

Development of Aluminosilicate Aerogel Impregnated Oxide Foams for Structurally Integrated Thermal Protection Systems

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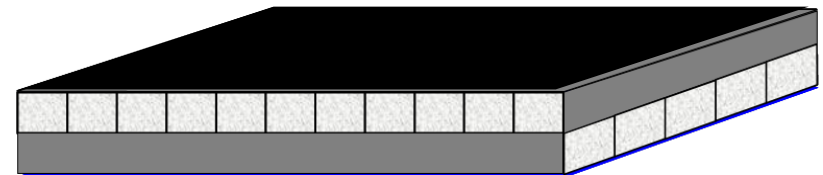
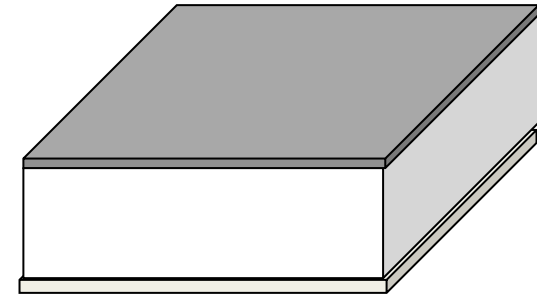
36th Annual Conference on Composites, Materials, and Structures
Cape Canaveral, FL, January 23-26, 2012

Insulating Cores for Structurally Integrated TPS (Integrated mechanical and thermal loads)

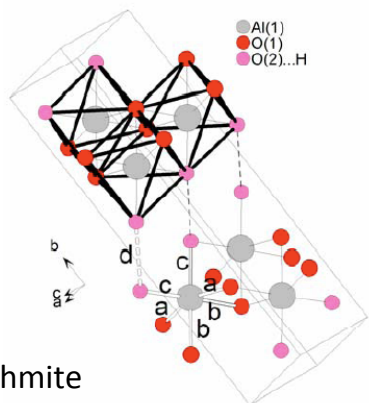
- Light-weight
- High volumetric heat capacity
- Low effective thermal conductivity
- Load bearing or non-load bearing
- Non-oxidizing
- Dimensional stability

Can aerogel incorporation reduce thermal conductivity while maintaining dimensional stability, allowing for lighter weight structural elements?

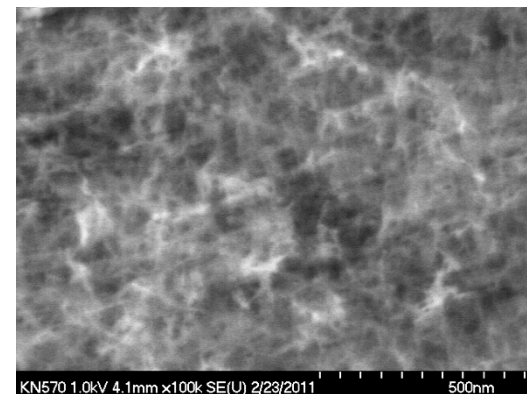
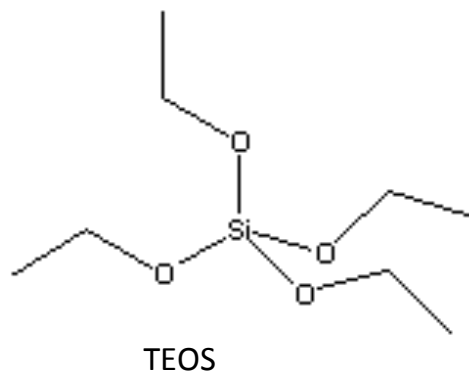
Susan White, Dan Rasky, “Fibrous-Ceramic/Aerogel Composite Insulating Tiles”, NASA Tech Briefs 2004



Boehmite [γ -AlO(OH)]+ TEOS \rightarrow hydrogel \rightarrow aerogel

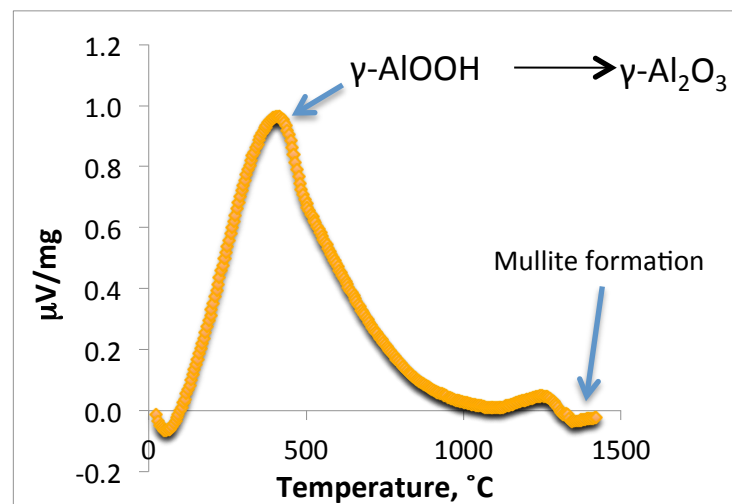
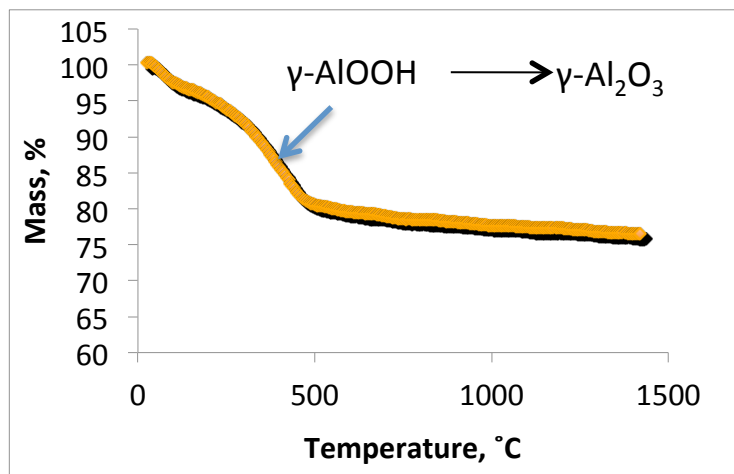


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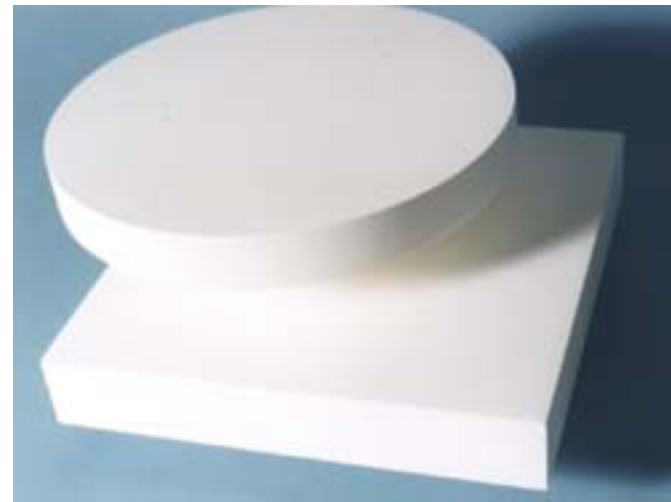
S. Bruhne, Cryst. Growth Des., 2008, 8 (2), pp 489–493n

P2W 3Al:1Si, 412 m²/g

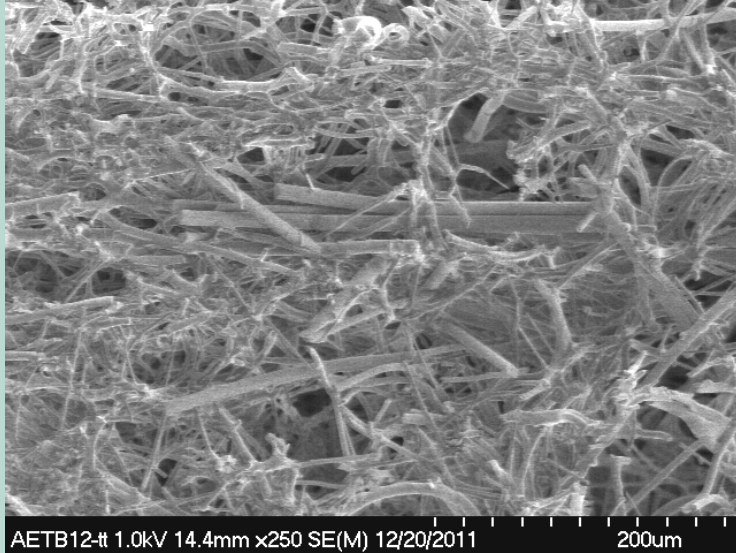


Oxide Foam Properties

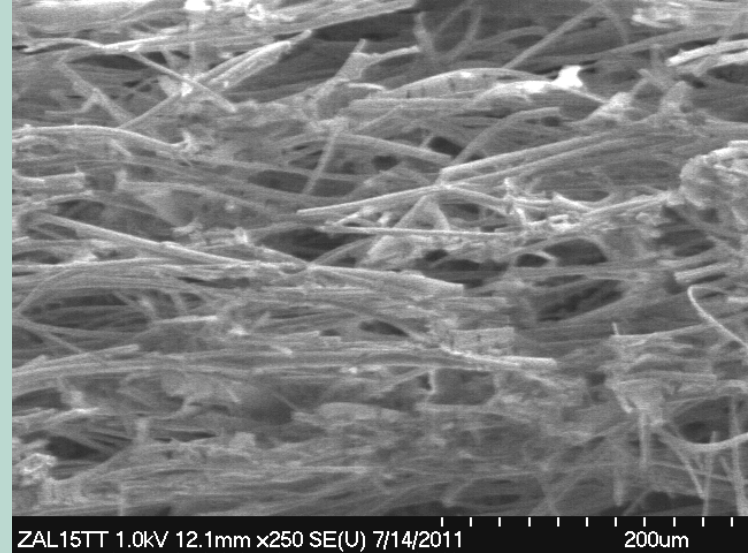
Material	Density (g/cc)	Thermal Conductivity (W/m-K)	Specific Heat (J/kg-K)	Al ₂ O ₃	SiO ₂	Binder	Source
AETB-12	0.192	0.064 (predicted)	628	20%	68%	Glassy phase; Inclusion of silica and aluminoborosilicate fibers provides bonding	TPSX
M15	0.240	0.16	1050	85%	15%	High Purity Silica	Zircar Zirconia
M2-35	0.624	-	1050	85%	15%	Mullite	Zircar Zirconia
ZAL-15	0.240	0.16	1047	85%	15%	High Purity Silica	Zircar Ceramics



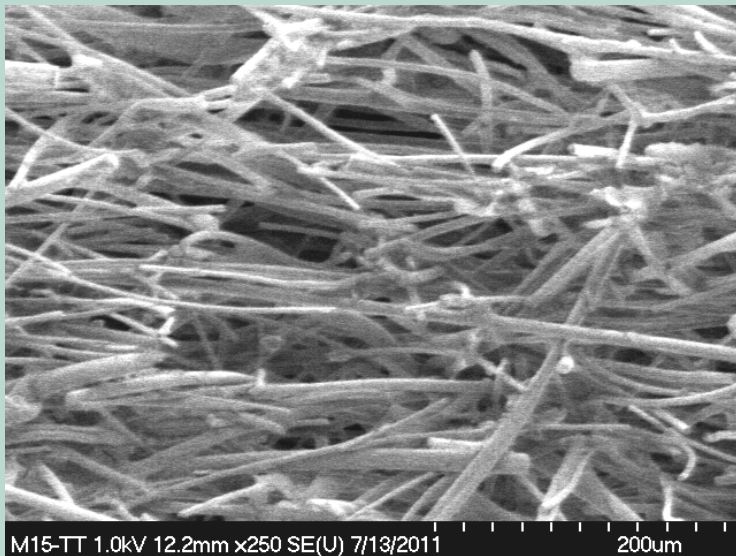
Microstructure: As-received foams



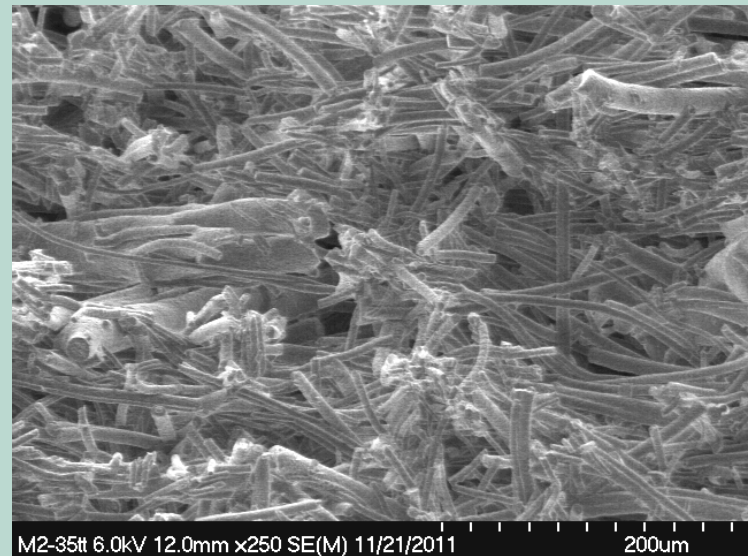
AETB-12



ZAL-15

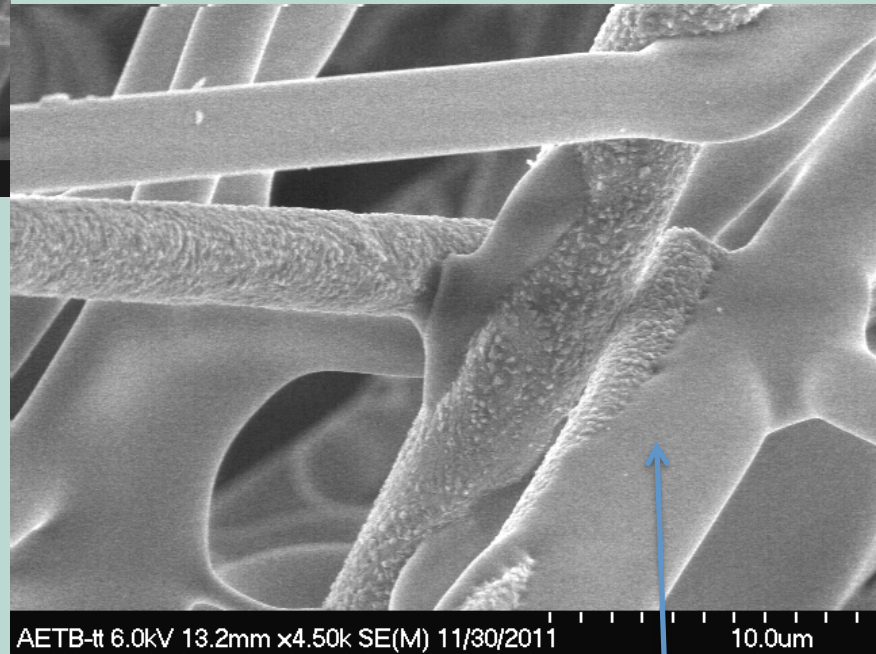
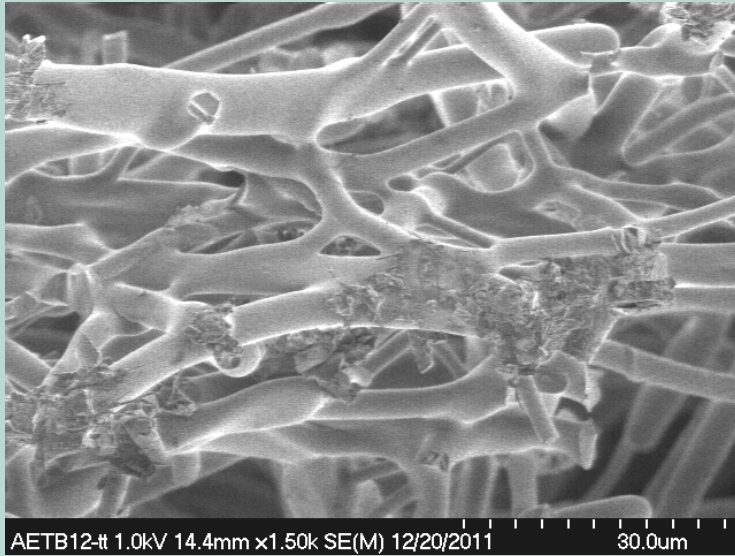


M-15



M2-35

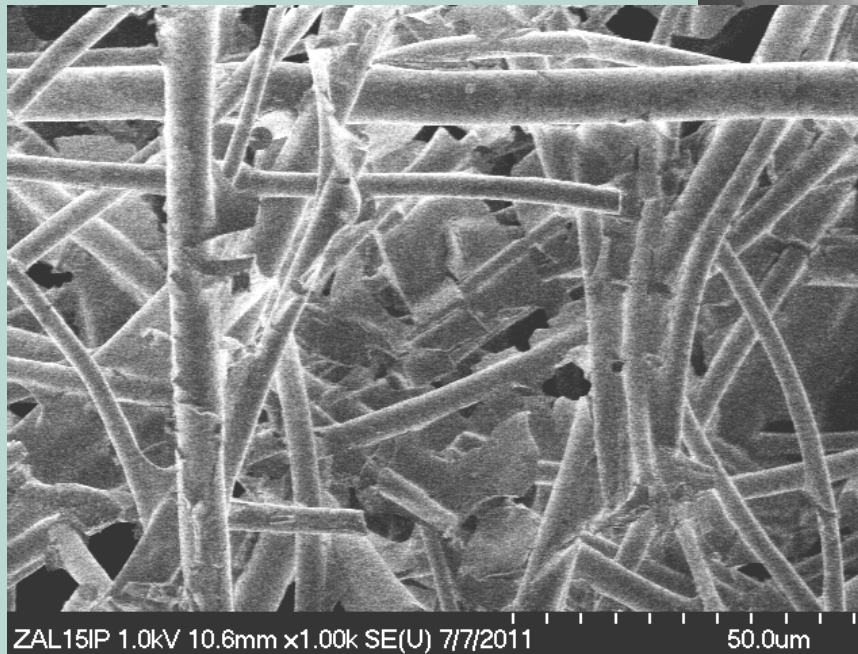
AETB-12



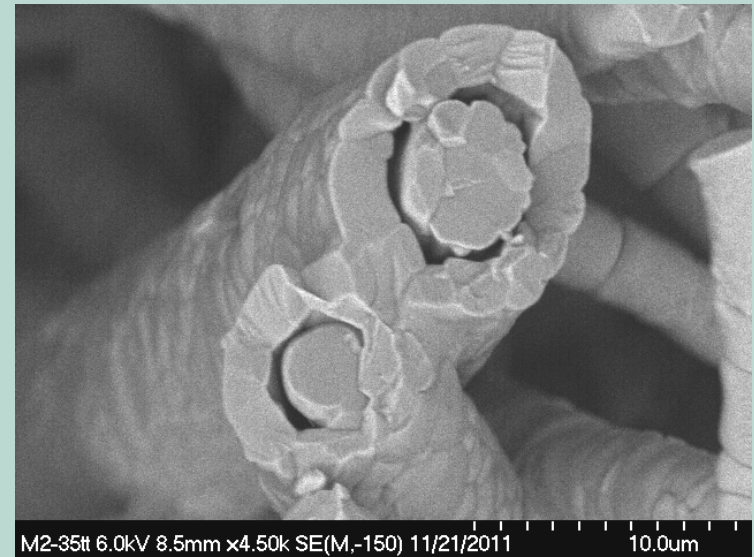
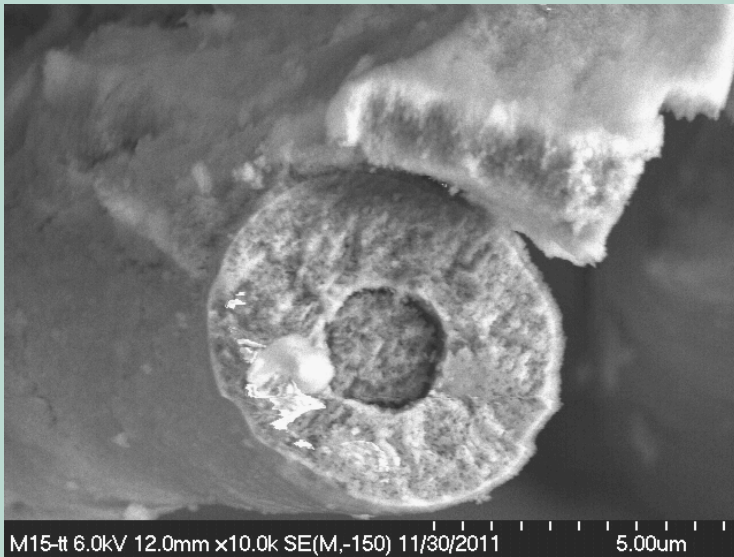
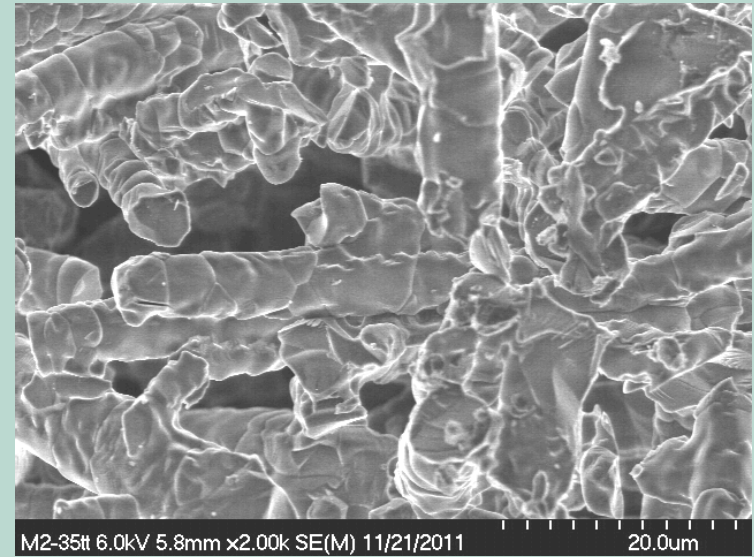
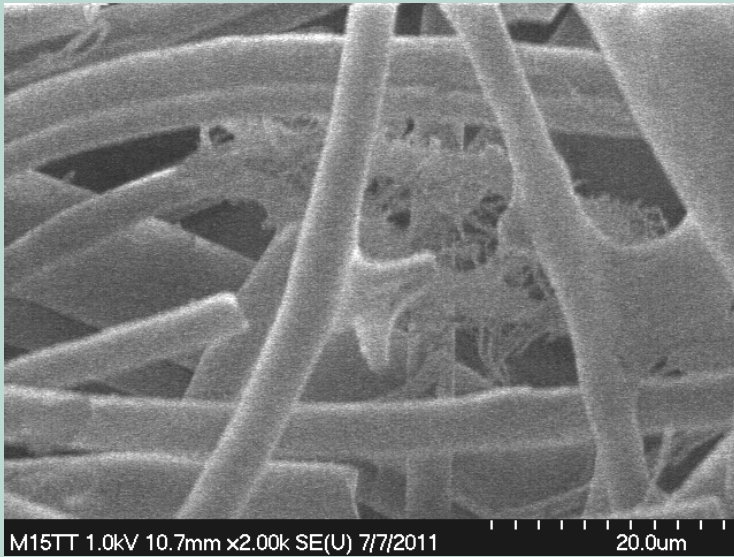
**Microstructure:
As-received foams**

SiO₂

**Microstructure:
As-received foams**



ZAL-15

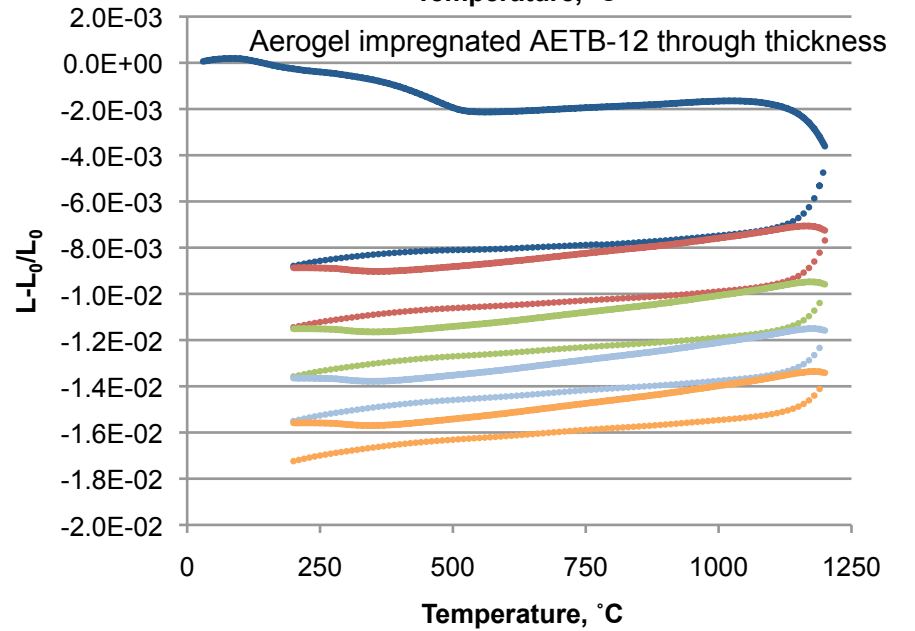
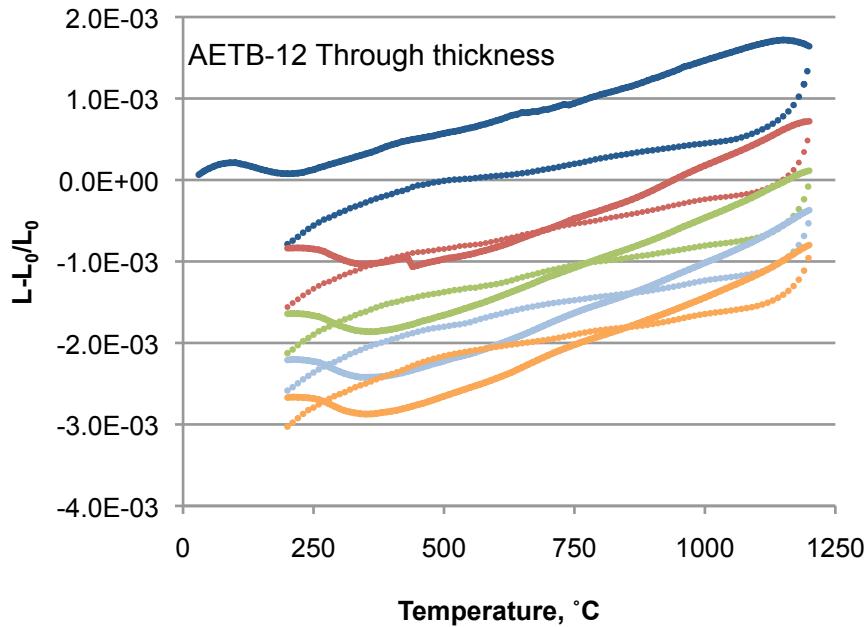
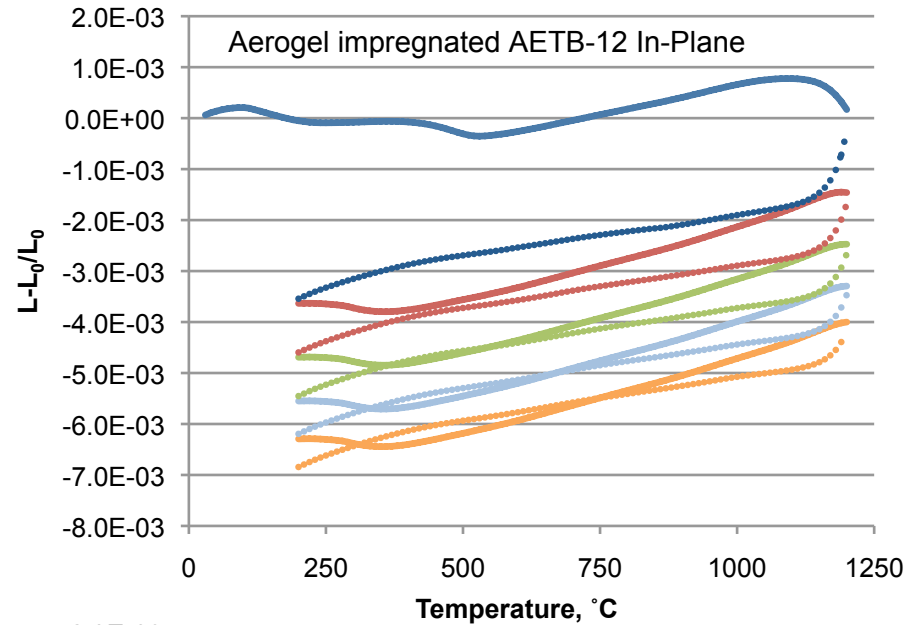
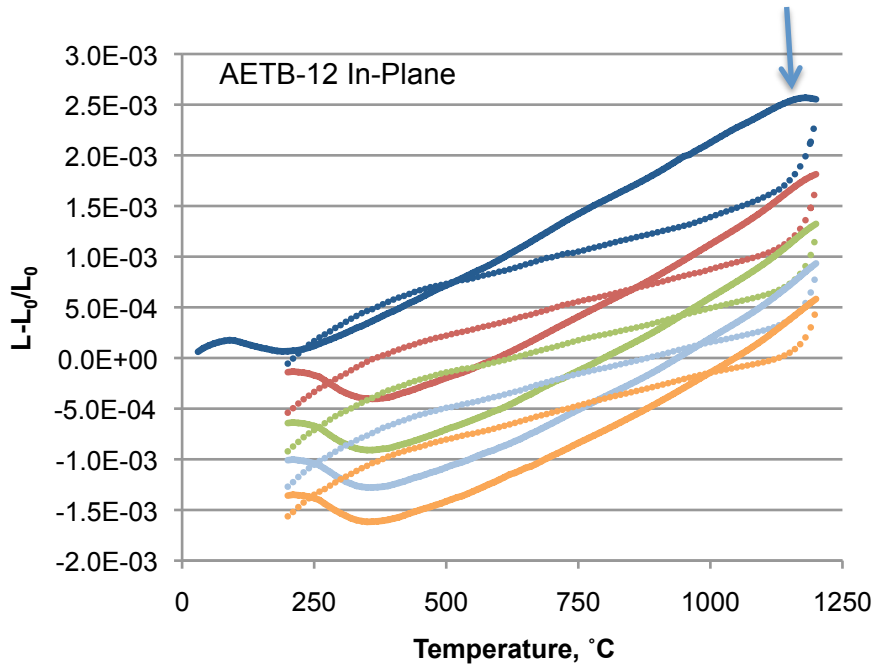


M-15

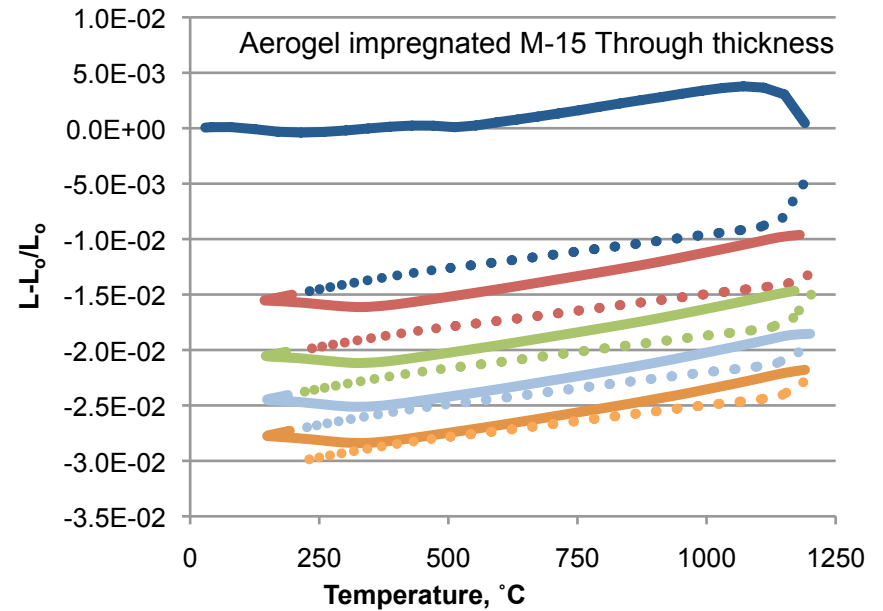
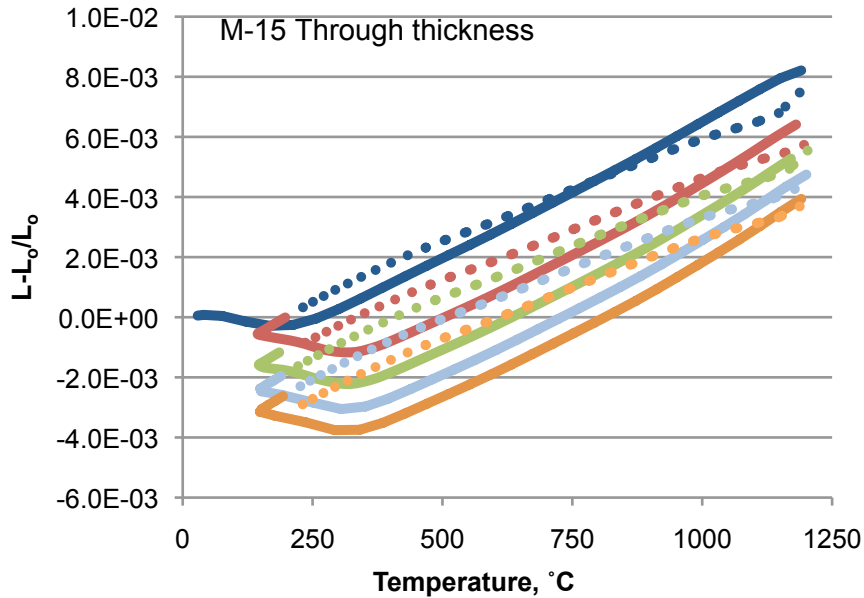
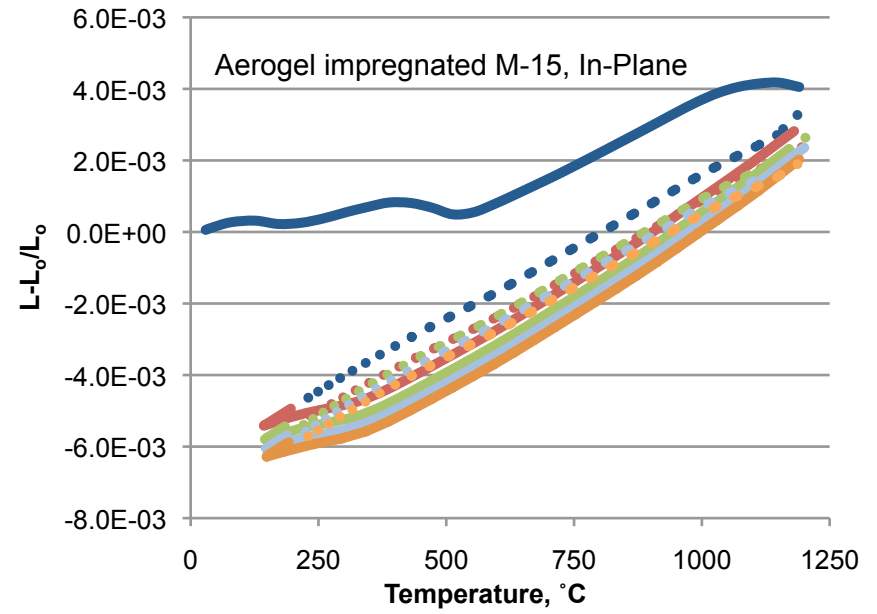
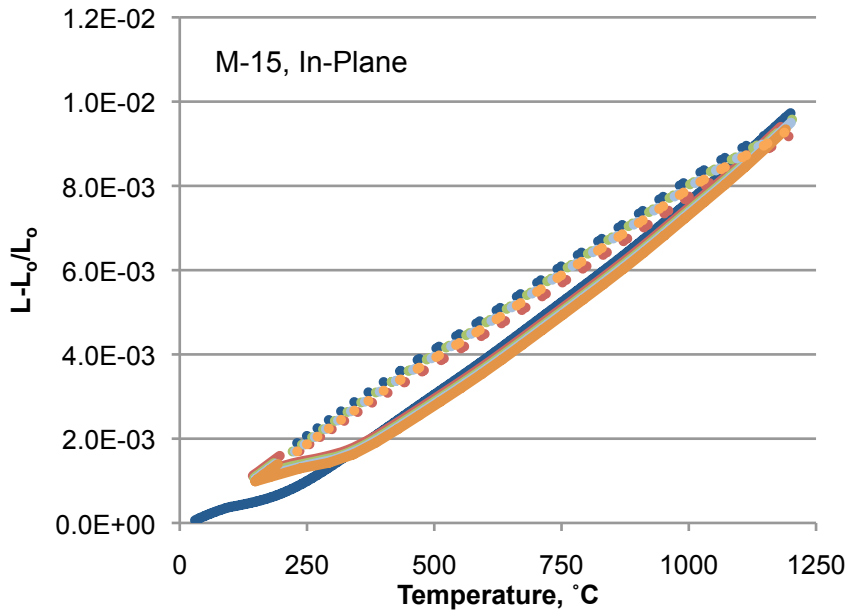
M2-35

Microstructure: As-received foams

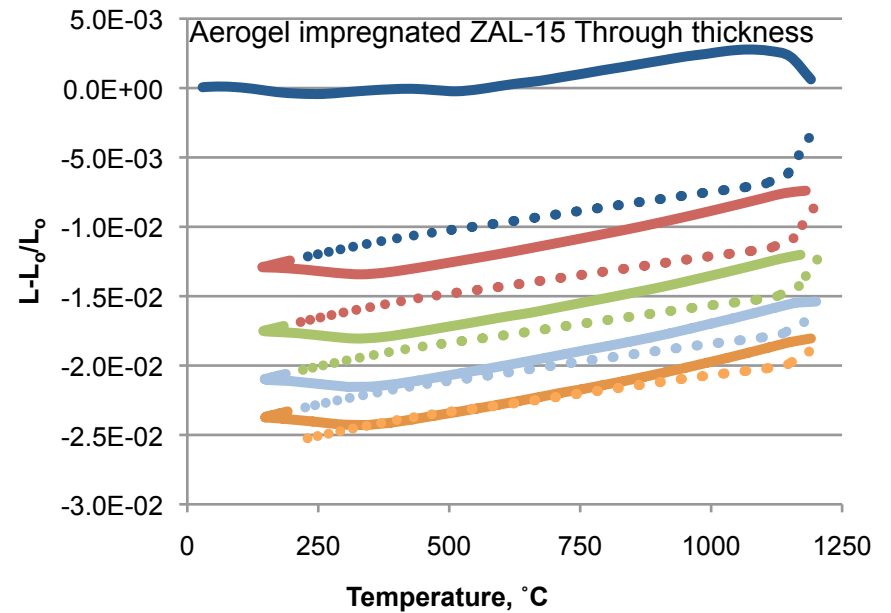
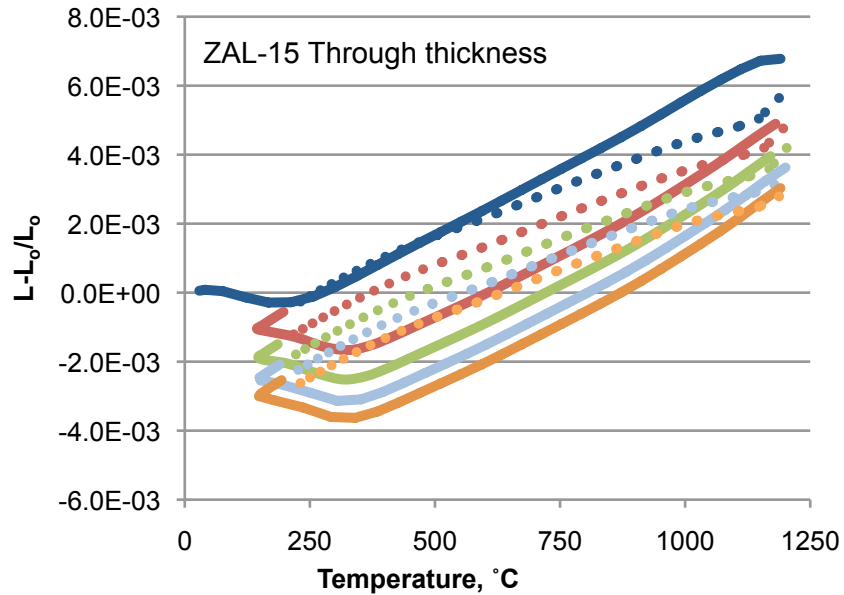
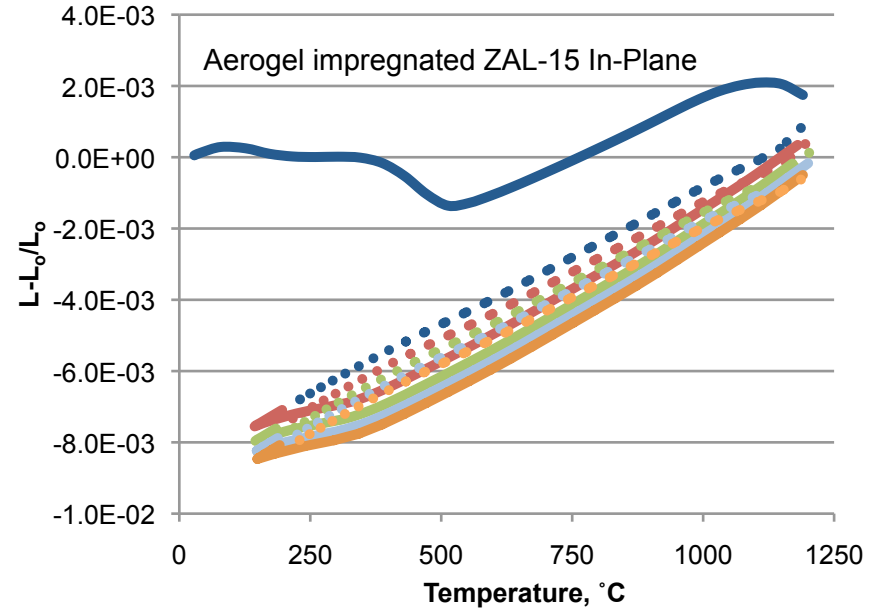
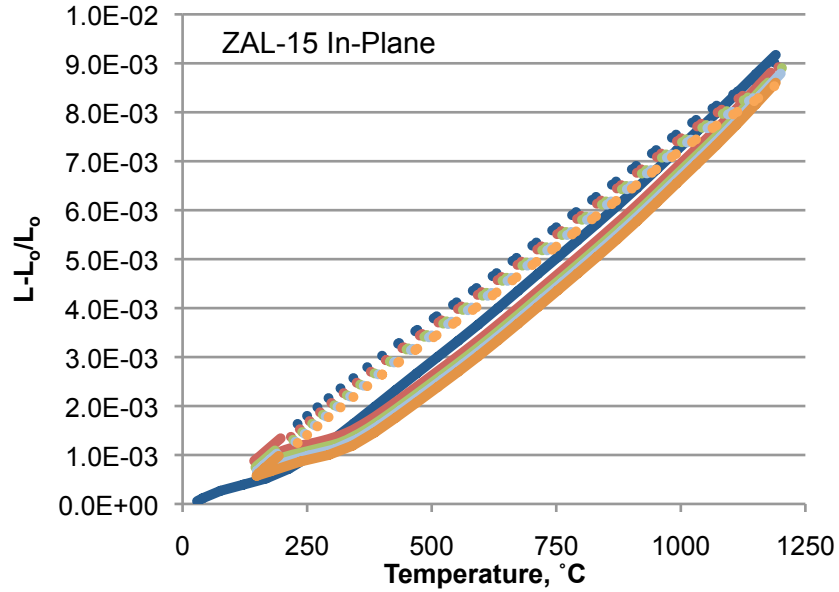
Dilatometry: AETB-12



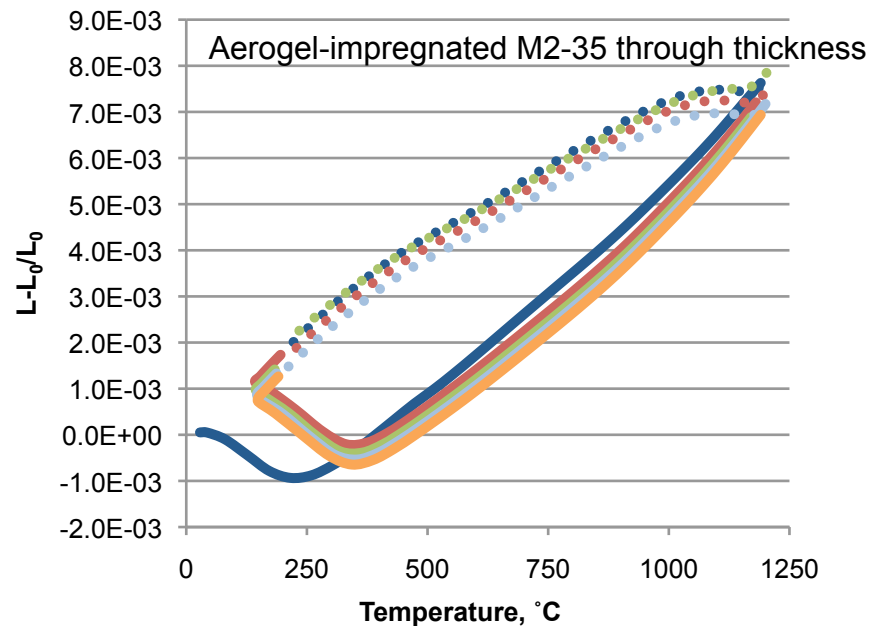
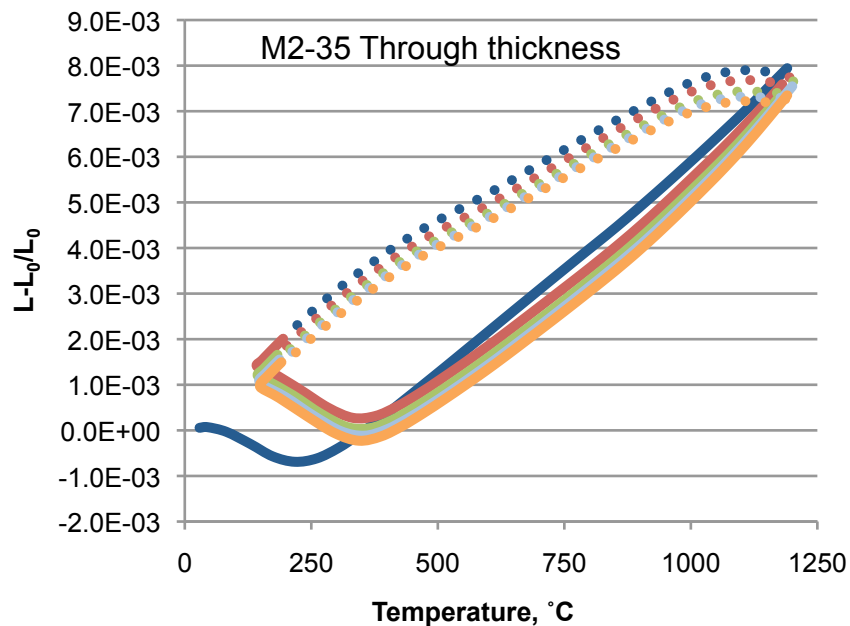
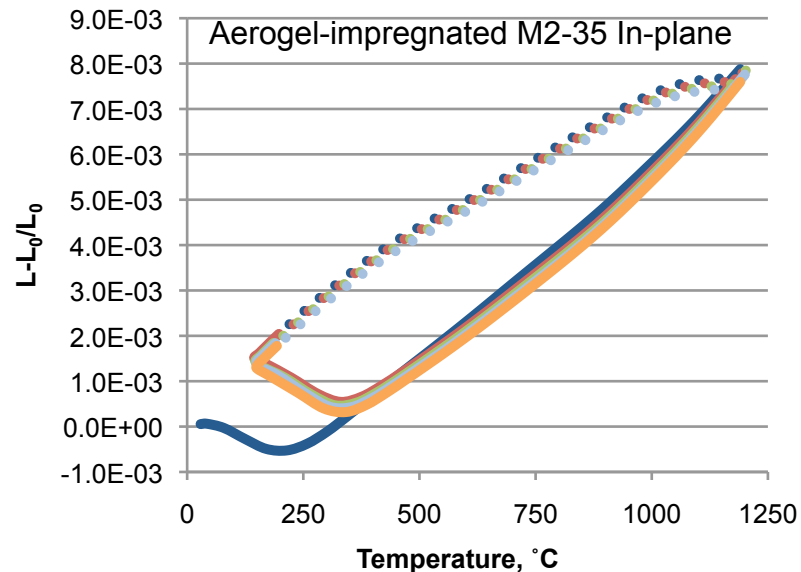
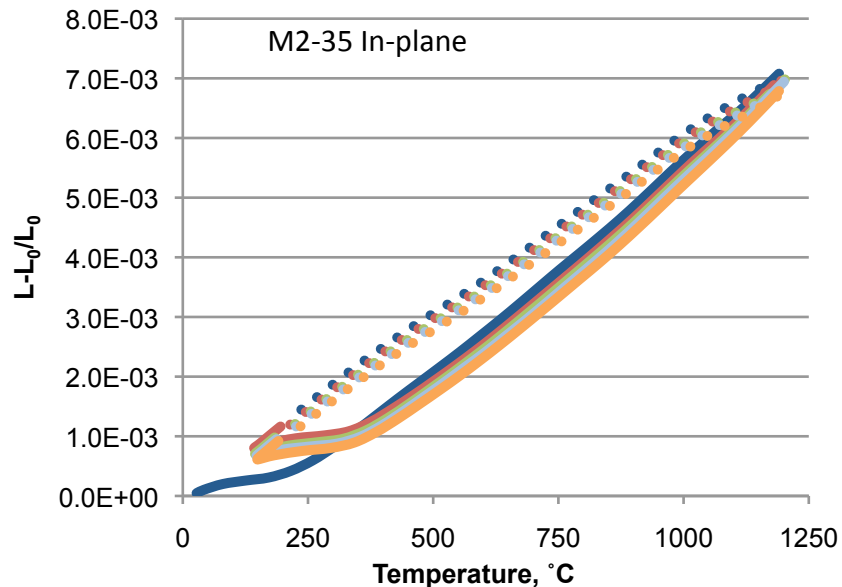
Dilatometry: M-15



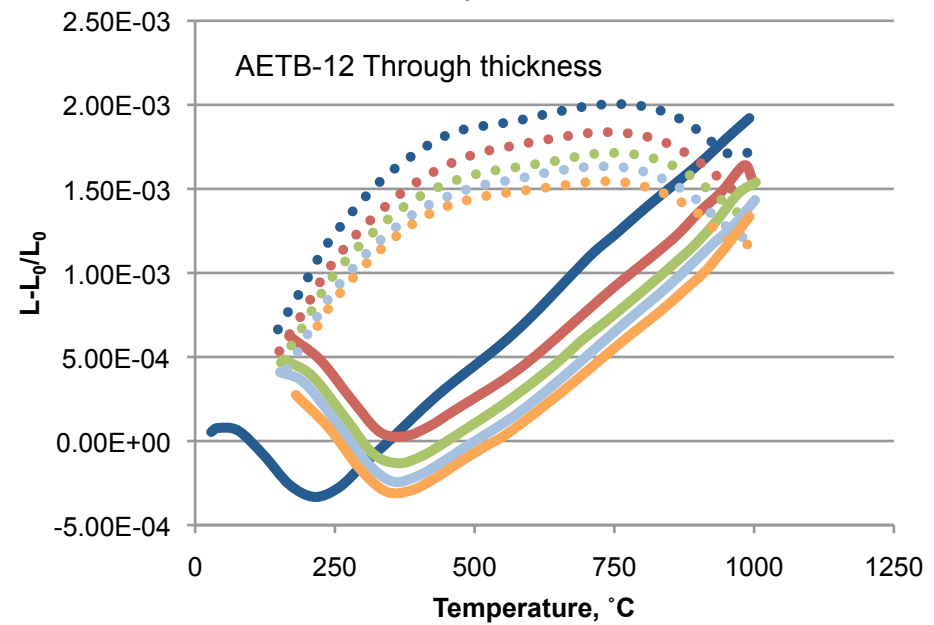
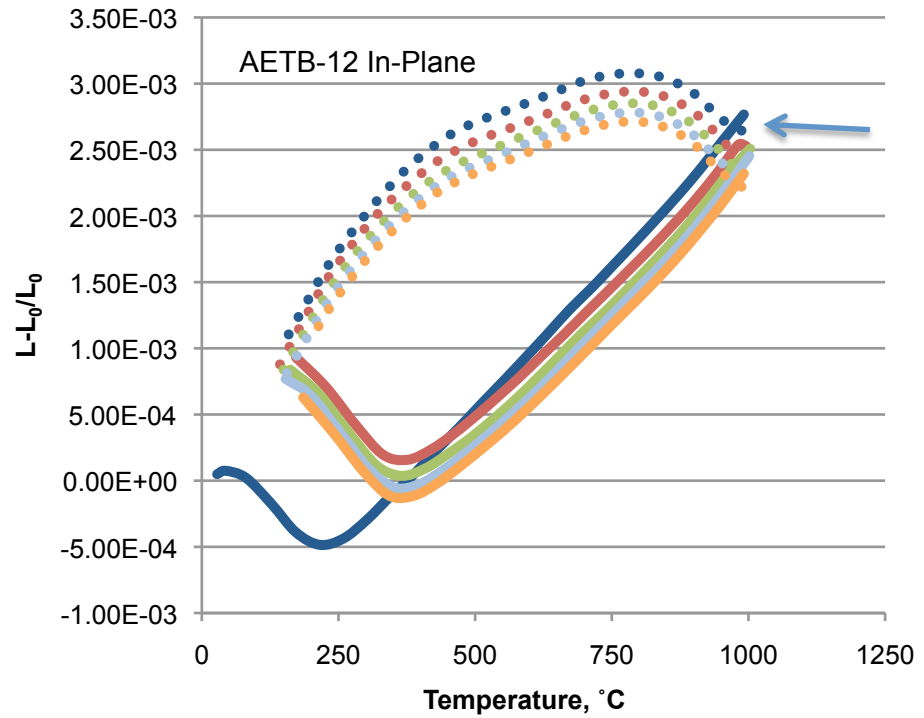
Dilatometry: ZAL-15



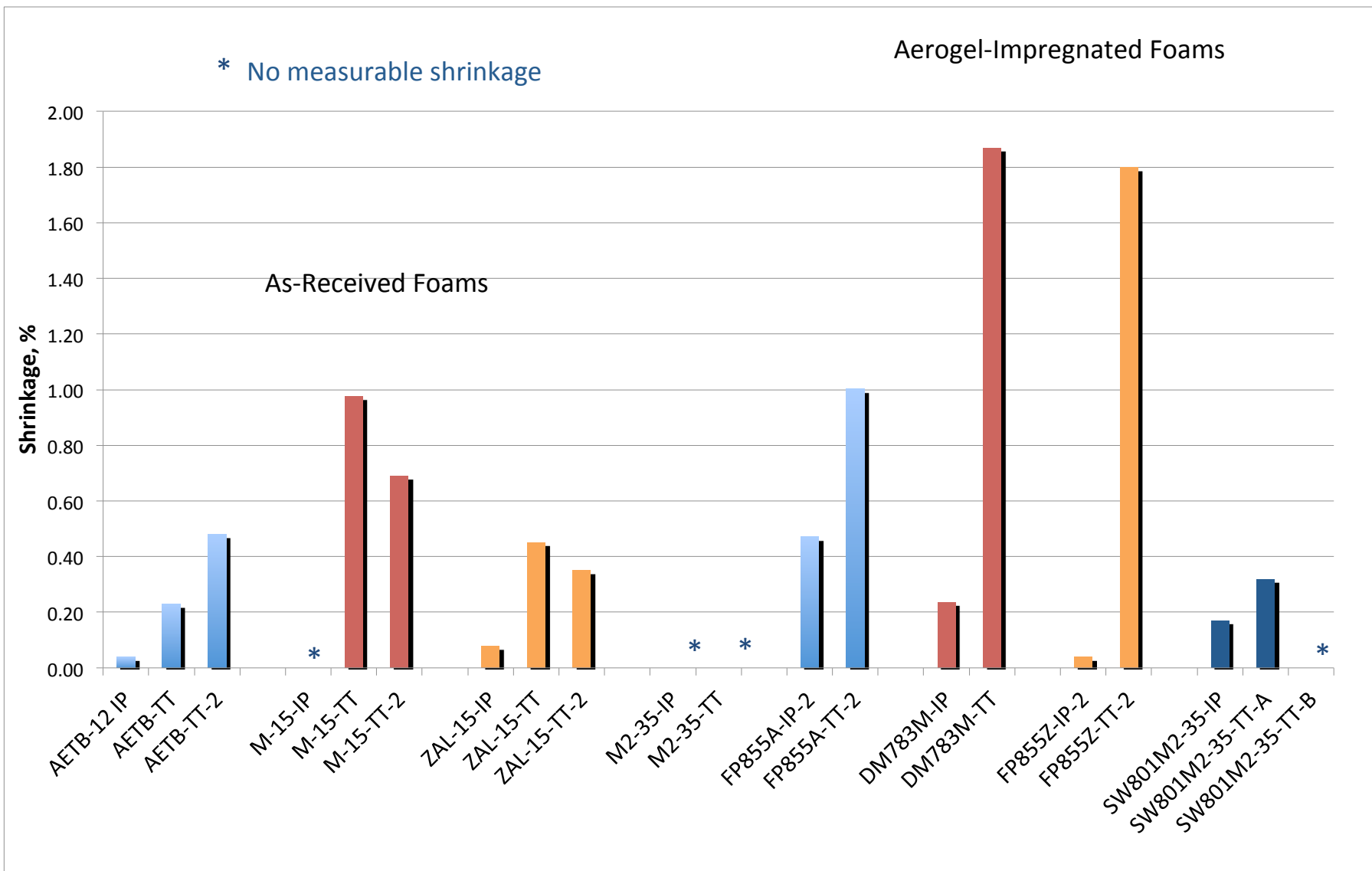
Dilatometry: M2-35



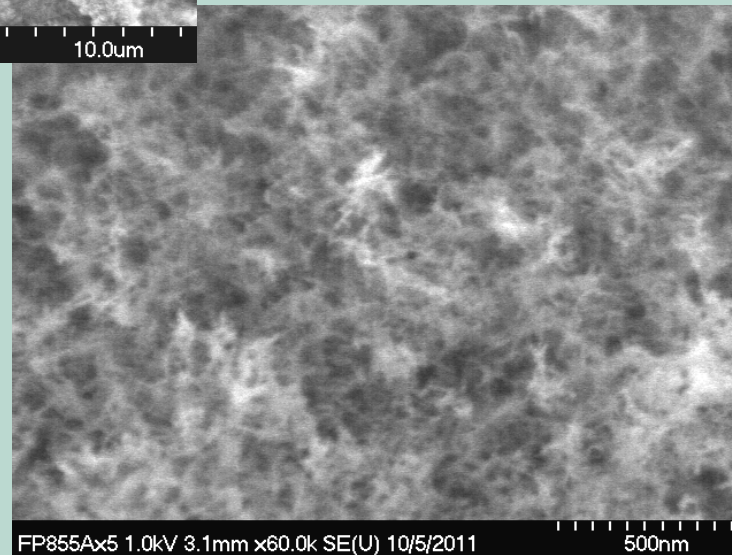
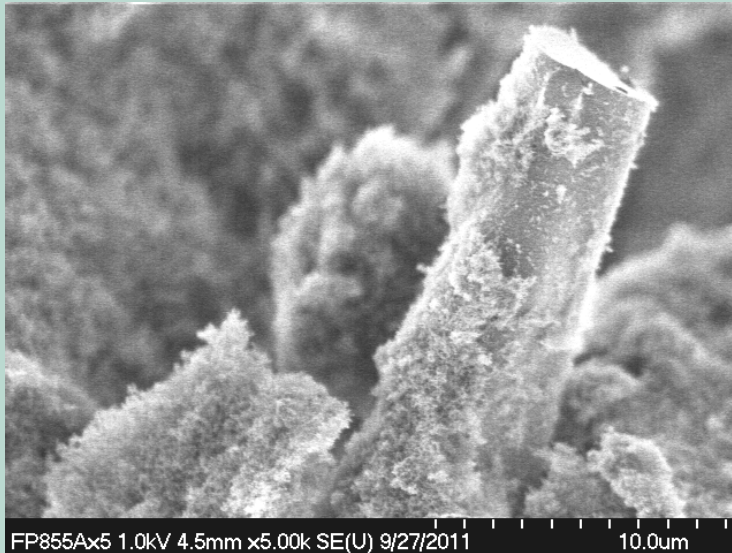
Dilatometry: AETB-12



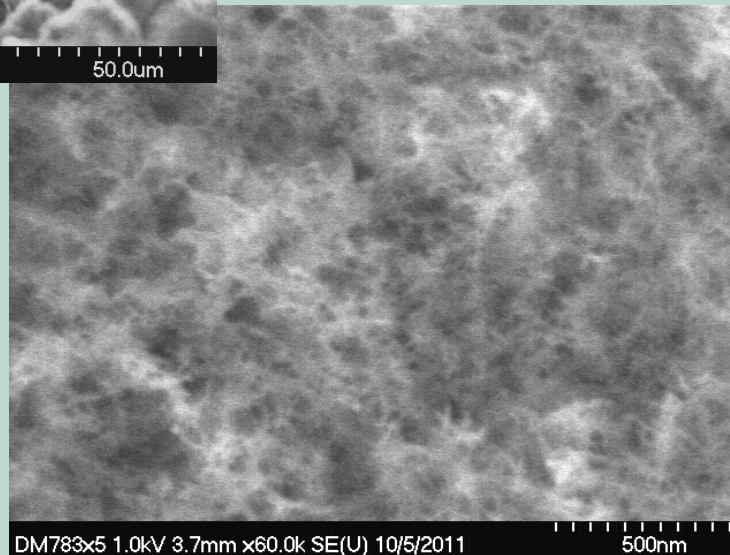
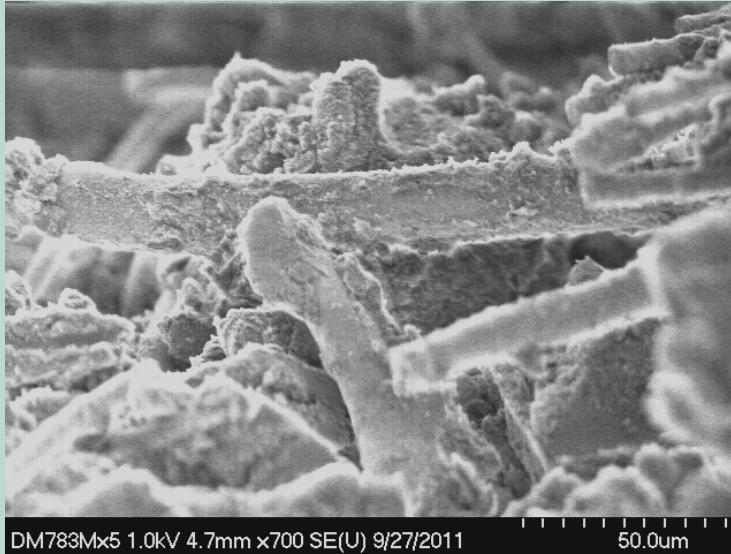
Dilatometry: Dimensional changes after 5 cycles to 1200°C



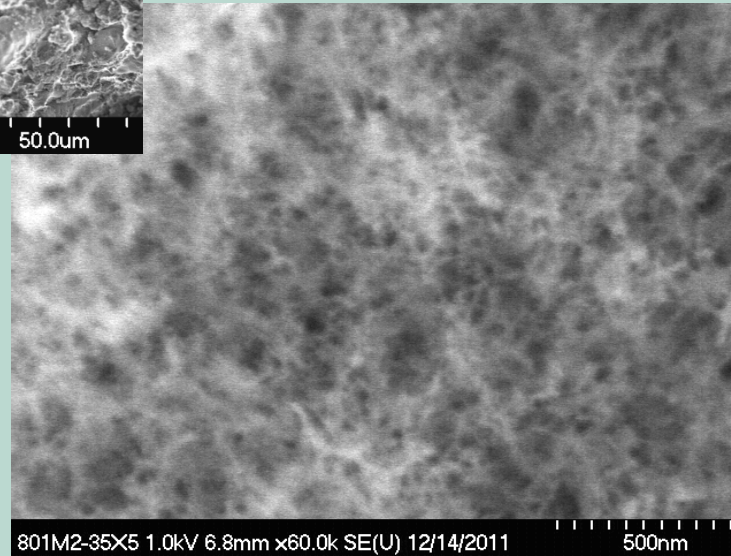
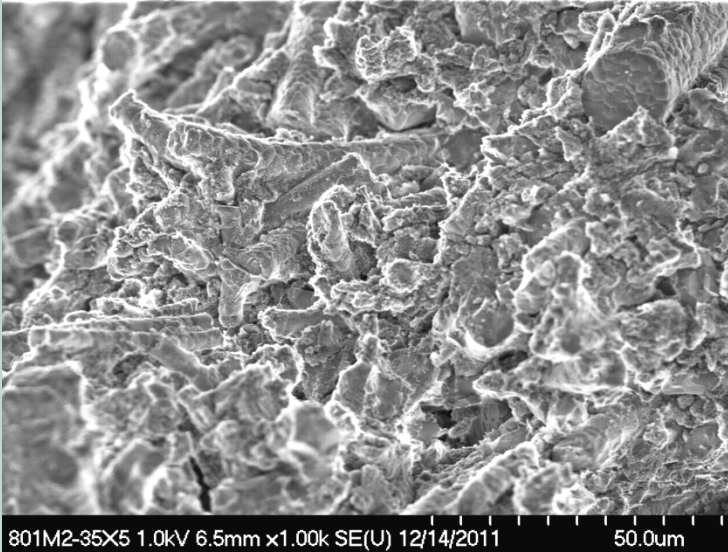
Aerogel-infiltrated AETB-12 Post 5 cycles to 1200°C



Aerogel-infiltrated M-15 Post 5 cycles to 1200°C



Aerogel-infiltrated M2-35 Post 5 cycles to 1200°C



X-ray Diffraction: As-received foams

AETB, as received

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	Aluminum Oxide	Rhombohedral	04-003-5819	53
Al _{4.44} Si _{1.56} O _{9.78}	Aluminum Silicate	Orthorhombic	01-074-4143	35
SiO ₂	Silicon Oxide	Tetragonal	04-008-7636	1
? Al _{2.5} B _{0.5} O _{4.5}	Aluminum Boron Oxide	Orthorhombic	04-012-8917	11

Significant glassy phase

M-15, as received

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	Alpha alumina	Rhombohedral	01-088-0826	71
Al _{4.52} Si _{1.48} O _{9.74}	mullite	Orthorhombic	01-074-4144	21
Al ₂ O ₃	Theta alumina	Monoclinic	01-086-1410	8

ZAL-15, as received

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	Aluminum Oxide	Rhombohedral	01-089-7717	61
Al ₂ (Al _{2.544} Si _{1.456}) O _{9.728}	Aluminum Silicon Oxide	Orthorhombic	01-074-8556	18
Al ₂ O ₃	Aluminum Oxide	Monoclinic	04-008-4095	12
? B ₆ O _{0.787}	Boron Oxide	Rhombohedral	01-087-2286	10

Samples after 5 cycles to 1000°C are very similar, with possible very small SiC phase present in AETB.

X-ray Diffraction: Thermally cycled composites

Aerogel impregnated AETB, 1200°C x 5

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	alpha alumina	Rhombohedral	01-089-7717	53
Al _{4.44} Si _{1.56} O _{9.78}	mullite	Orthorhombic	01-074-4143	40
? Si C	beta SiC	Cubic	01-075-0254	2
?Si O ₂	cristobalite	Tetragonal	04-005-4875	4

Significant glassy phase (SiO₂)

Aerogel impregnated M-15, 1200°C x 5

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	alpha alumina	Rhombohedral	01-088-0826	69
Al _{4.52} Si _{1.48} O _{9.74}	mullite	Orthorhombic	01-074-4144	21
Al ₂ O ₃	Theta alumina	Monoclinic	01-086-1410	10

Aerogel impregnated ZAL-15, 1200°C x 5

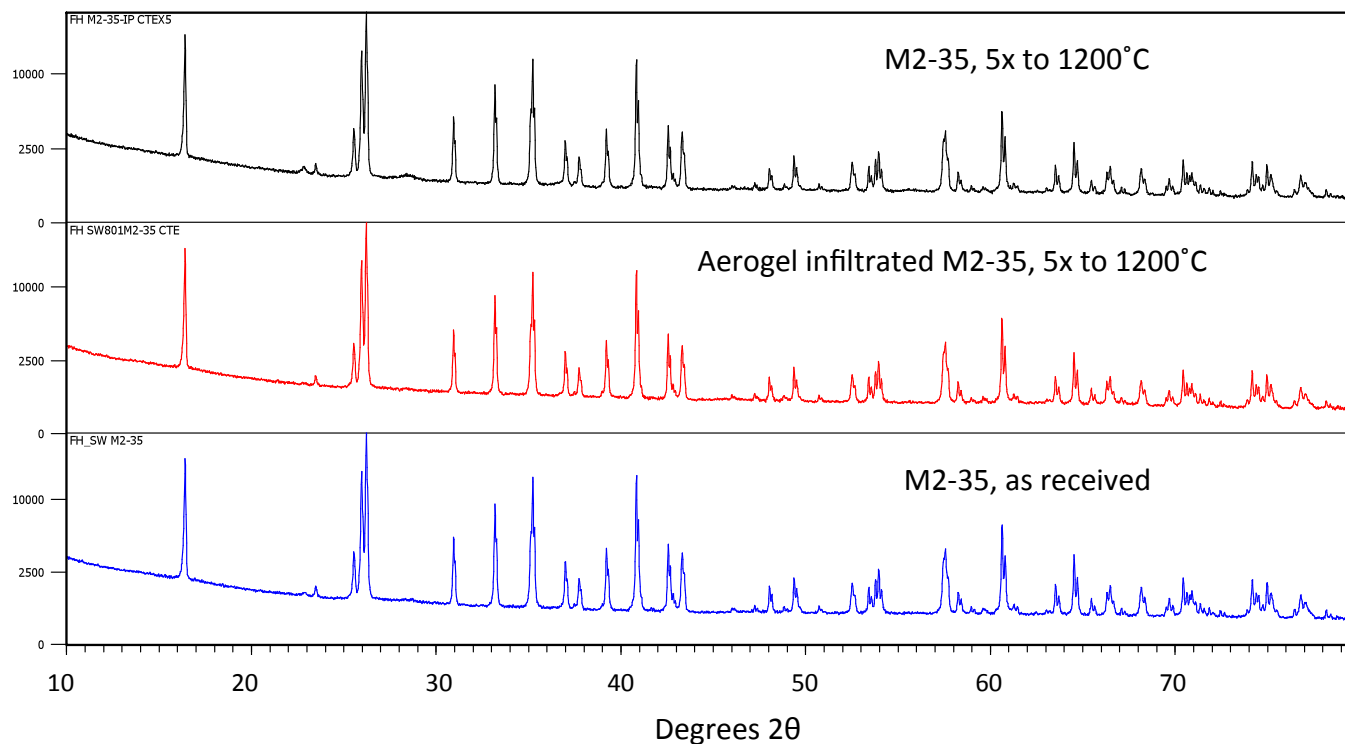
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Al ₂ O ₃	alpha alumina	Rhombohedral	01-076-8056	64
Al ₂ (Al _{2.556} Si _{1.444}) O _{9.722}	mullite	Orthorhombic	01-074-8552	19
Al ₂ O ₃	Theta alumina	Monoclinic	01-086-1410	16
?Si O ₂	cristobalite	Tetragonal	04-008-7641	1

Note1: there is a small glassy component to this sample.

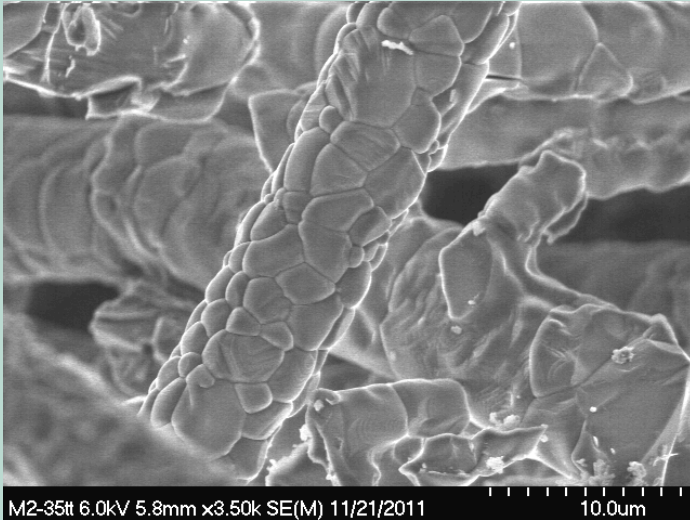
X-ray Diffraction: M2-35

M2-35 As received

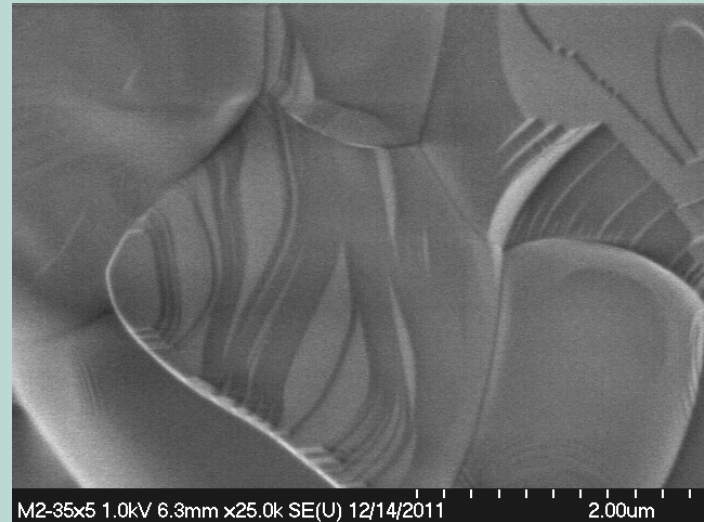
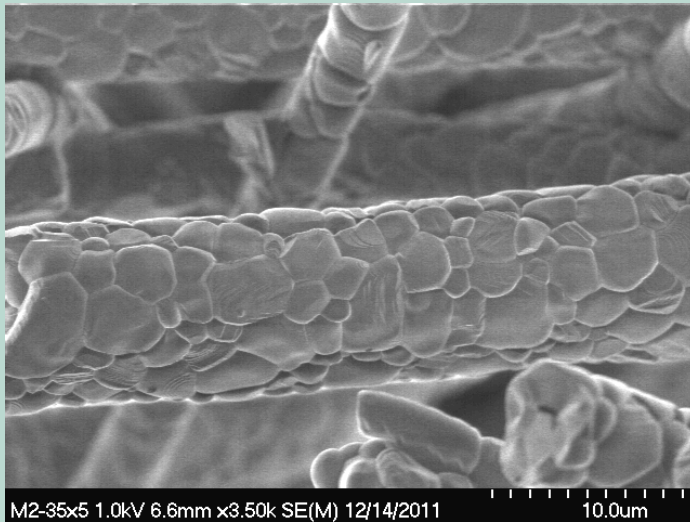
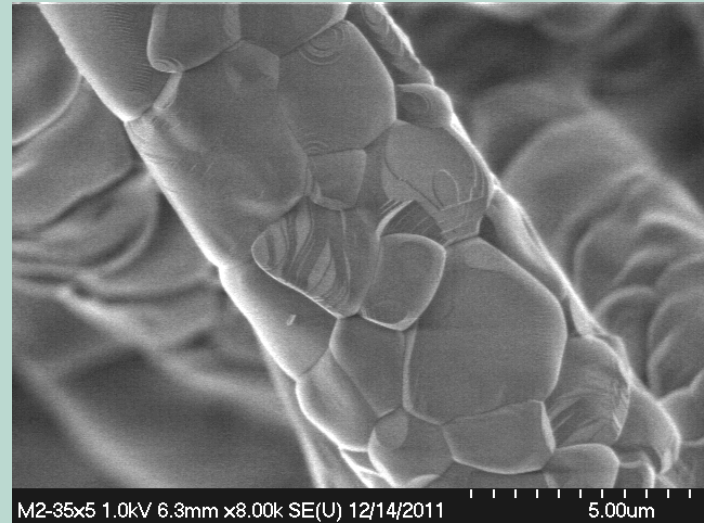
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
(Al _{2.34} Si _{0.66}) O _{4.83}	Aluminum Silicate	Orthorhombic	01-076-2579	84
Al ₂ O ₃	Aluminum Oxide	Rhombohedral	01-073-6190	11
?Ni (P ₄ O ₁₁)	Nickel Phosphorus Oxide	Anorthic	01-073-5532	6



M2-35 microstructure



M2-35 As received



Post CTE 5 cycles 1200°C

Thermal conductivity and heat capacity measurements of as-received and aerogel impregnated oxide foams in progress.

- Laser flash method being evaluated
- Samples being prepared comparative rod measurements

**Ongoing work:
Additional Oxide Foams**

Material	Density (g/cc)	Thermal Conductivity (W/m-K)	Specific Heat (J/kg-K)	Al ₂ O ₃	SiO ₂	Binder	Source
A-15	0.240	-	1050	97+%	-	Alumina	Zircar Zirconia
M2-15	0.240	-	1050	85%	15%	Mullite	Zircar Zirconia

All Al₂O₃ aerogels

CONCLUSIONS:

- Oxide foams (AETB-12, ZAL-15, M-15) containing *silica binders* and *glassy phases* undergo shrinkage on heating above 1100°C. Foams continue to shrink with repeated thermal cycling.
- Incorporation of aluminosilicate aerogels exacerbates shrinkage in AETB-12, ZAL-15, M-15, particularly in through thickness dimension.
- Mullite foams (M2-35) offer considerable improvement in dimensional stability, including samples incorporating aluminosilicate aerogels. Commercially available M2-35 carries a weight penalty; however, trial fabrication of lower density M2-15, and a lower density all Al₂O₃ foam, is in progress.
- Thermal conductivity measurements of the foams, with and without aluminosilicate incorporation, are underway.
- A Boehmite-derived, all Al₂O₃ aerogel, will be compared with aluminosilicates.

ACKNOWLEDGMENTS:

NASA ARMD Hypersonics Project

NASA Undergraduate Student Research Program

Derek R. Miller