Industry Trends in High Modulus Fiber and UHT Technology

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Review of Carbon Fiber Transformations at UHT Temperatures

- Carbon fiber undergoes a transformation at UHT temperatures which affect
  - Crystallite Structure
  - Thermal Conductivity
  - Electrical Conductivity
  - Fiber Modulus
  - Fiber Strength

Transformation of Carbon Fibers at UHT Temperatures

- Carbon fiber produced at typical HT temperatures may have only 93% carbon with a significant percentage of nitrogen, and a fractional percentage of hydrogen.
- High modulus fibers are relatively pure carbon.
- Mean inter-layer distance decreases with increased UHT temperatures

Transformation of Carbon Fibers at UHT Temperatures

- The crystallite dimensions of PAN carbon fibers increases with increased temperature
- Many of the carbon fiber properties change as a result of the crystallite changes. These include the carbon fiber modulus, thermal conductivity, and electrical conductivity.

Transformation of Carbon Fibers at UHT Temperatures - CTE

- The coefficient thermal expansion (CTE) of a graphite crystal parallel to the basal plane is negative at room temperature.
- The CTE along the fiber direction tends to be negative for carbon fiber (more aligned with the basal planes).
- The CTE trends to decrease with maximum processing temperature due to the increased crystallinity.
- As the UHT final temperature increases the CTE of the fiber trends to become a larger negative valve.

Single Crystal Graphite	Room Temperature Thermal Expansion
Parallel to basal plane	-1.5×10^{-6} /°C
Perpendicular to basal plane	27.0×10^{-6} /°C

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Transformation of Carbon Fibers at UHT Temperatures – Electrical and Thermal Conductivity

- Carbon fiber electrical and thermal conductivity increase with increasing UHT temperatures
- The electrical and thermal conductivity increase due to the increased crystallite dimensions and orientation

High Modulus Fibers Require UHT Temperature Capabilities

- Published data shows continued increasing modulus with fiber heat treat temperature.
- The fiber modulus increases towards the basal/c11 plane theoretical modulus of 1050 GPa.
- Modulus Rises faster after 2000°C.

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High Modulus Fibers Require UHT Temperature Capabilities

- Higher final processing temperature will tend to increase final modulus.
- Higher final processing temperature does not always increase strength.
- Published data shows decreasing strength with final processing temperature.

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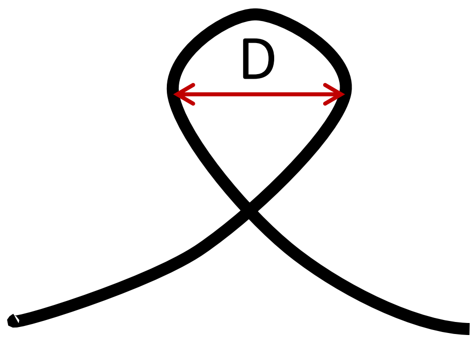
Knot or Loop Test

- Knot or loop test is a common quick method of determining the relative strength to modulus ratio of carbon fiber
- For PAN carbon fibers produced in HT furnaces the diameter of the loop to failure is small indicating a high strength to modulus ratio
- For PAN carbon fibers produced in UHT furnace system the diameter of the loop increases largely based on the increase in elastic modulus.



$$D_{Loop} \sim \left(\frac{d}{\epsilon}\right)_{Fiber} = \left(\frac{d * E}{\sigma}\right)_{Fiber}$$

$$d = fiber\ diameter,$$

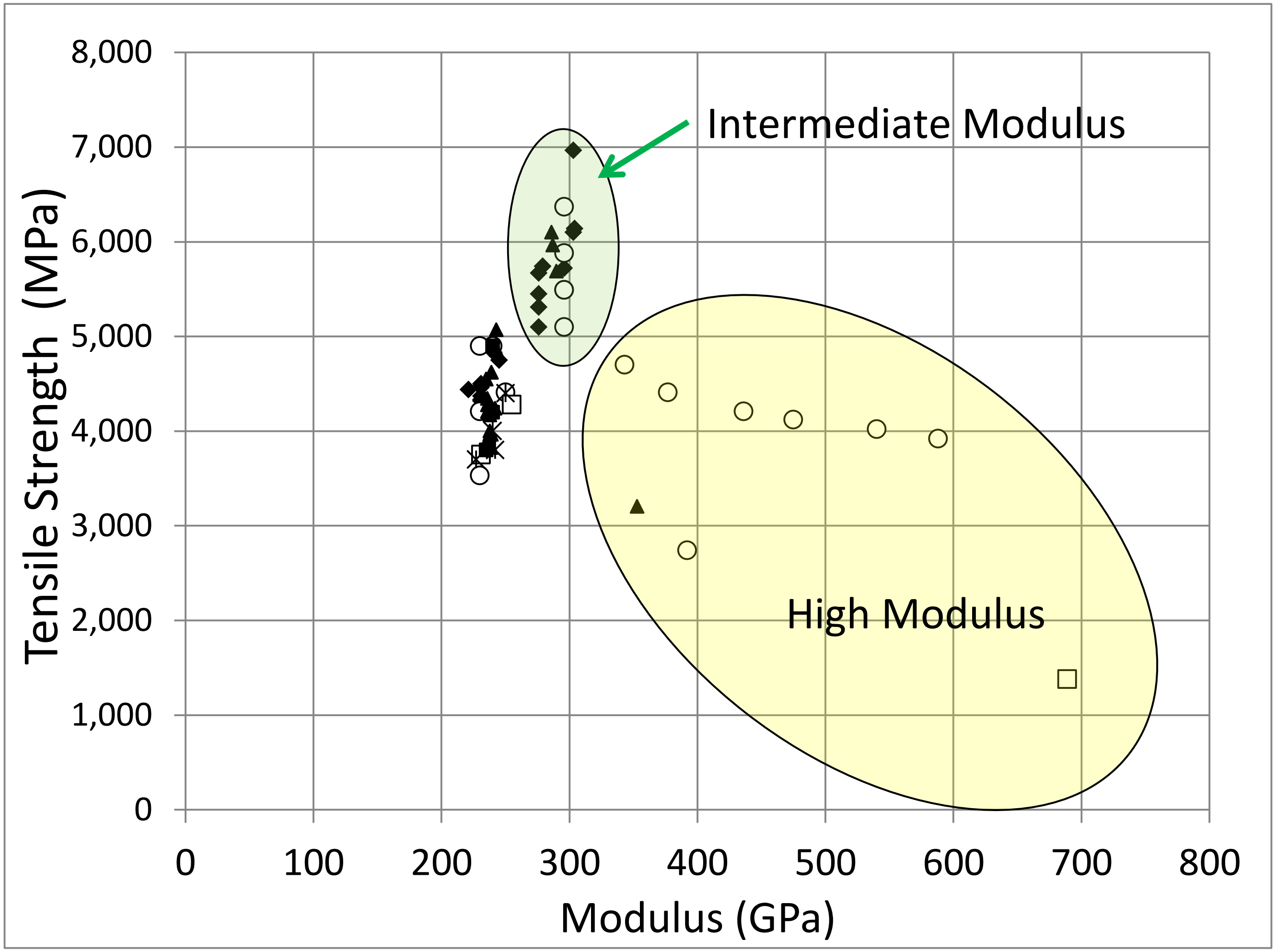
$$E = Modulus,$$

$$\sigma = tensile\ strength,$$

$$\epsilon = strain\ to\ failure$$

High Modulus Fiber On the Market

- The tensile strength and tensile modulus on the market shows the trend of lower strength fiber with higher modulus.
- High modulus fiber is typically above a tensile modulus of 350 GPa



Harper Pilot Scale UHT

- Multiple UHT pilot unit installations
- Years Operation 2300°C to 2650°C prior to element or graphite replacement

Width: 152mm / 6 inches
Heated Length: 1524 mm / 60 inches
Maximum Temperature: 2800°C

Width: 76mm / 3 inches
Heated Length: 914 mm / 36 inches
Maximum Temperature: 2800°C

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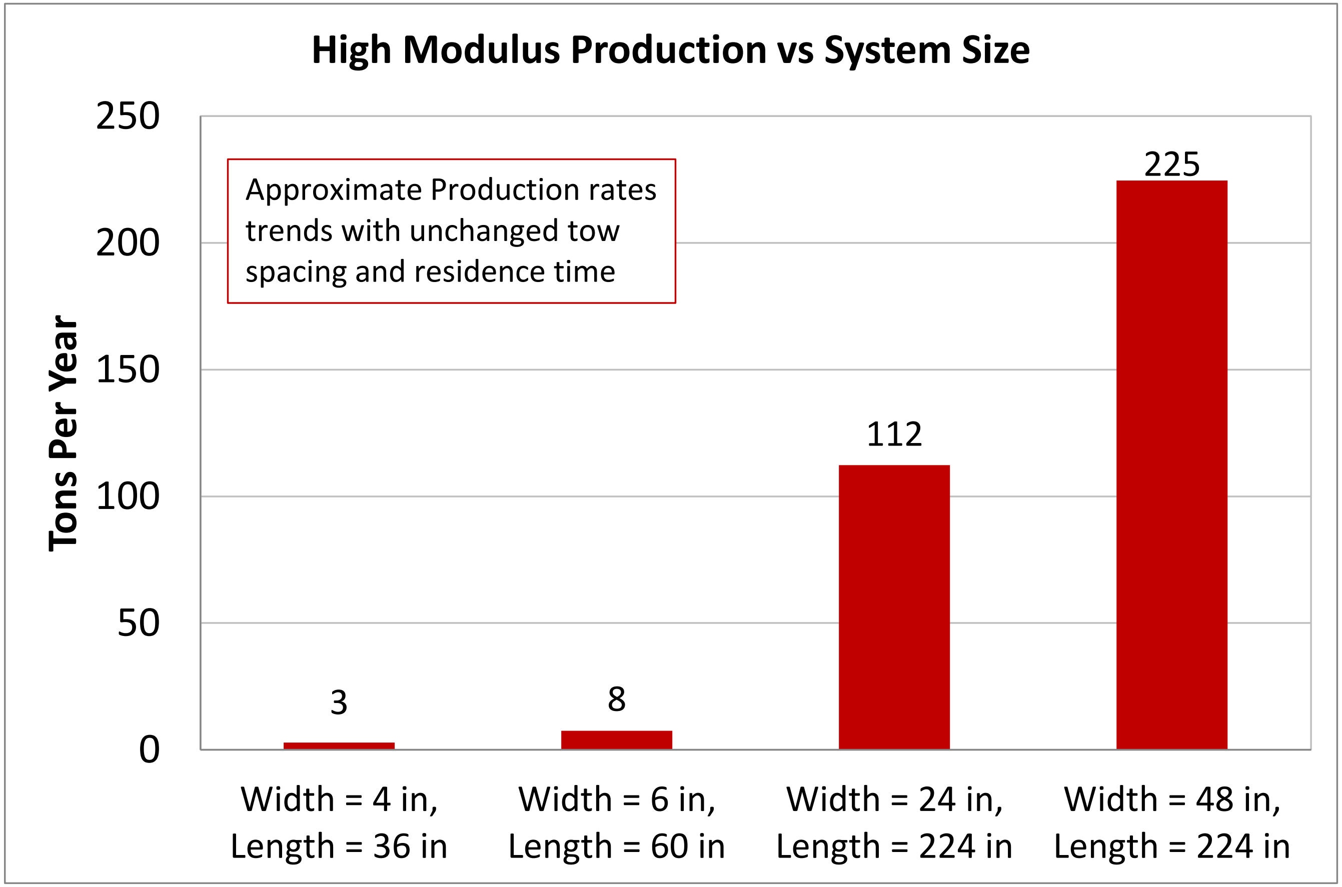
Trend is to Larger Multiple Zoned UHT Systems
Why scale-up? Capacity of Larger System

- Increased demand for high-modulus fibers
- 6″ tube system provides limited production
- Production rates increases significantly with scale



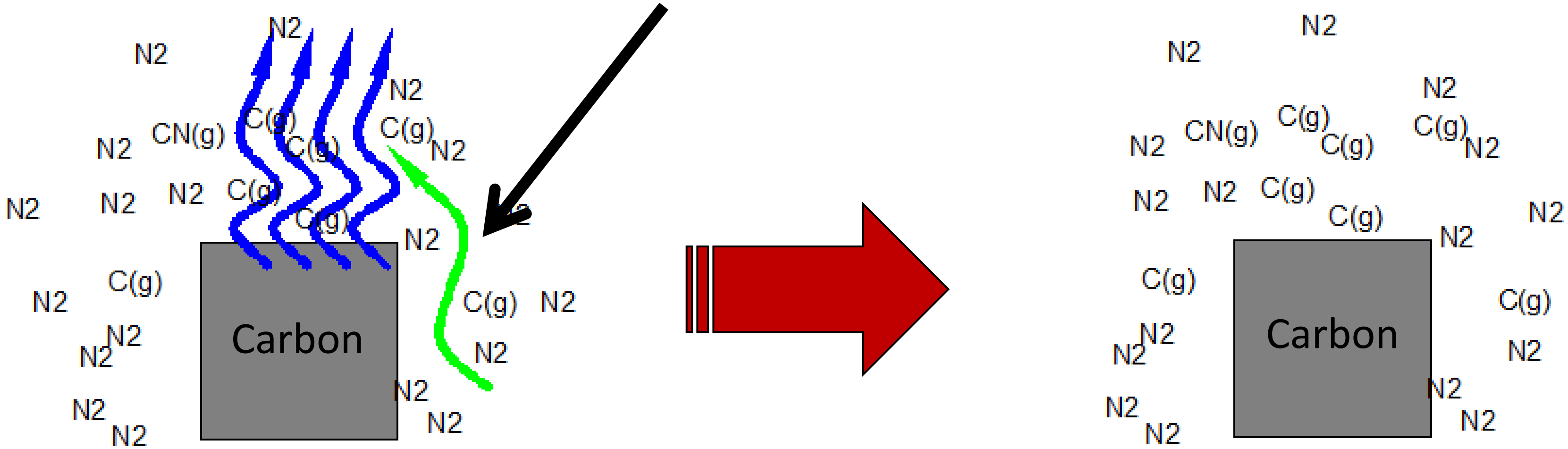
Protective Atmosphere

Higher the N2 purge rate → Increased carbon loss

Minimization of required heating chamber purge rates increases element and furnace component life.

Partial Pressure of C species gasses swept out by N2 purge

Near Stagnant N2 in heating chamber reduces carbon loss



Harper's Superior Positive Seal Construction results in greatly enhanced furnace life

Protective Atmosphere

- Nitrogen is the most commonly used protective atmosphere for UHT's.
- However, at the UHT temperatures the formation of CN is known to occur.
- The loss rate of carbon to the atmosphere is strongly dependent on temperature.
- The carbon loss is dependent on the carbon and CN vapor pressure.
- Within the heating chamber the rate of carbon loss becomes dependent on the amount fresh nitrogen purged within the chamber.
  - Higher the N2 purge rate → Increased carbon loss to bring the carbon species vapor pressure to equilibrium.
- **Minimization of required heating chamber purge rates increases furnace life.**
  - Minimization is achieved through a multifaceted approach to superior gas tight construction
  - Recommendation is to turn the chamber N2 flow off at UHT temperature operations.

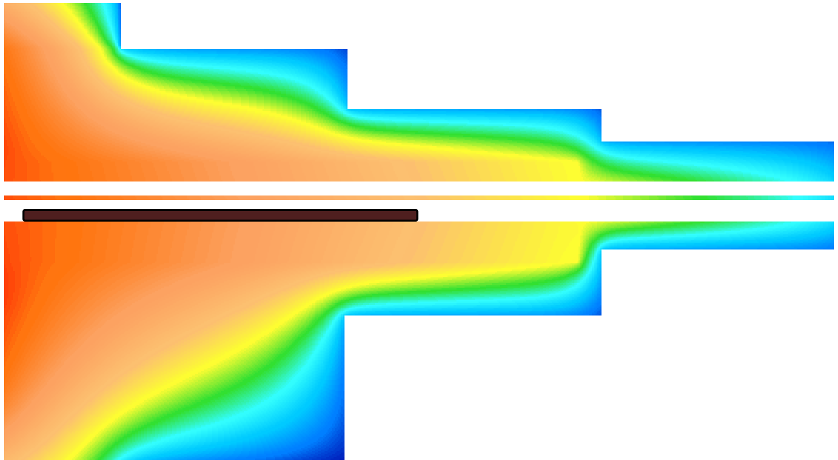
Advantages of Nitrogen vs. Argon at Production Scale

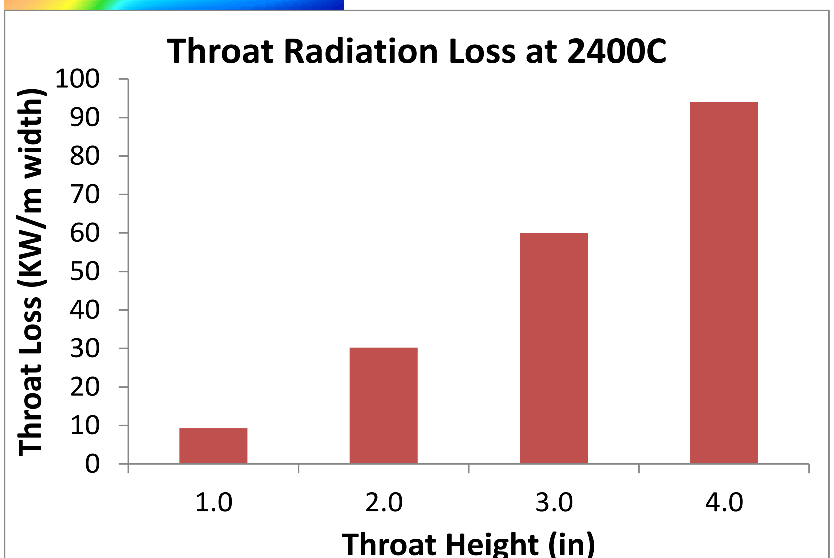
- Lab scale the consumption of the protective atmosphere is low.
- Argon costs ~8x per volume the cost of nitrogen
- At production scale the protective atmosphere (argon or nitrogen) is significant more than lab scale.
- The use of the Harper UHT low flow systems results in unparalleled performance and graphite life as well as lower overall operating costs for the Nitrogen protective atmosphere.

Gas	Boiling Point
Nitrogen	-195.8°C
Argon	-185.8°C
Oxygen	-183.0°C

Boiling point of argon and oxygen are close.

Throat Losses through Slot Openings: Throat Height affect Heat Loss out Furnace Ends





- At the throat height increase, the energy loss out the ends dramatically increases.
  - Loss proportional to increased area
  - Loss proportional to increased view factor based on slot H/L ratio
- Removable slot pieces to modify slot height and facilitate cleaning
- Cooling Section design accounted for large radiation and product thermal mass load.
- Insulated cooling design reduces overall thermal load to cooling section and improves thermal performance

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Harper Production UHTs

- UHT Production Unit Systems
  - 610 mm Slot Width
  - Multiple zone configuration
    - 5, 6, 7 or more zones
  - 4.1 – 6.5 m heated length
    (dependent on zone count)
  - Advanced purge chambers
  - Superior gas tight system

FJ210 UDRI Continuous Graphite System

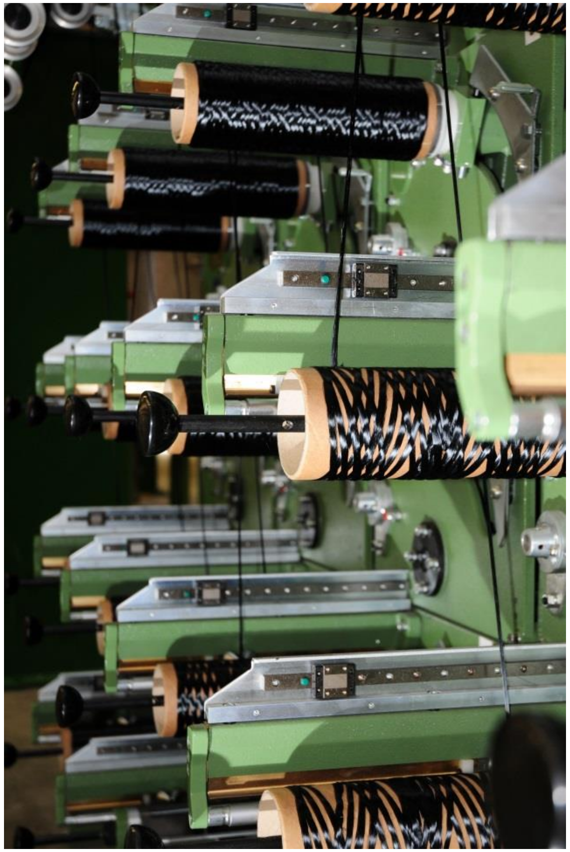
"Harper's ultra-high temperature (UHT) graphite furnace system has been rock solid in its performance. With the potential challenges a system that operates at 2500°C can offer, Harper's design has been dependable, consistent and reliable since 2006. With minimal rebuild and operation at 2500°C, the system remarkably still has original heating elements and graphitic parts, which would normally degrade quickly at such high temperatures. The furnace is used for process development of multiple applications and it has proven versatile for this purpose."

Nicholas Gagliardi
Composite Research Engineer
University of Dayton Research Institute

Ultra-High Temperature Graphite Furnace References

- 50+ Units Lab or Pilot Size at 2000°C+
  - 12 Units For Carbon Fiber
  - 9 Carbon Fiber Units above 2400°C

- 16 Production Units at 2000°C+
  - 8 Units For Carbon Fiber
  - 6 units above 2400°C



Thank you for your time!

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