High Thermal Conductivity, Mesophase Pitch-Derived Carbon Foams

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Keywords: Graphite Foam, Thermal Conductivity,Thermal Management

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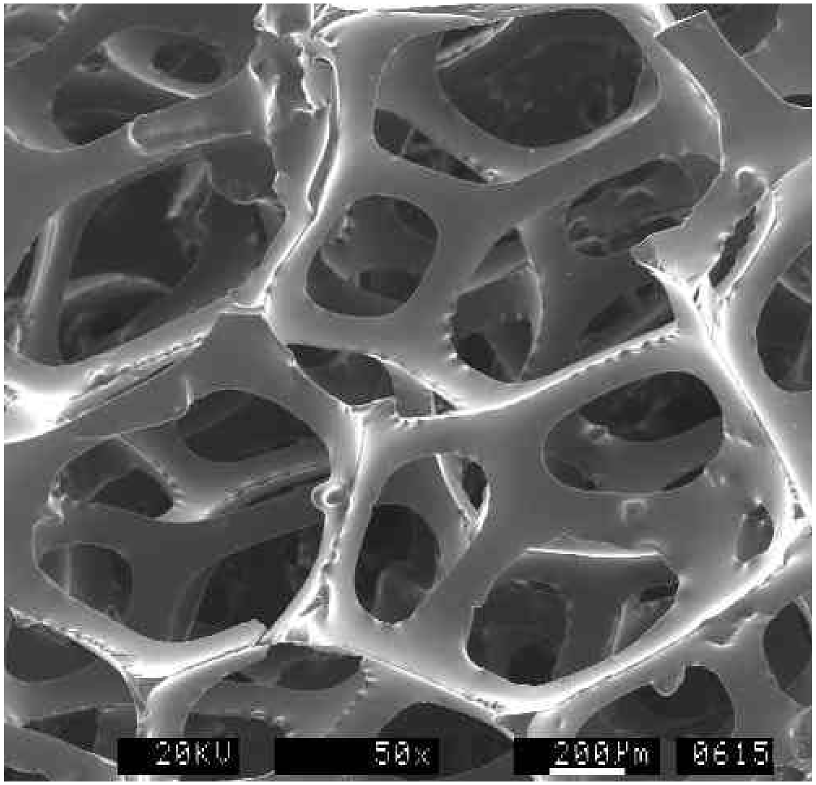
Carbon and Insulation
Materials Technology Group

Outline

- Graphite Foams
- Foam Structure and Properties
  - Scanning Electron Microscopy
  - Optical Microscopy - cross polarized light interference patterns
  - X-ray Analysis
  - Thermal properties - Xenon Probe Flash Diffusivity Technique
  - Mechanical Properties
- Engineered Graphite Foam Applications
  - Heat sinks
  - Heat Exchangers
  - Satellites
  - Heat Resistant Composites

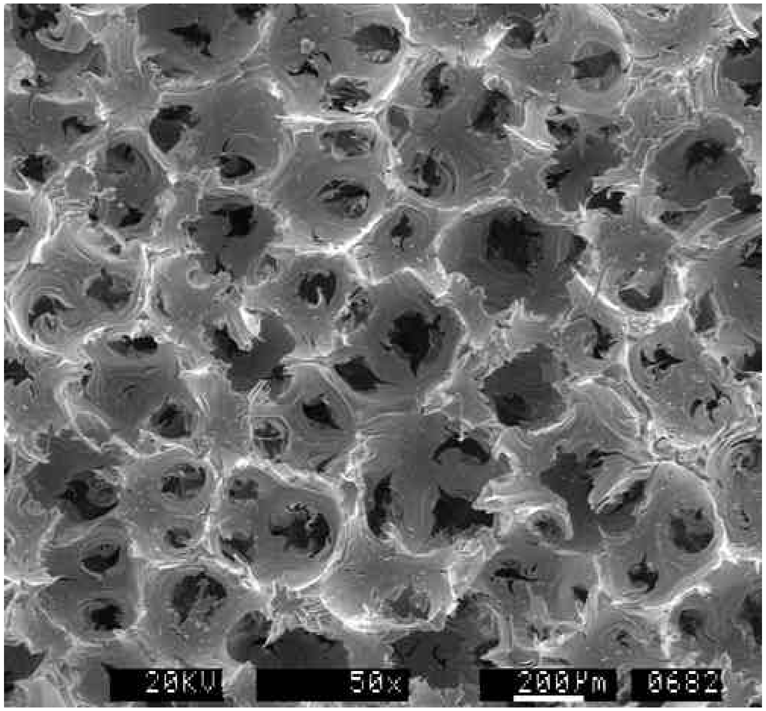
Typical Carbon Foams

- Made from amorphous carbons
- More recently made from pitches and mesophases
- 5-25% dense
- Thermal insulators
  - $\kappa < 10$ W/m·K
- strengths similar to honeycomb materials
- ability to absorb tremendous amounts of impact energy



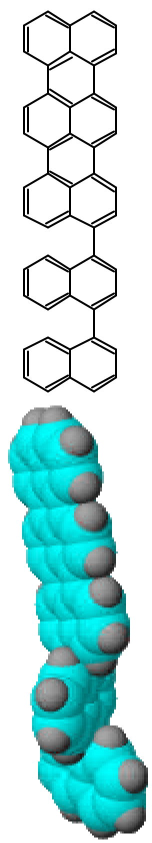
ORNL Mesophase-Derived Graphitic Foam

- Graphitic ligaments
  - Graphitic-like properties (high κ, E, σ)
- Dimensionally stable, low CTE
- No outgassing
- Open Porosity
- Excellent thermal management material

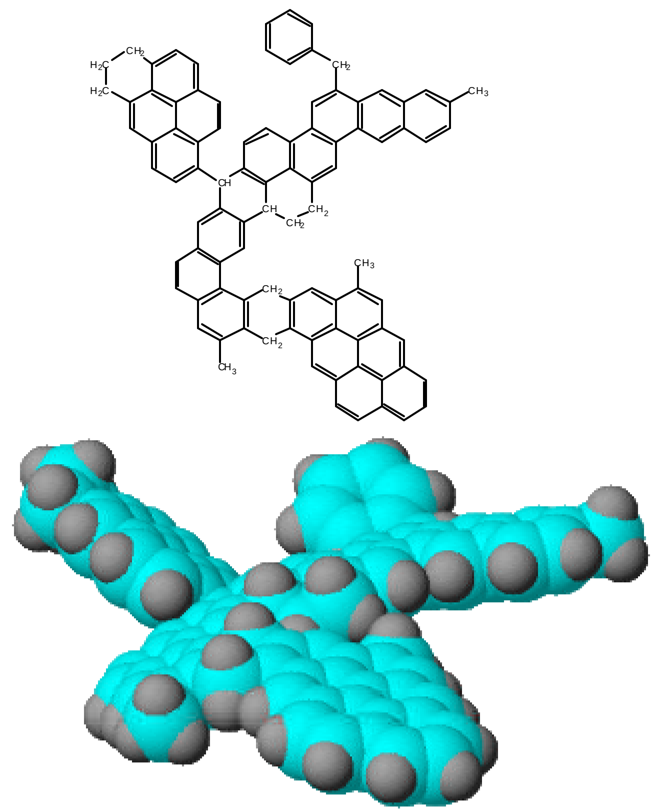


Mesophase Pitch

- Typical molecular structures are different
  - may affect shear orientation during processing
  - may affect mechanical and thermal properties



Mitsubishi AR Mesophase



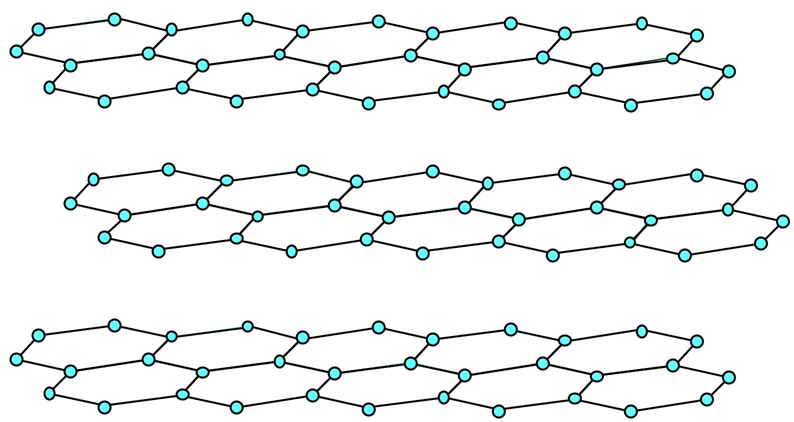
Typical Petroleum Derived Mesophase

Mesophase Pitch

- Under proper processing and heat treatments, the mesophase molecules become a Discotic Nematic Liquid Crystal
    - (400°C, 40 hours, Nitrogen Cover)

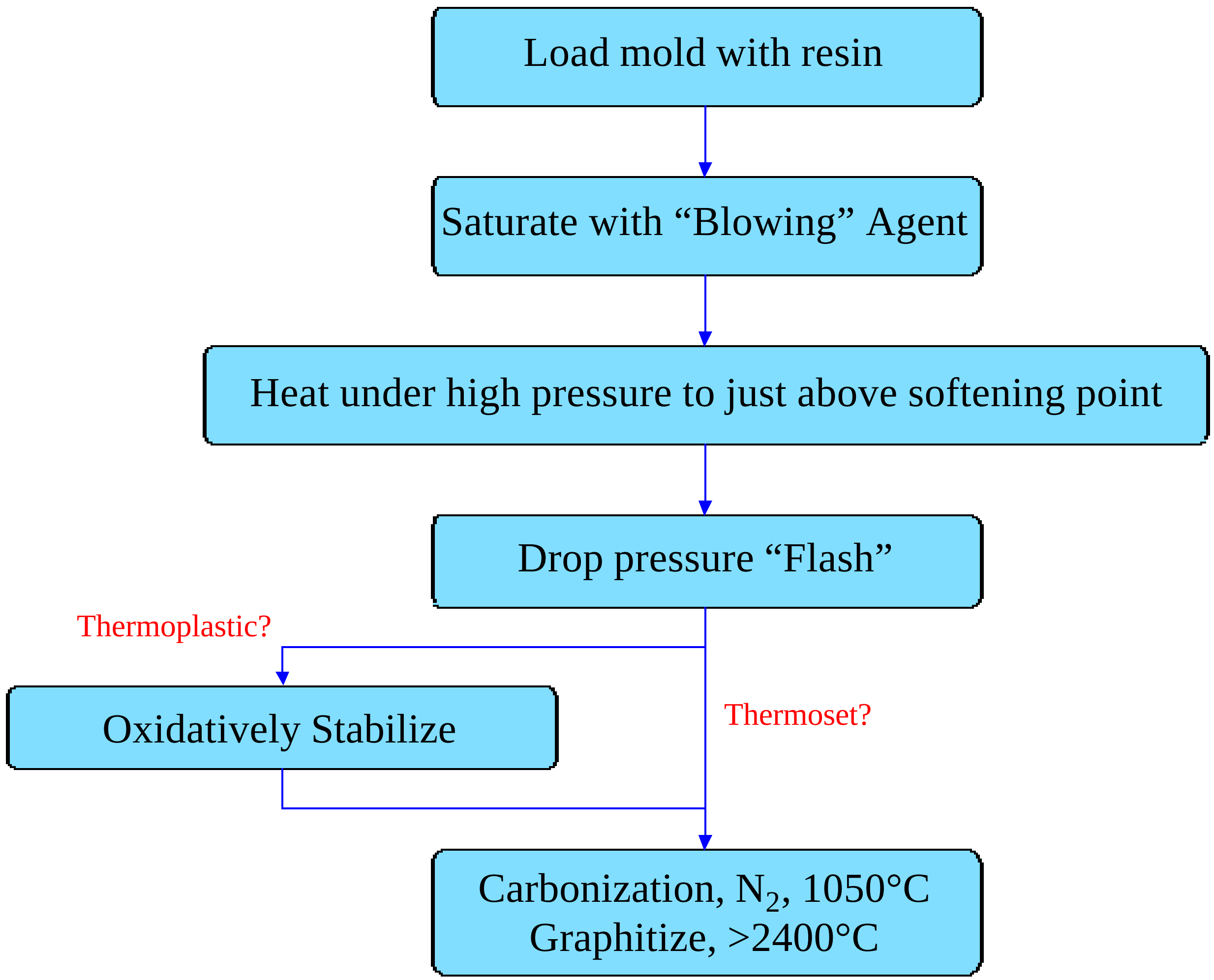
ΔT (3000°C)

Conversion to Graphite through Heat treatment



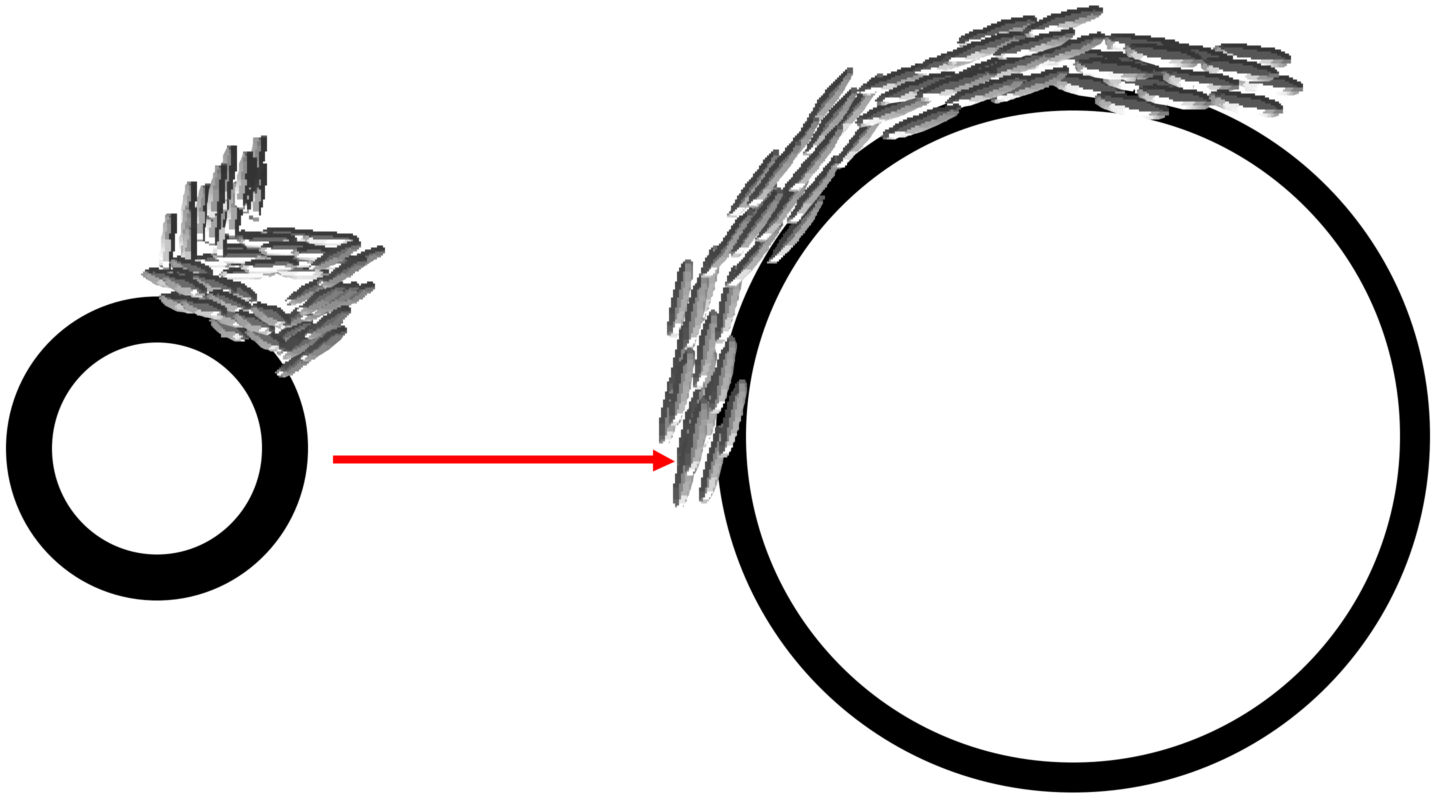
Traditional Carbon Foams - Manufacture

- Traditional "Blowing" techniques



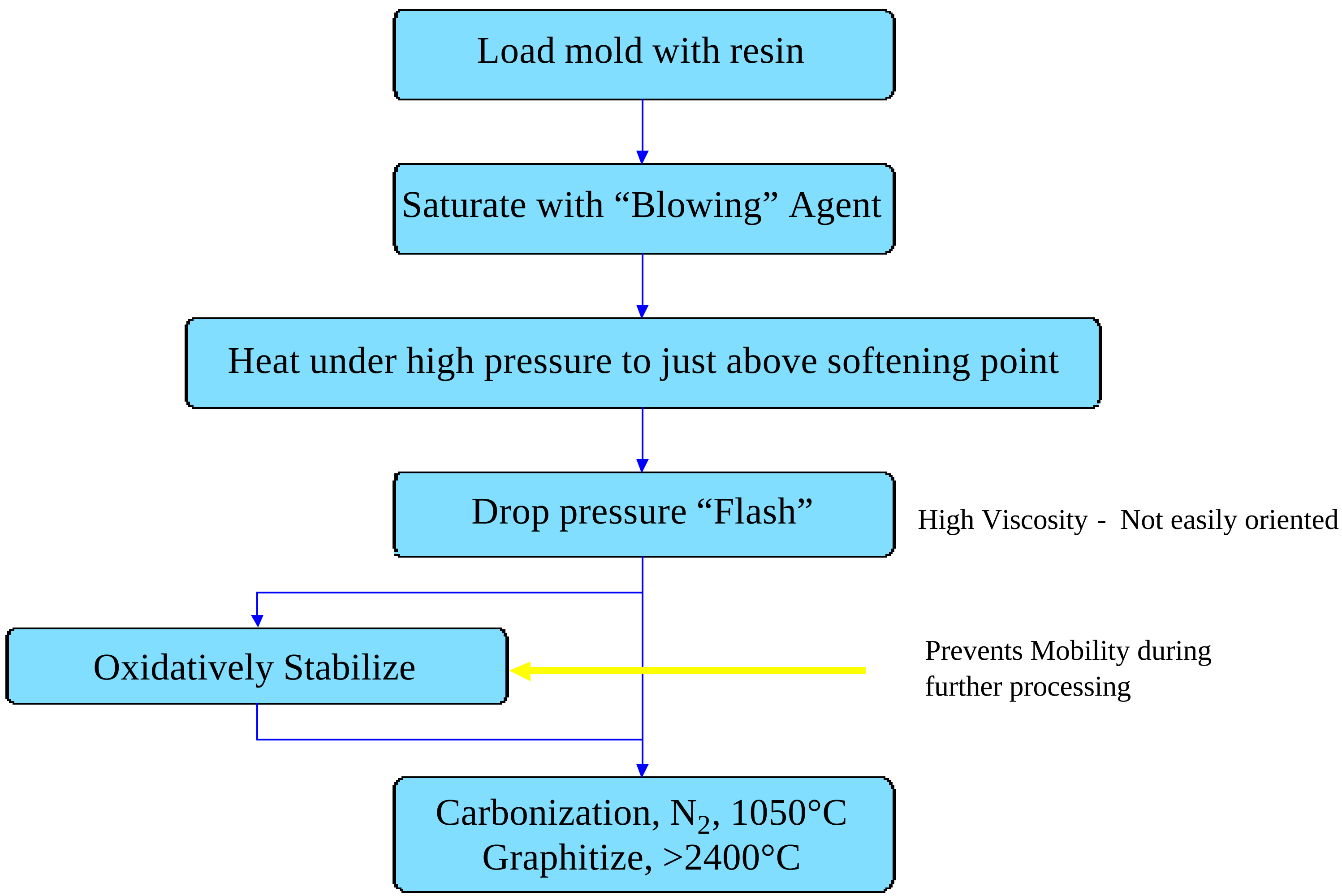
Bubble Growth

- Bi-Axial Extension causes liquid crystal to orient parallel to surface of bubble
  - similar to extension caused during formation of fibers.



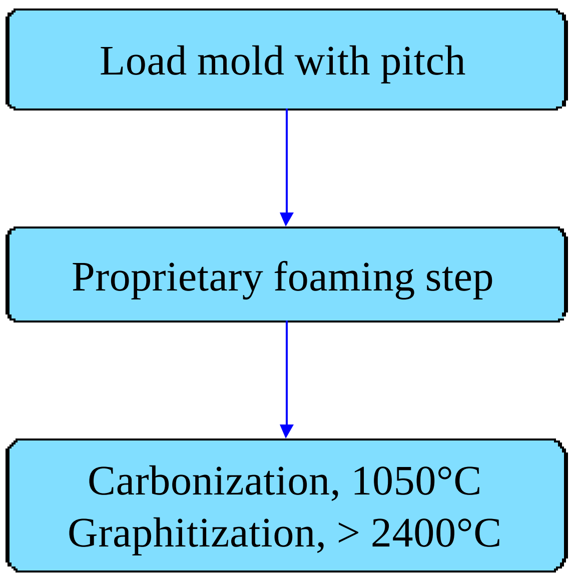
Traditional Carbon Foams - Problems

- Traditional “Blowing” techniques



Novel Production Method

- Proprietary method (many patents filed)
- Unlike traditional foaming techniques
  - No blowing (flashing) or pressure drop required
    - saves steps
  - No oxidative stabilization required
    - improved thermal properties



Mesophase Pitch Precursors

- Two separate 100% mesophase pitches
  - Synthetic mesophase from naphthalene
  - Proprietary high melting point mesophase from petroleum pitch

Mesophase	Softening Point [°C]	Mesophase Content [°C]	Carbon Yield @1000°C, N_2
Mitsubishi ARA 24	237	100	78
Conoco	355	100	87

Foam Processing

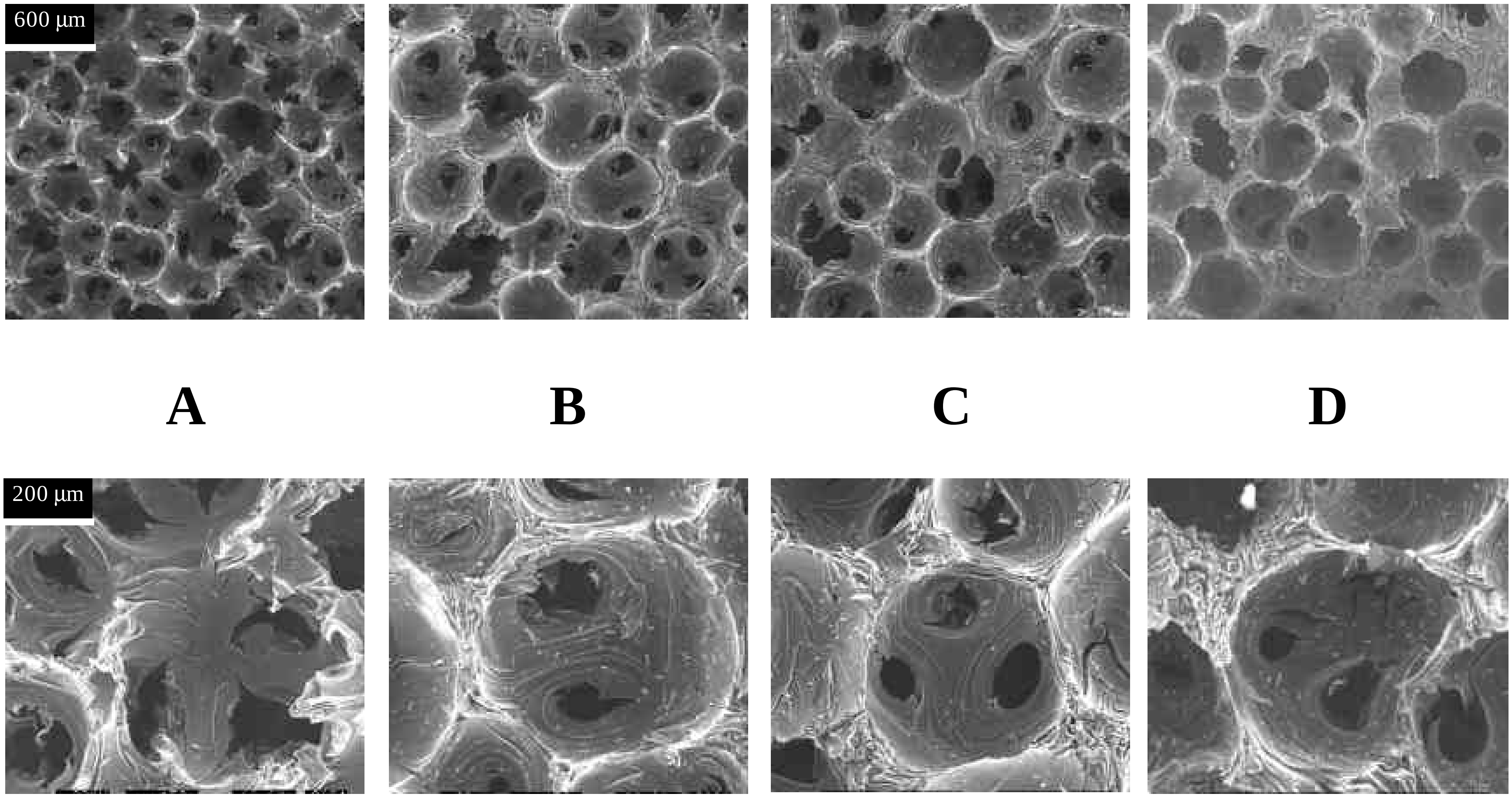
- Proprietary foaming method developed at ORNL
- Foams of both pitches were produced under 4 different processing conditions
  - A, B, C, D.
- The goal was to produce foams with varying density
  - properties as a function of density could be determined.
- Foams carbonized at 1000°C at 0.2°C/min
- Foams graphitized at 2800°C at 9°C/min

Properties of Graphitized Foams

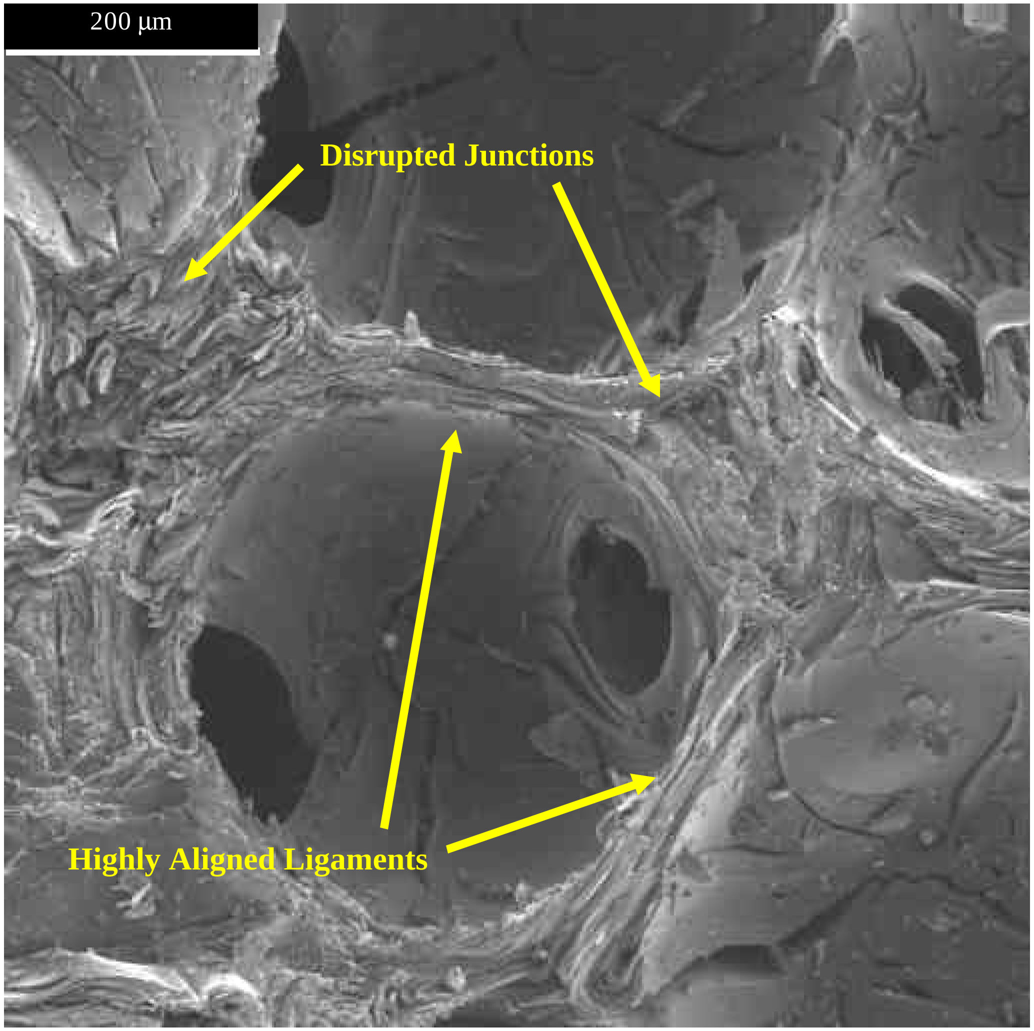
	AR Derived Foam		Conoco Derived Foam	
Processing Condition	**Density [g/cm^3]**	**Mean Pore Diameter* [mm]**	**Density [g/cm^3]**	**Mean Pore Diameter* [mm]**
A	0.25	354 ± 115	0.32	89 ± 79
B	0.39	361 ± 150	0.43	70 ± 54
C	0.48	293 ± 136	0.54	66 ± 65
D	0.57	275 ± 120	0.59	60 ± 49

*From optical image analysis

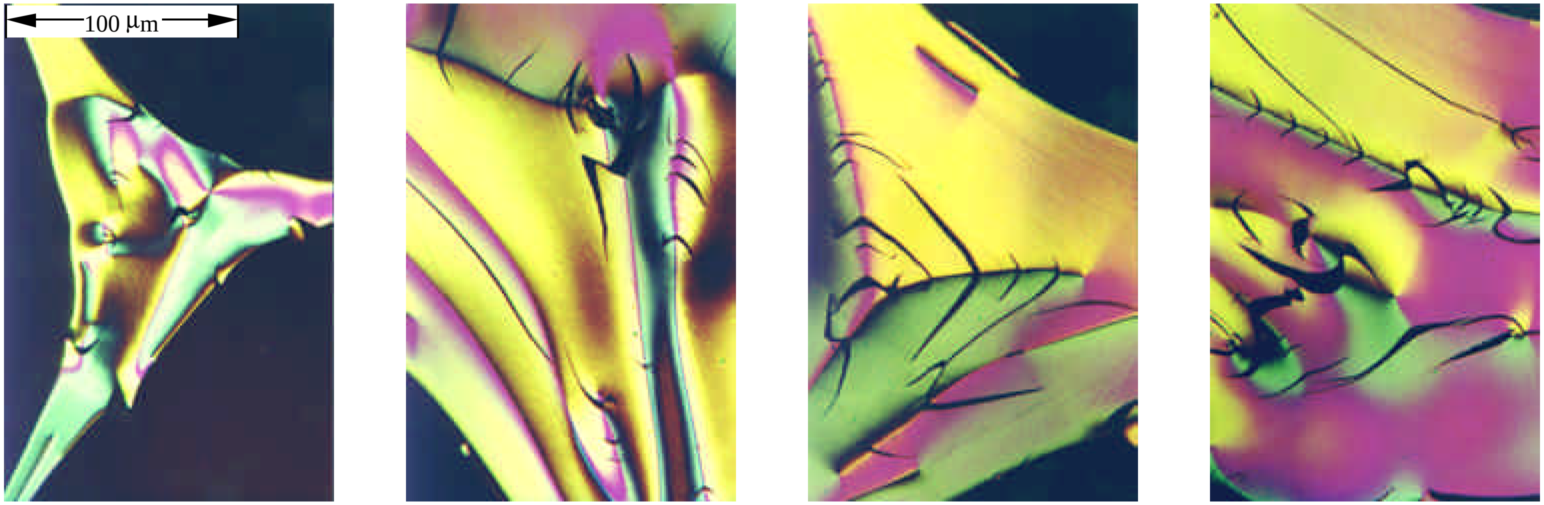
Foam Microstructure - AR Pitch



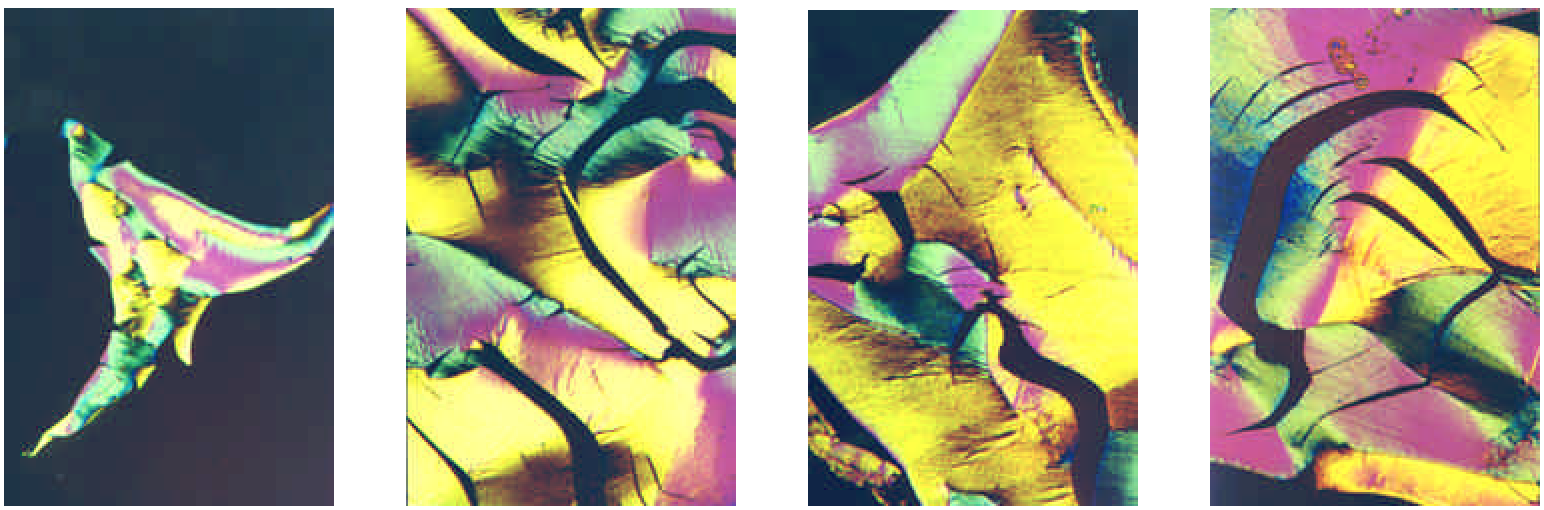
Graphitic Structure - AR Pitch -D



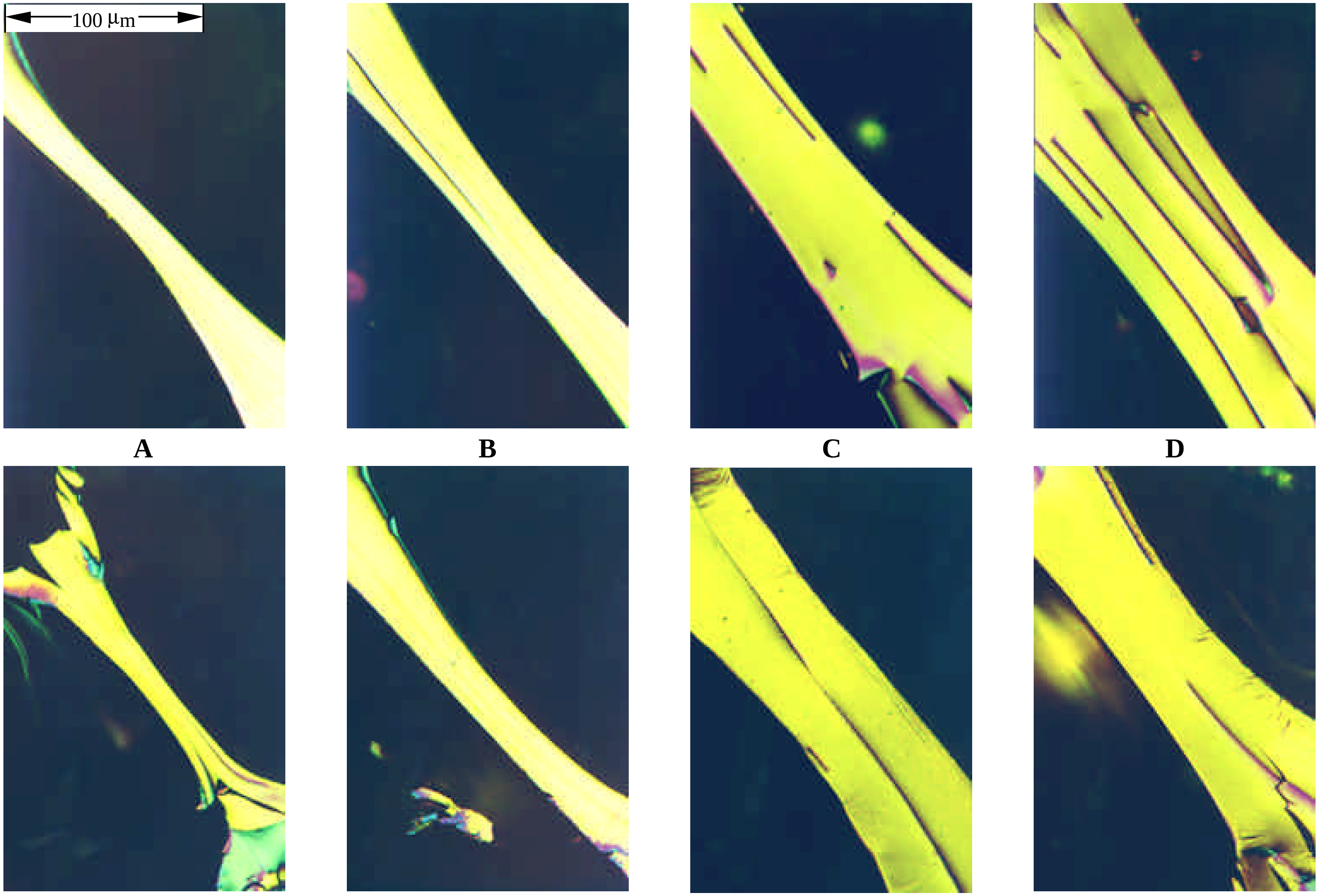
Graphitic Alignment and Structure - AR Pitch



A B C D

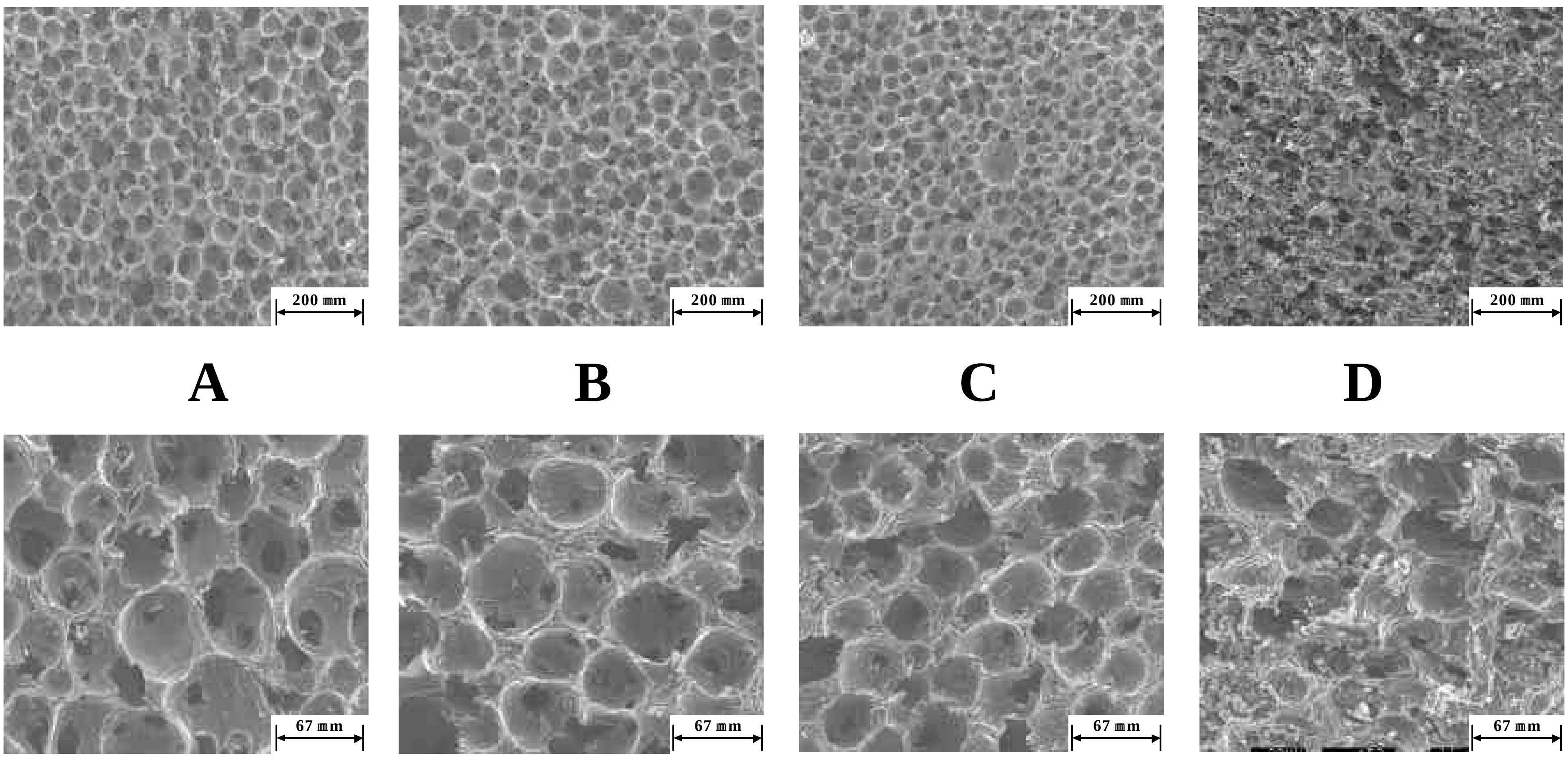


Graphitic Alignment and Structure - AR Pitch

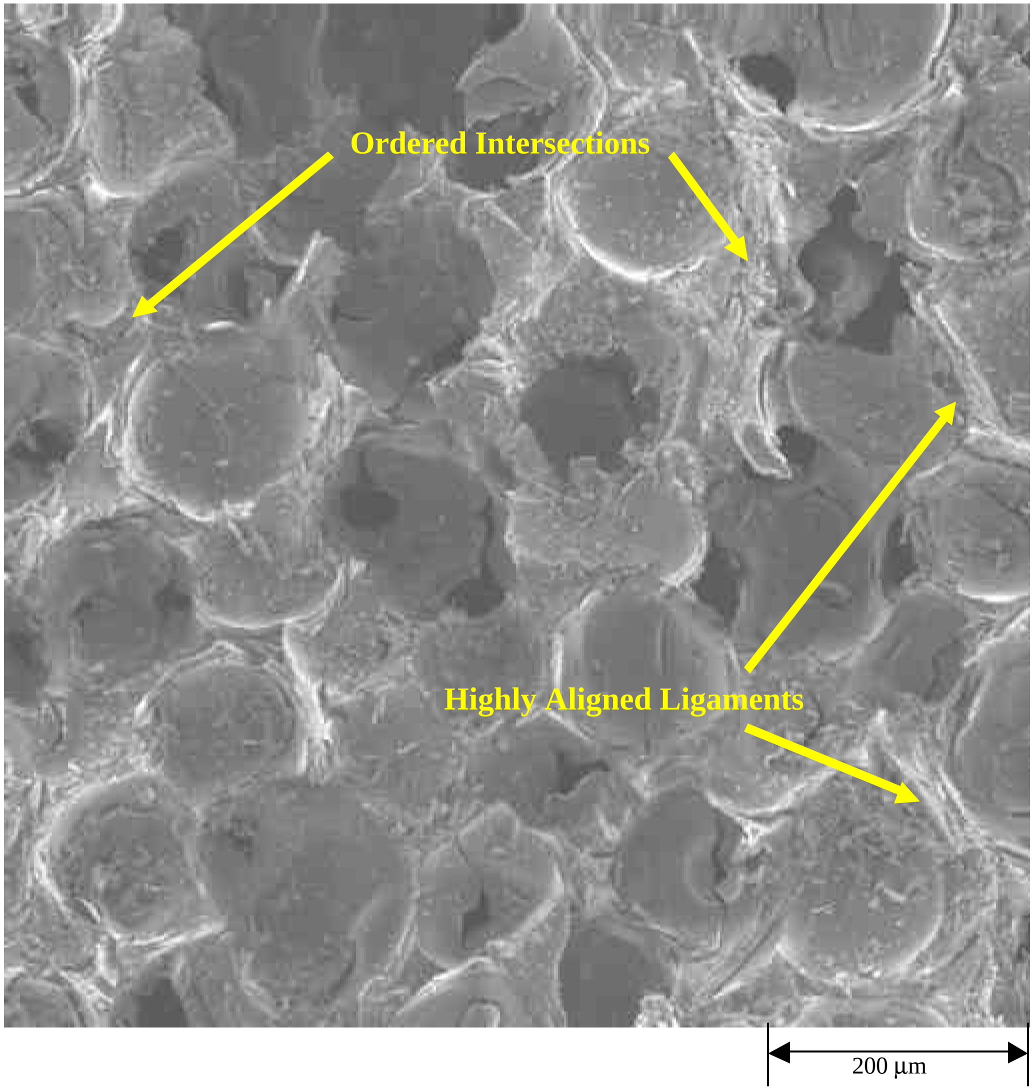


A B C D

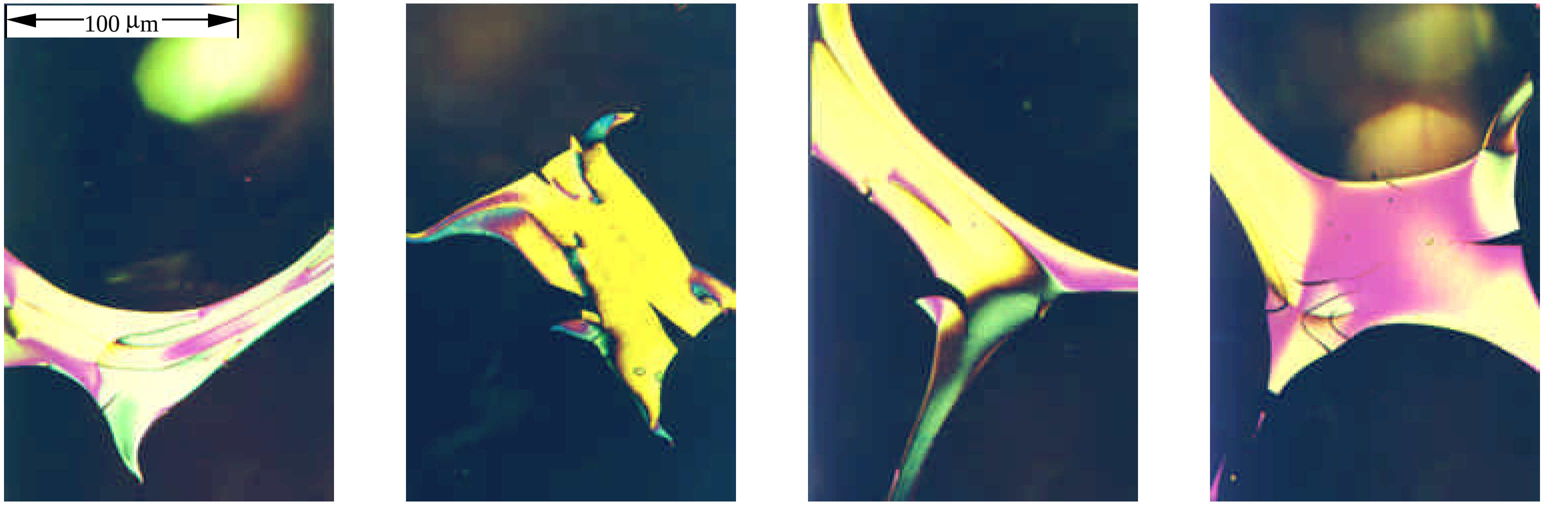
Foam Microstructure - Conoco Pitch



Graphitic Structure - Conoco Pitch -D

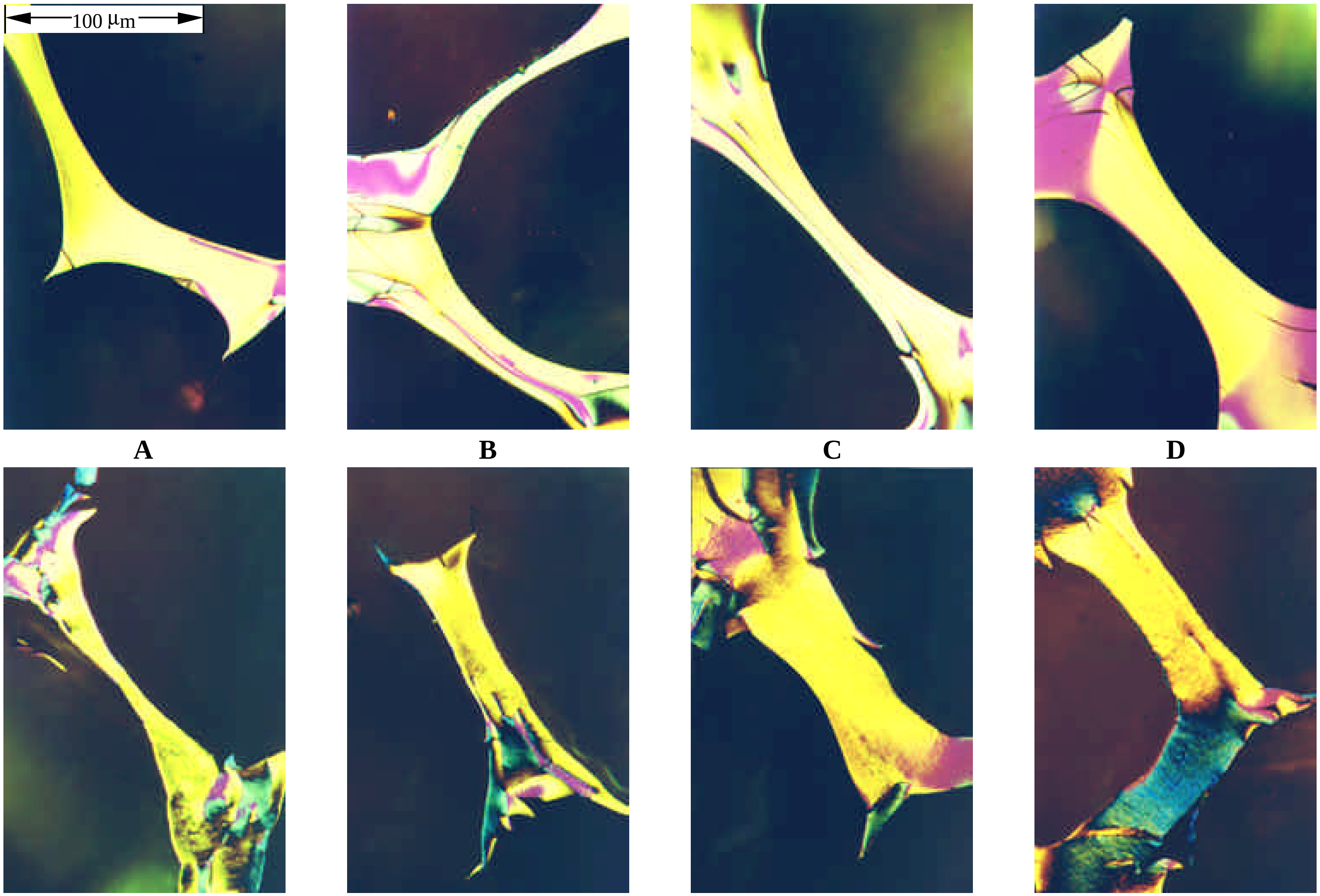


Graphitic Alignment and Structure - Conoco Pitch

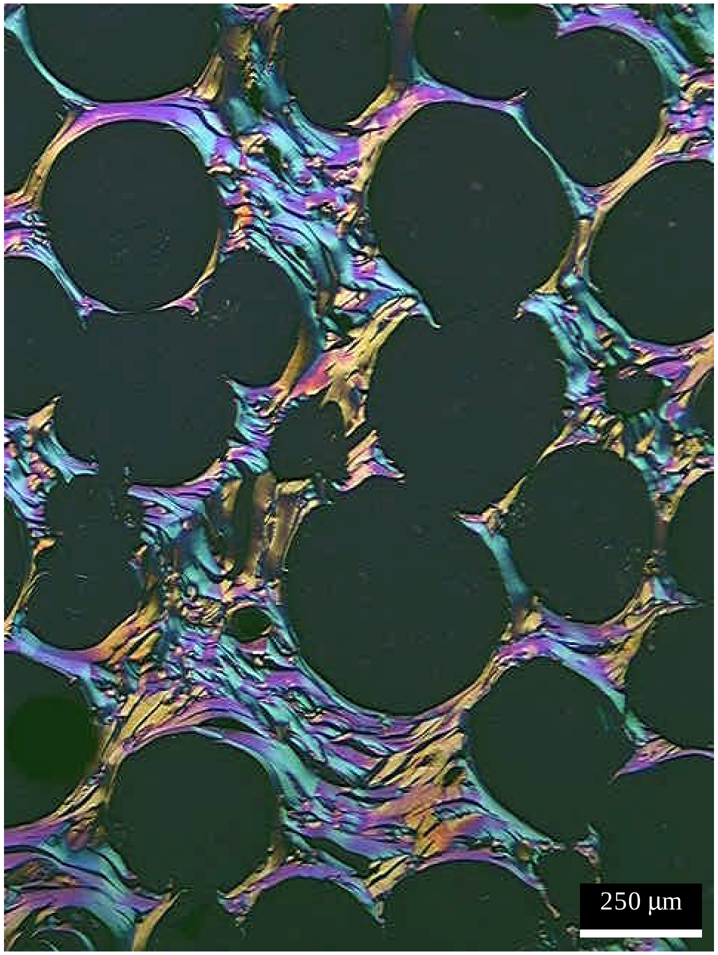


A **B** **C** **D**

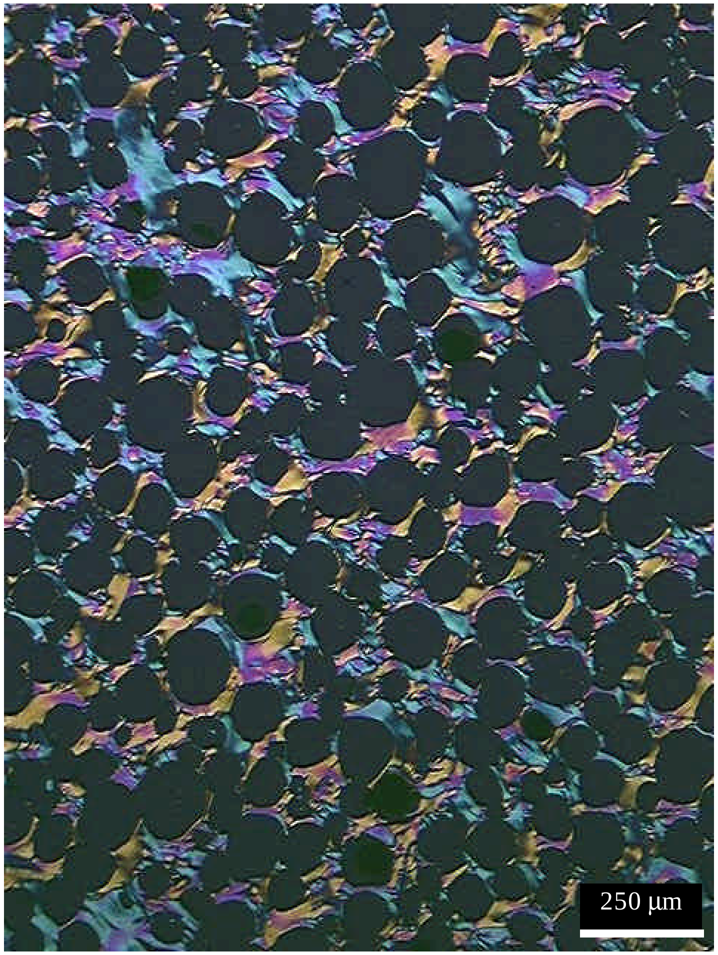
Graphitic Alignment and Structure - Conoco Pitch



Microstructures



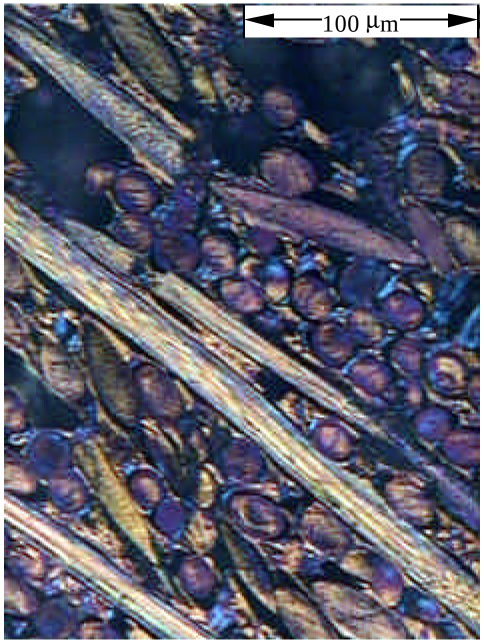
AR Derived Foam (D)

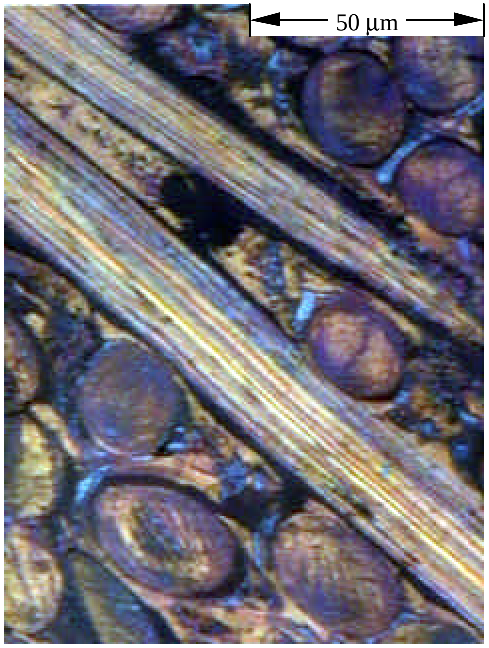


Conoco Derived Foam (D)

Comparison of Ligaments to High Performance Fibers

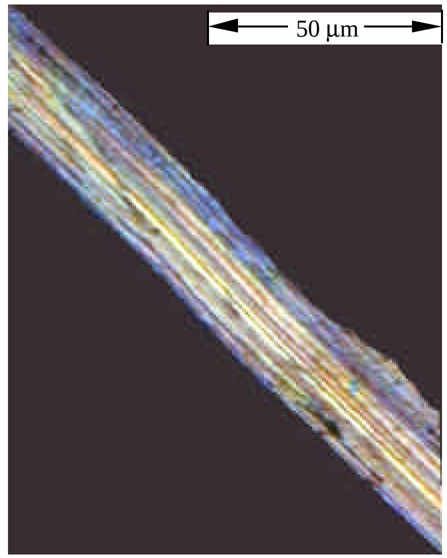
- Composites made with DKD-x fibers graphitized at 2800°C for 1 hour
- After high heat treatment DKD-x fibers very similar to K1100
- Estimated thermal conductivity is ~600-800 W/m·K



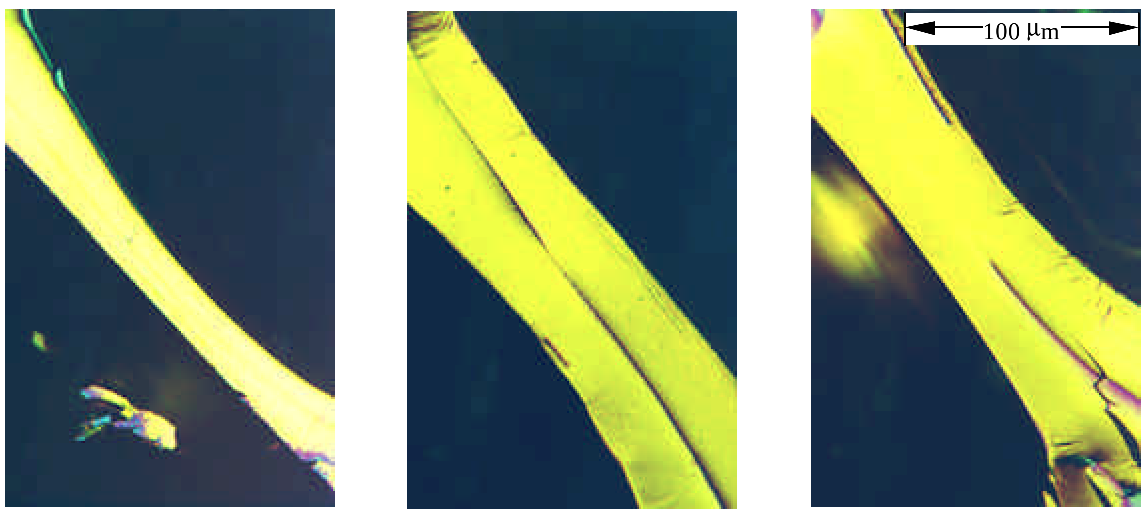


Comparison of Ligaments to High Performance Fibers

DKD-x® Fiber
2800°C

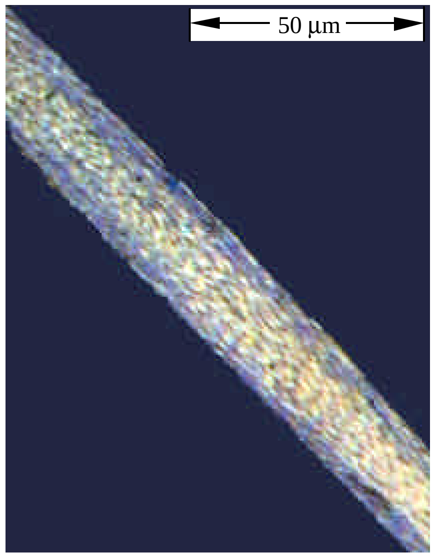


ORNL
Graphite Foam
2800°C

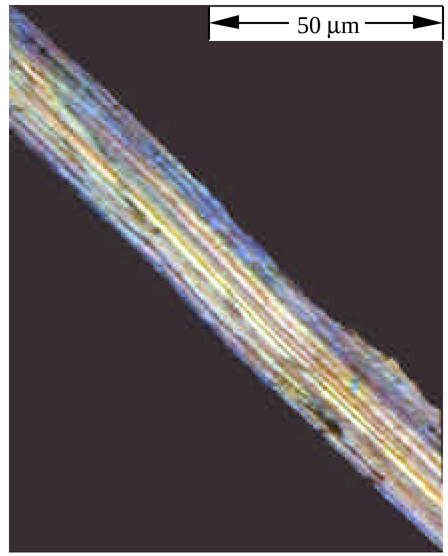


Comparison of Ligaments to High Performance Fibers

PAN Fiber
2800°C
κ ~ 50 W/m·K



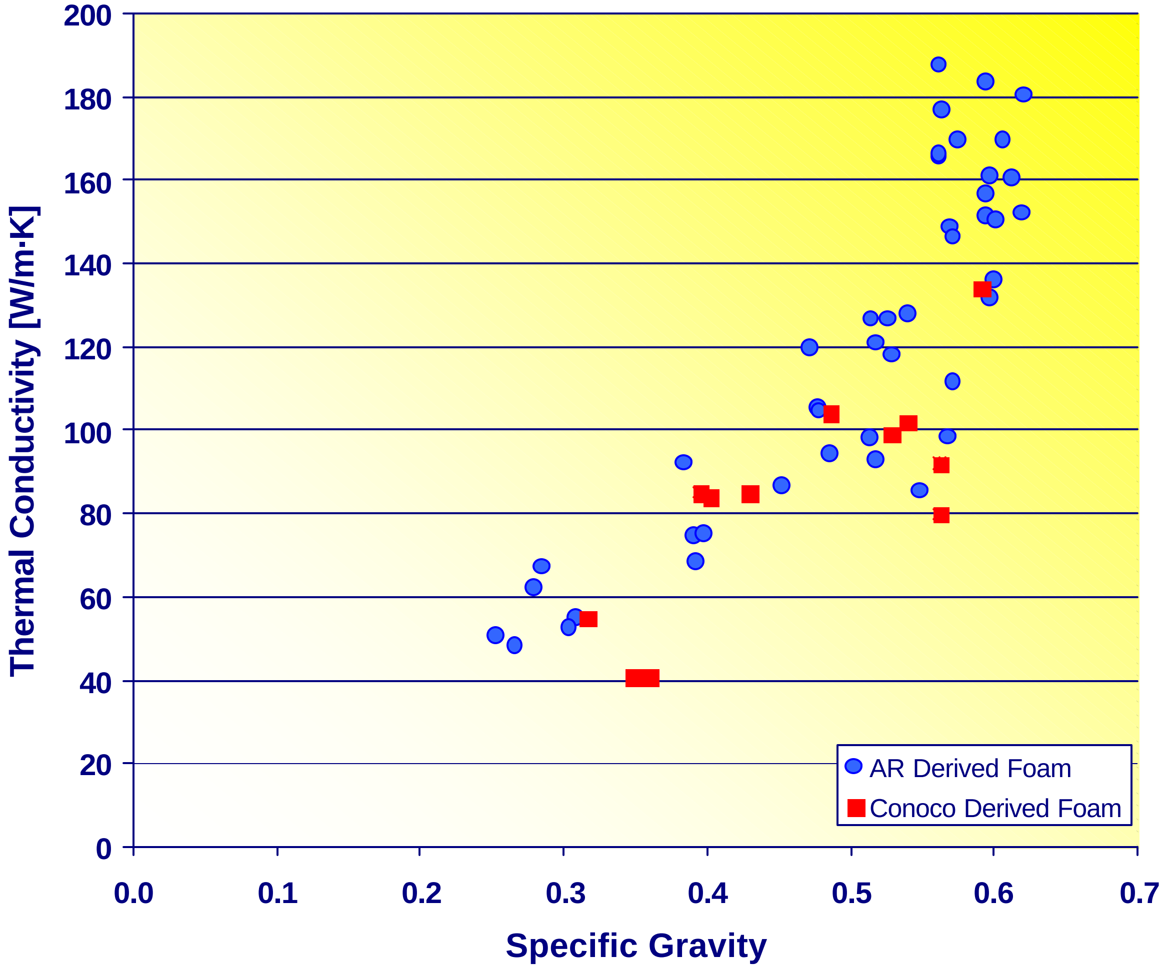
P-55 Fiber
2800°C
κ ~ 150 W/m·K



DKD-x® Fiber
2800°C
κ ~ 600 W/m·K

ORNL Graphite Foam
2800°C
κ ~ ?

Thermal Properties - Graphitized Foams



Helium Pycnometry - skeletal density

Material	Density	Thermal Conductivity
	[g/cm^3]	[W/m·K]
P55 fiber	2.00	120
P120 fiber	2.17	640
K1100 fiber	2.20	1000
ORNL Graphite Foam	**2.23**	**?**

Thermally Conductive Foams

$$k_{bulk} \approx 0.35\left(\frac{r}{r_{skel}}\right)k_{ligament}$$

	Relative Density [%]	Ligament Conductivity [W/m·K]	Bulk Conductivity [W/m·K]
Aluminum foam	25	180	~15
Copper foam	25	400	~40
Foam with P55 type ligament	25	120	~12
Foam with P120 type ligament	25	640	~60
ORNL Graphite Foam	25		***180***

Crystal Parameters of Foams

Foam	Specific Gravity	Interlayer Spacing d_{002}* [nm]	Crystal Size L_a [nm]	Stack Height L_c [nm]
Mitsubishi ARA24				
A	0.25	**.3364**	**11.8**	**48.2**
B	0.39	**.3362**	**17.8**	**46.6**
C	0.48	**.3360**	**21.5**	**79.3**
D	0.57	**.3355**	**18.4**	**82.4**
Conoco B				
A	0.35	**.3357**	**16.7**	**29.5**
B	0.40	**.3363**	**13.0**	**38.7**
C	0.49	**.3358**	**19.5**	**97.6**
D	0.59	**.3360**	**19.8**	**50.8**

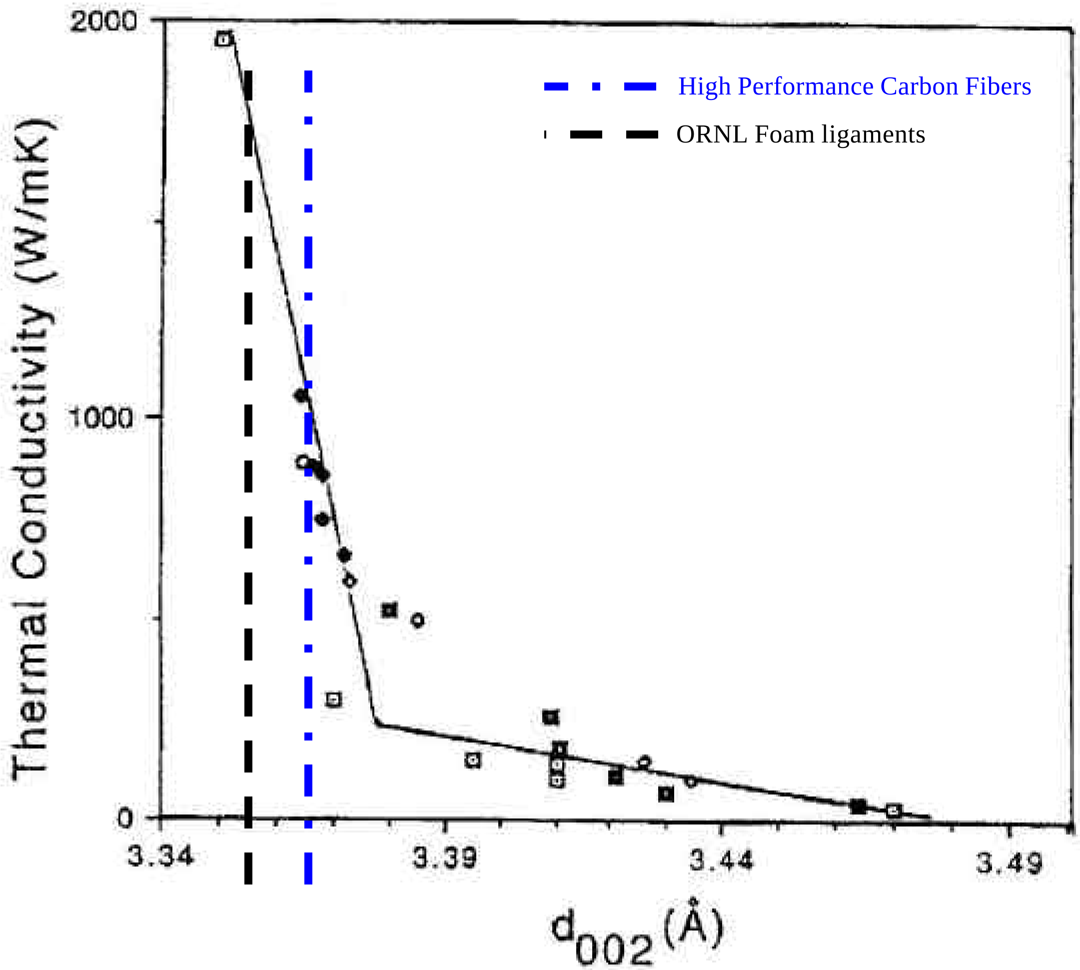
*perfect graphite is 0.3354

Comparison of Crystal Parameters to Fibers

Material	HTT	d_{002}-spacing*	L_a (crystal size)	L_c (stack height)	κ
	[°C]	[nm]	[nm]	[nm]	[W/m·K]
P30-x fiber[6]	2500	0.3375	50	32	>500
K321 fiber [6]	2500	0.3376	33	50	>500
EWC-600 [6]	--	0.3374	55	32	640
Clemson Ribbon [2]	2400	0.3380	32	12	950
K1100[3]	--	0.3366	85	51	1000
Fixed catalyst VGCF [1]	2800	0.3366	40[4]	37[4]	1950
AR Foam Ligament	***2800***	***0.3355***	***19***	***82***	***>1750***
Conoco Foam Ligament	***2800***	***0.3360***	***20***	***51***	***>1750***

* Turbostratic graphite = >0.3440 nm
Single crystal graphite = 0.3354 nm

Crystal Effects on Thermal Conductivity



(data from Rellick, et. al., (6))

Ligament Conductivity

- Compelling evidence to extremely high thermal conductivity in ligaments of ORNL Graphite Foam
  - optical microscopy
    - significantly larger monochromatic regions than K1100 fibers
  - Helium Pycnometry
    - higher skeletal density than K1100 fibers
  - X-ray analysis
    - d-spacing closer to pure graphite than K1100 fibers
    - plot of d-spacing indicates conductivity about 1800 W/m·K
  - Bulk thermal conductivity
    - order of magnitude greater than aluminum foams of similar relative density
    - anticipate ligaments to be order of magnitude greater than aluminum

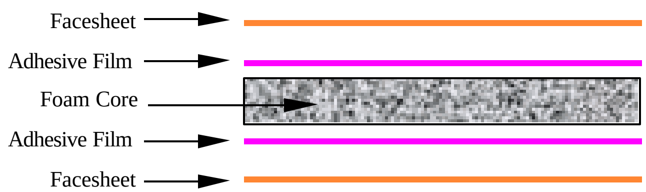
Thermal Properties vs Other Materials

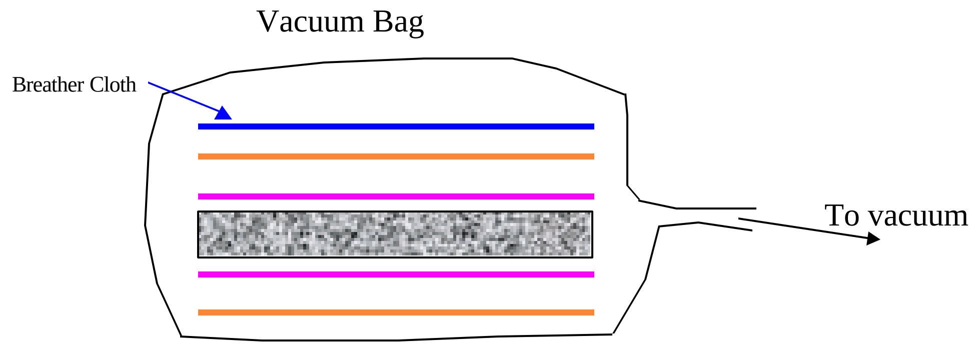
Material	Specific Gravity	Thermal Conductivity		Specific Conductivity	
		//	⊥	//	⊥
		[W/m·K]	[W/m·K]	[W/m·K]	[W/m·K]
AR Derived Foam D-2800	**0.56**	**187**	**187**	**334**	**334**
Conoco Derived Foam D-2800	**0.59**	**134**	**134**	**227**	**227**
Copper	8.9	400	400	45	45
Aluminum 6061	2.8	180	180	64	64
EWC-300/Epoxy Resin	1.72	109	1	63	1
K321/AR Pitch Carbon/Carbon	1.77	233	20	132	11
Amoco SRG	1.76	650	20	369	11
Aluminum Foam	0.5	12	12	24	24

†Specific Conductivity = Thermal Conductivity/Specific Gravity

Laminate Fabrication and Joining Techniques

- Autoclave process

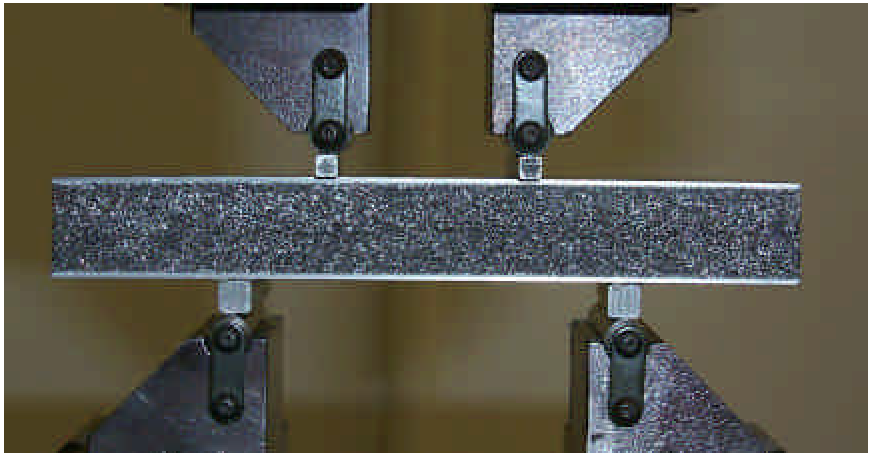




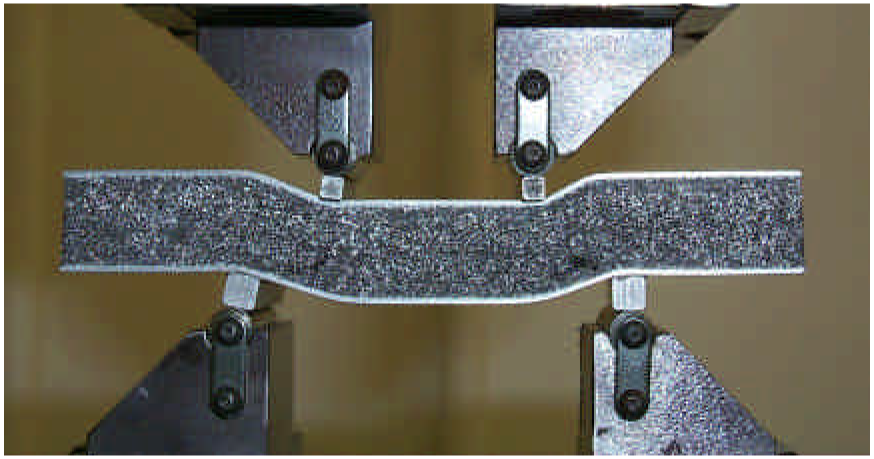
Cure at 35 psi, 150°C, 30 minutes

Flexural Testing

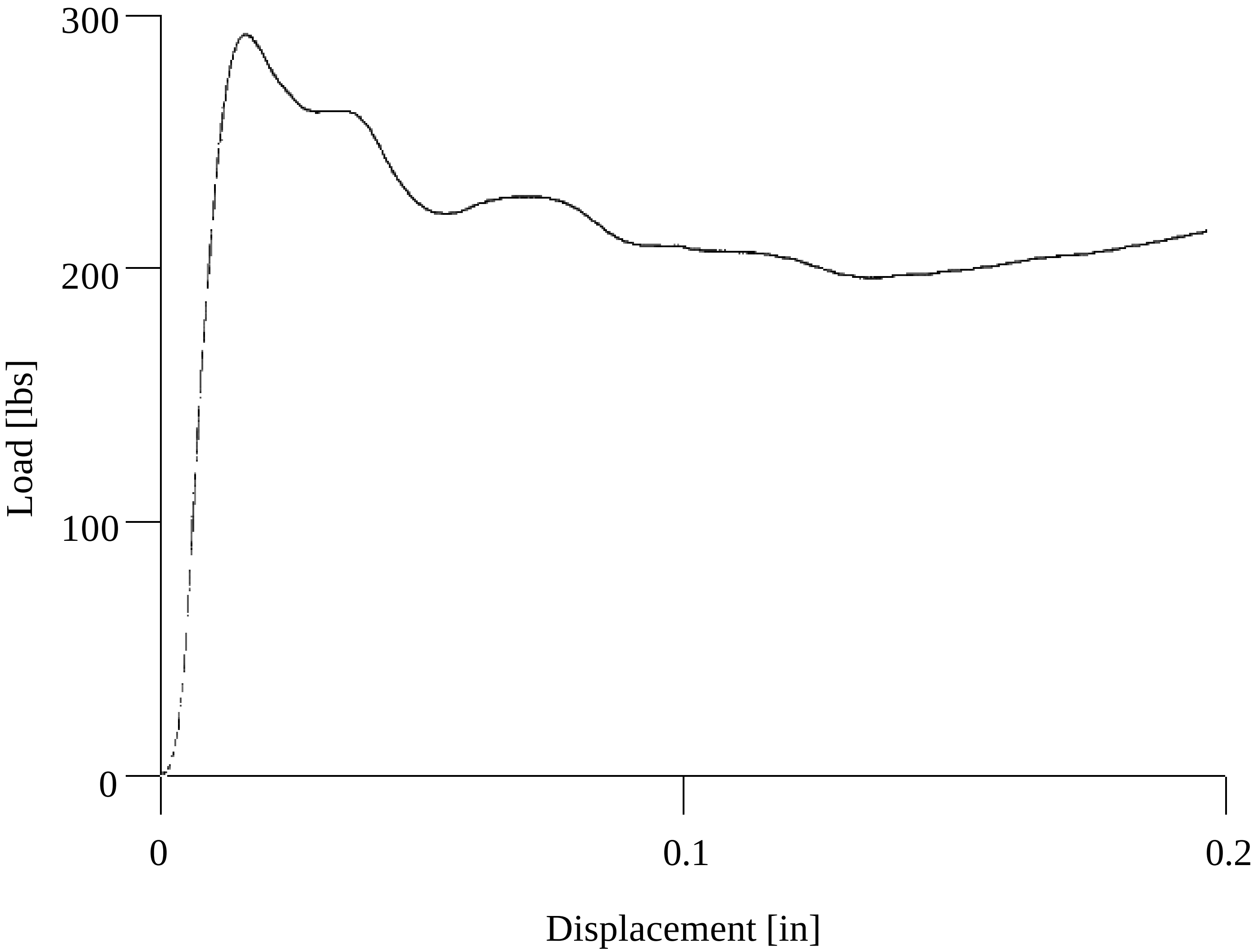
No Load



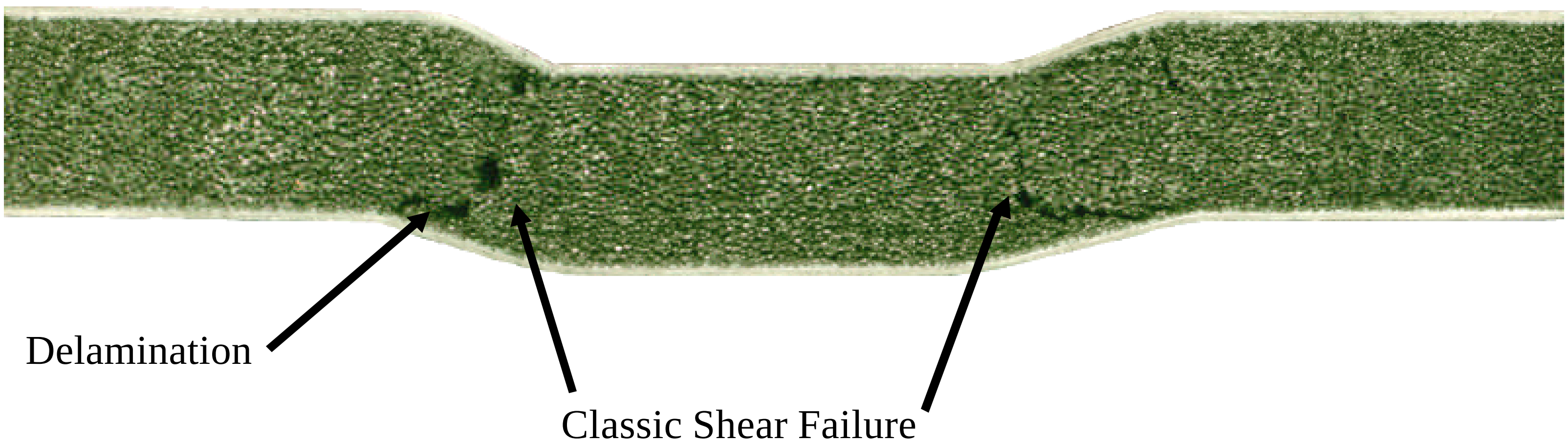
Load = 200 lb
Displacement = 0.17 in



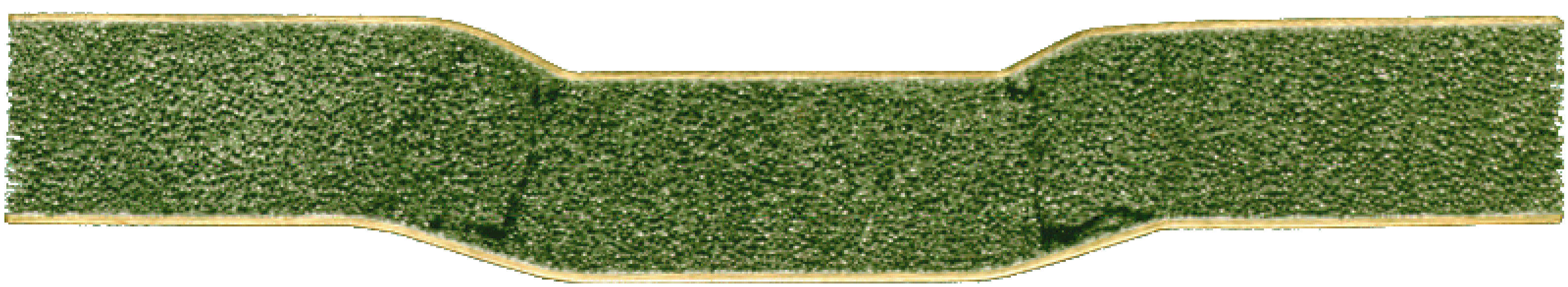
Typical Flexural Testing Results



Flexural Testing Results

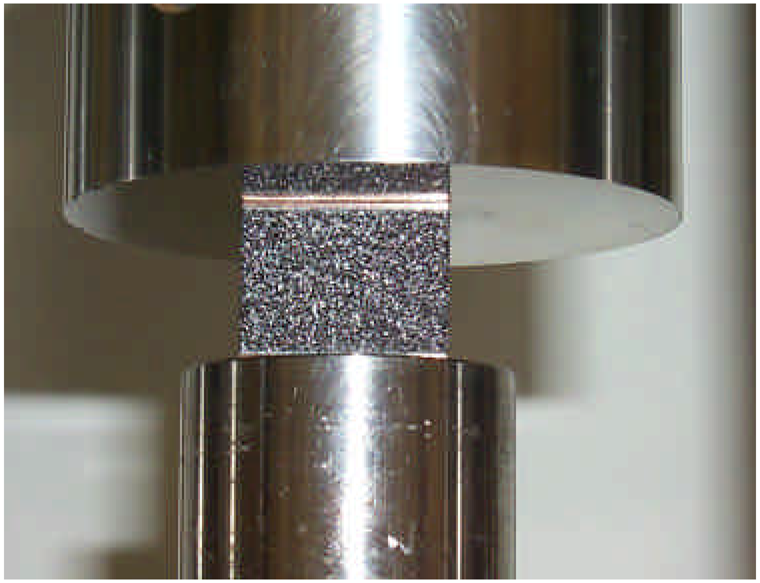


Aluminum Facesheets

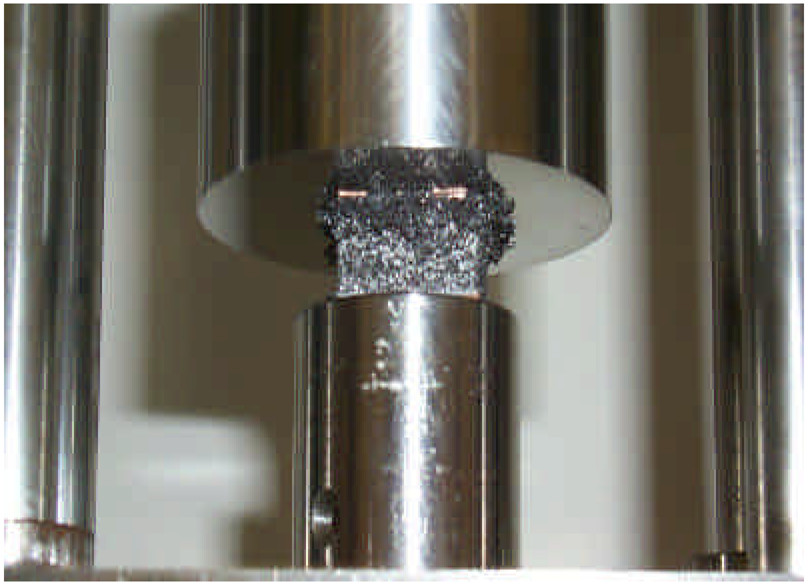


Copper Facesheets

Compression Testing

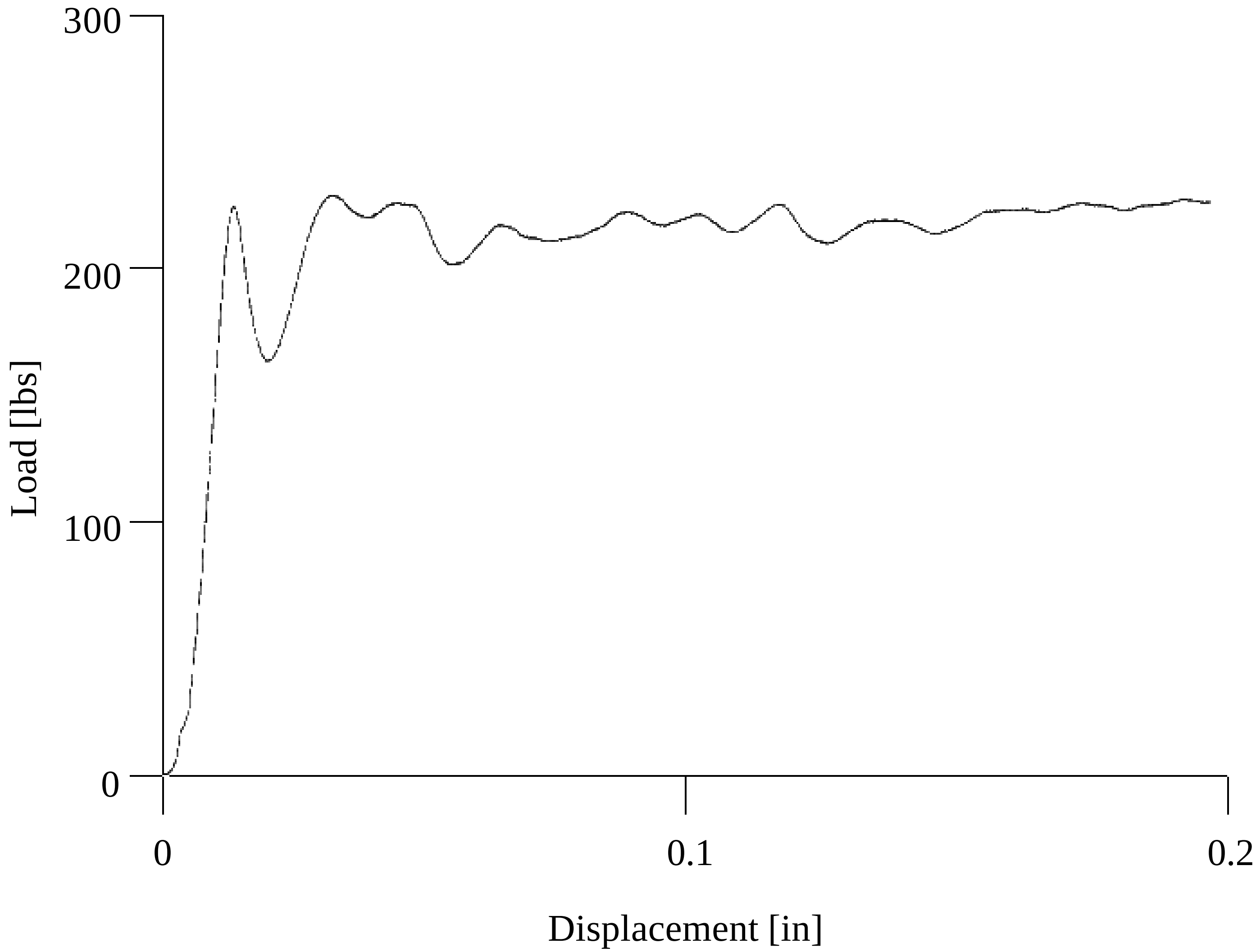


No Load



Load = 220 lb
Deflection = 0.2 in

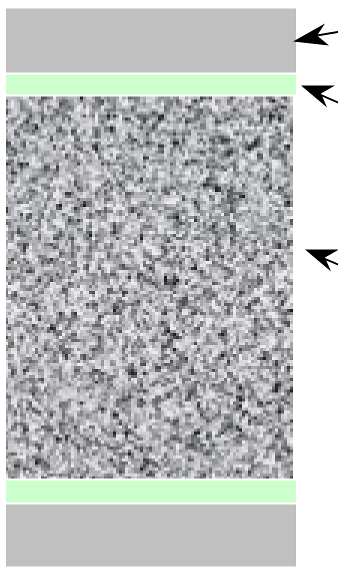
Typical Compression Testing Results



Thermal Testing of Laminates

Material	Specific Gravity	Thermal Conductivity		Specific Conductivity	
		//	⊥	//	⊥
		[W/m·K]	[W/m·K]	[W/m·K]	[W/m·K]
Al-A	***0.75***	***~150***	***51***	***200***	***68***
Al-B	***0.75***	***~150***	***64***	***200***	***86***
Cu-A	***1.17***	***~150***	***60***	***128***	***51***
Cu-B	***1.21***	***~150***	***55***	***124***	***45***
EWC-300/Epoxy resin (1)	1.72	109	1	63	0.6
K321/AR Pitch Carbon-Carbon (2)	1.88	233	20	124	10.6
Aluminum	2.77	150-200	150-200	54-72	54-72
Aluminum Foam (3)	0.50	12	12	24	24
Aluminum Honeycomb (4)	0.19	--	~10	--	52

Predicted Thermal Conductivity



Aluminum	$t = 0.025$, $\kappa = 200$ W/mK
Copper	$t = 0.025$, $\kappa = 400$ W/mK
Adhesive	$t = 0.008$, $\kappa = 8$ W/mK
Foam	$t = 0.5$, $\kappa = 120$ W/mK

Predicted $\kappa_{\text{aluminum laminate}}$ 78 - 88 W/mK

Predicted $\kappa_{\text{copper laminate}}$ 79 - 90 W/mK

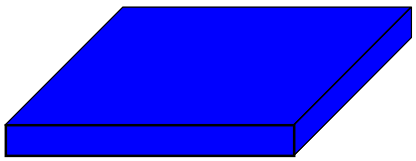
The limiting factor in the thermal conductivity is the adhesive.

Potential Applications

"Out of the Box" Thinking

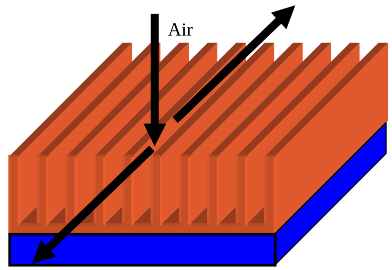
Foams as Heat Sinks

Heater @ 90% output



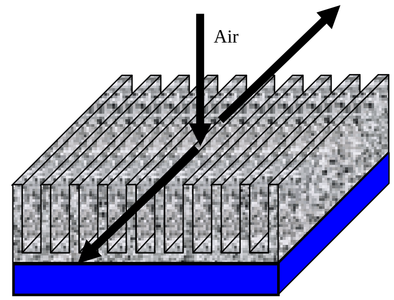
Mass of Sink = 0 g
Temperature = 170°F

Standard Aluminum
Heat Sink



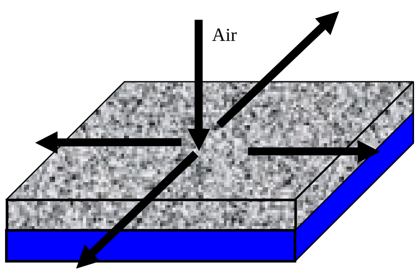
Mass of Sink = 44 g
Temperature = 99°F

Finned Foam
Heat Sink



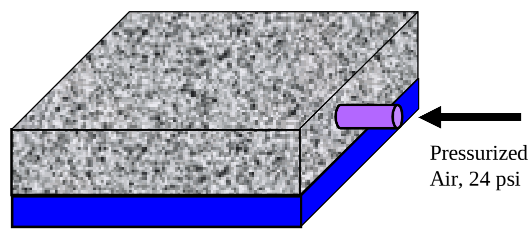
Mass of Sink = 8 g
Temperature = 93°F

Thin Foam
Heat Sink



Mass of Sink = 4 g
Temperature = 103°F

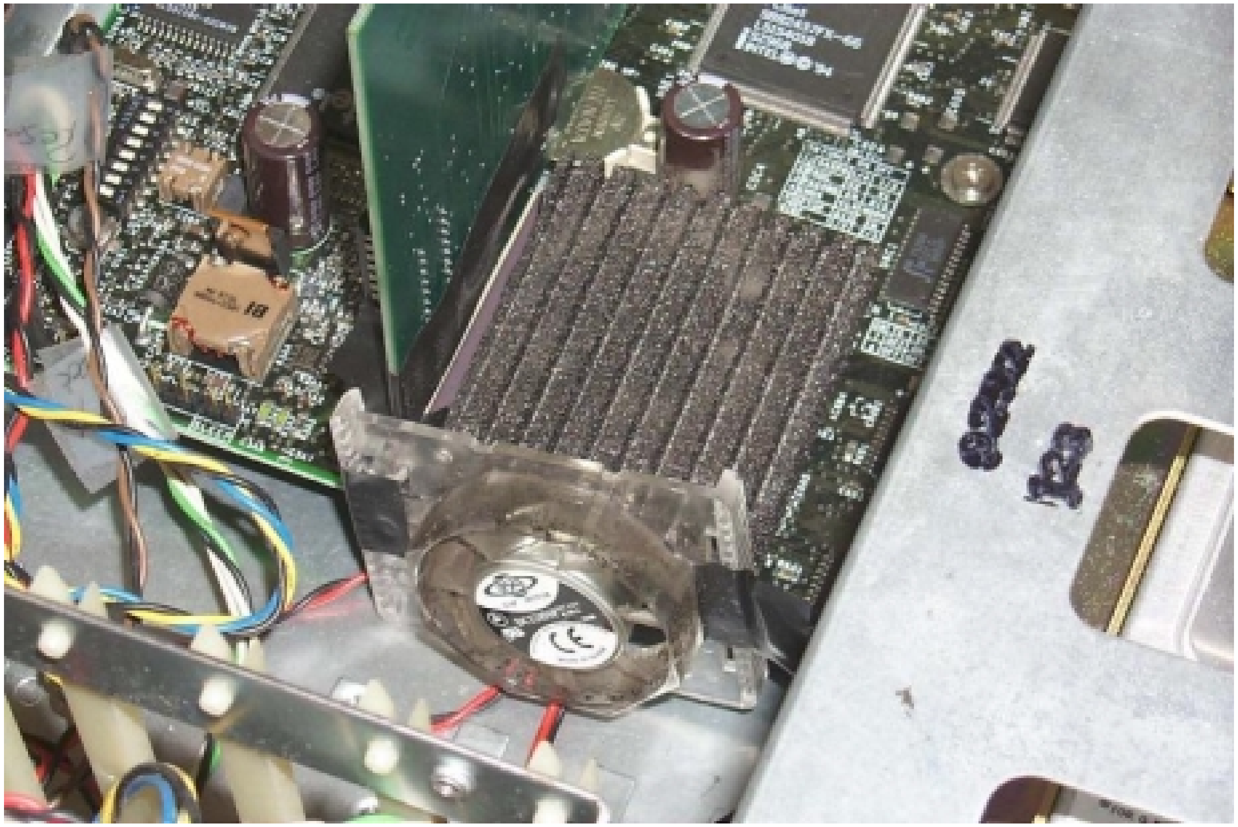
Foam Heat Sink
with Forced Flow



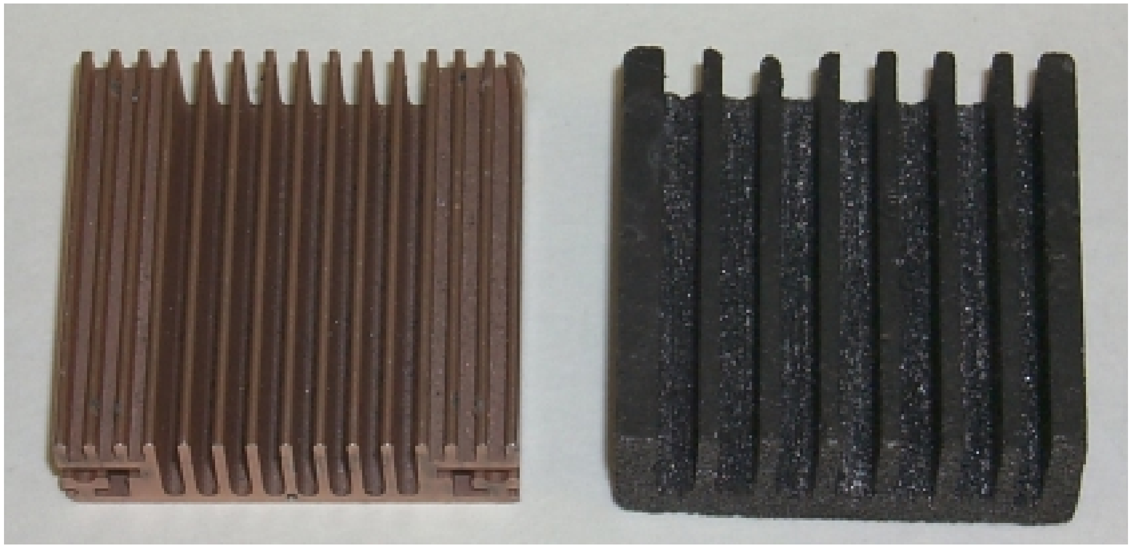
Mass of Sink = 11 g
Temperature = 99°F

Actual devices

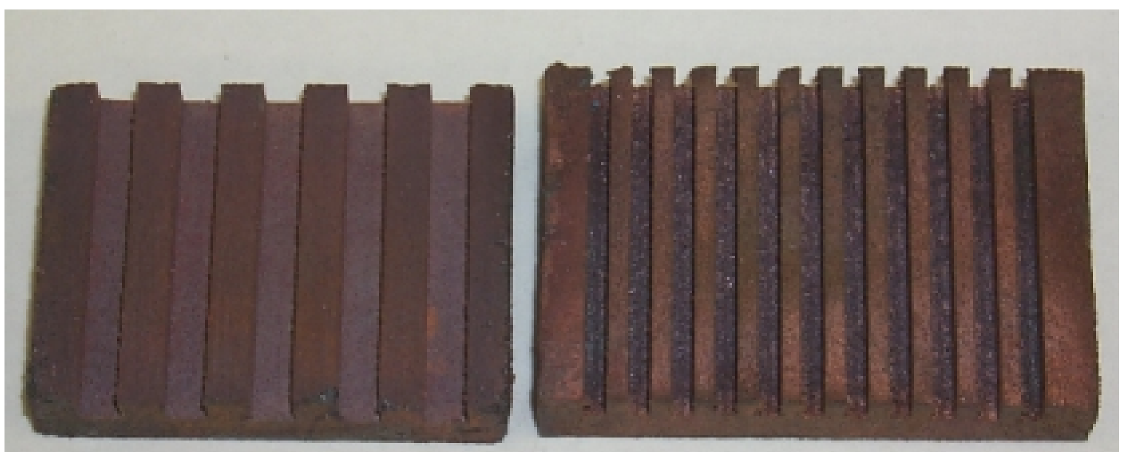
- Finned foam heat sink running in Pentium 133 computer since December 12, 1998.



Other Finned Heat Sinks



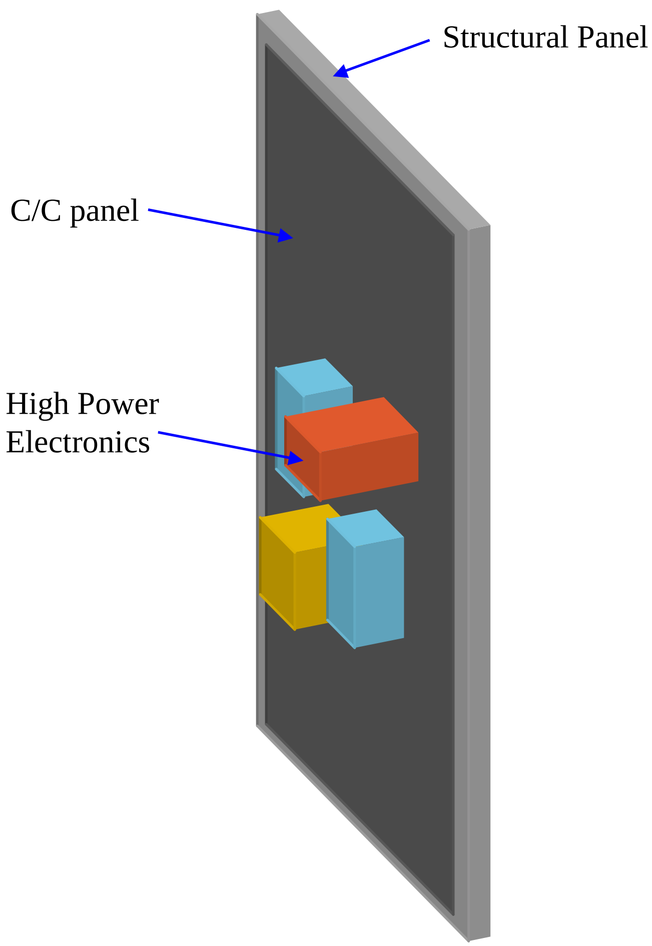
Aluminum Heat Sink from P133 Computer **Finned Foam Heat Sink**



Copper Plated Foam Heat Sink **Copper Plated Foam Heat Sink**

Satellite Applications?

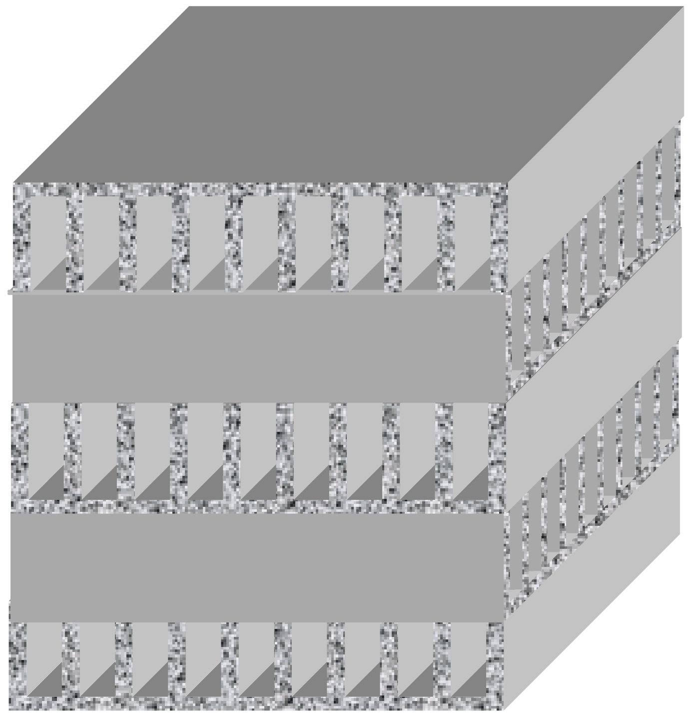
Thermal Doubler Panel



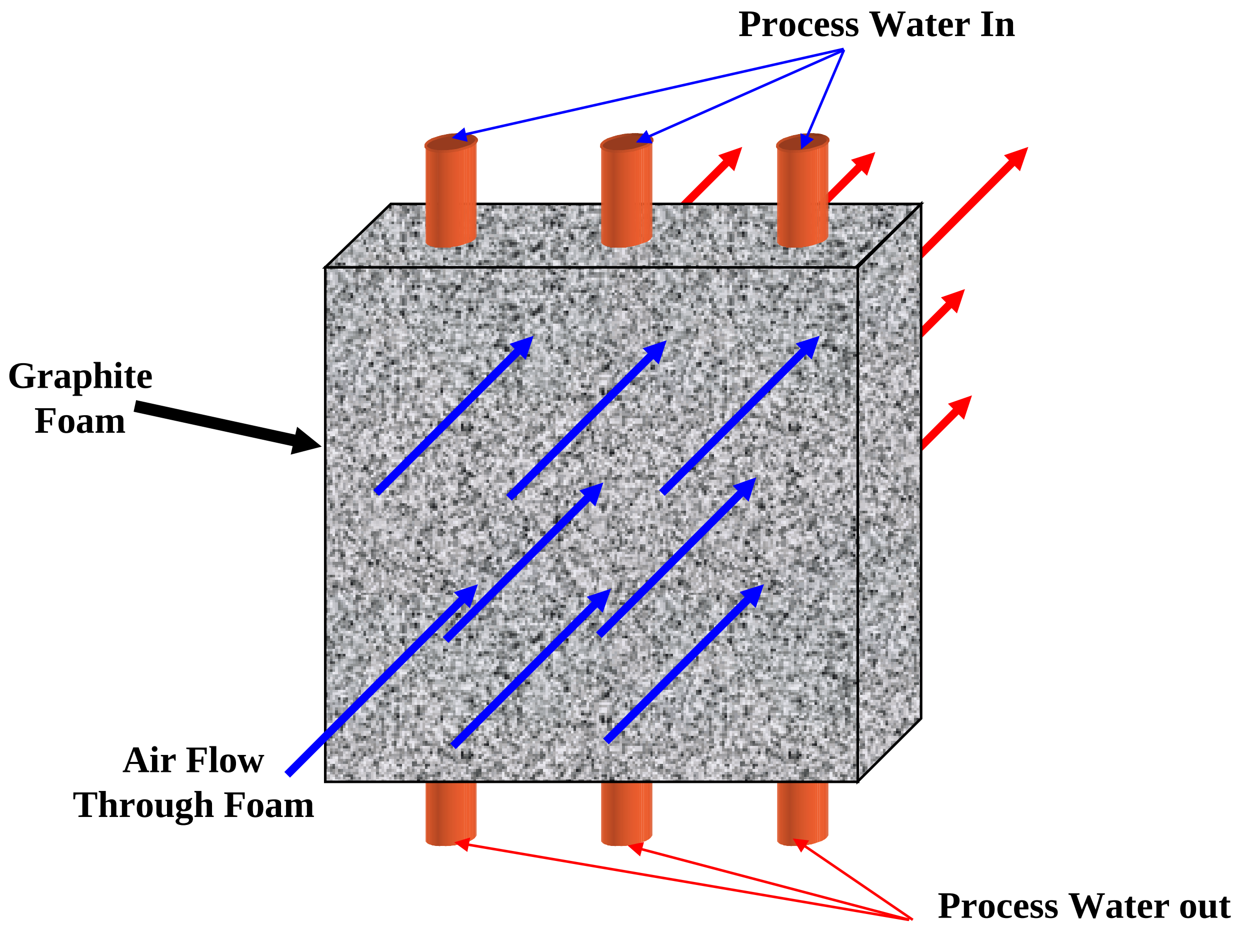
- Current concept spreads heat across larger area & reduces temperature
- Heat is rejected to space with T^4 relationship
- A very low through thickness thermal conductivity of current carbon-carbon (20 W/m·K) and honeycomb core limits heat rejection
- The higher through-thickness thermal conductivity of the foam (180 W/m·K) will increase temperature on outside surface
- High temperature on outside surface will increase radiation
- Smaller panel footprint, or more electronics can be utilized.

Cross Flow Heat Exchangers

- Foam rigidized with Carbon CVI for dramatic improvement in durability
- Surface skin produced during manufacture would become impermeable to H_2 (already demonstrated in Fuel Cell Bi-polar plate testing)
- Can be bonded together or "Glued" together during the CVI Process
  - porous structure allowed deposition to bond structure together



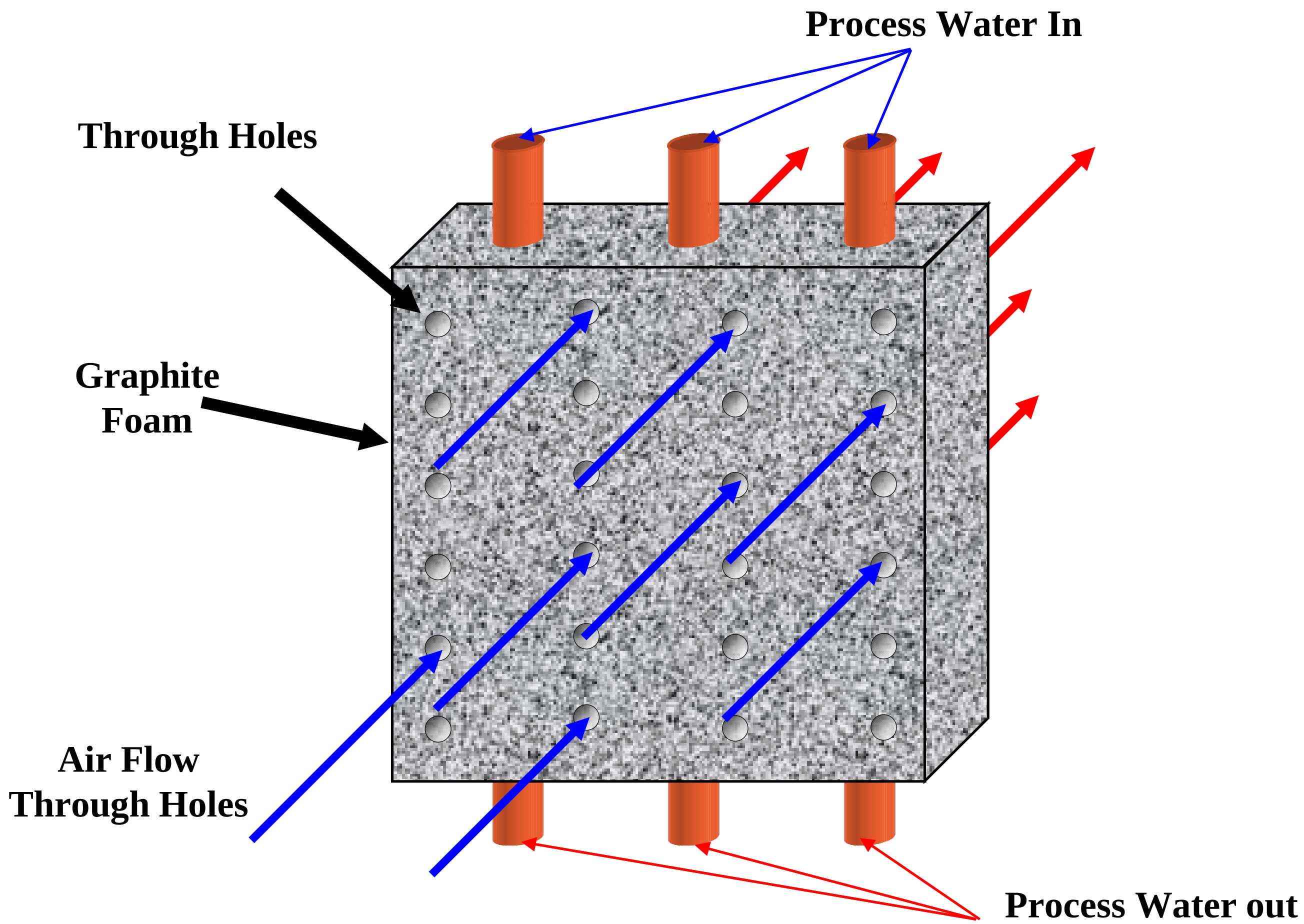
Heat Transport - Forced Diffusion



***Measured U_o* = 6, 000 - 11,000 W/m^2 ·K depending on air humidity**

an increase by a factor of more than 2 orders-of-magnitude
over typical radiators

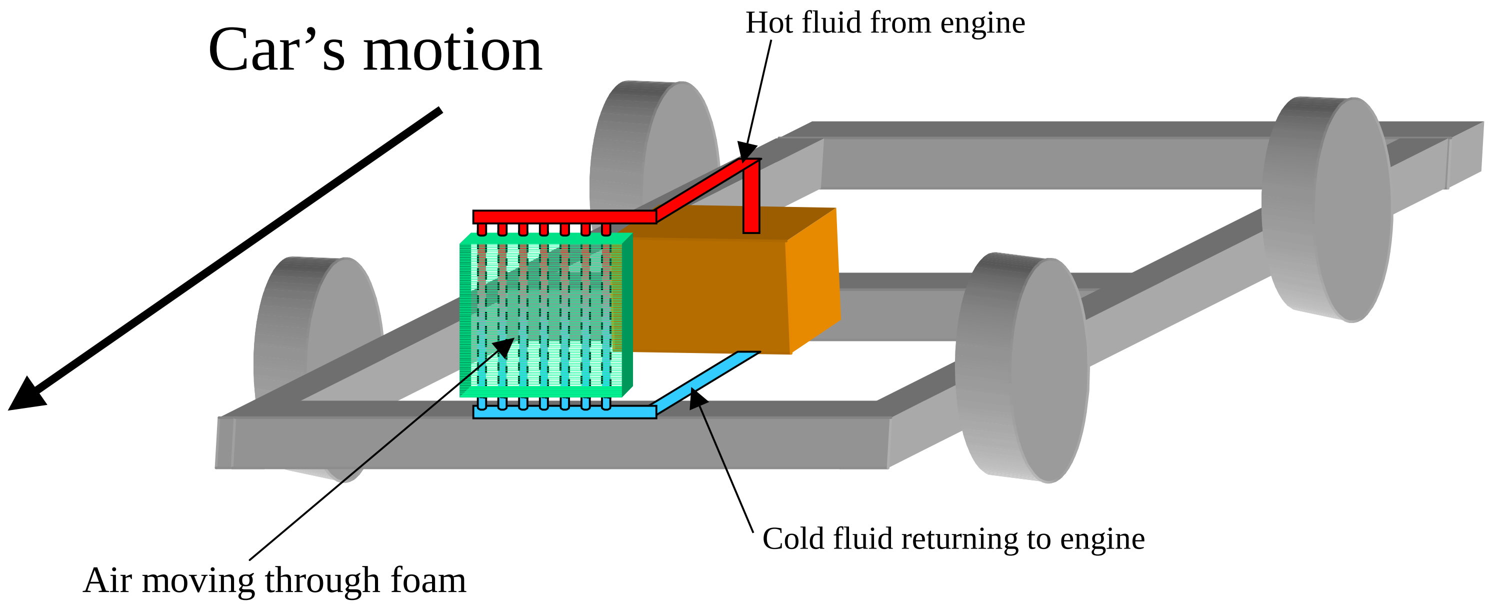
Heat Transport - Forced Convection

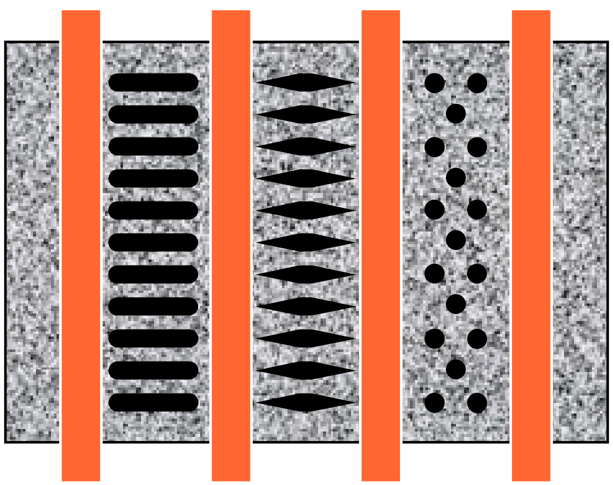


Measured $\boldsymbol{U_o}$ **= 1000 W/m^2 ·K depending on air humidity**

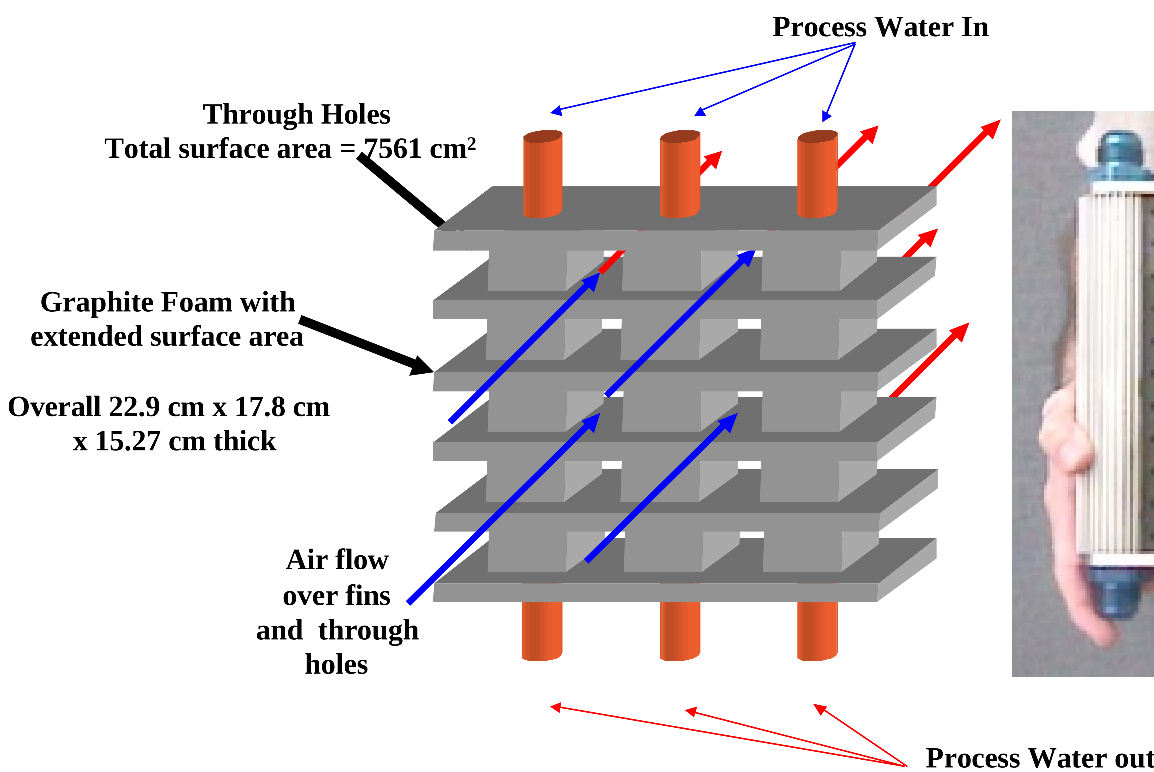
1 order-of-magnitude improvement

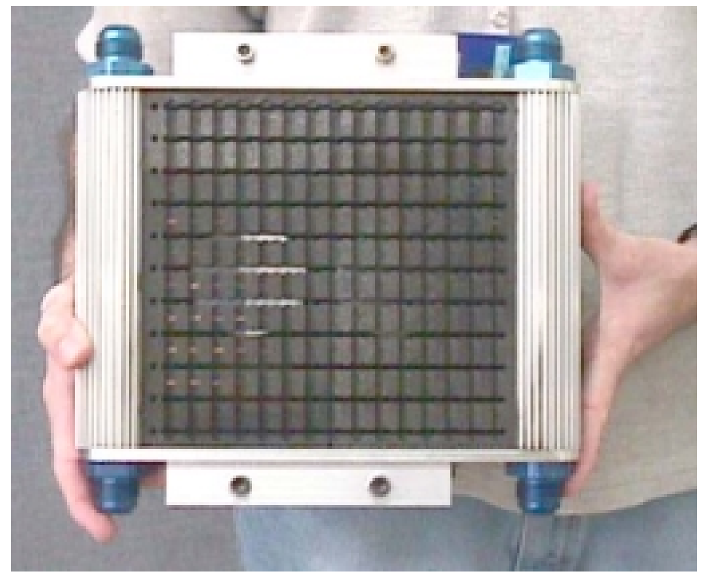
Heat Exchangers- Forced Convection





Current Radiator Demonstrated

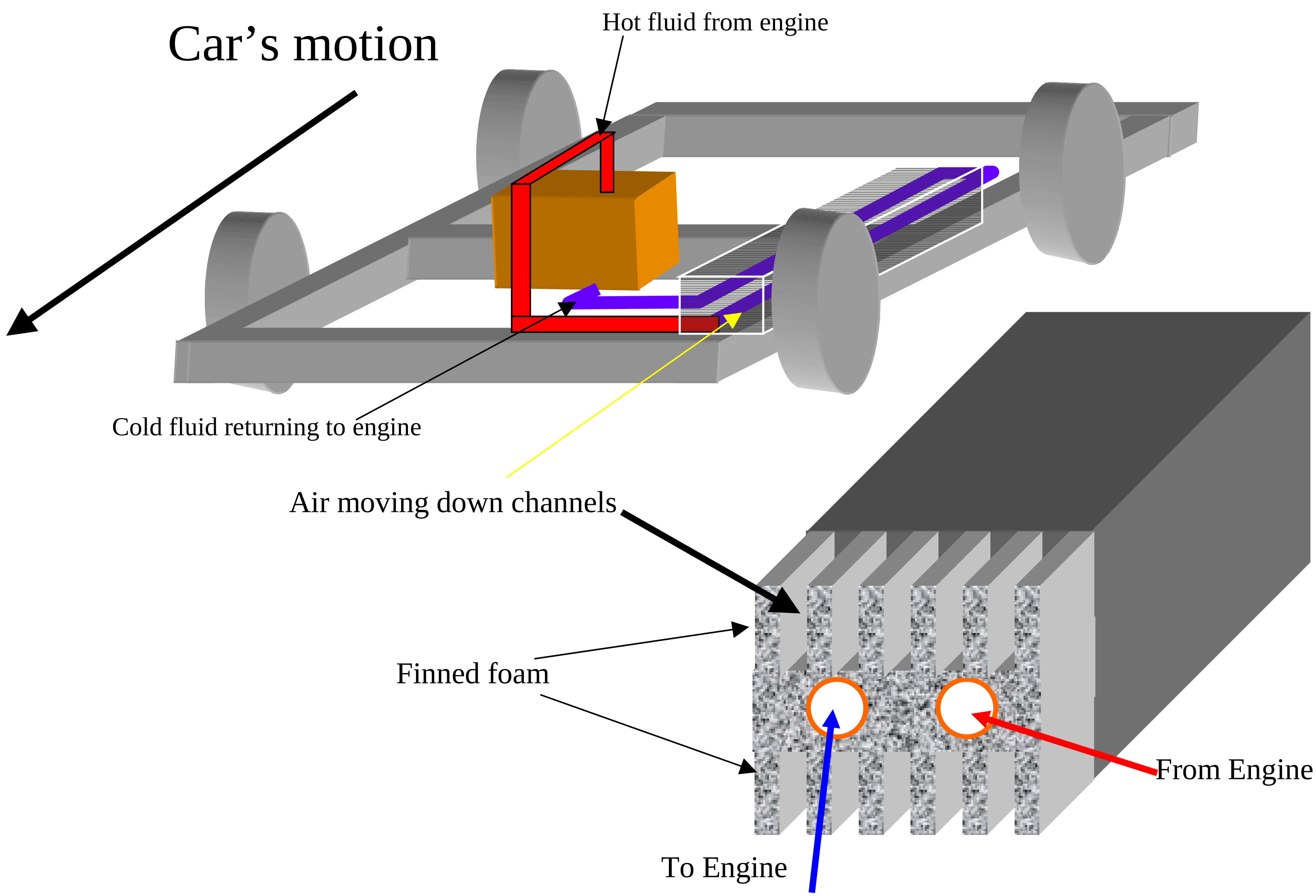




Measured U_o **= 1000 W/m^2 ·K depending on air humidity**

Similar design tested for 800 hp racing engine

Heat Exchangers- Forced Convection



Energy Balance

- Current heat exchanger utilize high flow rates and low temperature changes.

$$q = \dot{m}\, c_p\, \Delta T$$

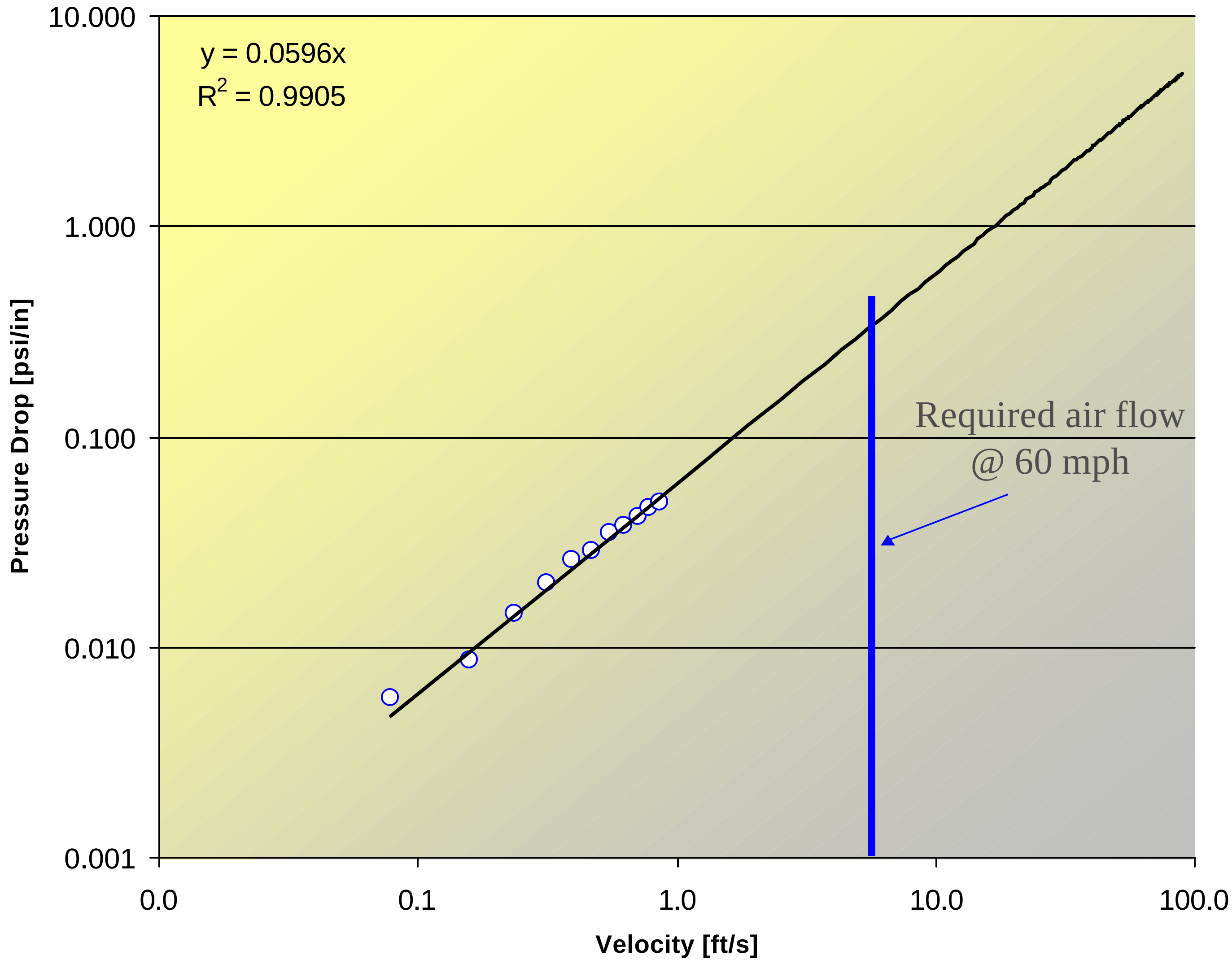
  - for example: automotive radiator for 150 hp engine
    - Current: ΔT < 5°F
    - Target: ΔT ~ 100°F
      - radiator fluid temperature cannot fall below ~200°F
    - Allows for a decrease in mass flow (m) of air by a factor of at least 20.

$$q = \dot{m}\, c_p\, \Delta T$$

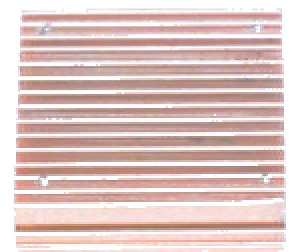
Decrease by 20

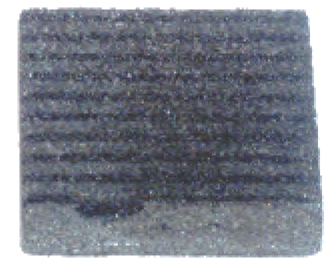
Increase by 20

Pressure drop through graphitic foam



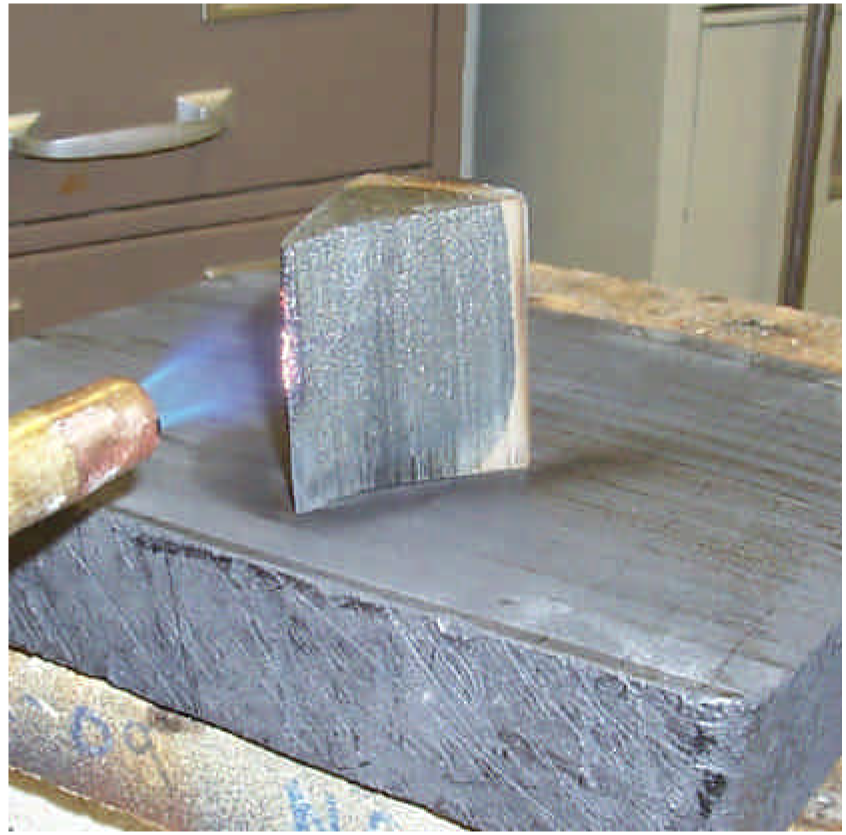
Workability





Heat Resistant Composites

Standard Polymer



Foam/Polymer

Conclusions

- By engineering process of producing pitch foams, thermal conductivity can be varied with density to achieve desired targets
- Light weight materials with thermal conductivities as high as aluminum can be produced
- Porous media heat exchangers can be designed that are dramatically smaller
- Out-of-the-Box designs can be used for the development of novel and radically different heat exchange devices
- Laminated foams can be used for structural members where high thermal conductivity and light weight are necessary.

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