Survey of Breakthrough Materials

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Compiled by
Charles E. Harris
The Center of Excellence for Structures and Materials
NASA Langley Research Center
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Executive Summary

1. Five NASA Field Centers contributed to the materials survey. Properties and development status reports were compiled for 53 materials, including structural, thermal protection, radiation protection, and electronics.

2. *Caution!* The best properties of a material that you will ever see is when you first see the properties! The history of new materials development is that when the final "-ilities" get worked the weight goes up, the use temperature goes down, and the operational environment limits performance.

3. <u>In the near-term</u>, numerous advanced materials exist that have attractive properties and can mature to a TRL of 6+ within <u>5 to 10 years or less</u>, but only with a compelling technology pull and the associated resource investment.

4. <u>In the far-term</u>, biomimetic, nanostructured materials, especially carbon nanotubes, are attractive for every materials application but dramatic breakthroughs will be required to realize the potential of the materials systems within the <u>next 10-20 years</u>.

5. Applications of new materials must be evaluated in a systems context. For example, advanced structural design methods and highly efficient structural concepts will be required to fully exploit the potential benefits of biomimetic, nanostructured, multifunctional materials in revolutionary aerospace vehicles. Also, the building-block approach to manufacturing scale-up will be essential to validate the advanced materials and concepts.

Executive Summary, continued

6. Structural materials for vehicles and habitats: a factor of 2 gain in weight savings can be achieved by carbon fiber reinforced polymers, metal matrix composites, and intermetallics; carbon nanotube reinforced polymers (and metals) may offer a factor of 10 gain in weight savings.

7. Structural materials for propulsion components: ceramics may offer a factor of 2 gain in use temperature but may never achieve attractive structural design allowables; advanced metallic alloys and intermetallics may offer a factor of 2 gain in weight savings but only modest temperature improvements; polymer matrix composites, including carbon nanotubes, may offer significant weight savings but at a reduction in the use temperature.

8. Materials for radiation shielding: Near-term gains by selecting structural materials only offer modest improvement in shielding potential (10-20%); dramatic improvements in radiation protection may be achieved by nonconventional vehicle and habitat configurations.

9. Thermal protection systems: breakthroughs will not come from improved material properties but from revolutionary concepts and capabilities such as sharp leading edges, rapid heat transfer, all-weather durability, self-diagnostics and self-repair.

10. Electronic and photonic materials: dramatic breakthroughs will occur from functionalized nanostructured materials enabling the fabrication of nano-electro-mechanical systems (NEMS).

Breakthrough Materials to Enable Exploration

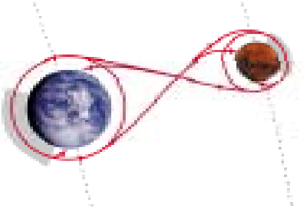
Space Access Vehicles

- Nanostructured, functionalized materials for ultralightweight, highly efficient structure
- Integrated thermal structure/TPS/cryo-insulation
- High temperature, durable materials for propulsion components
- Integrated vehicle health monitoring / management system for high reliability
- Validated, physics-based computational tools for reliability-based design methodology

In-Space Vehicles and Propulsion Systems

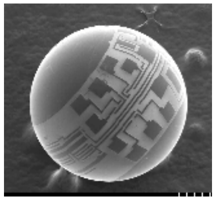
- Cryogenic propellant tanks and novel vehicle configurations
- Radiation shielding materials and integrated vehicle/habitat configurations
- Self-assembled, self-diagnostic, and self-healing materials and in-space fabrication methods
- On-site habitat construction using regolith mining and fabrication methods

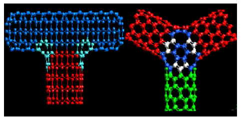
Planetary Entry Vehicles



- TPS materials and concepts to enable vehicle to change directions
- All-weather, self-diagnostic, and self-healing TPS materials
- TPS materials/concepts constructed from in-situ resource utilization

Avionics and Electronics





Self-Assembling Electronics

- Wide bandgap semiconductors for high-temp, high-power, and high-strength MEMS devices
- Multifunctional materials
- Nanostructured, functionalized materials for NEMS devices
- Biomimetic materials for electronic devices and molecular computing

I. Materials for Vehicle Structure and Habitats

First Generation RLV

Second Generation RLV

Third Generation RLV

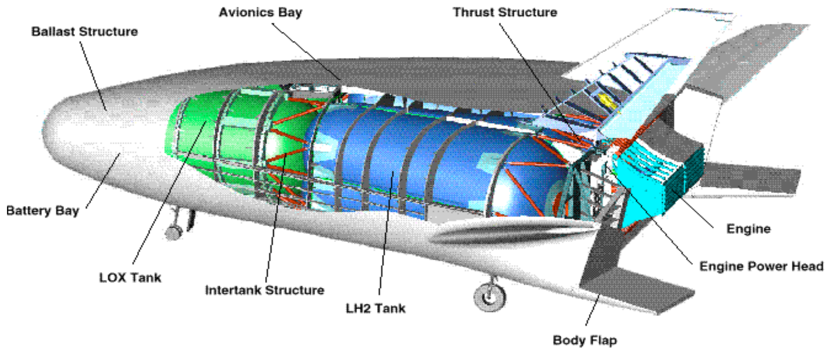
Application of Advanced Materials to 2nd Gen. RLV

Leading Edges / Nose Caps

- Hot-structure control surfaces (TRL=5)
- High-temperature heat pipes (TRL=4)
- Active cooling (TRL=4)

Thermal Protection System

- High-temperature metallics (TRL=5)
- Advanced ceramics (TRL=4)
- Refractory composites (TRL=4)
- Advanced flexible insulation (TRL=6)



Primary Structure

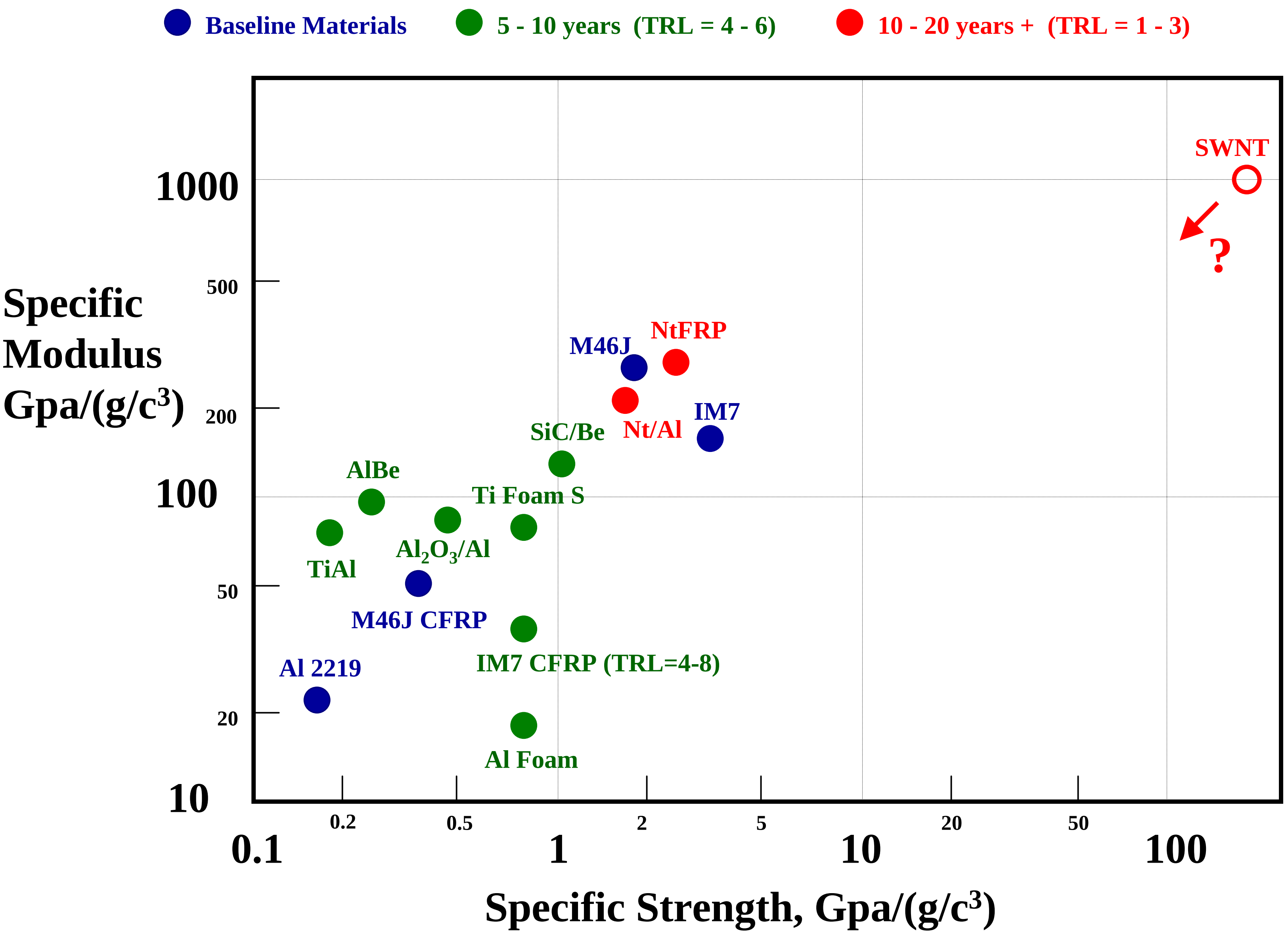
- High-temperature polymeric composites (TRL=5)
- High-temperature metal composites (TRL=4)
- Manufacturing process scalability (TRL=4
- Validated design and analysis methods (TRL=4)
- Nondestructive evaluation (TRL=4)

Cryotanks

- Nonautoclave curing (TRL=3)
- Manufacturing process scalability (TRL=4)
- Nondestructive evaluation (TRL=4)
- Vehicle health monitoring (TRL=3)
- Integrated TPS / cryoinsulation (TRL=2)

Technology Readiness Level (TRL) Scale is 1 - 9

Properties of Materials for Vehicles and Habitats



Metallic and MMC materials for vehicle structure and habitats

	reference Aluminum 2219-T87 ISS Crew Modules	5-10 yrs TiAl Alloy (measured)	5-10 yrs Al_2O_3 / Al Composite (measured)	5-10 yrs Aluminum Foam (theoretical)	5-10 yrs Al-Be Alloy (measured)	5-10 yrs Ti Foam Sandwich (measured)	5-10 yrs SiC / Be Composite (estimated)	10-20 yrs NT / Al Composite (theoretical)
Tensile Strength	0.46 Gpa	0.70 Gpa	1.65 Gpa	1.0 Gpa	0.5 Gpa	0.75 Gpa	2.1 Gpa	3.3 Gpa
Tensile Modulus	73 Gpa	280 Gpa	241 Gpa	20 Gpa	210 Gpa	90 Gpa	280 Gpa	300 Gpa
Elongation	10 %	1.7 %	0.8 %	20 %	5 %	5 %	3 %	6%
Density	2.83 gm/cc	3.8 g/cc	3.4 g/cc	1.3 g/cc	2.1 g/cc	1.1 g/cc	2.2 g/cc	2.0 g/cc
Specific Strength	0.16	0.18	0.49 (3x Al)	0.8 (5x Al)	0.25 (1.5x Al)	0.7 (4x Al)	1.0 (6x Al)	1.65 (10x Al)
Specific Modulus	26	74 (3x al)	71 (3x Al)	15	100 (4x Al)	80 (3x Al)	130 (5x Al)	150 (6x Al)
Thermal Cond’ty	121 W/mK	18 W/mK	94 W/mK	50 W/mK	200 W/mK	5 W/mK	n/a W/mK	120 W/mK
Use Temp.	150 C	800	375	150	500	600	750	400
Manufacturability	TRL = 9	TRL = 6	TRL = 5	TRL = 4	TRL = 3	TRL = 4	TRL = 3	TRL = 1

TiAl Alloy

Description

A light weight replacement for Ti and Ni alloys in structural applications in oxidizing environments

Processing Method(s)

Complex airfoils, housings and cases are made by casting. Sheet, rods, fasteners, disks are made by ingot/powder preforms plus hot working.

Current State of Development

Successful aero engine tests provide technology for space transportation applications. Lower strength, stiffness limited parts are more mature. Higher strength alloys have not been tested to same level.

Critical Issues

Damage tolerance is only moderate and must be confirmed for specific applications. Hydrogen resistance is expected to be poor.

Alumina (Al_2O_3) fiber/ Aluminum matrix MMC

Description

Low cost precursor materials in tape or wire form of fibers (Al_2O_3 or SiC) in aluminum matrix. Precursor forms are thin and flexible for laying into composite or selectively reinforcing metallic structures. Useable temperature range exceeds PMC and Al alloys. Reduced weight attained through improved structural efficiency and higher specific properties. AMC is believed to offer inherently superior cryogenic containment.

Processing Method(s)

Braze in air to form composite panel or to selectively reinforce metallic structures. Composite panels can be manufactured by continuous laser brazing of tapes using fiber winding techniques. Composite panels can also be fabricated by laying up tape followed by hot pressing.

Current State of Development

Al_2O_3 continuous fiber in pure Al matrix wire in use for electrical line supports to extend distance between cable supports. Continuous laser brazing using fiber winding techniques under development for fabricating curved composite panels. Other processing methods using aluminum alloys are possible.

Critical Issues

Availability of precursor tapes and/or wires. Process development and scale-up issues for fabrication of composite panels from precursor materials need to be studied further.

Aluminum alloy foam core structures

Description

Open and closed cell aluminum alloy foams with controlled densities (up to 95% porosity) and varying pore sizes (up to 200 ppi) for use as the core of sandwich structures, castings and extrusions.

Processing Method(s)

Syntactic foams produced by compaction and/or sintering of metal powder precursors

Reticulated foams produced by direct foaming of liquid metal and/or castings

Current State of Development

Applications include damage containment, acoustic damping, thermal management (aircraft), secondary structures, e.g. telescopes, heat exchangers (space vehicles), energy absorption (automotive), armor piercing protection (military).

Critical Issues

Forming to complex configurations, core-to-face sheet and panel-to-panel joining for primary structure applications.

Aluminum Beryllium (Al-Be) alloys

Description

Ultra-low density Al-Be binary alloys (ρ = 2.1gm/c^3) and Al-Be-Mg ternary alloys (ρ = 2.3 gm/c^3) comparable with PMC's.

Processing Method(s)

Powder metallurgy using cold isostatic pressing (CIP), extrusion followed by cross-rolling to sheet.

Current State of Development

Binary alloy (Al-62Be) has been produced and used in limited aircraft applications for decades (YF12, F-16). Ternary alloys (e.g. Al-40Be-5Mg) are under research and development.

Critical Issues

Cryogenic fracture toughness of binary alloy. Tensile and fracture toughness at cryogenic, ambient and elevated temperatures. Potential cryotank and TPS application if mechanical and thermal properties at extreme temperature ranges (-250^{o}C to 500^{o}C) are favorable.

Titanium alloy foam core sandwich structure

Description

Ultra-low density foams (up to 95% porosity) fabricated from advanced titanium alloys. Provides structural efficiency, weight reductions, and enhanced performance for hot structures.

Processing Method(s)

- Deposition of titanium-based material onto polymeric foam pre-forms, followed by high-temperature processing to remove organic volatiles.
- Spray deposition of hollow titanium-based spheres followed by sintering.
- Direct foaming of molten titanium-based materials.
- Other techniques include gas entrapment solid state processing.

Current State of Development

Only limited development activities are ongoing. Titanium foams are currently produced from conventional titanium alloys using vapor deposition onto polymeric foam preforms. Foams are not currently produced in intermetallics such as titanium-aluminides and titanium-beryllides

Critical Issues

Deposition of lightweight intermetallics without losing low-density elements through volatilization. Development and scale-up of high-deposition-rate processes for large-scale production of foam. Development of useful levels of ductility in intermetallic foams. Joining processes for incorporating foams into sandwich structure.

Silicon Carbide (SiC) fiber/ Beryllium matrix MMC

Description

Continuous SiC fiber reinforced beryllium. 0.0056 in. diameter fibers, 30-40 volume percent fiber. Dual coating on fibers for fiber/matrix compatibility at high temperatures.

Processing Method(s)

- Tape cast powder with binder and vacuum hot press (VHP) or hot isostatically press (HIP).
- Plasma spray Be on drum-wound fibers and VHP or HIP.
- Foil/fiber/foil layup and VHP or HIP.

Current State of Development

Largest piece ever made is approximately 6 in. x 9 in. x 6 ply. Room temperature mechanical properties. Material system has not been actively developed anywhere in the free world since 1989.

Critical Issues

Public mind set against Be use. Fiber/matrix interactions. Need better fiber exhibiting minimum reaction with Be during high temperature processing and service, or stable fiber coatings.

Carbon Nanotube (NT) fiber/ Aluminum matrix MMC

Description

Short carbon nanotube (NT) fiber reinforced aluminum alloy.

Processing Method(s)

Mechanically mix NT with Al alloy powder. Vacuum hot press (VHP) and/or extrude.

Current State of Development

Very small quantities produced in laboratory. A few experimental tensile data. Preliminary microstructures exist with 2 µm long NT and a 10 volume percent fiber in pure Al matrix.

Critical Issues

NT production, availability in bulk. Longer NT. NT dispersion, alignment control in matrix. Other matrix metals.

Carbon and PMC materials for vehicle structure and habitats

	reference Aluminum 2219-T87 ISS Crew Modules	reference Carbon Fiber M46J (handbook)	reference Carbon Fiber IM7 (handbook)	reference CFRP Q-I M46J/7714A Terra Spacecraft	5-10 yrs CFRP Q-I IM7/8552 (handbook)	10-20 yrs NTFRP Q-I Comp (theoretical)	20-30 yrs SWNT Single crystal (Theoretical)
Tensile Strength	0.46 Gpa	4.2 Gpa	5.3 Gpa	0.7 Gpa	1.3 Gpa	2.5 Gpa	180 Gpa (60 Gpa exp.)
Tensile Modulus	73 Gpa	440 Gpa	300 Gpa	86 Gpa	58 Gpa	240 Gpa	1200 Gpa
Elongation	10 %	1.0 %	1.8 %	1.0 %	1.58 %	6 %	15 %(6 % exp)
Density	2.83 g/cc	1.84 g/cc	1.77 g/cc	1.64 g/cc	1.59 g/cc	0.98 g/cc	1.2 g/cc
Specific Strength	0.16	2.3	3.0	0.42 (3x Al)	0.80 (5x Al)	2.5 (16x Al)	170 (1000x Al)
Specific Modulus	26	240	170	52 (2x Al)	36 (1.5x Al)	240 (9x Al)	1000 (40x Al)
Thermal Cond'ty	121 W/mK	50 W/mK	50 W/mK	5 W/mK	5 W/mK	5 W/mK	<5000 W/mK
Use Temp.	150 C	N/A	N/A	120 C	120 C	120 C	1200 C / 400 C
Manufacturability	TRL = 9	TRL = 9	TRL = 9	TRL = 9	TRL = 5+	TRL = 1	TRL = 1

Carbon Fiber Reinforce Polymer Composite (CFRP)

Description

The carbon fiber reinforced polymer composite (CFRP) is the IM7/8552 material system, a toughened epoxy resin reinforced with unidirectional carbon fibers or a woven preform. The IM7 fibers are intermediate modulus carbon filaments. The 8552 epoxy is a damage-resistant system, recommended for structural applications requiring high strength, stiffness, and damage tolerance. The properties in the table are taken from the Hercules Development Data Sheet and correspond to a $[0/+45/-45/90]_s$ quasi-isotropic (Q-I) laminate stacking sequence and a 60% fiber volume fraction.

Processing Method(s)

Conventional thermoset resin equipment and techniques can be used to process IM7/8552 prepreg tape. The laminates fabricated out of prepreg tape are typically cured in an autoclave at 350 F.

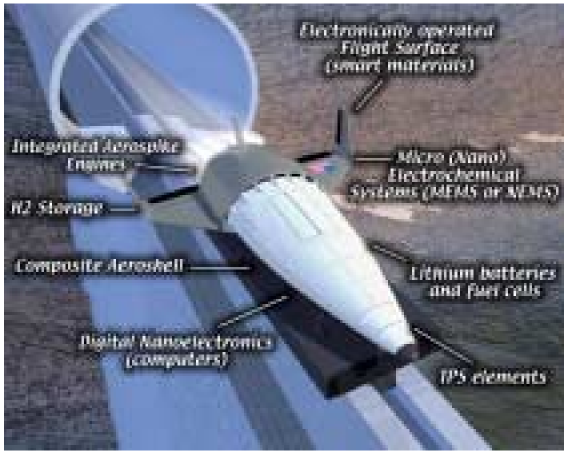
Current State of Development

CFRP are fully mature for some applications but not yet fully mature for all aerospace structural applications. Numerous CFRP composites have been developed by industry to a TRL of 9. The successful liquid hydrogen cryogenic tank on the DC-XA was fabricated out of IM7/8552. However, we are still encountering unanticipated failure modes when composites technology is extended to a new large-scale structural applications.

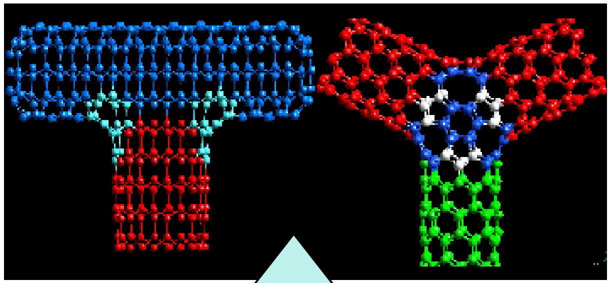
Critical Issues

Relatively immature design and analysis practices, manufacturing scale-up, and NDI for bonded construction are some of the primary technical issues that currently limit the full potential of CFRP’s.

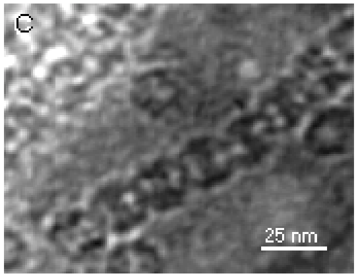
Nanostructured, Biomimetic Materials

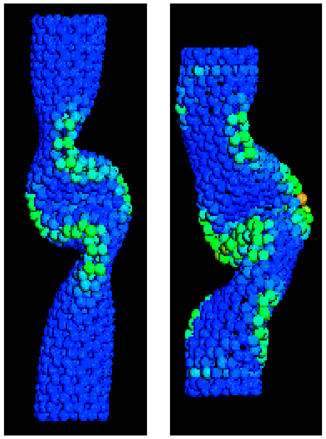


Self-Assembling Electronics

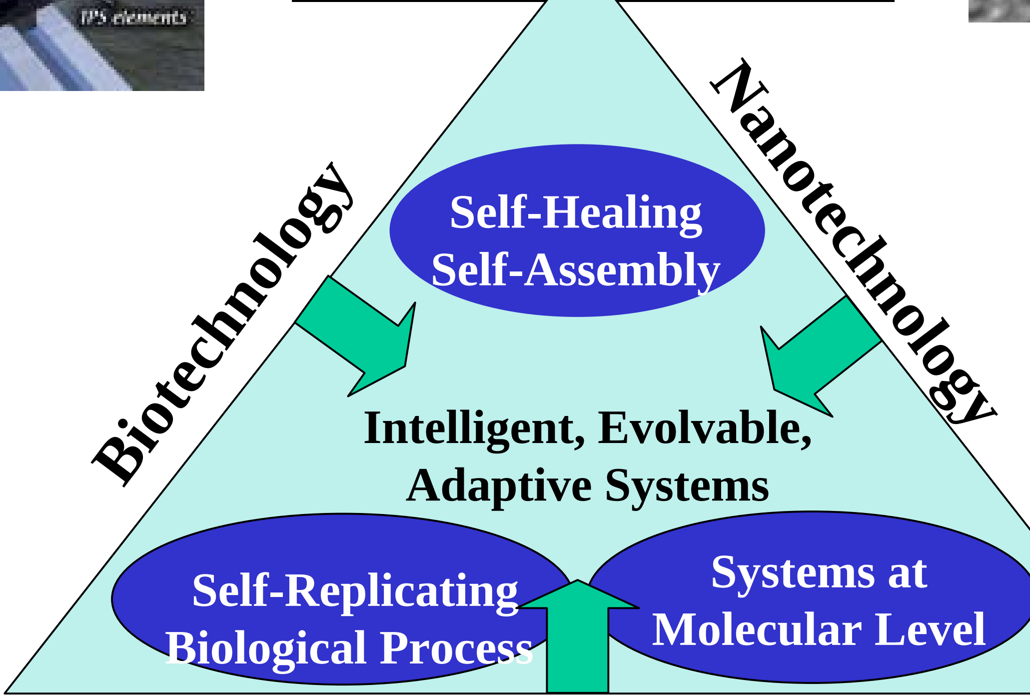


Protein





Structural Deformation



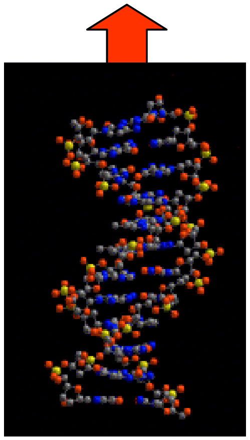
Self-Healing
Self-Assembly

Intelligent, Evolvable, Adaptive Systems

Self-Replicating Biological Process

Systems at Molecular Level

Information Technology



"DNA"

Single Wall Carbon Nanotubes (SWNT)

Description

A single-wall carbon nanotube (**SWNT**) is a graphene sheet rolled into a cylindrical shape so that the structure is virtually one-dimensional with axial symmetry. Tube diameters vary between about 0.7 nm to 10.0 nm.

Multiwall carbon nanotubes (**MWNT**) are concentric cylinders of individual SWNT's with various diameters. The SWNT are thought to be held together by relatively weak frictional forces.

A **single crystal** SWNT refers to a **membrane** of aligned, long, continuous SWNT's which were formerly held together by van der Waal forces, coalescing into a crystalline form which arises from decreased entropy during continued alignment.

Processing Method(s)

The laser vaporization synthesis uses a laser to vaporize a graphite target and nanotubes form in the condensing vapor of the heated flow tube at 1200 C.

The carbon arc method uses carbon rod electrodes and vaporizes the carbon atoms into a plasma at >3000 C with the nanotubes forming on the negative electrode.

The high-pressure gas-phase growth process (HipCo) uses high temperature (900-1200 C) and pressure (10-100 atm) to create a highly turbulent gas mixture that nucleates carbon nanotubes from a mixture of CO and a Fe/Ni carbonyl catalyst. Carbon nanotubes grow from metal clusters that form during this process.

Current State of Development

SWNT's have been fabricated at discontinuous lengths approaching microns and **ropes** of entangled SWNT's have been fabricated into paper-like mats. **(The following 5 pages contain tables of SWNT and MWNT properties reported in the literature.)**

Critical Issues

Production of large quantities of useable nanotubes with macroscale lengths has not yet been achieved.

Carbon Nanotube Reinforced Polymer Composite (NTFRP)

Description

Carbon Nanotube containing composites are estimated to have about 20% loading of the nanotubes or they will be crossplied materials that will afford no more than about 20% of the unidirectional nanotube properties because of processing/interface problems. The strength of the SWNT was limited to about 1% strain or about 10-12 Gpa. This estimate will be low if processing and translation of properties can be overcome. A ‘Blue Sky’ estimate would be about 3X this number.

Processing Method(s)

Processing will involve dispersing nanotubes in binders which will be molecular in nature (monolayer thickness). Layups and fabrication will have to be non-conventional and are yet to be determined. Processing of complex forms should offer no major technical problems. There is hope that molecular self-assembly can be employed which will create ‘near perfect’ molecular order.

Current State of Development

To date only crude prototypes have been made where carbon nanotubes have been dispersed at about a 5% level in room-temperature-curing epoxies..

Critical Issues

Carbon nanotube scaleup is in its infancy with only gram quantities available for experimentation. The ability to disperse nanotubes in binders has not been worked as is the case for the other processing issues.

Properties of SWNT and MWNT, 1 of 5

Mechancial										
Property	**Material**	**Type**	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Strength, Compressive	MWNT		150	GPa			X			Wagner
Bulk Modulus	SWNT		0.191	Tpa	.192 to .19	X		Force-constant		Lu
Bulk Modulus	SWNT	ropes	0.022	TPa	033 to .015	X		Force-constant		Lu
Bulk Modulus	MWNT		0.194	TPa	.194 to .19	X		Force-constant		Lu
Euler spring const				nN/A	4.0 to 1.6	X		Cerrius -MD		Yao
Poisson ratio	MWNT		0.269	-	280 to .269	X		Force-constant		Lu
Poisson ratio	SWNT		0.279	-	.28 to .277	X		Force-constant		Lu
Poisson ratio	SWNT		0.18	-		X		Force-constant		Halicioglu
Shear Modulus	MWNT		0.48	TPa	541 to .436	X		Force-constant		Lu
Shear Modulus	SWNT		0.45	Tpa	478 to .436	X		Force-constant		Lu
Strain to failure	MWNT	outer layer	0.12	strain	NA		X	SEM	Sem with loading stage	Yu
Strain to failure	MWNT	in polymer film	0.075	-			X	Tensile test	Instron	Wagner
Strain to failure	SWNT	Ult. Strain at various strain rates		%	35 to 28	X		MD		Yakobson

Properties of SWNT and MWNT, 2 of 5

Mechancial										
Property	**Material**	**Type**	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Strength	MWNT	outer layer	32.8	Gpa	63 to 20		X	SEM	Sem with loading stage	Yu
Strength, bending	MWNT		14.2	GPa	22 to 6		X	AFM	AFM, bending	Wong
strength, shear		Nanotube-polymer interfacial shear strength	500	MPa		X		Single fiber fragmentation model		Wagner
Young Modulus	MWNT	full tube		Gpa	68 to 18		X	SEM	Sem with loading stage	Yu
Youngs Modulus	MWNT	outer layer		GPa	950 to 270		X	SEM	Sem with loading stage	Yu
Youngs Modulus	MWNT	in polymer film	2	GPa			X	Tensile test	Instron	Wagner
Youngs Modulus	SWNT		fig	TPa	1.4 to .3	X		Mechanics		Sinnott
Youngs Modulus	SWNT	Diamond composite	Fig	TPa	1.3 to 1.28	X		Mechanics		Sinnott
Youngs Modulus	SWNT	func of geometry	fig	TPa	1.2 to .97	X		Cerrius -MD		Yao
Youngs Modulus	SWNT		0.974	TPa	975 to .971	X		Force-constant		Lu
Youngs Modulus	SWNT	ropes	0.56	TPa	.795 to .43	X		Force-constant		Lu

Properties of SWNT and MWNT, 3 of 5

Mechancial										
Property	**Material**	**Type**	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Youngs modulus	SWNT		1.8	TPa	4.15 to .4		X		TEM	Treacy
Youngs modulus	SWNT	BN tubes	1.22	TPa			X			Chopra
Youngs Modulus	SWNT	ropes	0.63	TPa		X		MD		Yakobson
Youngs modulus	SWNT		0.5	TPa		X		Force-constant		Halicioglu
Youngs Modulus	MWNT			TPa	1.12 to .97	X		Cerrius -MD		Yao
Youngs modulus	MWNT		1.28	TPa	1.87 to .79		X	AFM	AFM, bending	Wong
Youngs Modulus	SWNT		1.1	TPa	1.11 to .97	X		Force-constant		Lu

Properties of SWNT and MWNT, 4 of 5

Structural								
Property	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Wall Thickness	3.4	A		X		Cerrius		Yao
Euler Buckling force of MWNT		nN	464 to 6.25	X		Cerrius		Yao
Young's modulus of C SWNT,normalized wrt wall thickness	0.26	TPa	.275 to .247	X		Tight-binding calcs.		Hernandez

Thermal								
Property	**Value**	**Units**	**Error**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Thermal Conductivity SWNT mat	35	W m-1 K-1			x	Longitudinal Thermal Conductance	Thermal Comparator - Constantan Rod	Hone
Thermal Conductivity SWNT mat	1750-5800	W m-1 K-1		x		Electrical Conductivity Ratio		Fischer

Physical								
Property	**Value**	**Units**	**Error**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Weight Loss Peak Rate	627	deg C			X	TGA	TGA	Shaffer
Viscosity of NT dispersion	fig	Pas	100 to .1	X	X			Shaffer

Properties of SWNT and MWNT, 5 of 5

Electrical								
Property	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Resistivity of Al-C composite	5.1	µΩcm	6.6 to 3.4		X			Xu
Conductivity of CNT pellet (MWNT)	40	Siemens/cm			x	Four Probe Method		Fan

Density								
Property	**Value**	**Units**	**Range**	**Simulated**	**Measured**	**Technique**	**Equipment**	ref
Density of SWNT diamond composite	fig	g/cm^3	3.4 to 3.0	X		Mechanics		Sinnott
Wall density of SWNT	2020.48	kg/m^3		X		Cerrius MD		Yao

Properties of SWNT and MWNT, References

1. Chopra, N. G. and A. Zettl (1998). Solid state Communications **105**: 297.
2. Cornwell, C. F. and L. T. Wille (1998). “Critical strain and catalytic growth of single-walled carbon nanotubes.” Journal of Chemical Physics **109**(2): 763-767.
3. Fan, J., M. Wan, et al. (1999). “Synthesis, Characterizations, and Phyical Properties of Carbon Nanotubes Coated by Conducting Polypyrrole.” Journal of Applied Polymer Science **74**: 2605.
4. Fischer, J. E., H. Dai, et al. (1997). “Metallic Resistivity in Crystalline Ropes of Single-Wall Carbon Nanotubes.” Physical Review B **55**: R4921.
5. Frackowiak, E., S. Gautier, et al. (1999). “Electrochemical storage of lithium multiwalled carbon nanotubes.” Carbon **37**: 61-69.
6. Halicioglu, T. (1998). “Stress calculations for carbon nanotubes.” Thin Solid Films **312**: 11-14.
7. Hernandez, E., C. Goze, et al. (1998). “Elastic properties of single-walled nanotubes.” Applied Physics A **68**: 287-292.
8. Hone, M. W., C. Piskoti, et al. (1999). “Thermal Conductivity of Single-Walled Nanotubes.” Journal of Physical Review **59**(4): R2514.
9. Kong, J., N. R. Franklin, et al. (2000). “Nanotube Molecular Wires as Chemical Sensors.” Science **287**(5453): 622-625.
10. Lambin, P., V. Meunier, et al. (1998). “Elastic Deformation of a Carbon Nanotube Adsorbed on a Stepped Surface.” Carbon **36**(5-6): 701-704.
11. Lordi, V. and N. Yao (1998). “Radial compression and controlled cutting of carbon nanotubes.” Journal of Chemical Physics **109**(6): 2509-2512.
12. Lu, J. P. (1997). “Elastic Properties of Carbon Nanotubes and Nanoropes.” Physical Review Letters **79**(7): 1297-1300.
13. Shaffer, M. S. P., X. Fan, et al. (1998). “Dispersion and Packing of Carbon Nanotubes.” Carbon **36**(11): 1603-1612.
14. Sinnott, S. B., O. A. Shenderova, et al. (1998). “Mechanical Properties of Nanotubule Fibers and Composites Determined From Theoretical Calculations and Simulations.” Carbon **36**(1-2): 1-9.
15. Treacy, M. M. J., T. W. Ebbesen, et al. (1996). “Exceptionally high Young's modulus observed for individual carbon nanotubes.” Nature **381**: 678.
16. Wagner, H. D., O. Lourie, et al. (1999). “Macrofragmentation and microfragmentation phenomena in composite materials.” Composites **30**: 59-66.
17. Wong, E. W., P. E. Sheehan, et al. (1997). “Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes.” Science **277**: 1971-1975.
18. Xu, C. L., B. Q. Wei, et al. (1999). “Fabrication of aluminum-carbon nanotube composites and their electrical properties.” Carbon **37**: 855-858.
19. Yakobson, B. I., C. J. Brabec, et al. (1996). “Nanomechanics of Carbon Tubes: Instabilities beyond linear response.” Physical Review Letters **76**(14): 2511-2514.
20. Yakobson, B. I., M. P. Campbell, et al. (1997). “High strain rate fracture and C-chain unraveling in carbon nanotubes.” Computational Materials Science **8**: 341-348.
21. Yao, N. and V. Lordi (1998). “Carbon nanotube caps as springs: Molecular dynamics simulations.” Physical Review **58**(19): 12649-12651.
22. Yao, N. and V. Lordi (1998). “Young's modulus of single-walled carbon nanotubes.” Journal of Applied Physics **84**(4): 1939-1943.
23. Yu, M.-F., O. Lourie, et al. (2000). “Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load.” Science **287**(5453): 637-640.

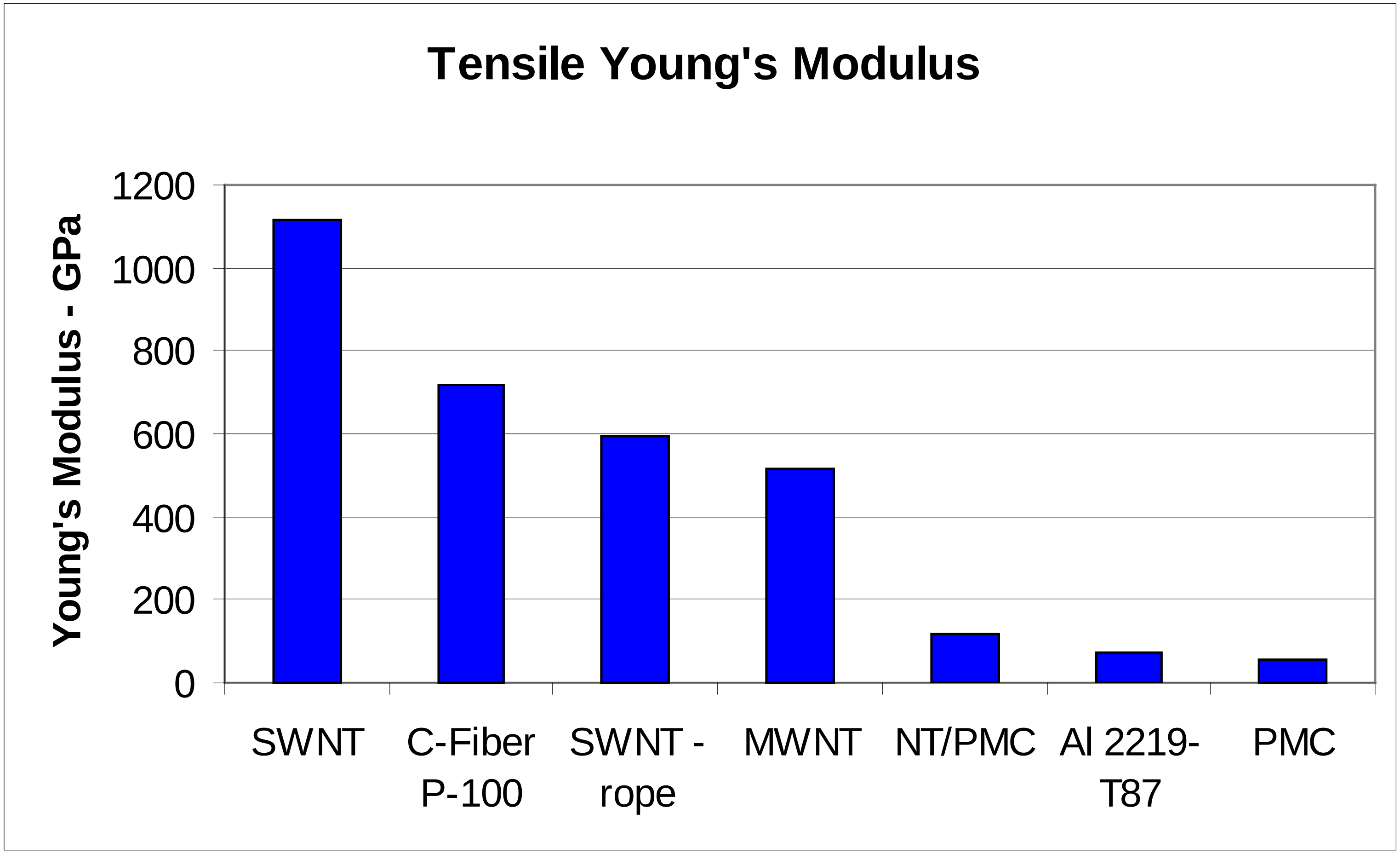
Application of Nanotubes in Heat Pipes

- **Inherent thermal properties are anisotropic; heat transfer is highest along their length ($l \sim$ 1-2 μm)**
- **Intrinsic axial conductivity of nanotube graphene sheet is comparable to that of diamond**
    - “metallic tube” bundles obey Wiedemann- Franz relation for high electrical and thermal conductivity (2150 W m^{-1} K^{-1} at 300 K) [1]
    - simulations by ARC show high thermal conductivity peak values at 300-500 K (2500 - 3000 W m^{-1} K^{-1}) [2]
    - calculations agree closely with intrinsic conductivity estimates from bulk mat by Hone *et. al* (1750 - 5800 W m^{-1} K^{-1}) [3]
- **Intrinsic transverse conductivity of nanotubes expected to be on the order of fullerenes ($\kappa_{C60} \sim$ 0.4 W m^{-1} K^{-1} at 300 K)**
    - transverse dimension of spherical fullerenes and nanotubes (~ 1 nm) is about one order of magnitude longer than the most probable phonon wavelengths
    - reductions in transverse conductivity of fullerenes in dielectric materials recently demonstrated in thin films [4]; notable reductions with just 5 wt.%

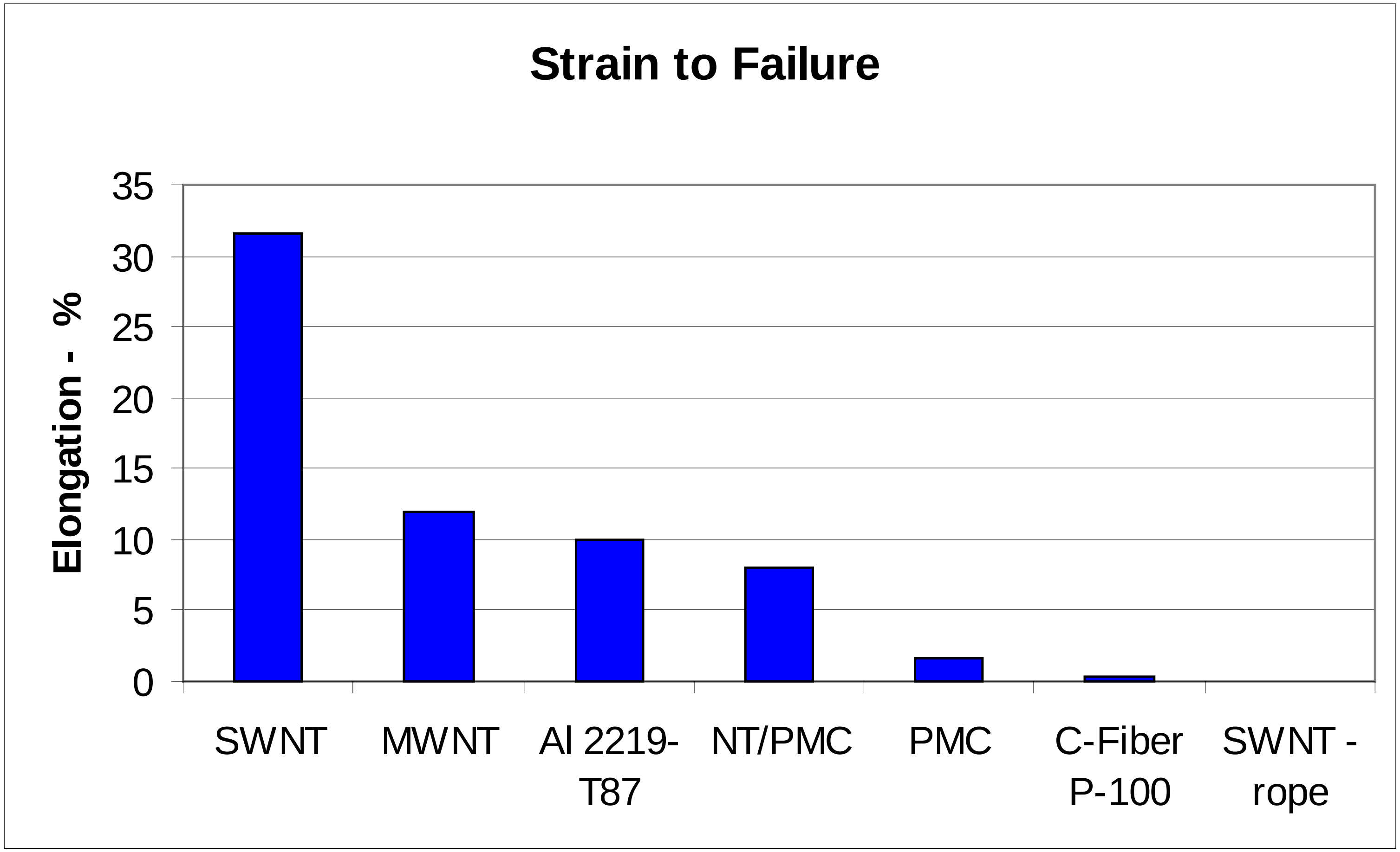
- **References:**

[1] A. Thess et. al, Science, 273, 483-487 (1996).
[2] M. Osman and D. Srivastava, Appl. Phys. Letters, (submitted 1-2000).
[3] J. Hone et. al, Phys. Rev. B, 59, R2514- R2516, (1999).
[4] K. Lozano et. al, Powder Materials Symposium, TMS Fall Meeting, (1999).

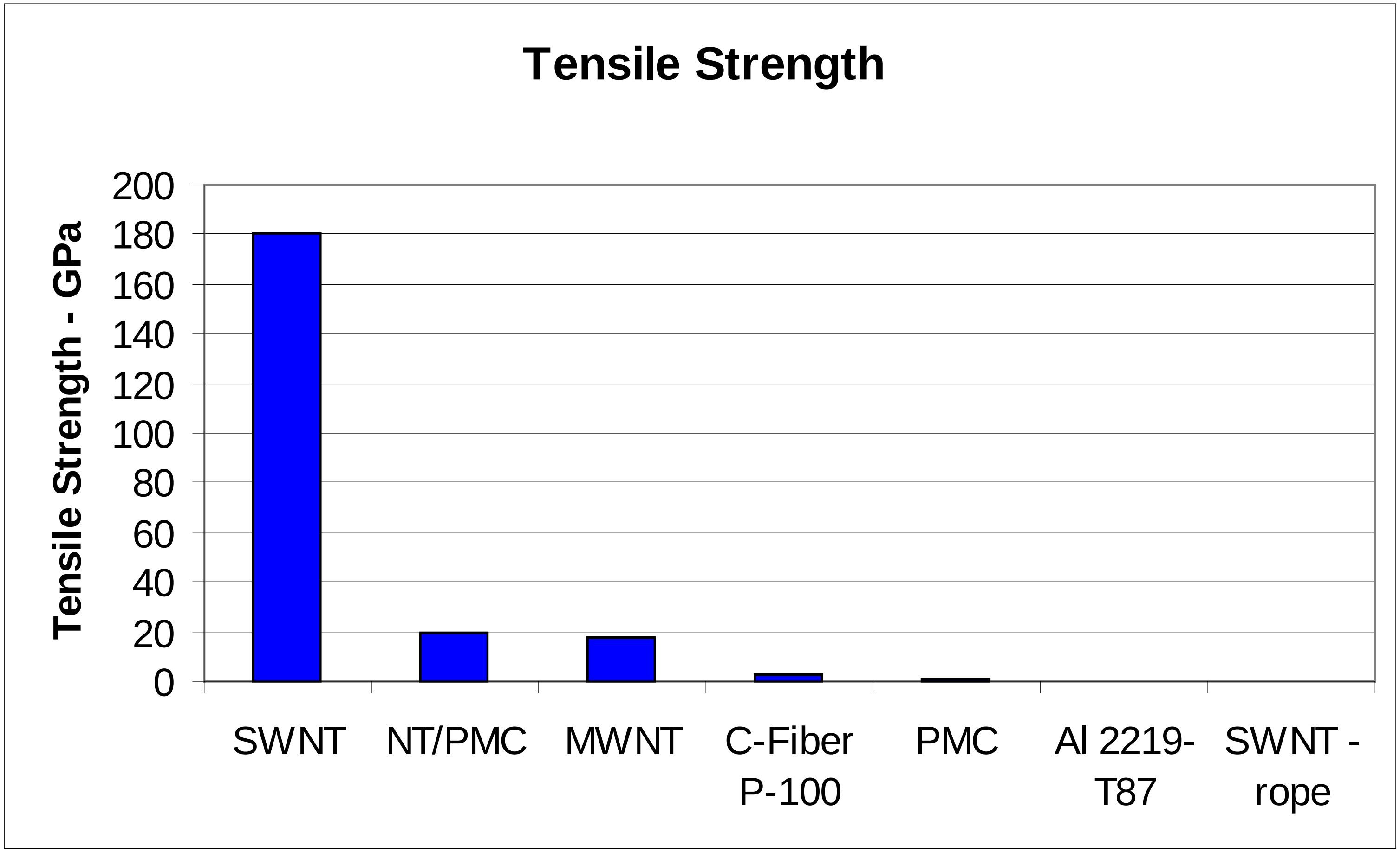
Comparison of Properties to SWNT and MWNT, Modulus



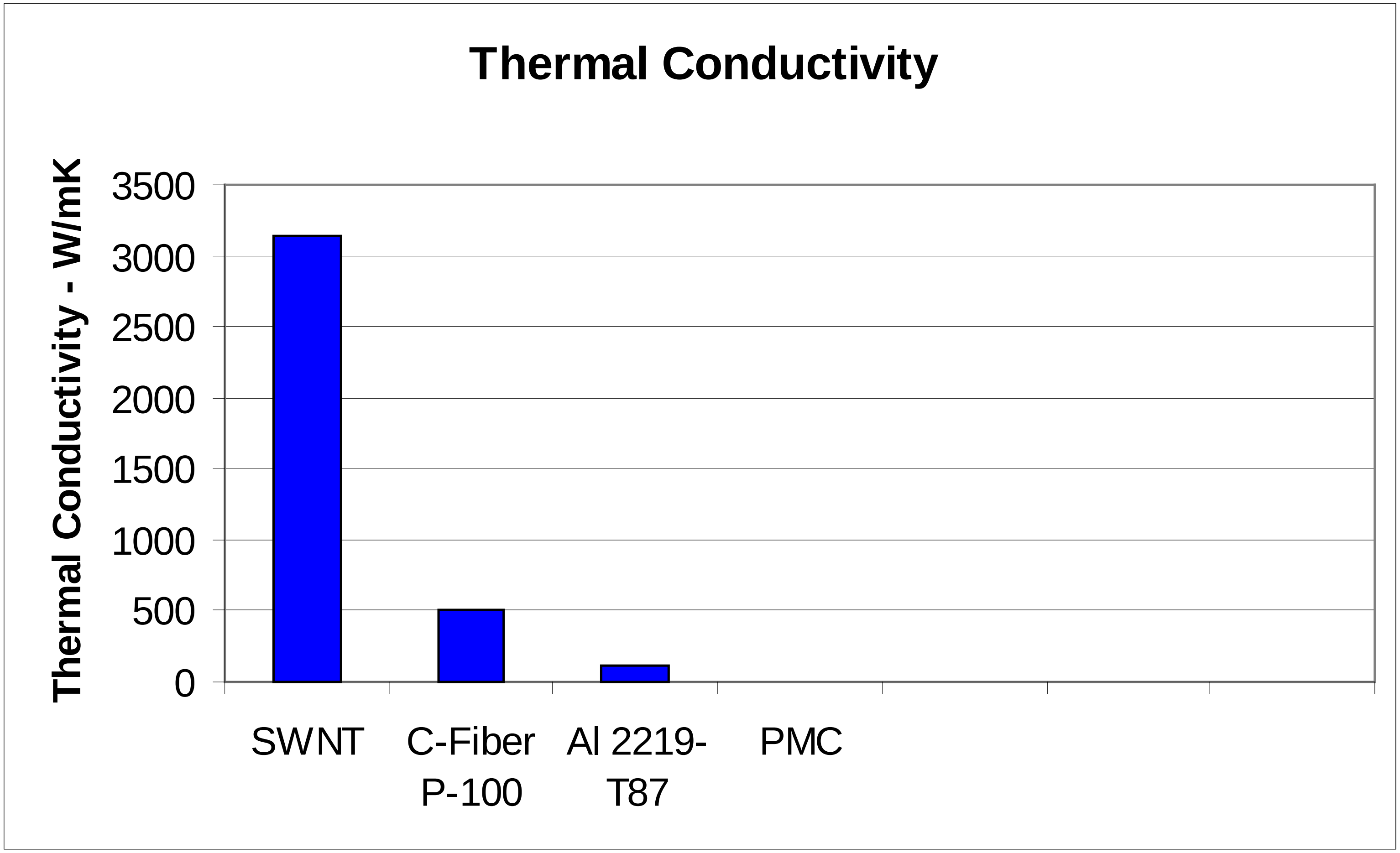
Comparison of Properties to SWNT and MWNT, <u>Strain</u>



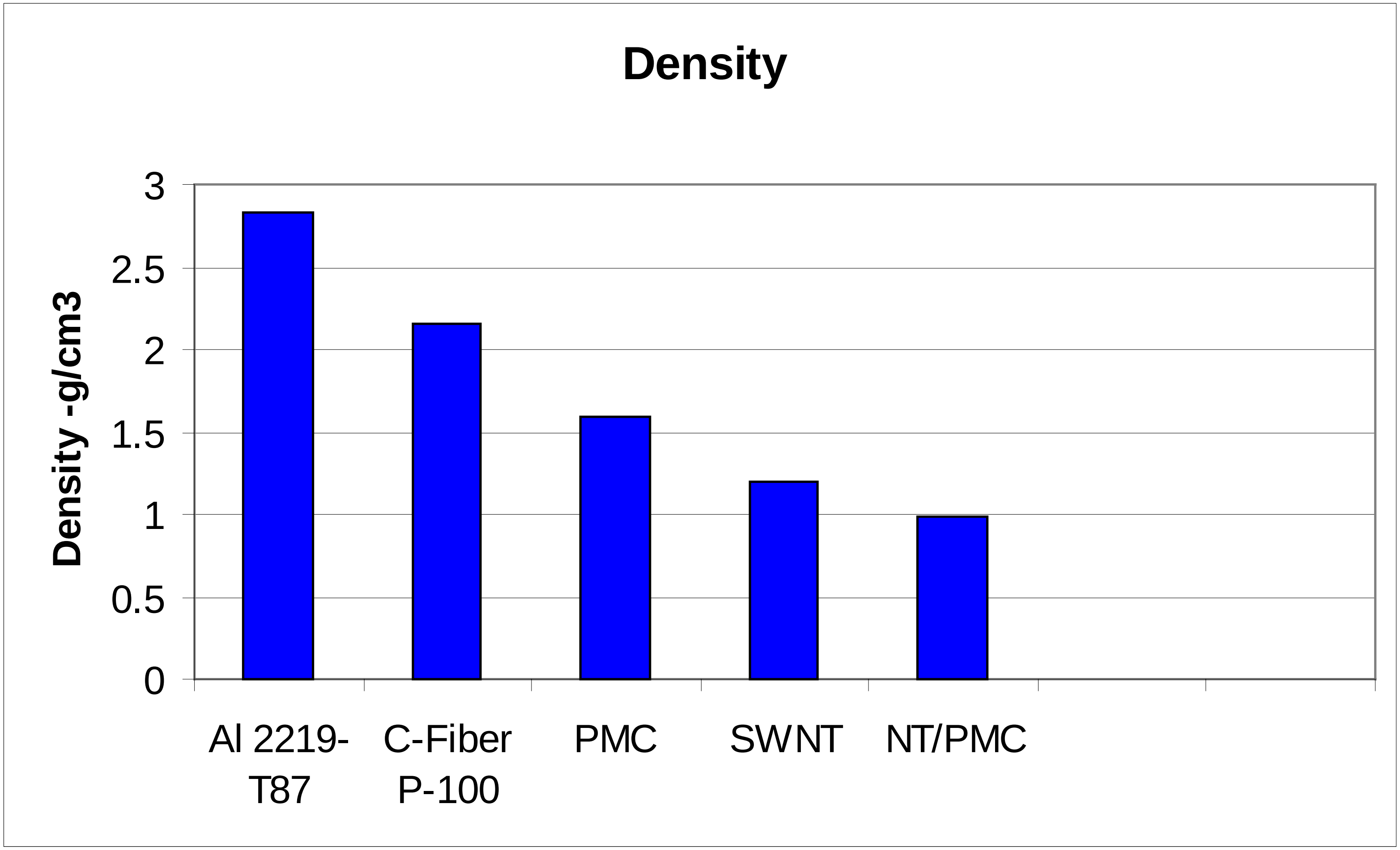
Comparison of Properties to SWNT and MWNT, Strength



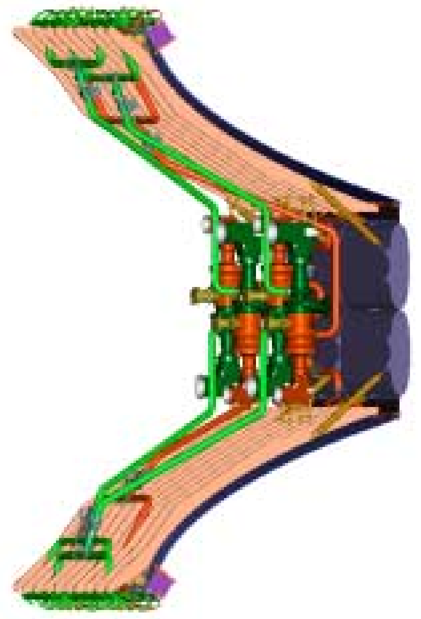
Comparison of Properties to SWNT and MWNT, Ther Cond



Comparison of Properties to SWNT and MWNT, Density

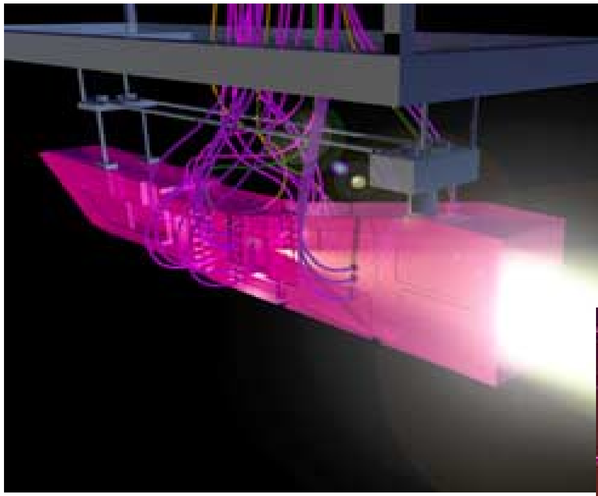


II. Materials for Propulsion Components



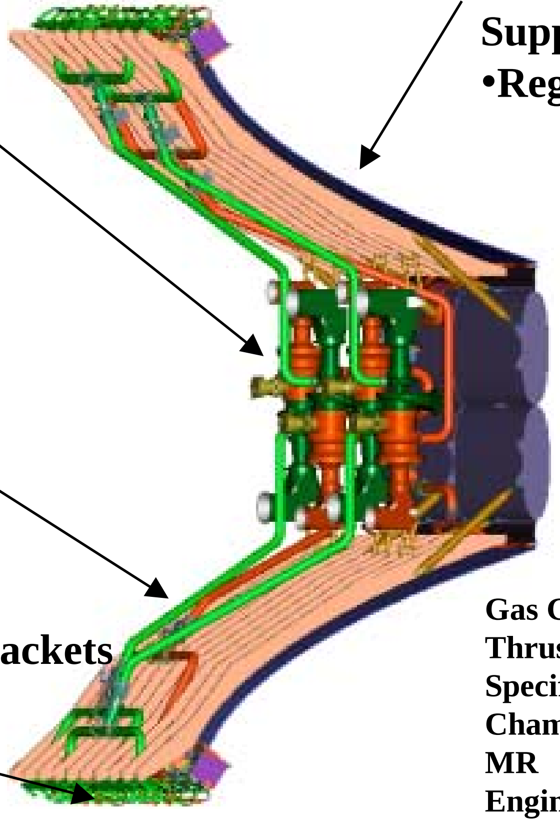
Aerospike Propulsion System (2nd Generation)

Rocket Combined Cycle System (3rd Generation)



Pulse Detonation and Turbine Combined Cycle (3rd + Generation)

Application of advanced materials to the Current Aerospike Propulsion System Concept



MMC Housings for turbopumps

Ceramic turbines in LOX and fuel turbopumps

- Metal disk with CMC blades, or
- CMC blisk

Composite ramp (CMC) & Structural Support

- Regen or dump cooling as required

Nanophase Al ducts w/ MMC flanges

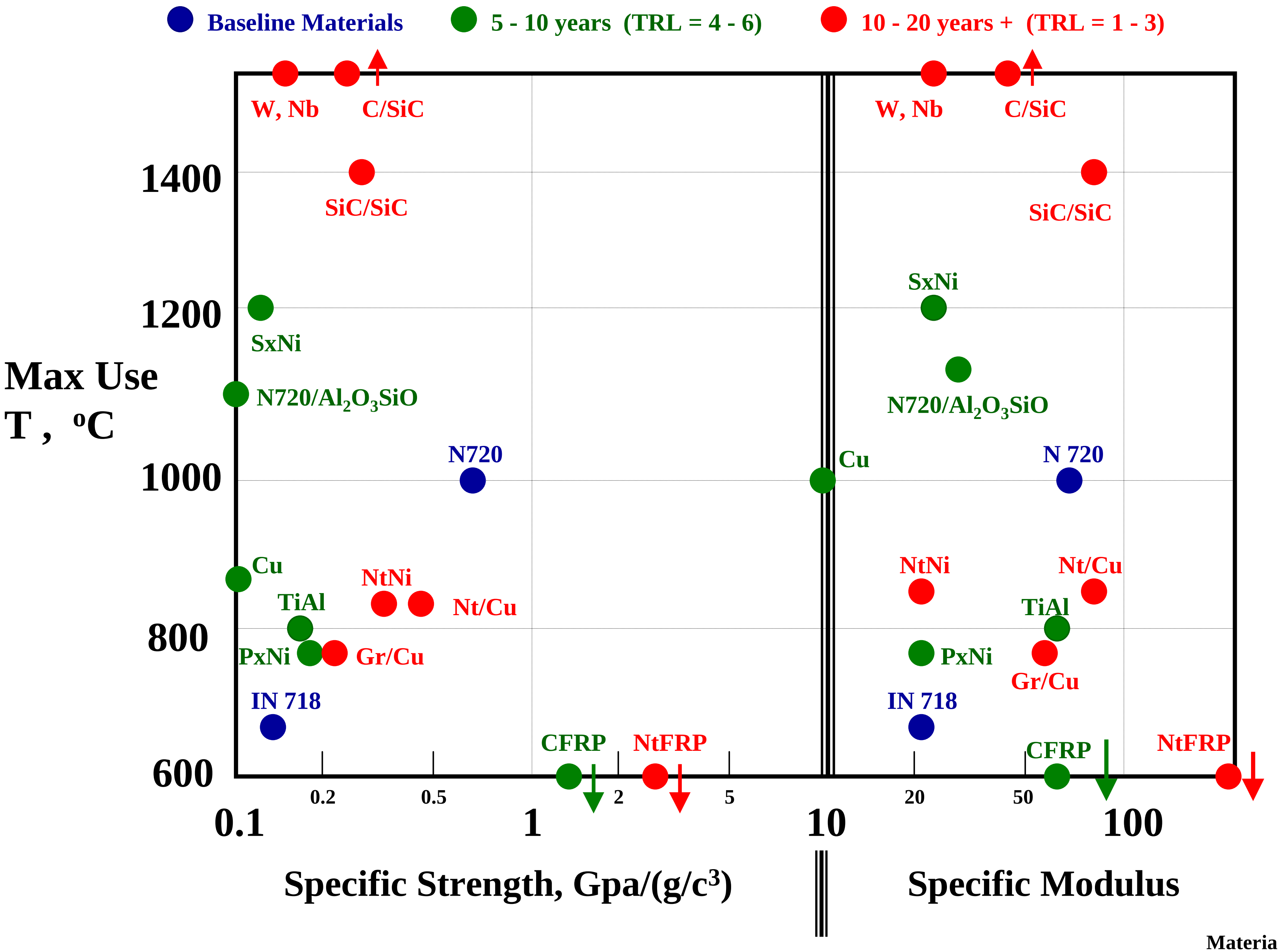
Dual Throat thrusters

- MMC or PMC Structural Jackets
- Ceramic injector body
- Cu-Cr-Nb Liners

Gas Generator Cycle

Thrust, S.L. [lbf]	450-475K
Specific Impulse, vac [sec]	454
Chamber Pressure [psia]	2,250/2,962
MR	6.0
Engine T/W (sea level)	75
Throttle Range [Nom. Thrust]	2:1
Life/MTBOH	100/20

Properties of Materials for Propulsion Components



Ceramic, CMC, and PMC materials for propulsion components

	reference Inconel 718 (handbook)	reference Nextel N720 fiber (handbook)	5-10 yrs N720 / Al_2O_3SiO (estimated)	5-10 yrs CFRP Composite (measured)	10-20 yrs C / SiC Composite (estimated)	10-20 yrs SiC / SiC Composite (estimated)	10-20 yrs NT/Polymer Composite (theoretical)
Tensile Strength	1.03 Gpa	2.1 Gpa	0.18	2.0	0.6	0.8	2.5
Tensile Modulus	190 Gpa	260 Gpa	77	90	83	250	240
Elongation	14 %	<1%	<1%	2.4 %	<1%	<1%	6 %
Density	8.2 g/cc	3.4 g/cc	2.6	1.3	2.2	2.7	1.0
Specific Strength	0.13	0.62	0.07	1.5 (10x IN)	0.27 (2x IN)	0.30 (2x IN)	2.5 (19x IN)
Specific Modulus	23	76	30	69 (3x IN)	38 (1.5x IN)	93 (4x IN)	240 (10x IN)
Thermal Cond'ty	15 W/mK	6 W/mK	6	8	11	20	20
Use Temp.	650 C	1000 C	1100 C	370 C	1650 C	1400 C	425 C
Manufacturability	TRL = 9	TRL = 9	TRL = 4	TRL = 5	TRL = 4	TRL = 4	TRL = 1

Nextel 720 fiber/alumino-silicate (Al_2O_3SiO) matrix CMC

Description

Nextel 720 fabric/alumino-silicate (Al_2O_3SiO) matrix, ~48% fiber volume, no interface coating, uses controlled matrix porosity for composite toughness.

Processing Method(s)

Sol-gel derived matrix infiltrated into woven Nextel 720 fabric. (Sol-Gel is a process where micron size particles are dispersed in a liquid and a solid is formed through chemical reaction rather than melting.) Infiltrated fiber weaves are laid up on tooling with final shape. Complex shape is vacuum bagged, then consolidated at low temperature and pressure (<300°F and <100 psi). Free standing post-care at ~1000°C-1100°C.

Current State of Development

Has been tested in exhaust systems for military applications.

Large parts have been fabricated and tested in engines.

Critical Issues

Fiber development: With currently available low temperature fibers, composite processing and use temperatures are limited to ~1100°C. With fibers that have greater thermal stability, processing temperature could be increased and mullite could be formed as the matrix. A mullite matrix and oxidation resistant fiber coating would lead to an oxide CMC with greater thermal stability and possibly higher mechanical properties.

CFRP Composite

Description

Improvements in matrix chemistry (polymer backbone and end-caps), better control of the resin-fiber interface, and the use of novel reinforcement approaches (e.g., alumino-silicate clay reinforced polymers) are expected to lead to improvements in mechanical performance, processability and long-term durability at high temperatures.

Processing Methods

New developments in resin chemistry will enable processing by a variety of methods including prepreg based methods (autoclave and compression molding, ATP) and resin infusion approaches (Resin Transfer Molding, Resin Film Infusion).

Current State of Development

Current high temperature systems have limited long-term durability at temperatures above 290 C. Processing of these conventional high temperature materials is limited to prepreg based methods.

Critical Issues

Need to identify/optimize resin chemistry to enable RTM processability without sacrificing high temperature performance and long-term durability.

C/SiC Composites

Description:

Carbon fibers in a silicon carbide matrix. Carbon fibers offer high temperature capability with the high modulus and oxidation resistance of a SiC matrix.

Processing Method(s):

Chemical Vapor Infiltration (CVI)- High strength; process well understood; largest database

Melt Infiltration (MI)- Highest thermal conductivity; lowest porosity

Polymer Infiltration Pyrolysis (PIP)- Initial processing at low temperatures; can form large complex shapes

Current State of Development:

C/SiC has been examined for use in forming blisks, nozzles, combustors, nozzle ramps, cooled components, leading edges, and control surfaces as well as other components. Work is being performed to determine the effects of oxidation on composite life. Variations are being made in each of the different processing approaches to determine ways to increase composite properties, densify thick sections, improve oxidation resistance, etc.

Critical Issues:

Life prediction, processing of components, reliability/reproducibility/uniformity, CTE mismatch between fiber and matrix, oxidation resistance

SiC / SiC Composite

Description:

Because of inherent oxidation resistance, low density, high strength, and creep-rupture resistance, continuous fiber-reinforced ceramic matrix composites (CMC) based on SiC fibers and SiC matrices can thermally outperform superalloys and thus are strong candidates for advanced hot structural components.

Processing Methods:

Variety of small-diameter (~10 μm) SiC-based fiber types, commercially available in multifilament tows, are woven or braided into 2D and 3D fiber architectures. Interphase coatings, typically based on C or BN, are deposited on fibers by chemically vapor infiltration either before or after architecture formation. SiC-based matrices from a variety of different precursors are infiltrated into coated fiber architectures by various combinations of gas, polymer, slurry, and/or molten silicon to achieve as dense a matrix as possible.

Current State of Development:

The feasibility of first generation SiC/SiC CMC have been examined in a variety of industrial, military, and commercial engine applications. Identified deficiencies, which are currently being addressed by a variety of governmental programs such as NASA UEET, include insufficient long term stability of constituents at high temperatures, particularly in moist combustion environments; fiber weave-ability for complex-shaped components; and high acquisition costs. Significant progress has been made recently by the development of stoichiometric SiC fibers, Si-doped BN interphases, dense melt-infiltrated matrices, and oxide-based environmental barrier coatings.

Critical Issues:

Process and property reproducibility, particularly in components. Interphase stability, particularly at intermediate temperatures. Fiber architectures for component scale-up. High fiber and CMC fabrication costs. Low projected market volume and thus stability of fiber and CMC vendors.

NT / Polymer Composite

Description

Properties of nanotube reinforced high temperature polymers are estimated at a nanotube loading level of about 20 weight %. The limited data published to date on nanotube reinforced polymers suggests that optimum levels of nanotube loading are in the range of 10 to 20 weight %. Properties of these material are assumed to be primarily reinforcement (nanotube) dominated and are estimated at 20% of the theoretical properties of the nanotubes. These estimates assume good NT-polymer adhesion.

Processing Methods

Novel processing methods and binder/sizing chemistries need to be developed to insure homogeneous distribution of nanotube reinforcements throughout the polymer matrix. Molecular level control of nanotube orientation and interactions with the matrix material is highly desired to obtain optimal properties and performance.

Current State of Development

There is sparse published data on nanotube reinforced polymers. Literature reports to date have been on crude composites from epoxies or acrylates at a nanotube loading level of up to 10 weight %.

Critical Issues

Need to develop an affordable, reproducible method to make large quantities of nanotubes with controlled size, geometry, chirality and purity. In addition, the proper chemistries have to be developed to control nanotube dispersion in the matrix without adversely affecting the mechanical integrity of the nanotubes.

Metallic and MMC materials for propulsion components

	reference Inconel 718 (handbook)	5-10 yrs TiAl Alloy (measured)	5-10 yrs Adv. Ni SinCrystal (measured)	5-10 yrs Adv. Ni PolCrystal (measured)	5-10 yrs Adv. Cu Alloy (measured)	10-20 yrs Gr / Cu Composite (estimated)	10-20 yrs Ns Ni Alloy (theoretical)	10-20 yrs NT / Cu Composite (theoretical)	10-20 yrs W, Nb Alloys (est'd)
Tensile Strength	1.03 Gpa	.70	1.0	1.55	0.45	1.0	2.45	2.0	2.4
Tensile Modulus	190 Gpa	280	180	231	90	300	230	450	350
Elongation	14 %	1.7	5	20	25	2	5	5	2
Density	8.19 g/cc	3.8	8.5	8.2	8.7	4.8	8.2	4.8	16.0
Specific Strength	0.13	0.18 (1.5x IN)	0.12	0.19	0.05	0.21	0.30 (2x IN)	0.42 (4x IN)	0.15
Specific Modulus	23	74 (3x IN)	21	28	10	63 (2.5x IN)	28	94 (4x IN)	22
Thermal Cond'ty	15 W/mK	18	17	17	320	400	17	500	140
Use Temp.	650 C	800	1200	750	850	750	850	850	1500
Manufacturability	TRL = 9	TRL = 6	TRL = 5	TRL = 5	TRL = 6	TRL = 2	TRL = 1	TRL = 1	TRL = 3

TiAl Alloy

Description

A light weight replacement for Ti and Ni alloys in structural applications in oxidizing environments

Processing Method(s)

Complex airfoils, housings and cases are made by casting. Sheet, rods, fasteners, disks are made by ingot/powder preforms plus hot working.

Current State of Development

Successful aero engine tests provide technology for space transportation applications. Lower strength, stiffness limited parts are more mature. Higher strength alloys have not been tested to same level.

Critical Issues

Damage tolerance is only moderate and must be confirmed for specific applications. Hydrogen resistance is expected to be poor.

Advanced Ni Single Crystal

Description

New single crystal alloys for jet engine turbine blades continue to push capability to higher temperatures.

Processing Method(s)

Directional solidification

Current State of Development

Very mature for jet engines. Applicability to space transportation not mature.

Critical Issues

Hydrogen resistance; must be evaluated. Specific alloy selection for space transportation issues would need to be addressed.

Advanced Ni Poly Crystal

Description

Advanced Ni alloys made by powder metallurgy and used for compressor and turbine disks. Higher strength and temperature capability compared to today's alloys used in aero and SSME engines.

Processing Method(s)

PM-extrude-forge

Current State of Development

Subscale processing demonstration and extensive mechanical property database exists

Critical Issues

H_2 resistance unknown

Advanced Cu Alloy

Description

Advanced Cu-alloy with improved temperature capability for thrusters, rocket nozzles, nozzle ramps, other high heat flux applications

Processing Method(s)

Powder metallurgy (PM) and Hot isostatic pressing (HIP), extrude, rolling

Current State of Development

Rocket test firing has demonstrated feasibility. Durability still needs to be examined. Coatings for extending life, performance need more work.

Critical Issues

Coating reliability. Performance limits need more definition. Applications other than thrust cells are immature.

Gr/Cu Composite

Description

High strength, conductivity, stiffness, lightweight material for hypersonic leading edges, actively cooled structures, radiators, heat pipes

Processing Method(s)

Pressure casting; Physical Vapor Deposition (PVD)

Current State of Development

Unidirectional plies are well developed and characterized. Woven composites are less mature but offer fewer weaknesses.

Critical Issues

Transverse properties are usually poor

Nano Structure Ni Alloy (Ns Ni)

Description

Nano structured nickel alloys with nanoscale grain size are projected to have 2x strength, 2x damping capacity, and 2x H_2 resistance.

Processing Method(s)

Cryomilling and PM

Current State of Development

Projections are based on similar results in other metals

Critical Issues

- General confirming of feasibility
- Concerned about low temperature damage tolerance

NT / Cu Composite

Description

Cu alloys with nanotubes, buckyballs, or diamond reinforcements are projected to have extremely high thermal conductivity, good stiffness and light weight.

Processing Method(s)

PM, Casting

Current State of Development

Cannot be fully explored until nano-reinforcements are more readily available

Critical Issues

Availability of nano-reinforcements

W, Nb, Mo Alloys

Description

Highest temperature capability available in a metal. High densities and poor H_2, O_2 resistance limit uses. Uniquely attractive for deep space missions and for nuclear propulsion.

Processing Method(s)

Cast and wrought or powder metallurgy are common. Chemical vapor deposition has also been used on rocket thrusters.

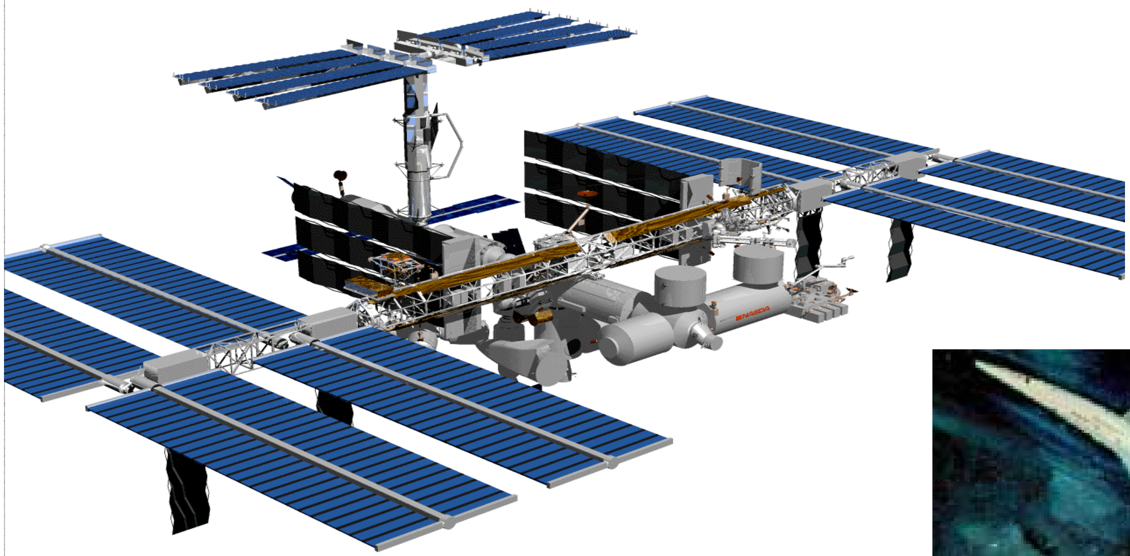
Current State of Development

Technology was worked heavily in the 60’s and 80’s. Alloys and processing are well developed. Coating efforts and alloy development for oxidation resistance are less mature but still hold promise.

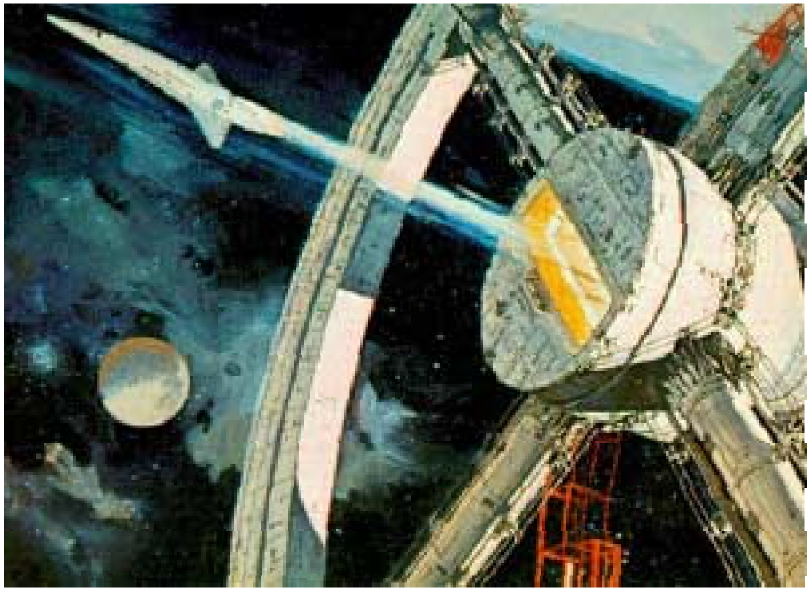
Critical Issues

Environmental resistance and coating reliability

III. Materials for Radiation Shielding

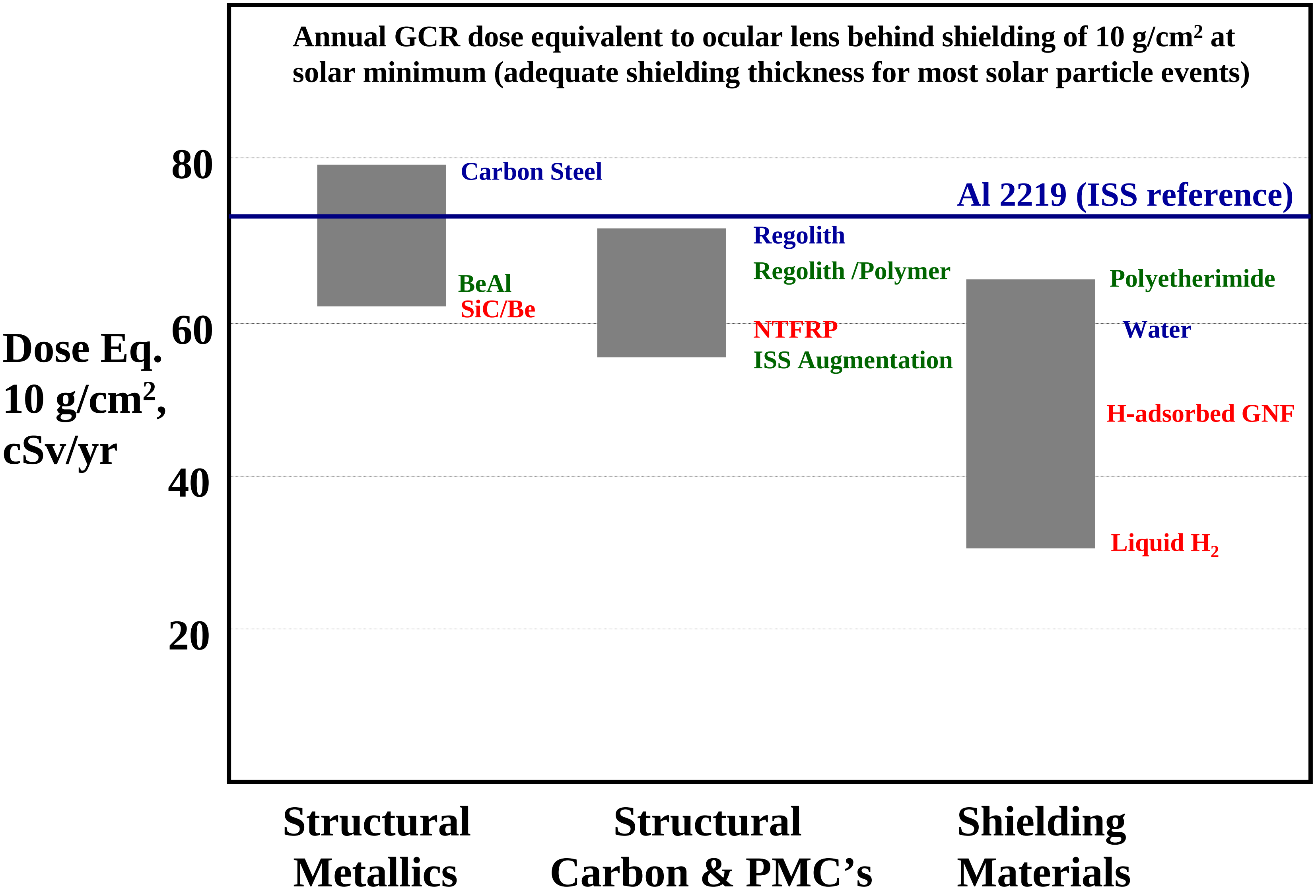


Near-Term: International Space Station

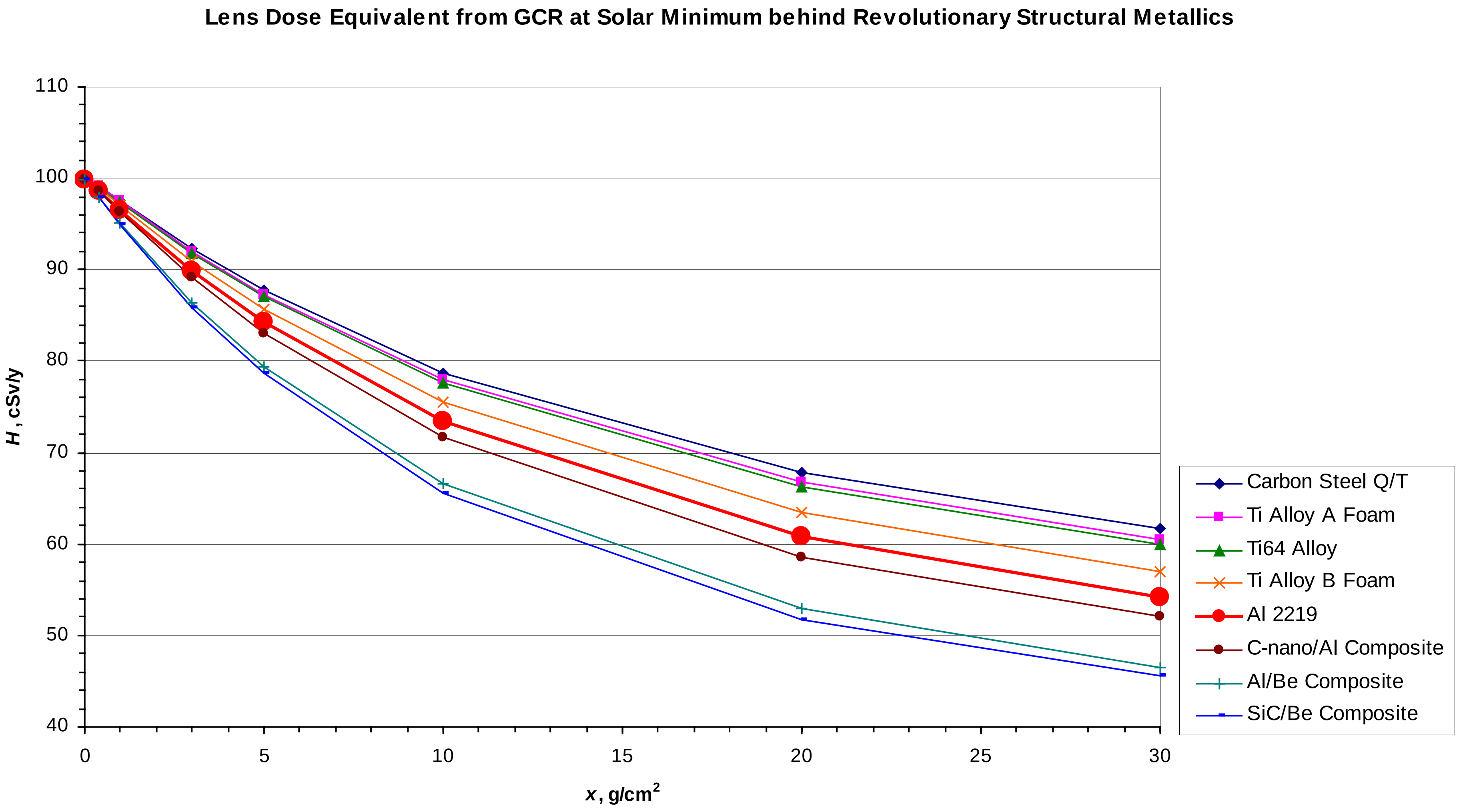


Far-Term: Routine Space Travel

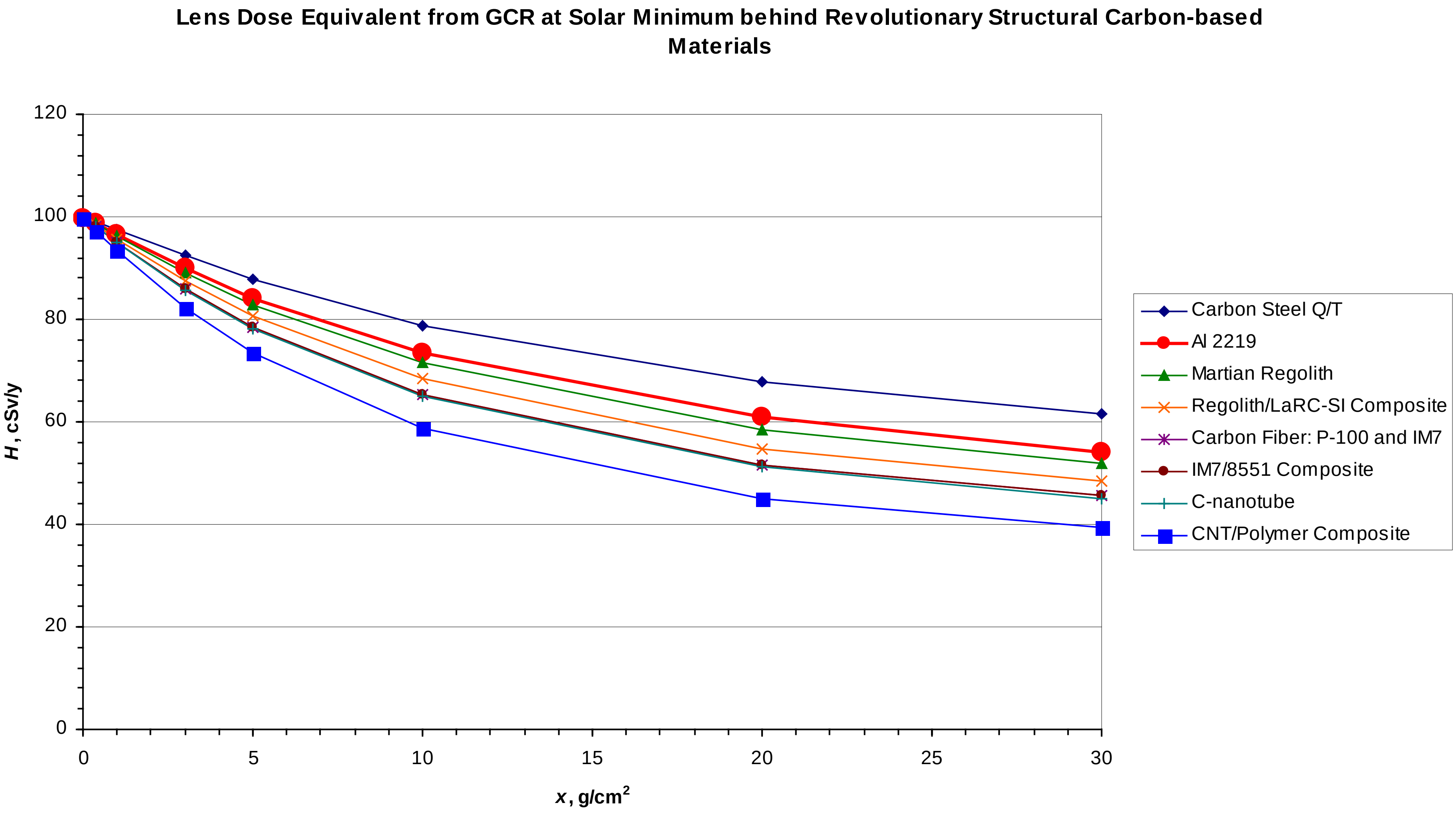
Properties of Materials for Radiation Shielding



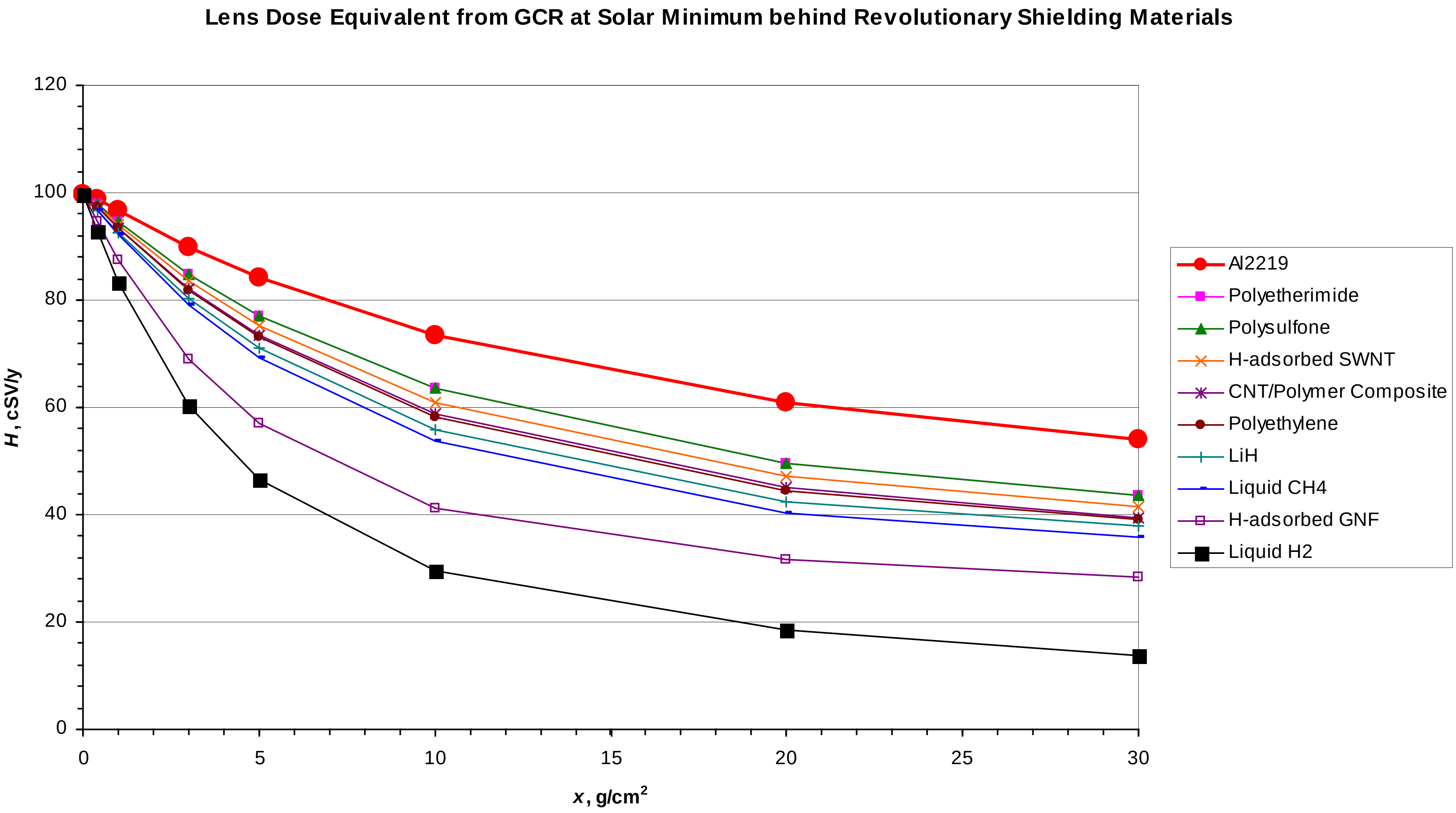
GRC Shielding Capability of Structural Metallics



GCR Shielding Capability of Carbon-based Material



GCR Shielding Capability of Shielding Materials



Radiation Shielding Materials

Revolutionary, Breakthrough Radiation Shielding Materials

- **Boron/Polymer Shielding Materials**
- **Regolith/Polymer Shielding Materials**
- **ISS Augmentation Type Shielding Materials**
- **Carbon Nanotube (CNT) Reinforced Polymer Composites (NTFRP)**
- **H-Adsorbed Graphite Nanofiber (GNF) with Herringbone Structure Composites**

Materials Under Development for Energy Applications – Could be Part of Shielding

- **Lithium Hydride (LiH)**
- **Liquid Methane (CH_4)**
- **Liquid H_2**
- **H-Adsorbed Single Wall Nanotube (SWNT)**

Commercially Available Materials – Could be Part of Shielding

- **Al 2219**
- **Polyethylene**
- **High Performance Polymers and Polymer Matrix Composites**
- **Water (consumables could be a part of radiation shielding)**

Boron/Polymer Shielding Materials

Description:

Boron/polymer microcomposites and composites

Processing Method (boron/epoxy microcomposites):

- boron powder and epoxy are combined and thoroughly mixed at a temperature of 66-71°C
- vacuum applied to the mixture at a temperature of 71-77°C until the mixture is de-aerated
- heated at the rate of 1-3°C/min to 121°C for 1 hr
- held at 121°C for 1 hr and then heated at the same rate to 177°C
- held at 177°C for 2 hr

Current State of Development:

- successfully processed using submicron amorphous boron powder and B_4C (boron carbide) whisker concentrations from 5% - 20% by weight
- polymers used: epoxy, LaRC-SI, PETI-5, K3B, 8515, Ultem, P1700, polypyromellitimide, and polyethylene
- improved mechanical properties
- excellent neutron absorption
- Boron/epoxy, B_4C/epoxy targets exposed to 1.05 GeV/amu Fe beam (1996); B_4C/PETI-5 target exposed to 1.05 GeV/amu Fe beam (1997) for radiation transport measurement and code validation
- other heavy ion beam tests, proton beam test, and other characterization tests planned

Critical Issues:

- development of processing protocol that enables both more boron for the best neutron shielding and more hydrogen for the ultra-lightweight shielding materials
- development of fiber reinforced composites using revolutionary boron fibers (boron deposited on carbon core)

Regolith/Polymer Shielding Materials

Description:

Regolith/polymer microcomposites

Processing Method:

Regolith/LaRC-SI polyimide

- LaRC-SI powder and regolith are combined and thoroughly mixed at room temperature
- heated at the rate of 1-3°C/min to 250°C
- heated at the same rate to 330°C under a pressure of 2.66 MPa (385 psi)
- held at 330°C for 1 hr under the same pressure to ensure the complete melting of crystalline regions

Regolith/polyethylene

- polyethylene powder and regolith are combined and thoroughly mixed at room temperature
- heated at the rate of 1-3°C/min to 121°C under a pressure of 0.7 MPa (100 psi)
- held at 121°C for 30 min under the same pressure
- cooled to 38°C under the same pressure and then released from the mold

Current State of Development:

Regolith/LaRC-SI polyimide

- successfully processed for regolith simulant concentrations from 5% - 90% by weight
- good properties up to 223°C by thermomechanical analysis (TMA) and thermogravimetric analysis (TGA)
- effective shielding property from 55-MeV proton beam test; the same shielding effects expected from other heavy ions
- heavy ion beam tests, neutron beam test, and other characterization tests planned
- one conceptual scheme for synthesizing LaRC-SI from Martian atmosphere as in-situ resource utilization (ISRU) proposed

Regolith/Polymer Shielding Materials, cont.

Current State of Development:

Regolith/polyethylene

- successfully processed a target for regolith simulant concentration of 85% by weight and shipped to the Heavy Ion Medical Accelerator (HIMAC), Chiba, Japan, for 290 MeV/amu carbon beam test scheduled for April 20-22, 2000, for radiation transport measurement and code validation
- other heavy ion beam tests, proton beam test, neutron beam test, and characterization tests planned
- conceptual schemes for synthesizing polyethylene from Martian atmosphere as in-situ resource utilization (ISRU) under investigation

Critical Issues:

- development of processing protocol that requires lower temperature and pressure
- feasibility of microwave processing
- transporting polymers to Martian surface versus manufacturing polymers on the surface by transporting various reagents and catalysts to the surface
- necessary processing equipment and adequate source of power on the surface presumed available from propellant manufacture
- development of robotic processing unit

ISS Augmentation Type Shielding Materials

Description:

Proposed ISS augmentation with graphite/epoxy composite face sheets and polyethylene core

Processing Method:

- sandwich construction with 8-ply quasi-isotropic graphite/epoxy laminate face sheets (0.28 g/cm² areal density)
- 7/16-inch-thick neat polyethylene core (0.98 g/cm² areal density)

Current State of Development:

- developed and implemented encapsulation schemes for multifunctional shield optimization: noise/radiation protection; structurally reinforced localized shielding technology
- fabricated target prototype and exposed to several beams: 250 MeV/amu Fe, 400 MeV/amu Ar, and 400 MeV/amu Ne beams at BNL/AGS during 11/11-17/1999 to validate shielding augmentation approaches
- localized shield optimization for ISS demonstration planned
- shipped to the Heavy Ion Medical Accelerator (HIMAC), Chiba, Japan, for 600 MeV/amu Ne beam test scheduled for April 20-22, 2000, for radiation transport measurement and code validation
- other heavy ion beam tests, proton beam test, neutron beam test, and design flight validation tests planned

Critical Issues:

- optimize encapsulation design to guarantee astronaut safety from outgassing of polyethylene
- optimize encapsulation design to achieve maximum structural property
- adapt ISS Habitat wall augmentation design for application to Mars Habitat module

Carbon Nanotube (CNT) Reinforced Polymer Composite (NTFRP)

Description:

LaRC proposed NTFRP as ultra-lightweight multifunctional material for structural and shielding applications

Processing Method:

- under development

Current State of Development:

- a novel approach to producing revolutionary shielding materials to protect humans and microelectronics from the hazards of space radiation has been proposed to the CETDP NRA
- theoretical shield performance against galactic cosmic rays is being studied at LaRC
- preliminary materials processing activity has been initiated

Critical Issues:

- development of processing protocol to introduce and bond hydrogen to carbon nanotubes
- development of carbon nanotube-based composite materials for lightweight shielding materials and structural elements with substantially higher strength-to-weight ratios than state-of-the-art composites

TRL:

- Current**:** TRL 1 Concluding**:** TRL 6

Time Line:

- 6 years

H-Adsorbed Graphite Nanofiber (GNF) with Herringbone Structure Composites

Description:

Multifunctional material for hydrogen storage and propulsion

Processing Method:

- experimental status in the research community

Current State of Development:

- being pursued by DOE for hydrogen storage in energy applications
- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- development of packaging method required to maintain 11.35 MPa (113 atm) pressure
- processing confirmation required for structural forms of the GNF to achieve the requirements of the DOE Hydrogen Plan

TRL:

- Current**:** TRL 1 Concluding**:** TRL 6

Time Line:

- 6 years

Lithium Hydride (LiH)

Description:

Material used primarily in batteries

Processing Method:

- commercially available

Current State of Development:

- used for nuclear reactor shielding, especially in space applications
- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- development of packaging method required to avoid contact with air and moisture

Liquid Methane (CH_4)

Description:

Material considered for propulsion fuel

Processing Method:

- commercially available

Current State of Development:

- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- development of advanced cryogenic insulation required in order to store liquid CH_4 over long time periods

Liquid H_2

Description:

Multifunctional material for propulsion fuel

Processing Method:

- commercially available

Current State of Development:

- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- development of advanced cryogenic insulation required in order to store liquid H_2 over long time periods

H-Adsorbed Single Wall Nanotube (SWNT)

Description:

Multifunctional material for hydrogen storage and propulsion

Processing Method:

- experimental status in the research community

Current State of Development:

- being pursued by DOE for hydrogen storage in energy applications
- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- requires about 100 atm to maintain
- processing confirmation required for very high, reversible adsorption of molecular hydrogen in nanotubes to achieve the requirements of the DOE Hydrogen Plan

Al 2219

Description:

Baseline material used on the ISS: primary structural material, including bulkheads, structural rings, and pressure shell

Processing Method:

- commercially available

Current State of Development:

- used in the aerospace industry and typically employed for spacecraft structural components
- fracture resistance, known allowables, and a long experience base for variable polarity plasma arc welding
- Al 2219 basic node 2 wall segment exposed to several beams: 250 MeV/amu Fe, 400 MeV/amu Ar, and 400 MeV/amu Ne beams at BNL/AGS during 11/11-17/1999 to validate shielding augmentation approaches
- Al 2219 basic node 2 wall segment shipped to the Heavy Ion Medical Accelerator (HIMAC), Chiba, Japan, for 400 MeV/amu Ne beam test scheduled for April 20-22, 2000, for radiation transport measurement and code validation

Critical Issues:

- impractical shielding material to ensure that radiation exposure is within as low as reasonably achievable (ALARA) principle
- significant dose contribution from neutrons produced from Al 2219
- greater consideration needed for angular distribution of secondary particles according to the theoretical result of variation in doses received for LEO orbit of 51.6 deg, 410 km

Polyethylene

Description:

Linear polymer with numerous commercial applications; widely used

Processing Method:

- commercially available

Current State of Development:

- excellent core material for radiation shielding because of its high hydrogen content
- used by nuclear and medical industries as a moderator of neutron fluxes
- principal neutron shielding material in non-aerospace sector
- polyethylene target exposed to 1.05 GeV/amu Fe beam at BNL/AGS during 10/17-25/1997 for radiation transport measurement and code validation

Critical Issues:

- development of packaging method required for space applications because of outgassing
- development of packaging method required for space applications to improve structural properties

High Performance Polymers and Polymer Matrix Composites

Description:

High performance polymers used for composite matrix materials and thick resin castings

Processing Method:

- commercially available

Current State of Development:

- various polymers available: epoxy, LaRC-SI, LaRC-IA, LaRC PETI-5, K3B, LaRC 8515, Ultem, P1700, polypyromellitimide, polycyanate ester, etc.
- theoretical shield performance against galactic cosmic rays is being studied at LaRC

Critical Issues:

- only moderate shielding efficiency achieved: hydrogen content in polymers and composites not maximized

Water (consumable materials could be part of shielding)

Description:

Water for use by astronauts

Processing Method:

- develop materials and geometry of storage containers for optimized radiation shielding

Current State of Development:

- water is an effective radiation shielding material; since it will be on board for the astronauts, it can be considered as part of the overall radiation shielding

Critical Issues:

- need to establish radiation shielding properties of water so that it can be taken into consideration as part of the overall radiation shielding
- need to optimize materials and geometry of storage containers
- as the water is consumed by the astronauts, the radiation shielding decreases; so have to consider the component of trash and biowaste also for radiation shielding

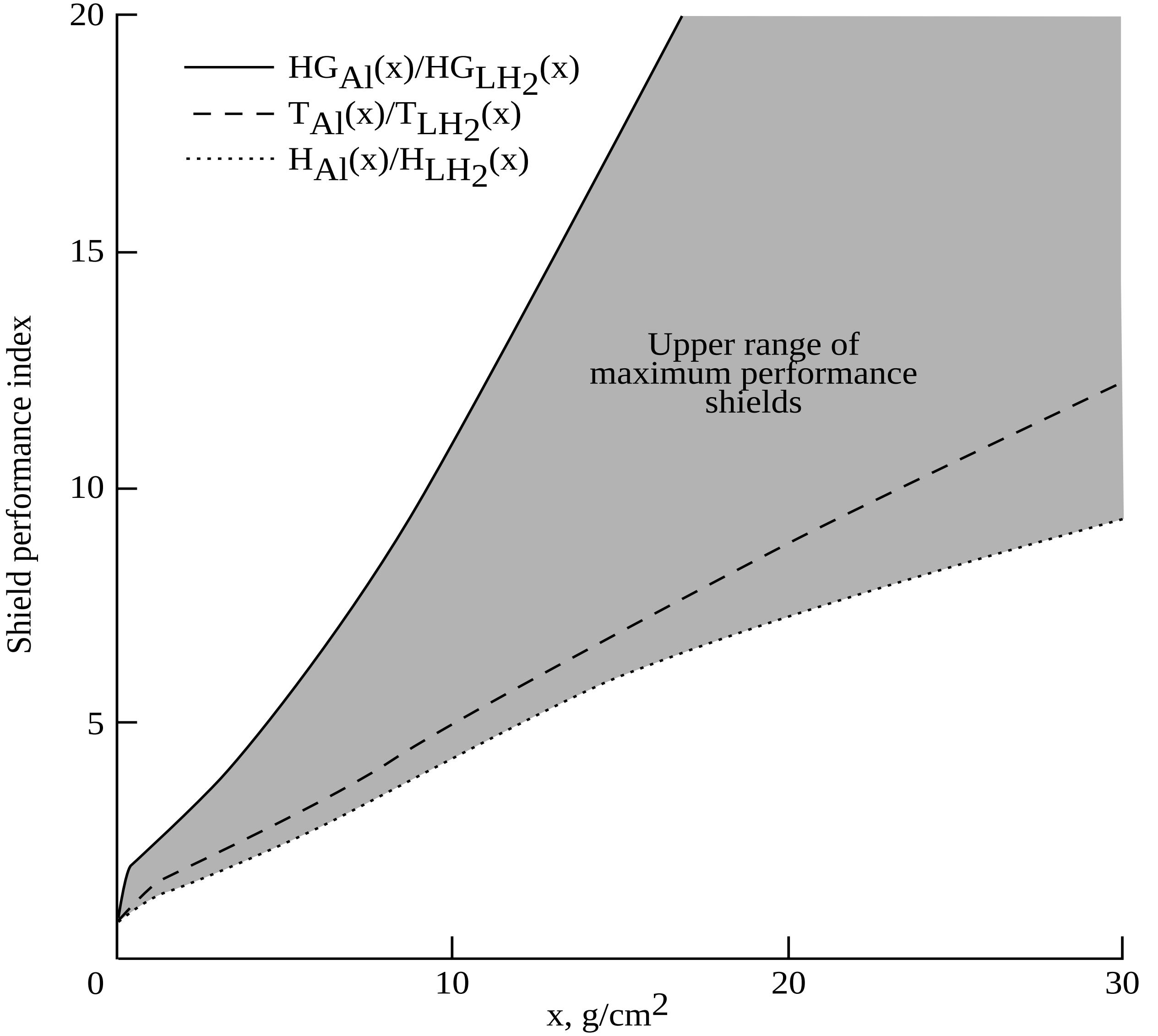
TRL:

- Current**:** TRL 4 Concluding**:** TRL 6

Time Line:

- 3 years

Maximum Shield Performance Factors Relative to Aluminum for Various Biological Models



Ionizing Radiation Analysis Methods: Development and Validation

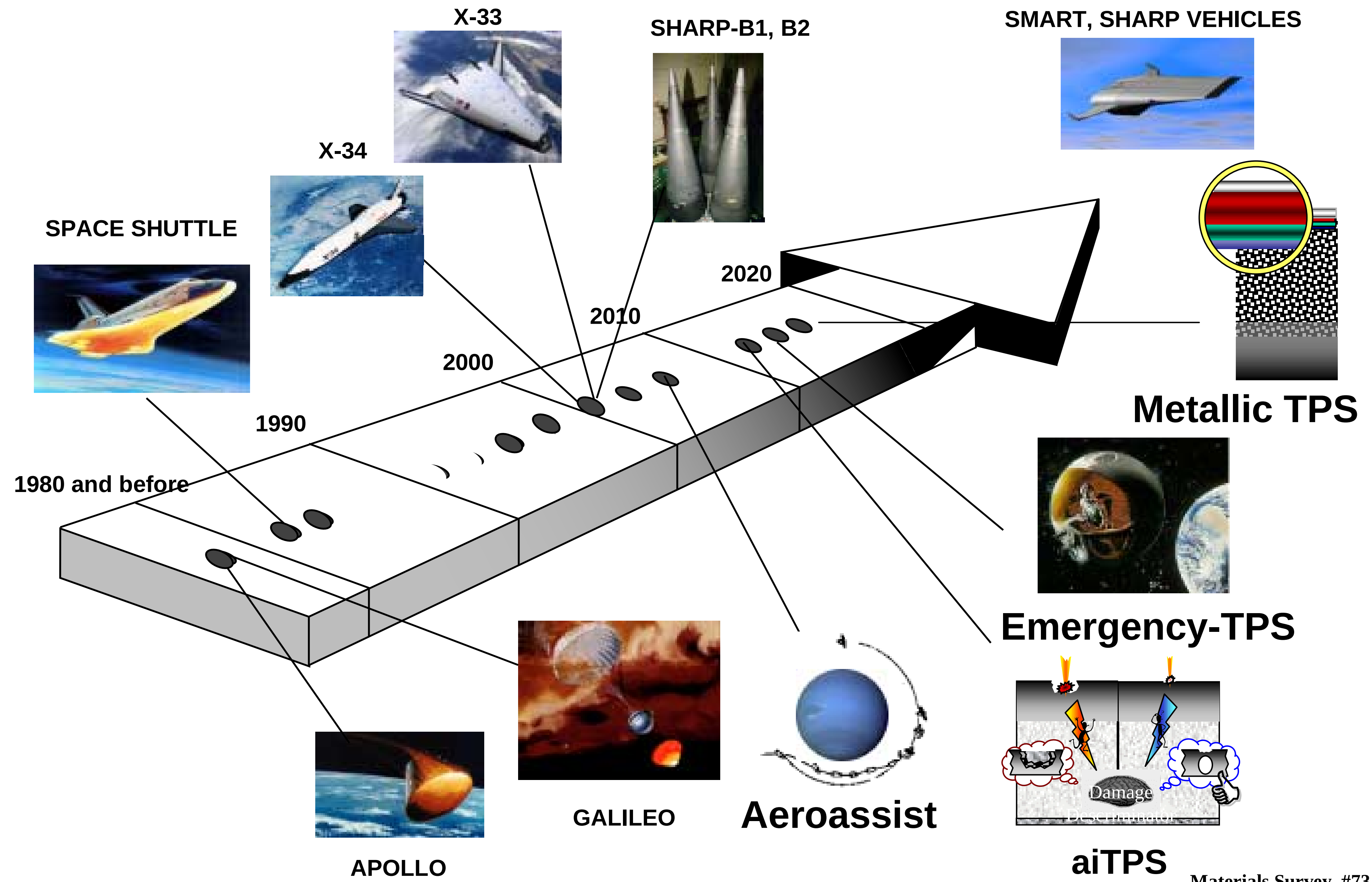
Present Status of Radiation Shielding Codes :

- **Monte Carlo Codes**
  - √ Lacks a heavy ion reaction model (TRL 1)
  - √ Does not transport heavy ions and their secondary particles (TRL 1)
  - √ *Slow computationally especially in complicated geometry
  - √ *Cannot be used in optimization processes due to slow computation times
- **HZETRN Code**
  - √ Has several alternate heavy ion reaction models available
  - √ Computationally efficient even in complex geometry
  - √ Can be used in optimization procedures
  - √ Currently used in Astronaut Radiation Health Program at JSC
  - √ Currently being applied to ISS redesign
  - √ *Does not transport secondary mesons
  - √ *Limited laboratory validation of database (TRL 4)
  - √ *Limited space flight validation (TRL 5)

- **GRNTRN Code**
  - √ Has several alternate heavy ion reaction models available
  - √ Limited laboratory validation (TRL 4)
  - √ Computationally efficient even in complex geometry
  - √ Can be used in optimization procedures
  - √ *Has not been space flight validated
  - √ *Does not transport protons, neutrons, mesons
  - √ *Only code which can be laboratory and space-flight validated and applied in shield optimization procedures (TRL 9)

* **Critical issues**

IV. Materials for Thermal Protection Systems



Rigid RSI Property Comparison

Properties	LI-900	LI-2200	FRCI-12	AETB-8	TUFI-HT	ROCCI
Density Lbs/Cu.Ft.	9	22	12	8	12	12
Tensile Strength						
IP (PSI)	68	181	256	55	40	50
TTT (PSI)	24	73	81	100	80	100
Modulus						
IP (KSI)	25	80	50	9	8	10
TTT (KSI)	7	27	10	22	22	25
Maximum Use Temperature (°F)						
Multiple Flights	2,400	2,500	2,500	2,500	3,000	3,200
Single Flight	2,700	2,800	2,800	2,800	3,100	3,300
Therm. Cond.,P= 10^{-3} Atm., T=1000°F (BTU-In/Ft-Hr°F)	0.021	0.030	0.027			
Year Developed	1973	1977	1980	1993	2001	2005

Novel TPS Currently Under Development

- **Advanced Rigid TPS: Ultra-TUFI, TUFI-HT, white-TUFI**
  Improved temperature capability and durability
- **Advanced Flexible Blankets: CFBI, High-Temperature felts**
  Reduced weights and costs
- **Integral Cryogenic Insulation/TPS: Incorporating aerogels and new MLI**
  Reduced weights and costs
- **New coatings: Surface and material characterization**
  Reduced weights and operations costs
- **Ultra-High Temperature Ceramics: Zr and Hf based ceramic composites**
  Significant increase in temperature and heat flux capability
- **Nano-phase Ceramic Insulations: Aerogel and zerogel composites**
  Reduced weight insulations
- **Organo-Ceramic Materials: QUIC-Fix, QUIC-Stick, QUIC-TUFI**
  Reduced fabrication, repair and maintenance costs
- **Light-Weight Ceramic Ablators: SIRCA, PICA, SPLIT**
  Reduced weight and fabrication costs
- **Metal Covered Blankets: DurAFRSI, DuraTABI**
  Increased rebustness, reduced fabrication costs

TPS for the Future

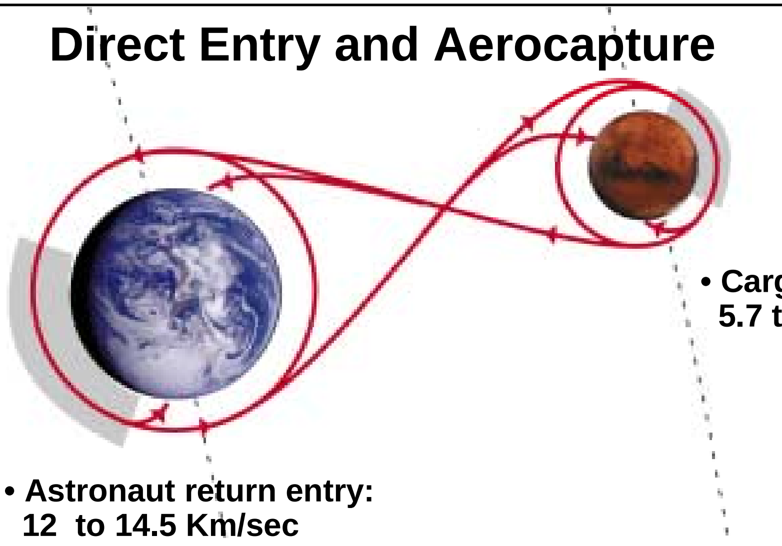
- **TPS Material Properties**
  - Critical TPS material property is weight
    - Apollo: TPS was approximately 30-50% of re-entry mass
    - Shuttle: TPS is approximately 15%of dry mass of the orbiter
    - Future HEDS mission: decrease TPS mass by half with added reliability and safety
  - Advances continue to be made in reducing TPS mass and increasing TPS strength
    - Lightweight Ceramic Ablators (PICA, SIRCA) invented at Ames are a factor of 5 times lighter than previous ablators like Carbon-Phenolic

- **TPS Breakthroughs will not come from improved material properties but from revolutionary capabilities and applications**
  - 5-10 years: Aeroassist technology utilizing sharp leading edges to optimize L/D; challenge is to design TPS for aeroassist and atmospheric entry; will allow a reduction in ...
  - 10-20 years: adaptive, intelligent TPS and emergency TPS...
  - 20 years: ISRU TPS development. Use in-situ resources (either on-vehicle or on-planet resources) to develop TPS on-site; the challenge is to develop a system that allows astronauts to simply and reliably assemble the TPS

Benefits from Aeroassist Technology

SHARP leading edges will enable aeroassist vehicles to change direction

Direct Entry and Aerocapture



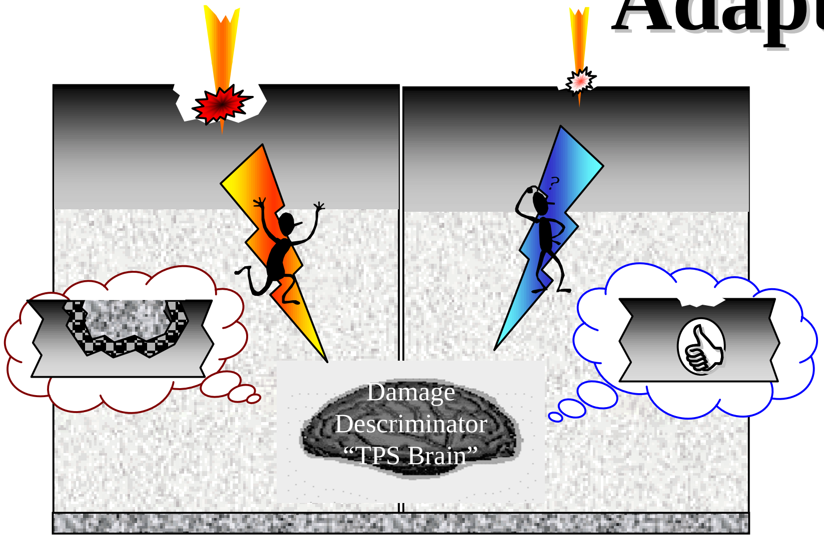
- Cargo/Human entry: 5.7 to 8.7 Km/sec
- Astronaut return entry: 12 to 14.5 Km/sec

- Aeroassist significantly reduces system complexity and mass of propulsion systems.

- Reductions in mass of vehicles -> Reduced launch requirements or direct increase in payload e.g., 20 -68 % reductions in IMLEO for Human mission.

- Aerocapture at Mars is efficient for orbit insertion which gives options for precision landing with reduced entry errors, entry in daylight conditions, or entry after an unexpected dust storm.

Adaptive Intelligent TPS (aiTPS)



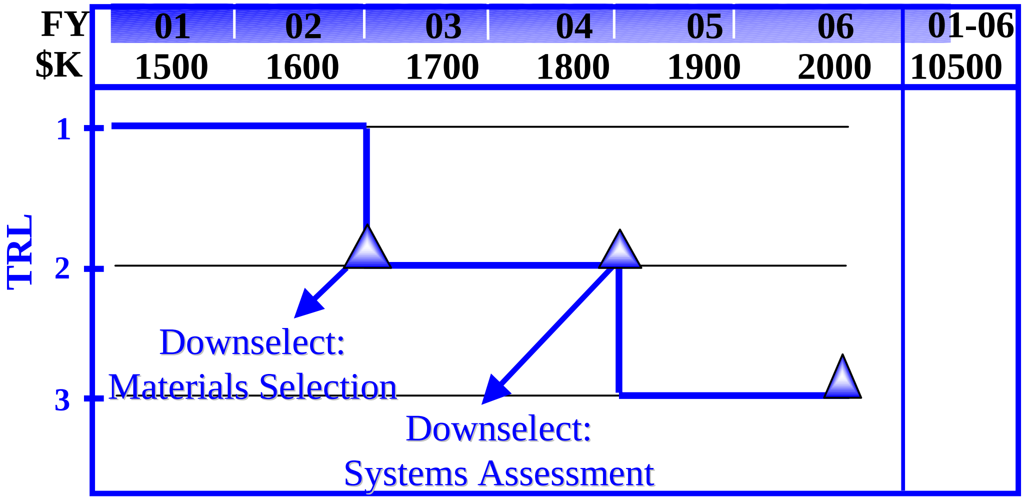
Adaptive TPS, with an intelligent material response to changes in the environment

Products / Benefits

- Products
  - Development of Adaptive Intelligent , self-healing Thermal Protection Systems
- Benefits
  - Increased reliability and safety through adaptation of the TPS structure/composition to the environment
- Customers
  - NASA (Exploration, HEDS, RLVs)
  - Commercial Launch Enterprises

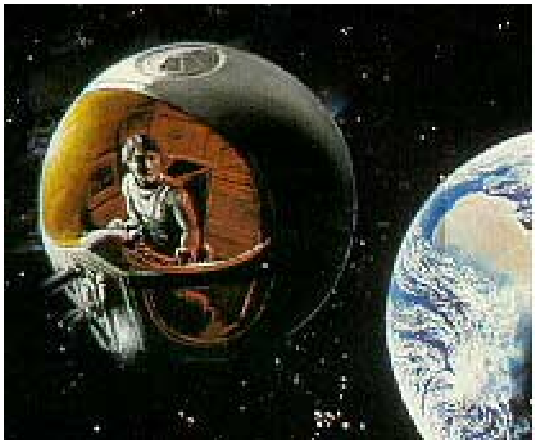
Implementation / Metrics

- Current State of the Art
  - Presently at TRL-1
- Performance Metrics
  - Measurable metric(s): Enhanced life-time, dynamic material properties
- Risks
  - Materials systems interactions and potential weight impact
- Participants
  - ARC (lead), JSC, KSC



FY	01	02	03	04	05	06	01-06
$K	1500	1600	1700	1800	1900	2000	10500

Emergency Thermal Protection Systems - eTPS



Deployable Crew Escape Option - Notional Image Only

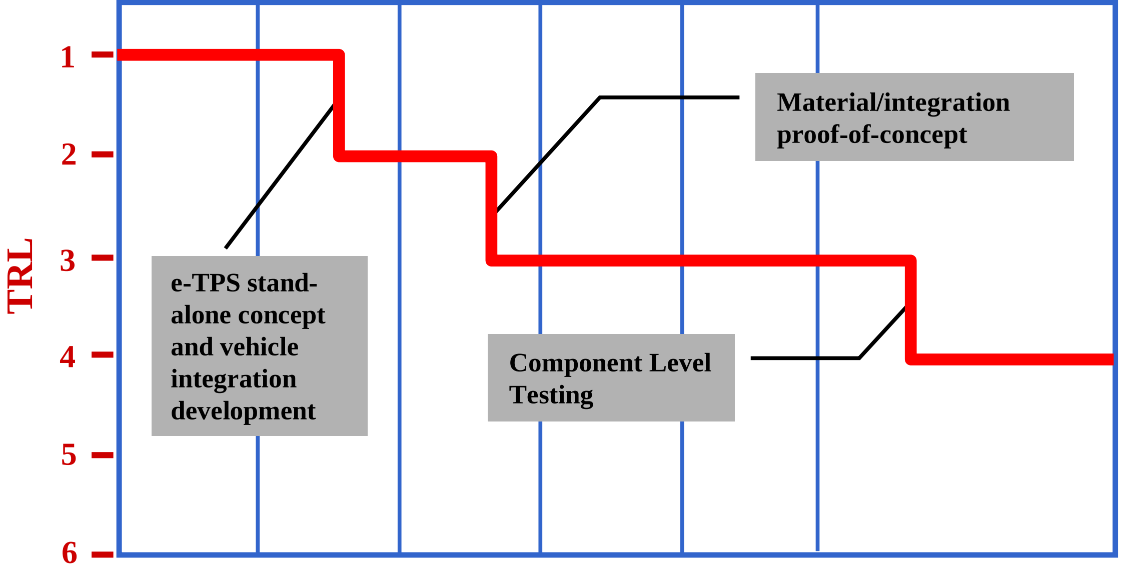
Products / Benefits

- Products
  - – A family of deployable thermal protection systems that can be used in an emergency for safe crew escape or vehicle abort
- Benefits
  - – e-TPS will assure crew survival in a catastrophic event
- Customers
  - – NASA (HEDS, RLVs)
  - – Commercial Launch Enterprises

Implementation / Metrics

- Current State of the Art
  - – No emergency-TPS currently available
- Performance Metrics
  - – 1,000,000 to 1 Crew Survivability
- Risks
  - – Meeting vehicle mass and volume requirements
- Participants
  - – ARC (Lead), JSC, KSC

FY	01	02	03	04	05	06	01 - 06
$M	0.70	0.70	0.75	0.80	0.80	0.80	4.55



In-Situ Resource Utilization TPS

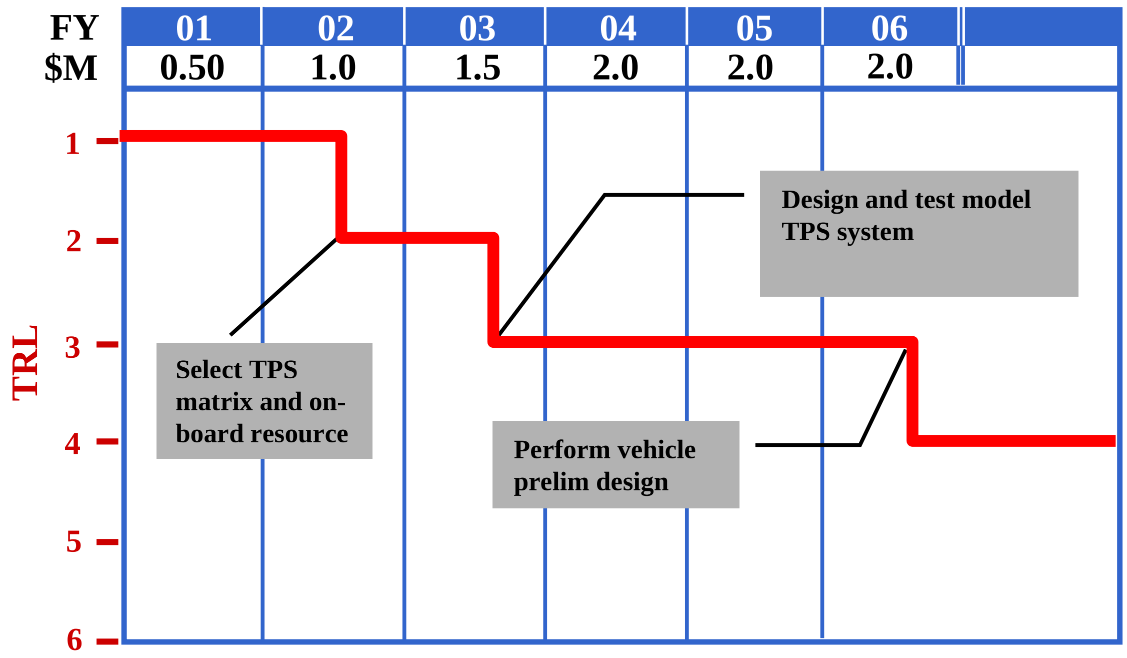
Notional picture of TPS Created from In-Situ Resources

Products / Benefits

- Products
  - Development of ablative TPS for planetary exploration vehicles that utilize on-board resources such as water, unneeded structure, plant wastes and/or planetary materials
- Benefits
  - Decrease vehicle mass by not needing a complete separate TPS system; increase payload, enhance reliability (weight savings could be 1/3 of entry vehicle weight)
- Customers
  - NASA (HEDS, Exploration,RLVs)

Implementation / Metrics

- Current State of the Art
  - TRL 1
- Performance Metrics
  - Decreased vehicle mass
- Risks
  - Meeting vehicle mass and volume requirements
- Participants
  - ARC (Lead), JSC, JPL



Development of Metallic TPS

Metallic TPS - General	**Critical TPS Needs Addressed**
• Metal system inherently all weather, durable and impact resistant. No re-processing, waterproofing, etc. req'd. (Research on field repairable coatings where needed is proposed) • Lee-side metal TPS likely not need coating. for 1000˚F operation. Ground handling minimized.	**Environmental Tolerance**
• Metal TPS typically will not require high temperature seals or adhesive development.. Seals are handled by the TPS configurations. (Ref. X-33)	**Joints/Seals**
• Metal TPS will not require water infiltration, contamination sensors. • Ref. X-33 experience - Individual TPS panels can be removed and replaced in ~ 10 minutes for back surface and subsurface inspection. Attachment schemes developed as part of new concept studies.	**Inspectibility/IVHM**
• Metals applicable to all vehicles. Can save weight, especially when used as aeroshell (Ref. X-33)	**Flexibility, Low Weight**

Development of Metallic TPS, continued

Alloy & Process Development

- **Emerging ODS alloys and processes for 2000 ˚F+ operation.**
  - **Ni, Fe, Cr base systems**
- **Intermetallics for 2300+ operation**
  - **Beryllium, titanium & nickel based intermetallics**
- **Ultra low density metallics**
  - **Porous materials, metallic foams, joining technology**
- **Nanostructured alloys and processes**
  - **Functionally graded, integrated aeroshell systems**
  - **Metal/ceramic/nanotube hybrids**
- **Innovative processing for sheet & foil product**
  - **Direct cast, Spray deposition, Laser sintering**

Critical TPS Needs Addressed

High Temperature Base M & P
Low Cost Manufacturing
Light Weight

Surface Modifications

- **Revolutionary nano-laminate, graded layer aeroshell**
- **Self-sensing, self regulating environmentally compliant surfaces**
  - **Surface modifications and/or coatings**

High Temperature Capability
Impact tolerance
Replaceability/Repairability

TPS Concept/Design Development

- **Advanced metallic TPS concepts & designs (Beyond X-33, & VentureStar) with emerging alloys and insulations.**
- **Models for thermal/mechanical optimization integrating substructures, insulation, and metal aeroshell.**
- **Integrated cryotank/substructure/TPS/aeroshell optimization**

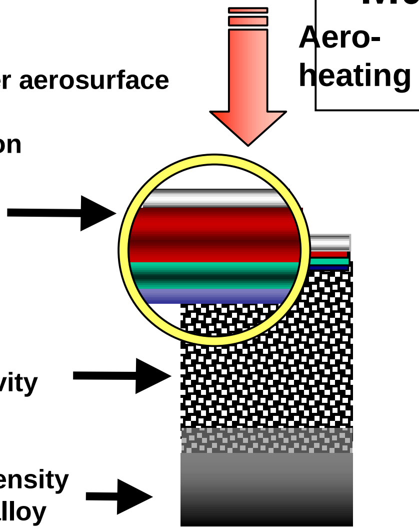
TPS/Vehicle Optimization/Validation

Multifunctional Metallic Integrated TPS/Aeroshell (*MITAS*) for RLV Acreage Application

- **Nano-laminate/graded layer aerosurface**
  - **Self sensing/regulating**
  - **Environmental protection**
  - **Thermal control**
  - **Impact resistant**
  - **All-weather**

High temperature reduced-conductivity metal/hybrid foam

Ultra low density structural alloy



Metallic Integrated TPS/Aeroshell with Environmentally Compliant Surface

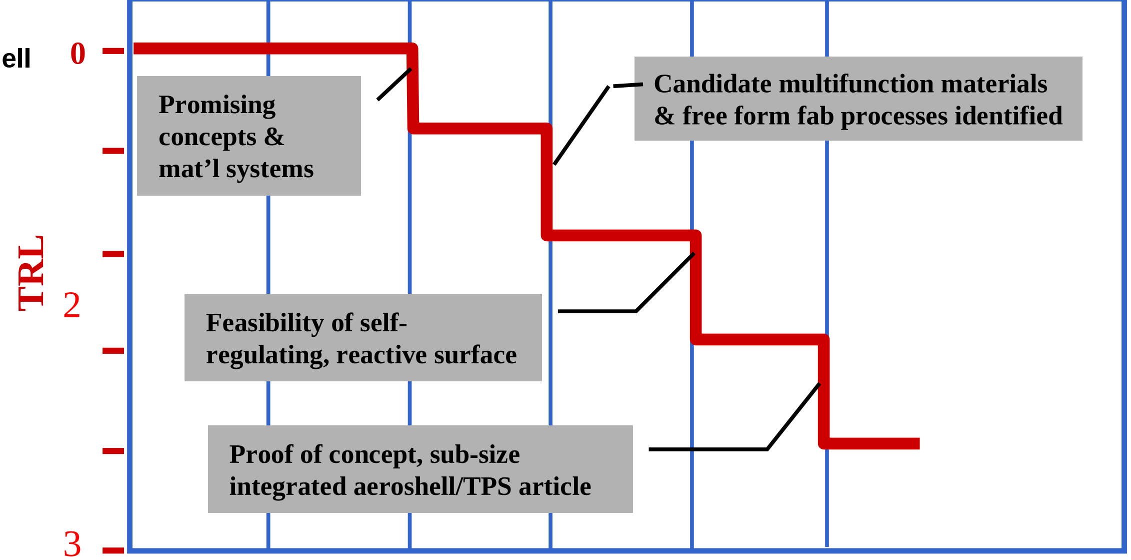
Products / Benefits

- Products
  - Integrated TPS/Aeroshell system for up to 2500 °F operation
  - Adaptable surface for optimum optical/chemical properties
  - Free-form fabrication practice for simplified manufacturing
- Benefits
  - Simple, totally reusable, all-weather, robust, light weight, reduced part count, minimal maintenance
- Customers
  - LaRC(SAEPO, AVSTPO), GRC, MSFC, SL100, DOD(SMV, SOV)
  - Gen2(1st stage of TSTO and 2nd stage orbiter)
- Common/enabling

Implementation / Metrics

- Current State of the Art
  - Separate structure, attachments, insulation, aero-shell
  - Fragile ceramic blankets, tiles
  - Weather constrained
  - Not fully reusable
- Performance Metrics
  - Thermal & structural efficiency
  - Surface optical/chemical properties (emittance, reflectivity, catalytic efficiency)
- Risks
  - Foam/dense materials compatibility (interfaces)
  - Self regulating surface
  - Nano-laminate process control
- USG participants
  - LaRC, GRC

FY	01	02	03	04	05	06	Total
$M	1.7	1.9	2.2	2.6	3.5	3.5	15.4



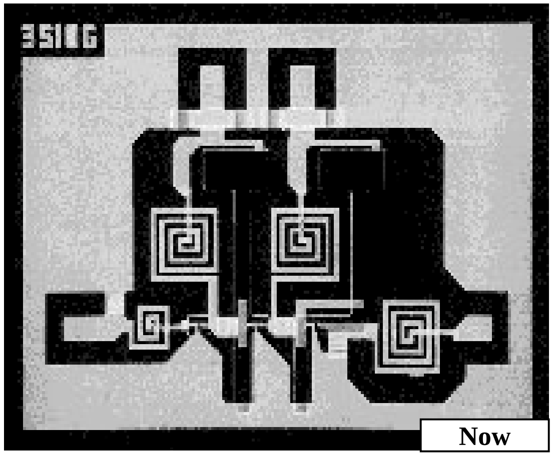
Promising concepts & mat'l systems

Candidate multifunction materials & free form fab processes identified

Feasibility of self-regulating, reactive surface

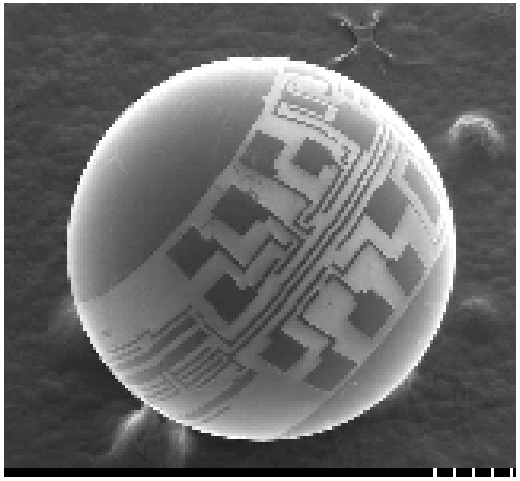
Proof of concept, sub-size integrated aeroshell/TPS article

V. Materials for Electronics and Photonics Systems



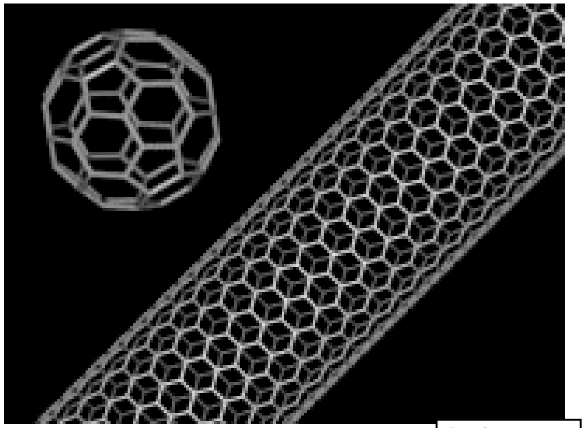
Now

Monolithic Microelectronic Integrated Circuit (MMIC) devices



5-10 years

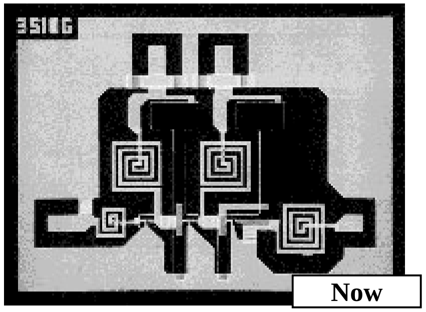
Integrated Intelligent system with on board sensing, data processing, and control.



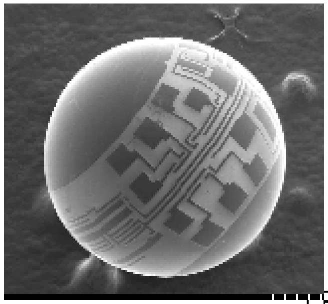
15-25 years

Self-deployed Smart integrated nano systems with networking

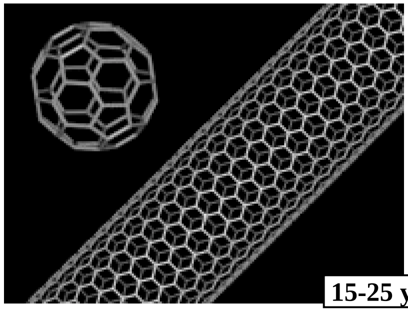
V. Materials for Electronics and Photonics Systems


Now

MMIC based devices


5-10 years

Integrated smart system


15-25 years

Self-propelled networking system

System Metrics:			
Mass	10 Kg	100 gms	1 gm
Power	20 W	2 W	10 µW
Function/mass	1	20X	20,000X

Objective: Develop materials to allow miniaturization of communications/data manipulation/ sensing/ power/ thrust systems to enable the deployment of fleets of intelligent satellites and robotics to more effectively explore Mars.

Leading Candidates with high potential payoff:

- Wide bandgap semiconductors for high temperature environments, high-power circuitry, and high-strength Micro-Electro-Mechanical Systems (MEMS) devices [TRL2-4]
- Multifunction materials compatible with data, energy handling and propulsion systems [TRL 1-3]
- Organic materials for active electronic devices/molecular computing [TRL1]
- Self-assembling materials -- just grow it [TRL 1]
- Self-healing materials. [TRL 1]
- Magnetoelectonic materials - “spintronics” [TRL 1]

Properties of Electronics and Photonics Materials

Property	reference Silicon micro-device (handbook)	1-5 yrs 4H-SiC micro-device (theoretical)	1-5 yrs 6H-SiC micro- (handbook)	5-10 yrs 3C-SiC micro- (report)	5-10 yrs GaN* micro- (report)	15-20 yrs SiC nano-device (theoretical)	15-20 yrs GaN nano-device (theoretical)
Bandgap (eV)	1.1	3.2	3.0	2.3	3.4		
Relative Dielectric Constant	11.9	9.7	9.7	9.7	9.0		
Breakdown Field $N_D = 10^{17}\ \text{cm}^{-3}$ (MV/cm)	0.6	//c-axis: 3.0	// c-axis: 3.2 ⊥ c-axis: > 1	> 1.5	2 - 3		
Thermal Conductivity (W/cm-K)	1.5	3 - 5	3 - 5	3 - 5	1.3		
Electron Mobility @ $N_D = 10^{16}\ \text{cm}^{-3}$ (cm^2/V-s)	1200	//c-axis: 800 ⊥c-axis: 800	//c-axis: 60 ⊥c-axis: 400	750	Bulk: 900 2 DEG: 1400		
Hole Mobility @ $N_A = 10^{16}\ \text{cm}^{-3}$ (cm^2/V-s)	420	115	90	40	30		
Donor Dopants & Shallowest Ionization Energy (meV)	P: 45 As: 54	N: 45	N: 85 P: 80	N: 50 P: 80	Si: 15		
Acceptor Dopants & Shallowest Ionization Energy (meV)	B: 45	Al: 200 B: 300	Al: 200 B: 300	Al: 270	Mg: 170		
1999 Commercial Wafer Diameter (cm)	30	5	5	None	None		
Device Manufacture-ability (TRL)	9	3	3	1	1		

* Gallium Nitride (GaN)