Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

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Overview

Timeline

- Start- 2004
- End- 2012
- Percent complete- ca. 50%

Barriers

- Barriers addressed
  - A. High cost of carbon fiber
  - B. High volume manufacturing of carbon fiber

Budget

- Already covered

Partners

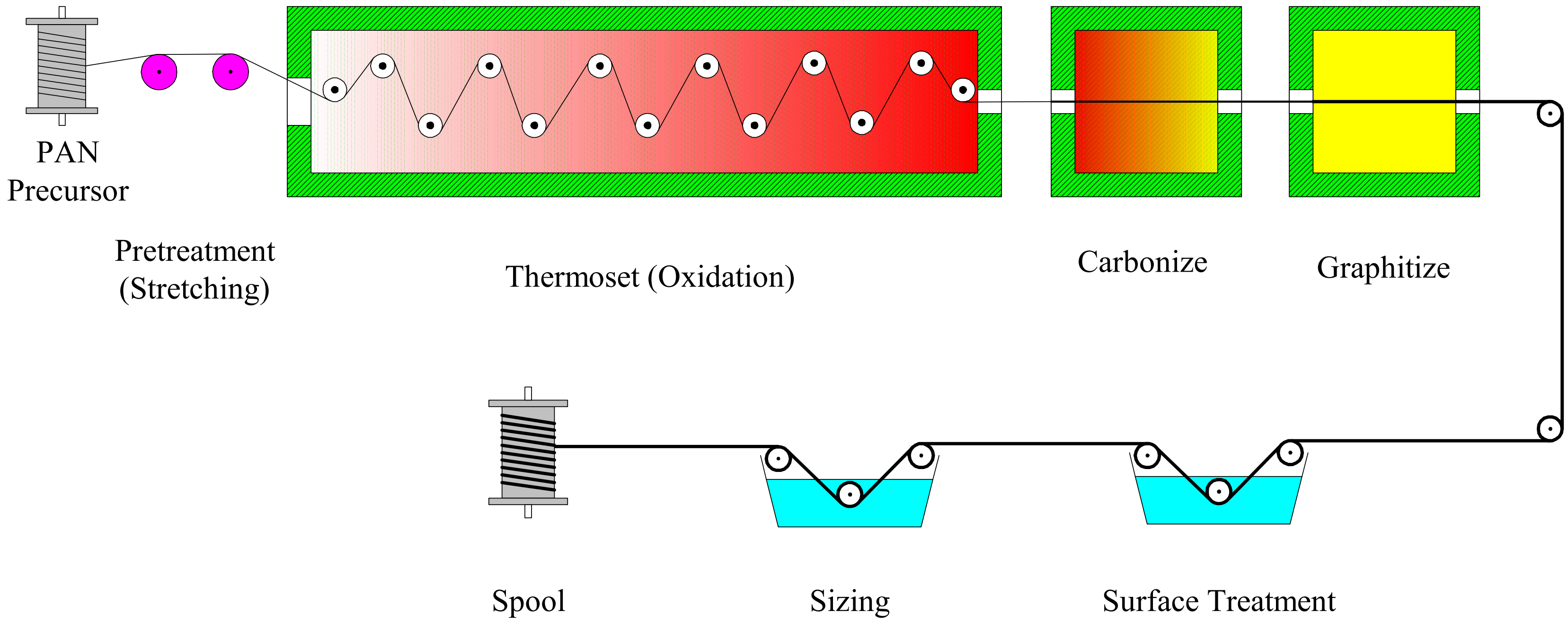
- ORNL (Host site)
- Sentech Inc. (Experimental site)

Objectives

- Rapid stabilization and oxidation of Pan-based carbon fiber precursor

- By developing a rapid stabilization and oxidation of a precursor a significant cost reduction in the most important step of carbon fiber conversion is achieved.

Conventional PAN Processing



Typical processing sequence for PAN –based carbon fibers

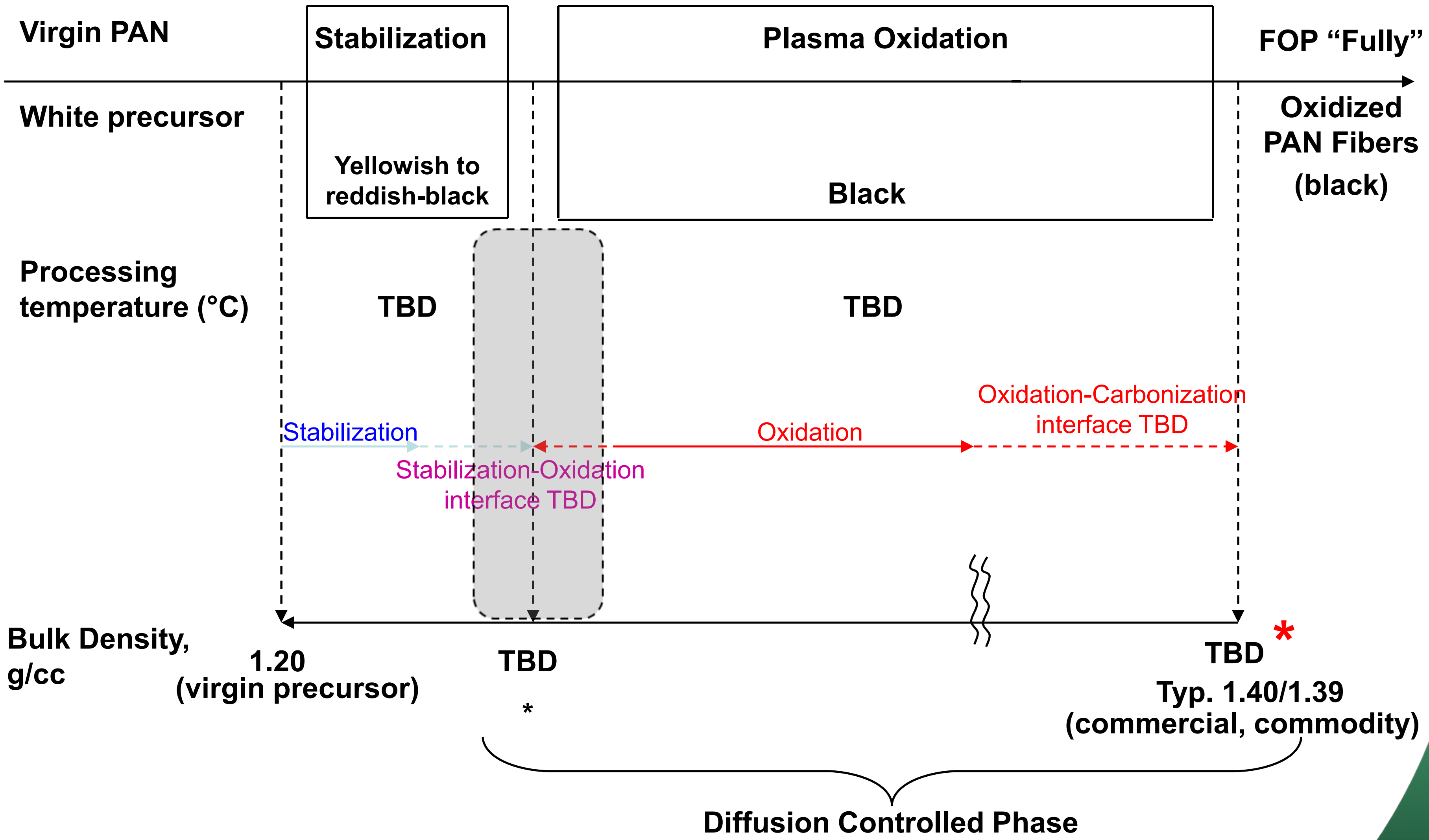
Major Cost Elements	
Precursor	43%
Oxidative stabilization	18%
Carbonization	13%
Graphitization	15%
Other	11%

Automotive cost target is $5 - $7/lb

Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain

ORNL is attempting major technological breakthroughs for major cost elements

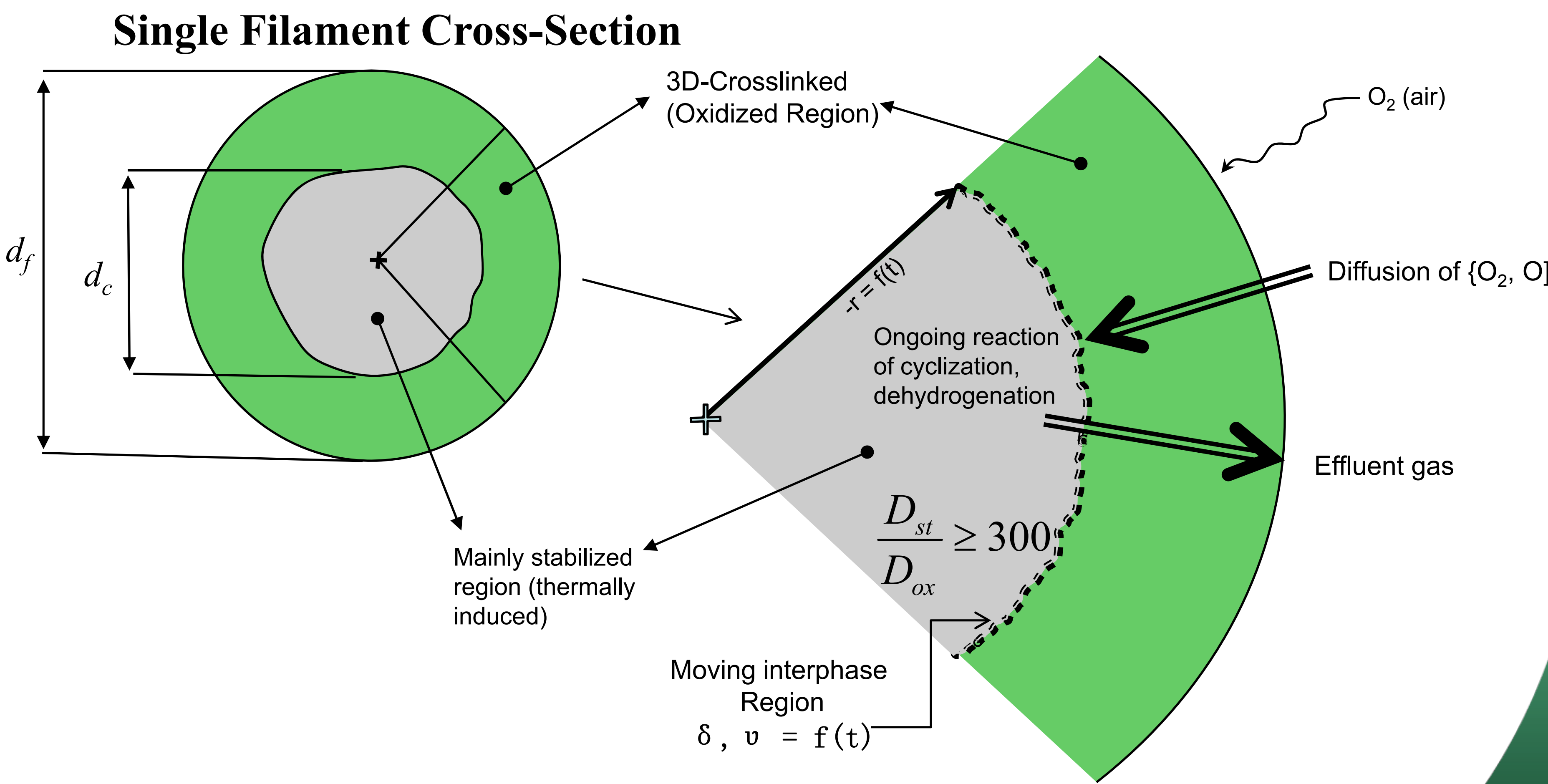
Oxidation Interfaces



Milestones

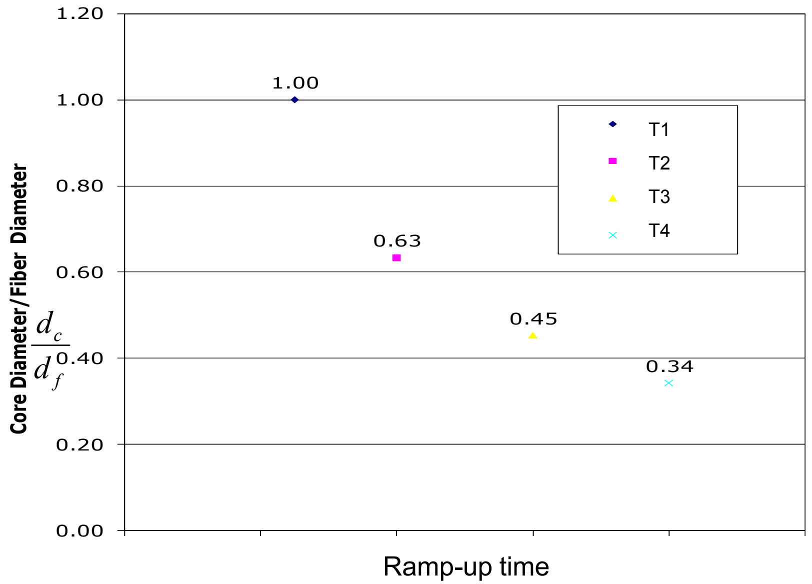
Date	Milestone or Go/No-Go Decision
Sep-08	Complete initial mapping and analysis of gas-phase FTIR data – delayed by AGT dissolution.
Dec-08	Commence scaling to > 3k tow size (deferred)
Mar-09	Complete equipment relocation. – Complete, experimental operations ongoing
Jun-09	First experimental results from experiments with > 3,000 filaments
Sept-09	Report tow mechanical properties of plasma oxidized, conventionally carbonized tow with ≥ 3k filaments

Approach: Reduce PAN-Oxidation Two Zones Morphology

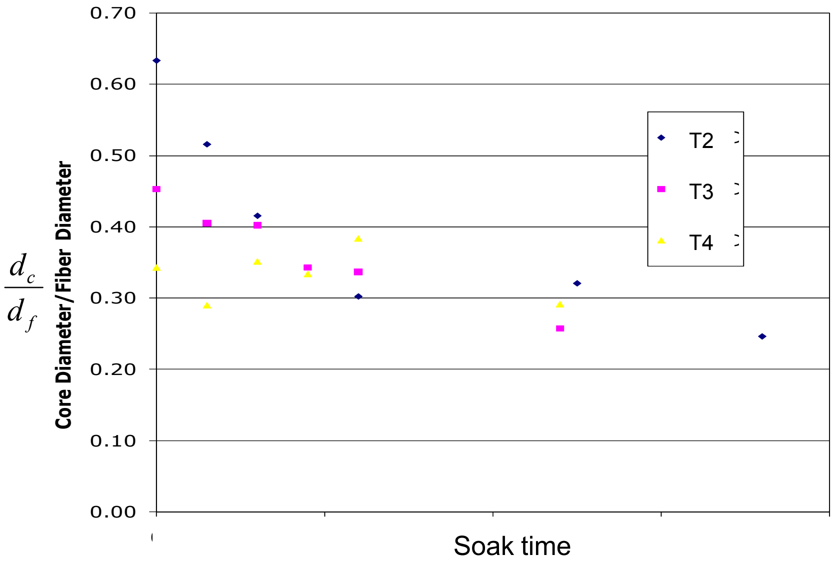


- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase

Approach: Evolution of Stable Fiber Core

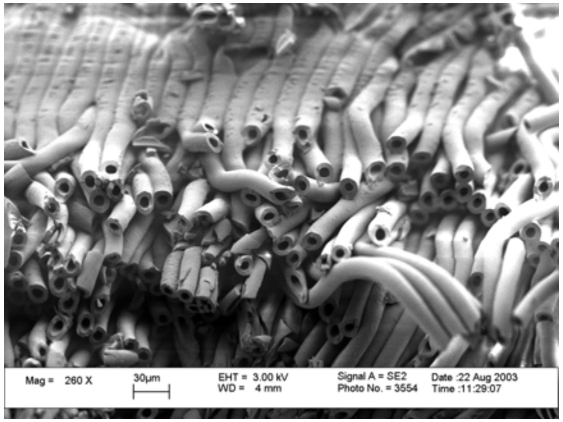


Fibers heated to specified temperature, no temperature soak



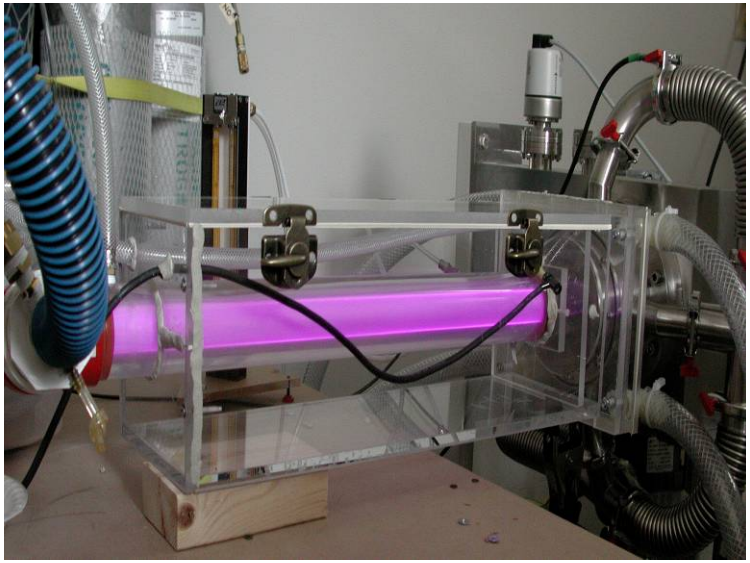
Fibers heated to specified temperature, followed by temperature soak

- **Fiber stabilizes from outer surface toward center**
- **Unstabilized core was digested in acid, then core diameter measured by microscopy**



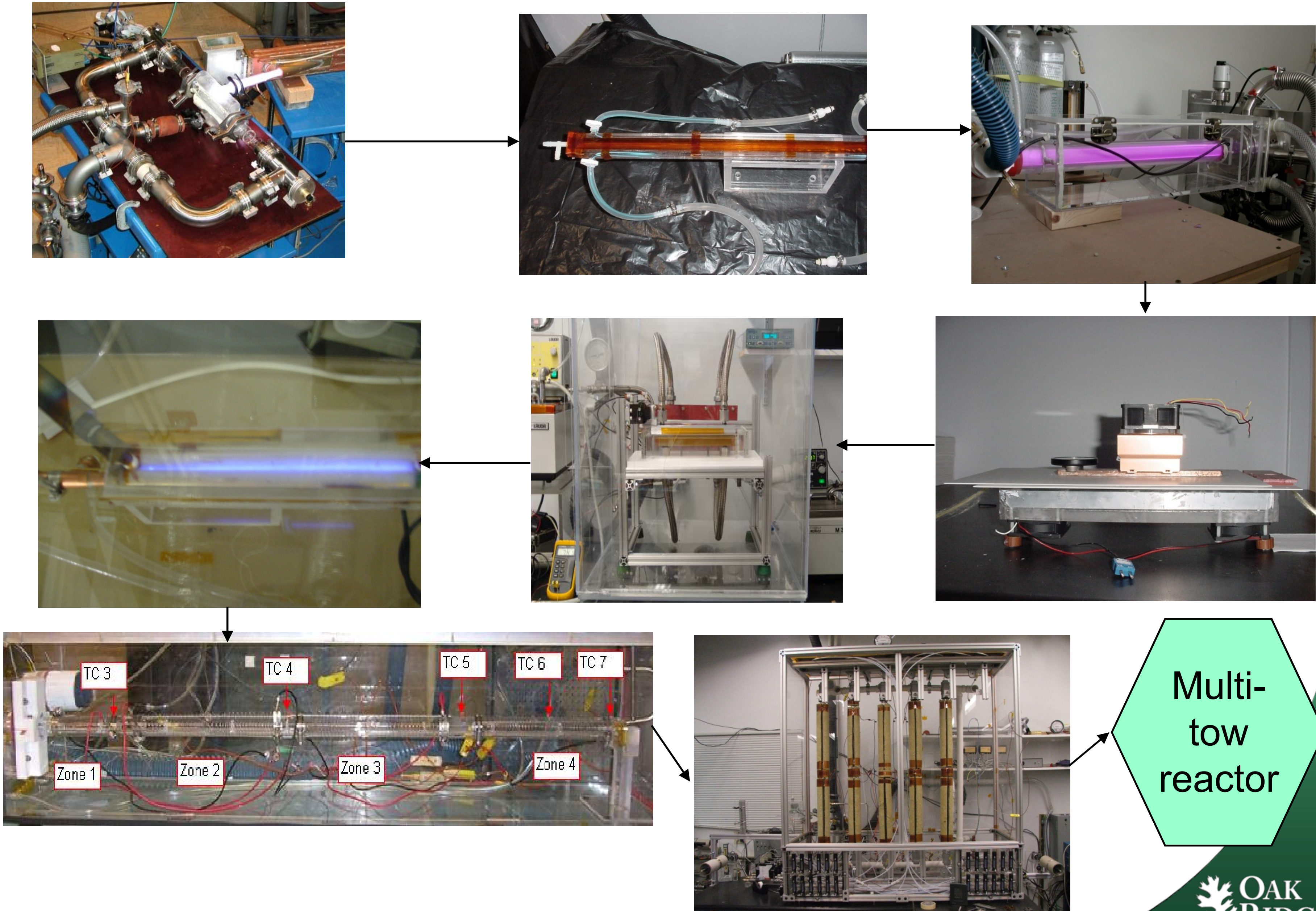
Approach: Advanced Oxidation

- **Addresses diffusion-controlled stages of conventional oxidation**
- **Based on nonthermal, atmospheric pressure plasma processing**
- **Physical and morphological properties good; carbonization and mechanical property validation underway**
- **Residence time reduced by ≥ 3X to date**
- **Fiber core better oxidized (digestion profiles)**
- **System design improvements and scale-up underway**



- **Initial need for fiber pre-stabilization was eliminated**

Advanced Oxidation Reactor Development Sequence

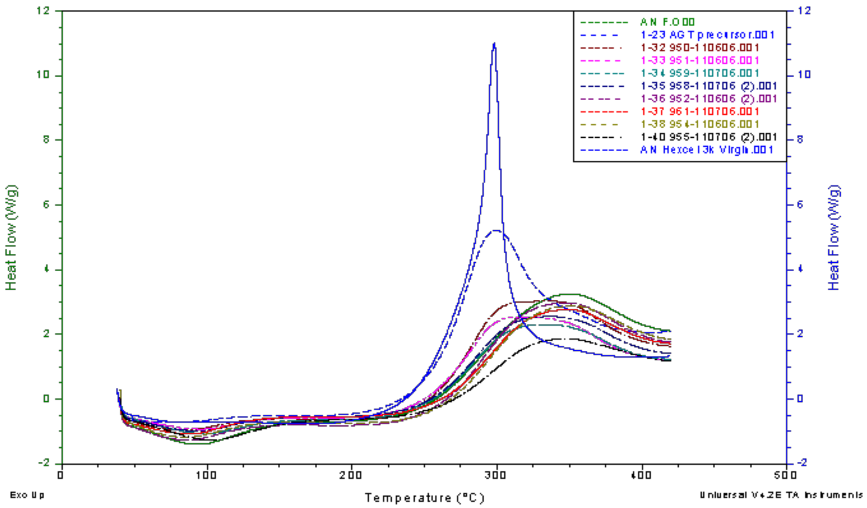


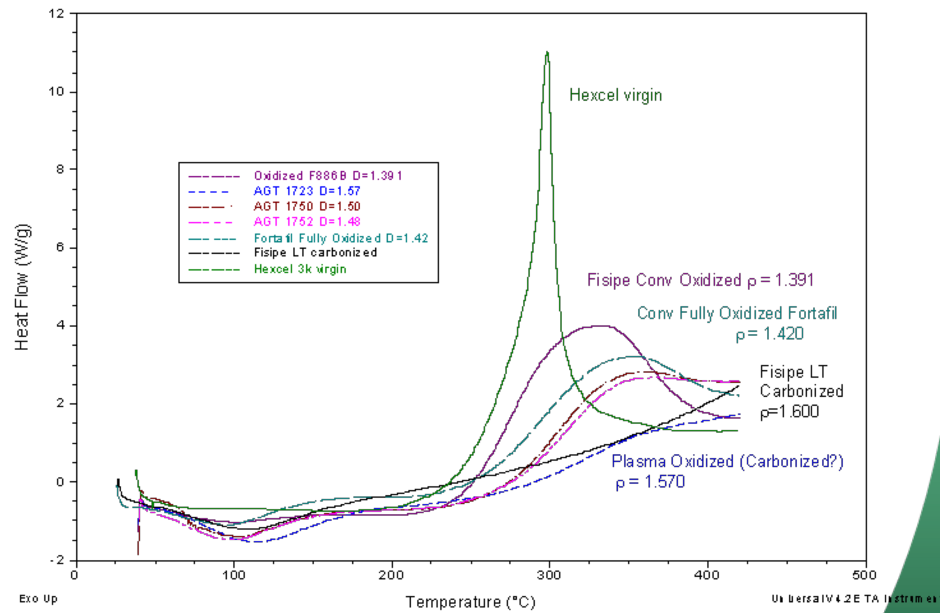
Stabilization Challenges

- Stabilization needs to be fast and inexpensive
- Thermochemical route
  - Conv. thermal – high line speeds require long oven(s)
  - Plasma-assisted – initially damaged virgin precursor, until we discovered a “good recipe”; integrates seamlessly with plasma oxidation
- Electron beam route
  - Unstable, accelerated oxidation process
    - There is further high cost reduction potential when we learn to control the oxidative reactions
    - IP has been disclosed on how to utilize this effect to advantage
  - Capital investment
- Ultraviolet route
  - Throughput demand
  - Nonuniformity

- Thermochemical stabilization route was down selected

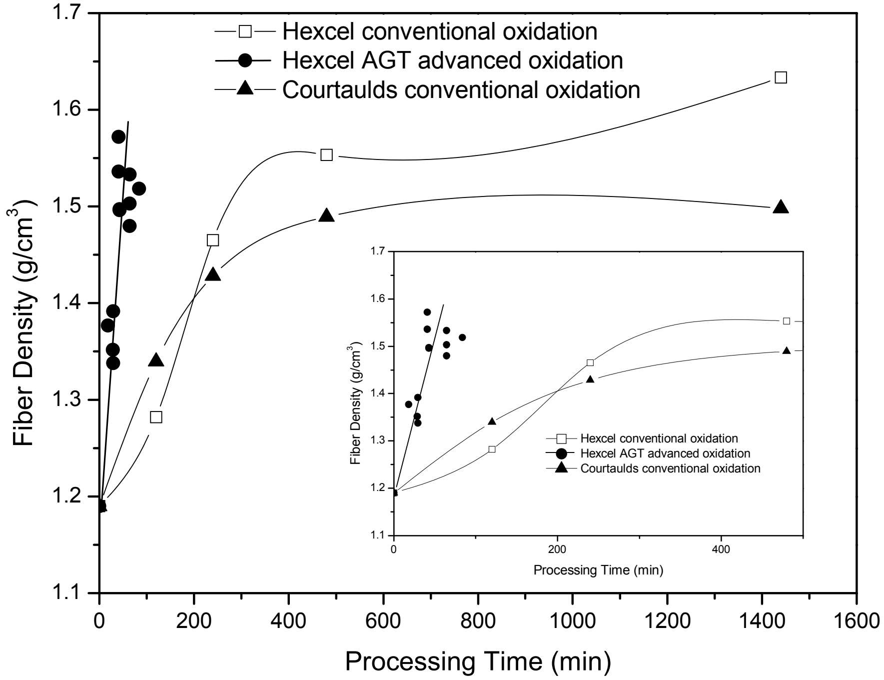
Technical Accomplishments/ Progress/Results





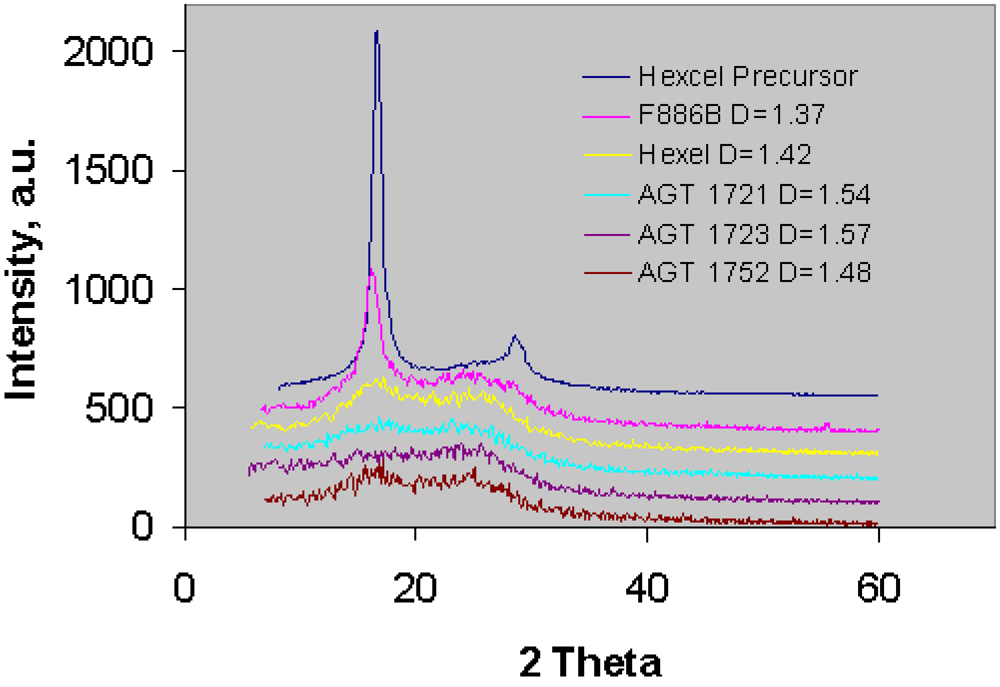
DSC thermograms of PAN fibers at different level of advanced and conventional oxidation are displayed in the figures. It is clear that advanced oxidized fiber has less heat of reaction in air than the other fibers.

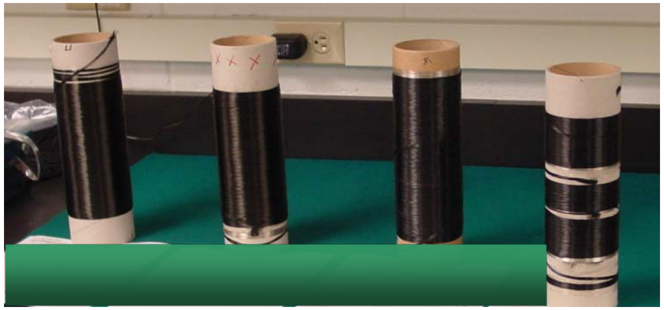
Technical Accomplishments/ Progress/Results



Accelerated oxidation is demonstrated in processing time vs. density profiles for fibers in conventional and ORNL proprietary oxidation process

Technical Accomplishments/ Progress/Results





Oxidized fiber spools

XRD Data indicate that there is less degree of order for the advanced oxidized fibers (sharpness of the peak due to precursor fiber orientation is reduced) in comparison to the conventionally oxidized fiber F886B D=1.37 g/cm^3 and Hexcel D=1.42 g/cm^3. This is due to higher degree of oxidation in advanced processed fibers

Technical Accomplishments/ Progress/Results

Measured mechanical properties of single filaments from various oxidized tows

Fiber ID #	Density (D) (g/cm^3)	Tensile Strength (Ksi)	Tensile Modulus (Msi)	Ultimate Elongation (%)
AGT 1411	1.3515	29.8 ± 3.4	0.77 ± 0.21	5.86 ± 1.19
AGT 1427	1.3378	31.7 ± 3.1	0.88 ± 0.16	6.10 ± 1.39
AGT 1552	1.3839	33.2 ± 3.0	0.84 ± 0.17	14.58 ± 3.81
AGT 1586	1.3769	35.1 ± 2.4	0.82 ± 0.16	18.02 ± 4.52
AGT 1750	1.5028	20.0 ± 3.7	0.70 ± 0.30	3.15 ± 0.60
AGT 1496	1.3914	42.6 ± 3.4	0.90 ± 0.30	18.5 ± 4.3
AGT 1723	1.5719	20.2 ± 1.9	1.1 ± 0.20	2.02 ± 0.37
AGT 1752	1.4799	21.5 ± 4.2	1.2 ± 0.30	2.23 ± 0.55
AGT 1754-1755	1.5182	17.1 ± 1.7	0.60 ± 0.20	3.27 ± 0.59
Conventional-Hexcel 3k 4 hours	1.4651	39.3 ± 5.4	0.93 ± 0.33	10.35 ± 1.87
Conventional-Hexcel 3k 24 hours	1.6333	26.2 ± 2.6	0.09 ± 0.20	3.62 ± 0.66

With increase in density, the ultimate elongation decreases. We can tailor the mechanical properties depending on the degree of oxidation. Tensile data show strength and elongation can vary from 17-45 ksi and 2-18%, respectively.

Future Work

- **Rest of FY09**
  - Conduct detailed investigation of stoichiometry in multiple tow reactor
  - Commence materials compatibility investigations
  - Evaluate properties of plasma oxidized, conventionally carbonized tows

- **FY10**
  - Complete stoichiometry investigations
  - Refine oxidation process to satisfy program requirements for carbonized tow properties
  - Assess energy balance and demand
  - Conduct preliminary investigations with alternative precursors

Date	Milestone
Jun-09	First experimental results from experiments with > 3,000 filaments
Sept-09	Report tow mechanical properties of plasma oxidized, conventionally carbonized tow with ≥ 3k filaments

Date	Milestone
Mar-10	First experimental results for plasma oxidation of textile PAN or lignin precursor
Sept-10	Carbonized tow properties satisfy program requirements

Summary

- This work directly supports petroleum displacement via improved fuel economy from vehicle weight reduction
- This work addresses the very important barrier of carbon fiber cost
- The approach is to develop a revolutionary new method for converting carbon fiber, which offers much higher potential for achieving significant cost reduction than evolutionary improvements to existing conversion technology
- Major performance measures are good
  - Cut 3k tow residence time by ~ 3X vs. conventional oxidation
  - Single-filament mechanical properties encouraging
  - Constructed and began operation of multi-tow reactor
  - Delivered 100 m of plasma oxidized, 3k tow to each domestic auto OEM
  - Successfully recovered from the dissolution of a key partner, now proceeding forward with a new partner
  - Some FY08 milestones deferred due to subcontractor bankruptcy
  - Kline report indicates high cost reduction opportunity
- We are now in the early stages of scaling the processes and equipment designs