory experiments planned)**
- **High temperature release rate does NOT exceed Cp**

Radiation Damage In Graphite Is Temperature Dependent



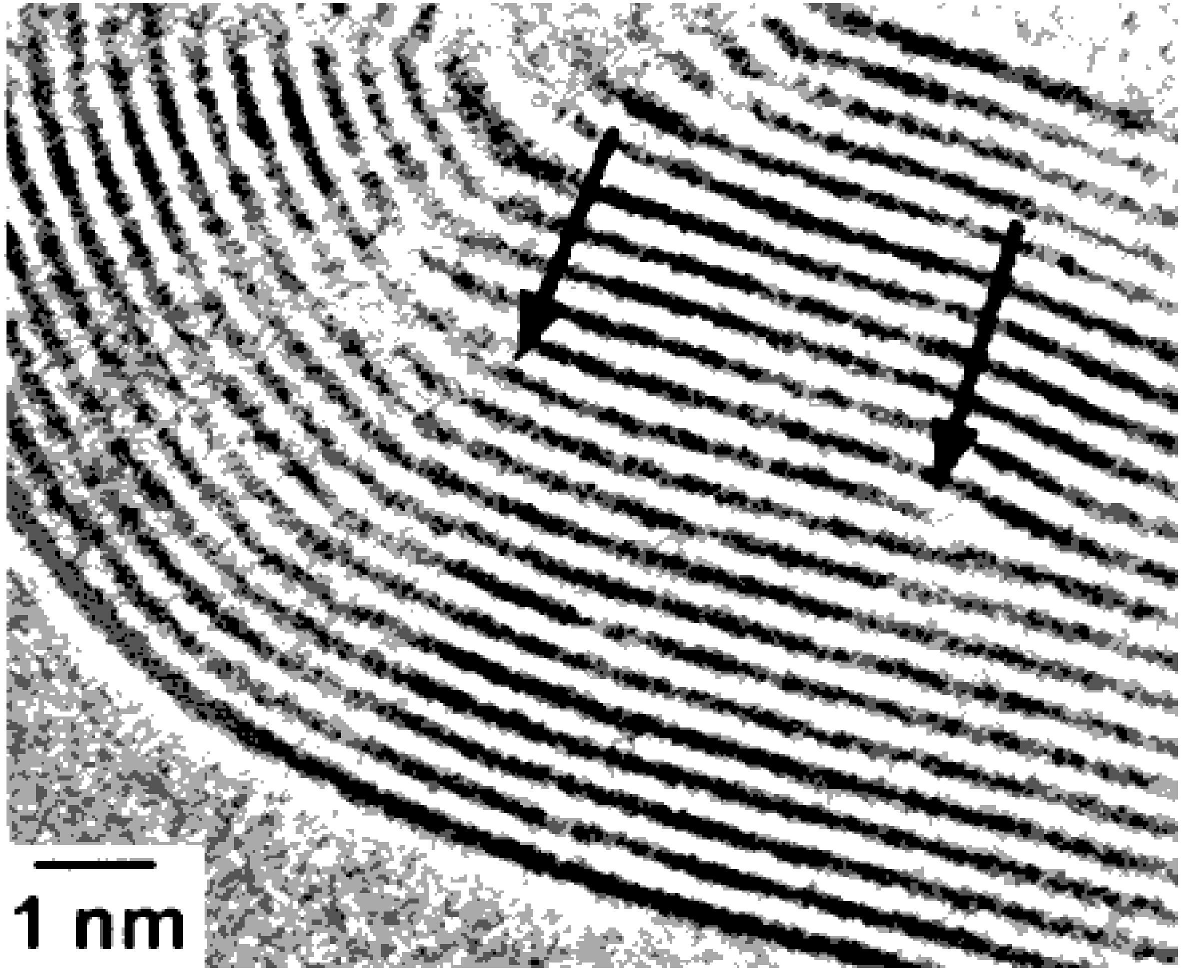
INTERSTITIALS

Mobile at room temperature.
Above ~200°C form into clusters of 2 to 4 interstitials.
Above 300°C form new basal planes which continue to grow at temperatures up to 1400°C.

VACANCIES

Immobile below 300°C.
300-400°C formation of clusters of 2-4 vacancies which diffuse in the basal planes and can be annihilated at crystallite boundaries (function of lattice strain and crystal perfection).
Above 650°C formation of vacancy loops.
Above 900°C loops induce collapsing vacancy lines.

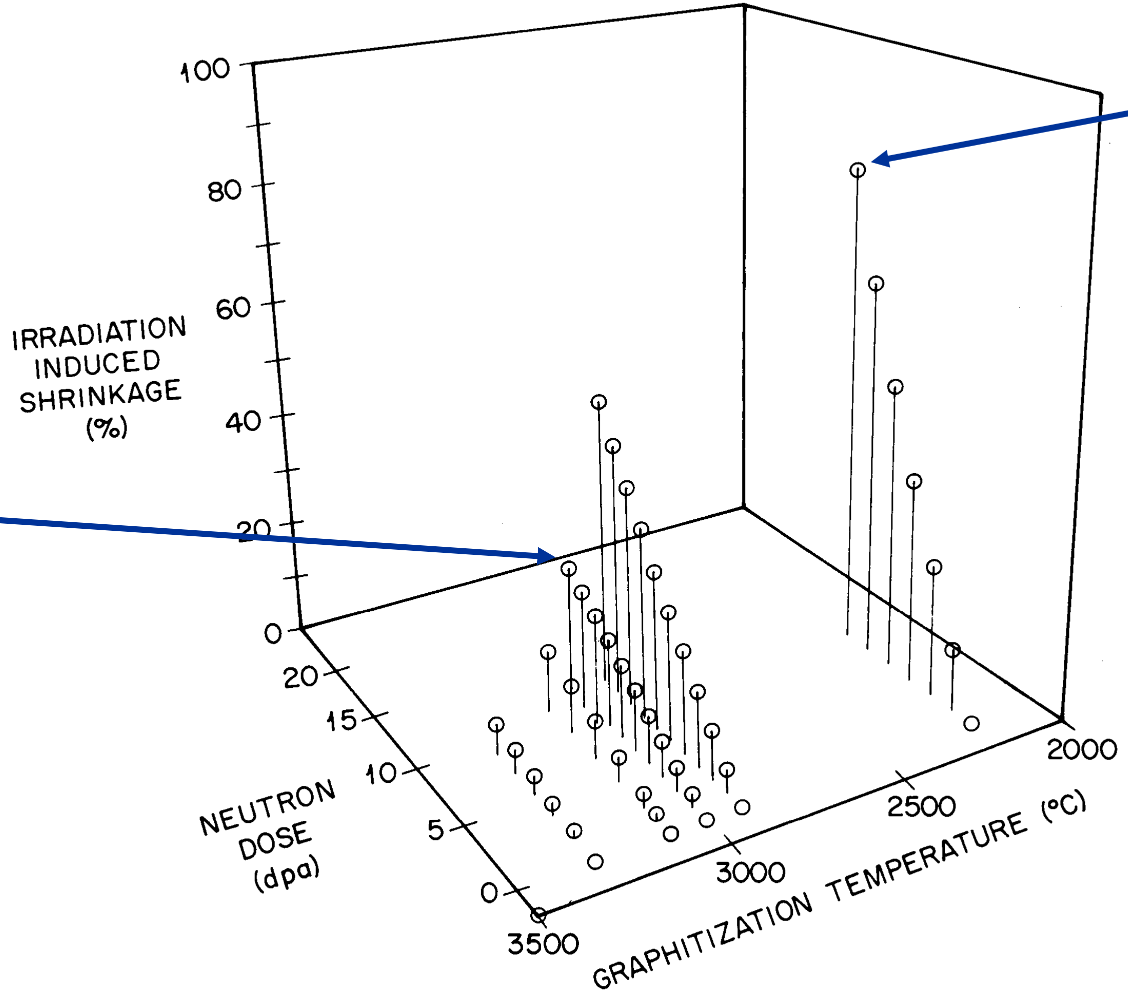
Basal Planes in Layered Graphitic Structures



A high-resolution electron micrograph showing the basal planes of a graphitic nano-particle with an interstitial loop between two basal planes, the ends of the inserted plane are indicated with arrows.

Banhart, F. *Rep. Prog. Phys.* **1999**, 62, 1181–1221.

The Influence of Crystallinity on the <a>-axis Shrinkage of Pyrolytic Graphite



L_c = 22 nm

L_c = 160 nm

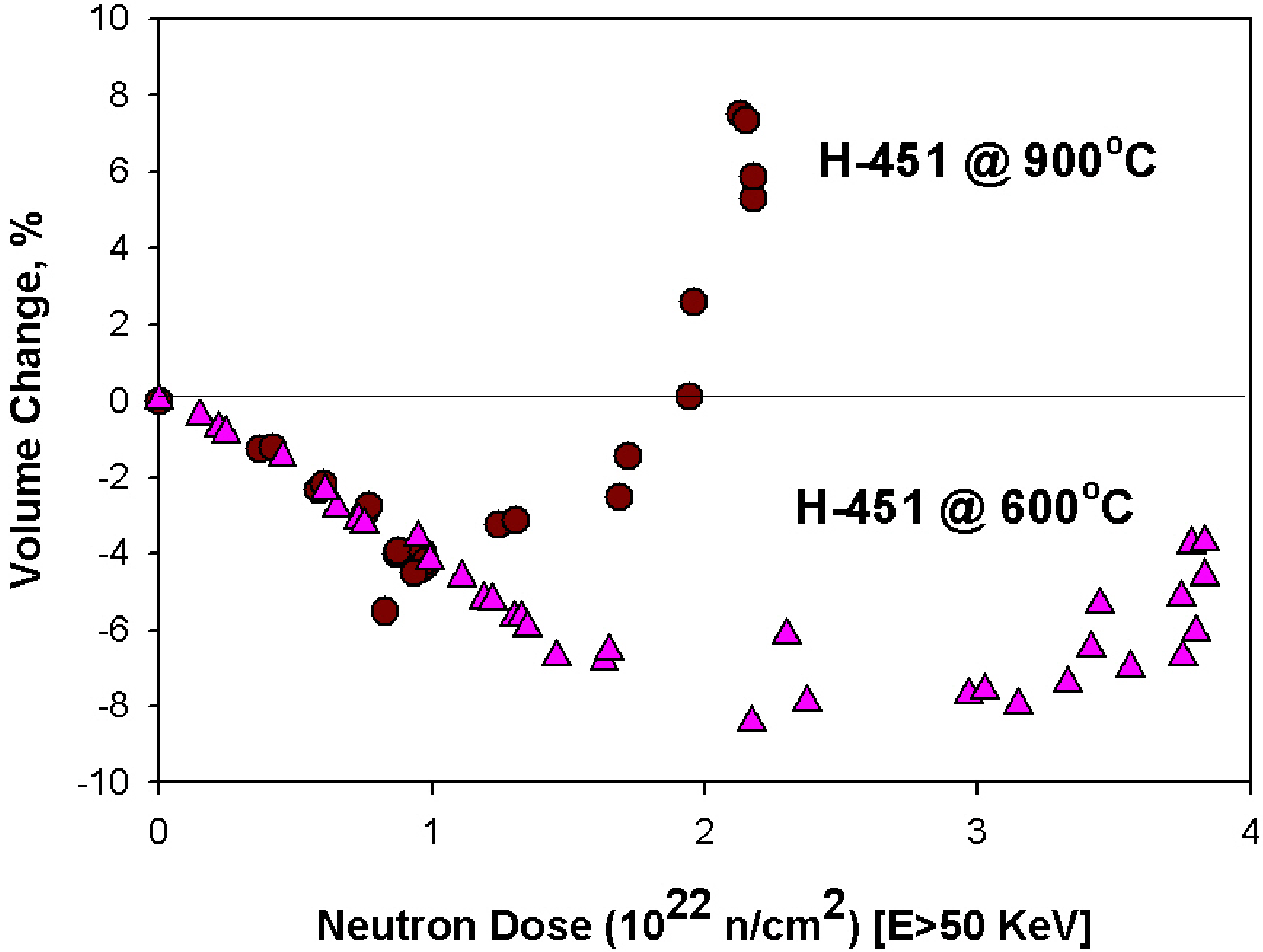
Neutron Irradiation Induced Dimensional Change

- Graphite dimensional changes are a result of crystallite dimensional change and graphite texture.
- Swelling in c-direction is initially accommodated by aligned microcracks that form on cooling during manufacture.
- Therefore, the a-axis shrinkage initially dominates and the bulk graphite exhibits net volume shrinkage.
- With further irradiation, incompatibilities in crystallite strains causes the generation of new porosity and the volume shrinkage rate falls eventually reaching zero.

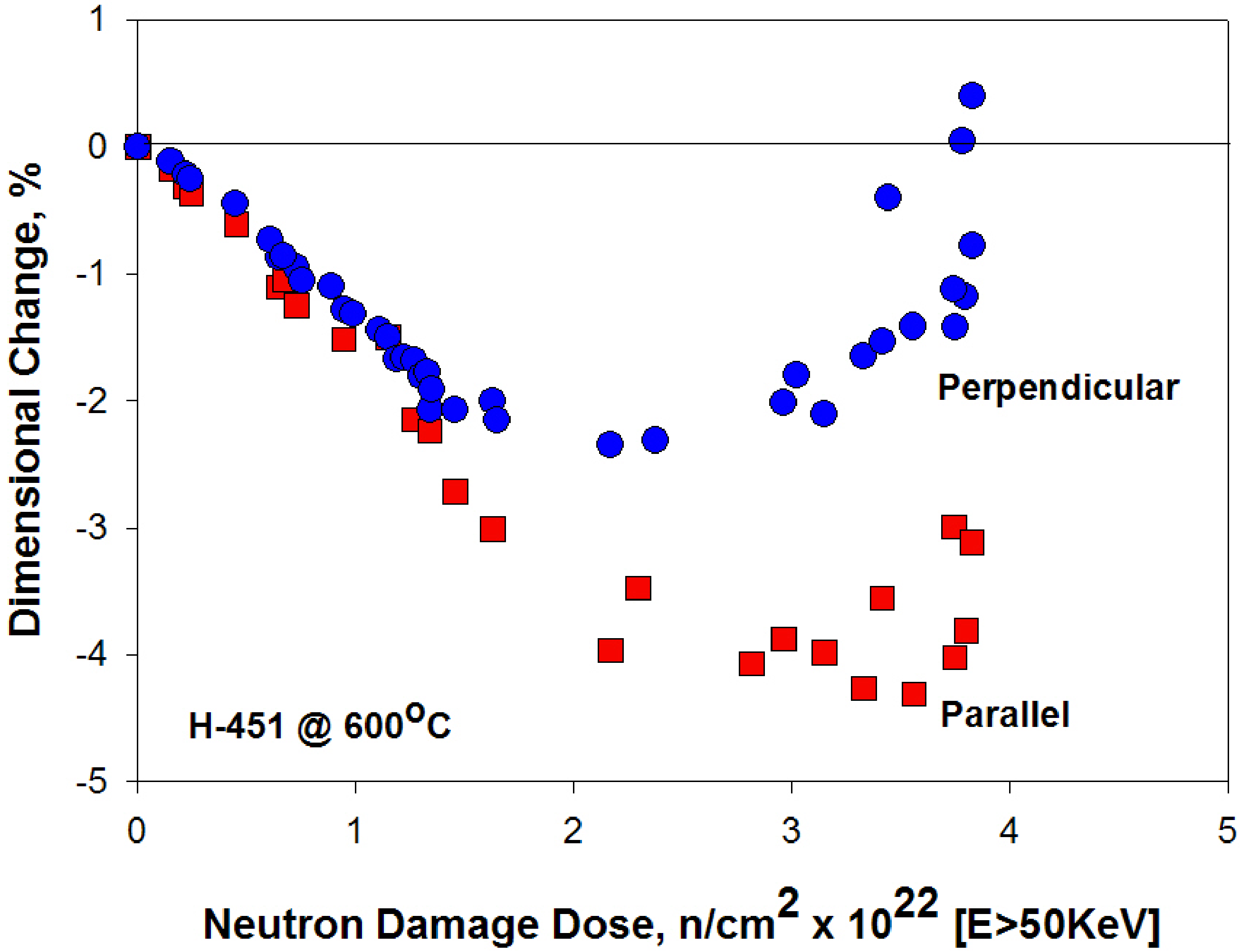
Neutron Irradiation Induced Dimensional Change (continued)

- The graphite begins to swell at an increasing rate with increasing damage dose due to c-axis growth and new pore generation.
- The graphite thus exhibits volume "turnaround" behavior from initial shrinkage to growth.
- Eventually loss of mechanical integrity occurs due to excessive pore/crack generation.

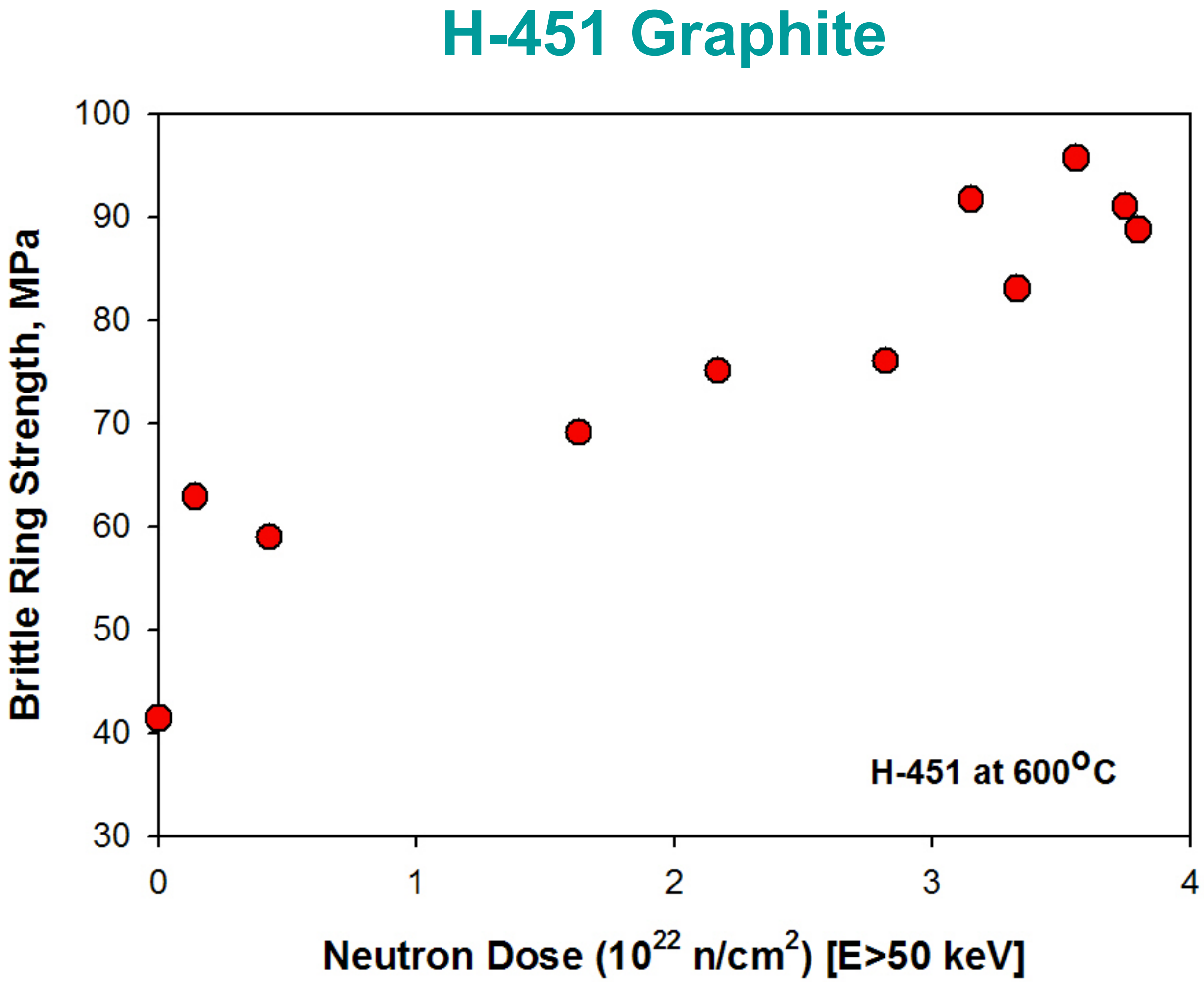
Radiation Induced Dimensional Changes in H-451 (Effect of Temperature)



Radiation Induced Dimensional Changes in H-451 (Effect of Texture)



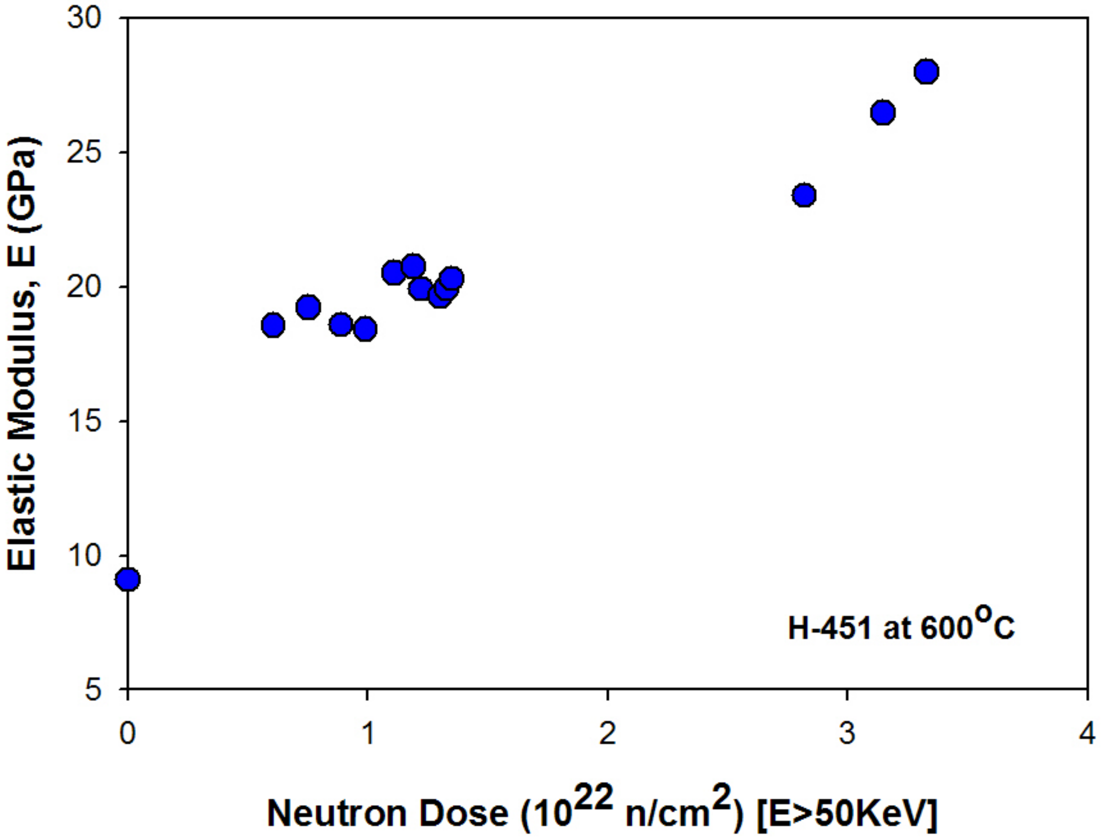
Neutron Irradiation Induced Changes in Fracture Strength



- Initial increase due to dislocation pinning
- Subsequent changes due to pore closure and new pore generation
- $K_{Ic}=\sigma[\pi c]^{1/2}$
- Critical flaw (unirradiated) approximately 1 mm

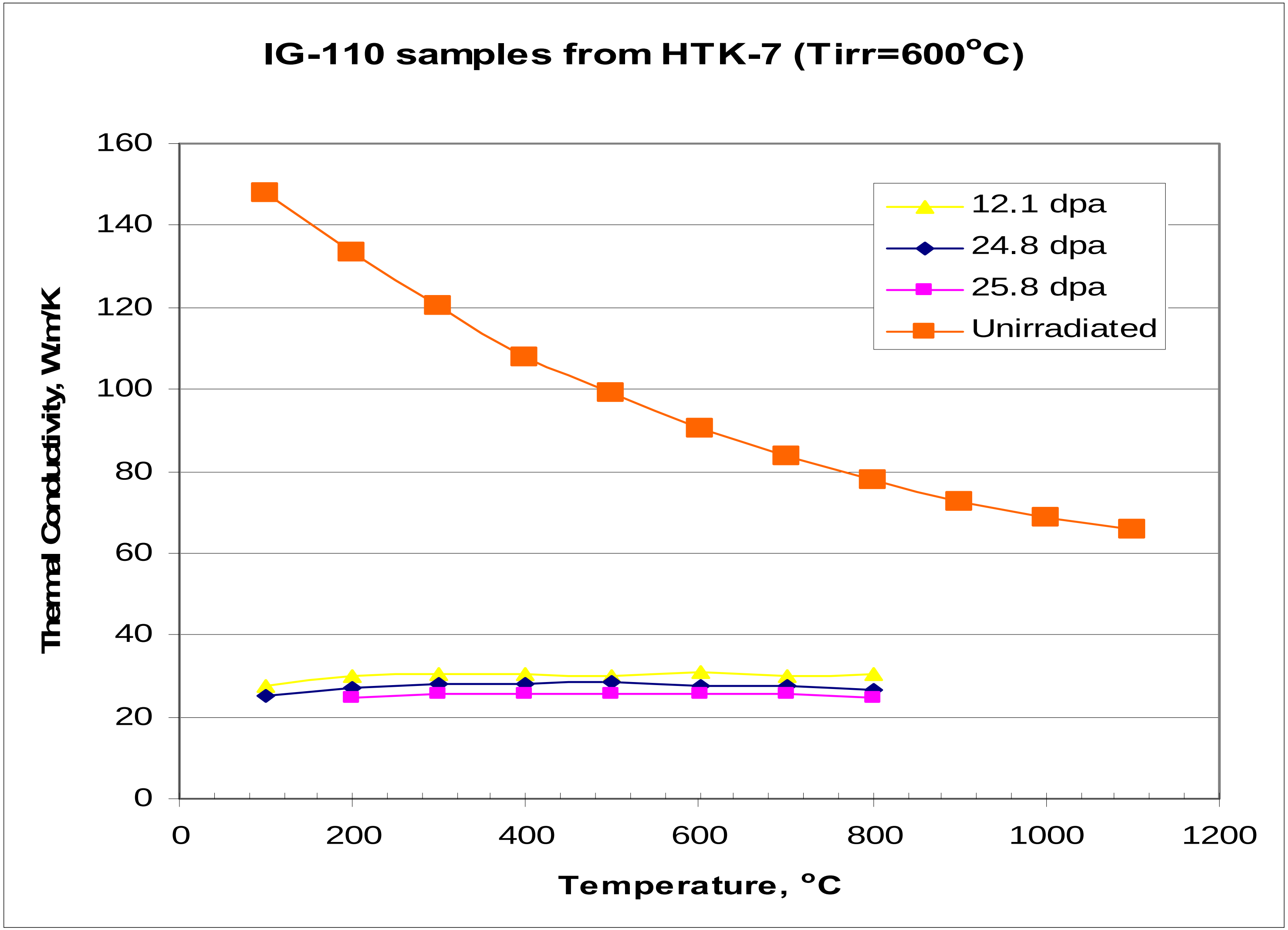
Neutron Irradiation Induced Changes in Young’s Modulus

H-451 Graphite



- Initial rise due to dislocation pinning
- Subsequent increase due to volume shrinkage (densification)
- Eventual turnover and reduction due to pore/crack generation and volume expansion
- $\sigma \alpha (E)^{1/2}$

IG-110 Thermal Conductivity Changes Umklapp and Defect Scattering



Irradiation Induced Dimensional Changes Result in Differential Strains

- **Weaker graphites crack (pore generation)**
- **Stronger graphites resist pore generation and strains creep out (irradiation creep)**
- **Radiation creep is a two stage phenomena**
- **Primary (reversible) creep strain α (1/E_0)**
- **Secondary (irreversible) creep strain f(σ,γ,E_0)**
- **Mechanism of creep subject of disagreement**
- **Two effects must contribute**
  - In-crystal deformation
  - Pore generation/pore re-orientation
- **At high doses we must allow for structural changes**
- **Irradiation induced creep in graphite is the subject of a new IAEA Coordinated Research Project**

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International Graphite Irradiation Programs

- **European Framework (5th, 6th, 7th, 8th ….)**
  - Comprehensive irradiation program of available candidate graphites
- **South Africa**
  - MTR program (conducted at ORNL) for NBG-18 covers relevant dose and temperature range to PBMR **(ON HOLD)**
- **China**
  - Plans an MTR Program relevant to HTR-PM (IG-110)
- **USA (DOE)**
  - NGNP Graphite irradiation program for candidate graphites (See Technology Development Plan)
- **International data will become available through the Gen IV International Forum**

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Radiolytic Oxidation is not a Problem In He Cooled HTRGs

- $CO_2 + \gamma = CO_2^*$, an activated species that can oxidize carbon at reactor temperatures
- Radiolytic weight loss can degrade physical properties
- Special measures include gaseous phase inhibitors
- Helium cooled reactors are immune from radiolytic oxidation
- Air/steam oxidation can occur in all graphite moderated reactors and will cause property degradation

Thermal Oxidation (Air and Steam)

- **Air/steam oxidation can occur in all graphite moderated reactors and will cause property degradation**
- **Air ingress accident**
  - $C+O_2 \rightarrow CO_2$
  - $CO_2+C \rightarrow 2CO$
- **Steam in Helium Coolant**
  - $C + H_2O \rightarrow CO + H_2$
  - $C + 2H_2 \rightarrow CH_4$
- **Oxidation = Loss of solid Carbon (Graphite)**

Thermal oxidation (Air and Moisture)

- **Properties degrade as a function of oxidative weight loss (burn-off)**
- **To predict burn-off we need to know:**
  - Kinetics of oxidation reactions over the appropriate range of temperature and partial pressure (or concentration) of oxidizing species
  - Local partial pressure (or concentration) of oxidizing species within core/graphite block (Effective Diffusivity)
- **Graphite purity also has an effect since some impurities act as oxidation catalysts**

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Graphite Wear/Abrasion

- **Tribological data are needed to establish wear of components**
- **Friction Coefficients (in Helium, effect of pressure and temperature)**
  - Graphite on graphite
  - Pebble on Pebble
  - Pebble on Graphite
- **Wear rates need to be established**
- **Wear products (dust) represents a possible fission product transport mechanism**

Outline

- Role in HTGRs
- Manufacturing processes
- Nuclear graphite for HTGRs
- Graphite and graphite testing standards
- Physical & mechanical properties and irradiation effects
- International graphite irradiation programs
- Graphite oxidation and other chemical reactions
- Wear of graphite – tribology
- Graphite performance modeling

Graphite Performance Modeling

Graphite Performance Modeling Requires:

- Whole core graphite behavioral model
  - How large are the stress?
- Fracture Model or Failure Theory
  - Do the stresses cause fracture?
- Assessment Criteria
  - What are the consequence of brick/block failure for core integrity?

Graphite Performance Modeling

- **Whole core graphite behavioral model requires:**
  - **Stress analysis, constitutive equation**
  - **$\varepsilon_{Total} = \varepsilon_e + \varepsilon_t + \varepsilon_d + \varepsilon_c$**
  - **Core temperature (T) and dose distribution (γ)**
  - **Dimensional change data and model**
  - **Creep data and model, f (T, γ, σ)**
  - **Property change data and models, Tc, CTE, E, σ as a f (T, γ)**

Graphite Performance Modeling

- Fracture Model or Failure Theory
  - Weibull model
  - Burchell model
  - CARES model
  - Fracture Mechanics
  - Maximum Deformation Energy Theory (ASME)
  - Maximum Strain Energy Theory
  - Maximum Principal Stress
  - Etc.

Graphite Performance Modeling

- Assessment Criteria
  - **Consequence of brick/block failure for core integrity**
  - **Core structural redundancy**
  - **Fitness for purpose**
  - **In core monitoring to confirm predictions and increase confidence in core integrity**
  - **Replaceable components**

Graphite Performance Modeling

- Need to determine the effect of weight loss on property
- Need to predict extent of property degradation
- Work in hand at INL and ORNL to determine oxidation kinetics and effect of oxidation on properties for candidate graphites
- Oxidation is a potential FP transport mechanism

Summary

- > 60 years experience with graphite as a solid moderator
- Mechanism of radiation damage well understood
- A few grey areas remain
  - High temp stored energy release
  - Whole core models (and material models)
  - Irradiation creep
  - Tribology & wear
  - Effective diffusivity (oxidative weight loss)

Suggested Reading

- **Nuclear Graphite –The First Years, W. P. Eatherly, J. Nucl. Mater. 100 (1981) 55-63**
- **Irradiation Behavior of Graphite at High Temperatures, G. B. Engle and W. P. Eatherly, High Temperatures-High Pressures, Vol. 4, pp.119-158 (1972)**
- **Radiation Damage in Graphite, J.H.W. Simmons, Pergamon Press (1965)**
- **Nuclear Graphite, R.E. Nightingale (Ed.), Academic Press (1962)**
- **Radiation Effects in Graphite and Carbon-Based Materials, T. D. Burchell. MRS Bulletin, Vol. XXII, No. 2, pp. 29-35 (1997)**
- **CARBON MATERIALS FOR ADVANCED TECHNOLOGIES, Edited by Timothy D. Burchell. Pub, Pergamon (Elsevier Science), 1999.**
  - CHAPTER 13: *FISSION REACTOR APPLICATIONS OF CARBON* by Timothy D. Burchell
- **Banhart, F. Irradiation effects in carbon nanostructures. *Rep. Prog. Phys.* 1999, 62, 1181–1221.**
- **Graphite for High Temperature Gas-Cooled Reactors, David Ball, ASME STP-NU-009 (2008)**