N93-12450

ADVANCED CERAMIC MATRIX COMPOSITES FOR TPS

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Abstract

Recent advances in ceramic matrix composite (CMC) technology provide considerable opportunity for application to future aircraft thermal protection systems (TPS), providing materials with higher temperature capability, lower weight, and higher strength and stiffness than traditional materials. The Thermal Protection Material Branch at NASA Ames Research Center has been making significant progress in the development, characterization, and entry simulation (arc-jet) testing of new CMC's. This presentation gives a general overview of the Ames Thermal Protection Materials Branch research activities, followed by more detailed descriptions of recent advances in very-high temperature Zr and Hf based ceramics, high temperature, high strength SiC matrix composites, and some activities in polymer precursors and ceramic coating processing. The presentation closes with a brief comparison of maximum heat flux capabilities of advanced TPS materials.

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Long Range Goal of the Ames Thermal Protection Materials Branch

To Provide Thermal Protection Materials, Systems, and Analysis Methods for Heat Shields of Entry, Aerobraking and Hypersonic Cruise Vehicles and Planetary Probes

THERMAL PROTECTION MATERIALS

AMES ⇄ VEHICLE DEVELOPER ➡ GROUND/FLIGHT EXPERIMENTS ➡ FLIGHT TPS

TPS TECHNOLOGY DEVELOPMENT, ARC JET TESTING & COMPUTATIONAL ANALYSES

PAST: 1970-1982

- KEY SHUTTLE TPS CONTRIBUTIONS:
  - LI2200*
  - FRCI-12*
  - RCG COATING*
  - AFRSI**
  - GAP FILLERS*
- IN FLIGHT PROOF OF CATALYTIC EFFECTS
- ARC-JET TESTING FOR SHUTTLE, GALILEO, APOLLO, DOD VEHICLES
- X-24B/C FIRST SUPERSONIC FLIGHT TEST OF TILE TPS

* AMES PATENT
** TECH BRIEF

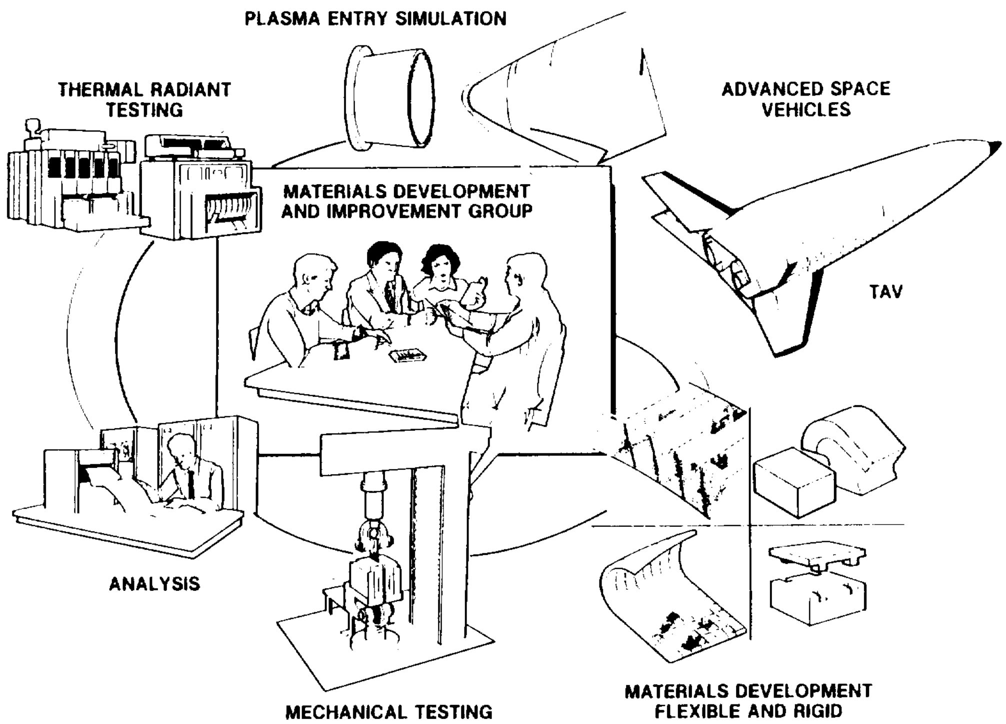
1982 - PRESENT

- NASP:
  - CMC & COATINGS TMP'S
  - GWP #93 & #95
  - ARC-JET TESTING
- LEAD CENTER FOR SEI AEROBRAKE TPS
- 3 AFE EXPERIMENTS
- 3 OEX EXPERIMENTS
- PEGASUS FLIGHT EXP'S
- NEW MATERIALS AND TPS:
  - AETB*, TUFI*
  - TABI*, CFBI*
  - CMC DEVELOPMENT
  - TOP HAT*
- NUMEROUS APPLICATIONS OF AMES TECHNOLOGY: ATF, B-2, TITAN-IV

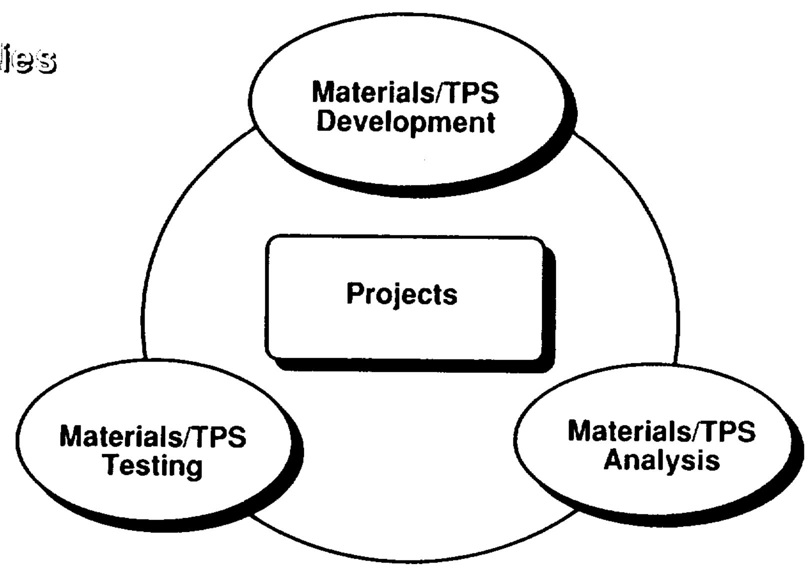
FUTURE TO 2005

- NEW 4000°F + REUSABLE CERAMICS AND TPS
- HOT STRUCTURE CMC TPS
- DURABLE ALL-WEATHER TPS
- ADVANCED ABLATORS:
  - CERAMIC/POLYMER
  - VOLUME REFLECTING
- TPS FOR FUTURE PROGRAMS:
  - X-30, DELTA CLIPPER
  - HYFLEX, JSC FLIGHT EXP.
  - MESUR, NEPTUNE PROBE
- CATALYTIC EFFECTS FOR MARS ENTRY
- NUCLEAR ROCKET REENTRY
- ADVANCED TPS MODELING

THERMAL PROTECTION SYSTEM DEVELOPMENT PROCESS



Activities



- A Synergistic, Multi-disciplinary Approach
- Continual Research/Technology Development Supports Projects

Projects

NASA Programs

- SEI: Recent Langley "Aerobrake Assembly with Minimum Accommodation" study performed by Lockheed baselined Ames developed "TOP HAT" CMC/rigid tile TPS.
- Shuttle: Working with KSC, JSC, NASA HQ and Rockwell to fly Ames developed TUFI TPS on the Orbiters in high erosion areas.
- MESUR: Performed initial TPS sizing and trades. Identified a light weight silicon rubber TPS (SLA-561) which allows a 50% increase in scientific payload.
- Pegasus: Teaming with Dryden and LaRC for boundary layer cross flow transition experiment (scheduled to fly in FY92). Constructing Pegasus Wing-Glove and PI for and TPS performance evaluation experiment. Wing fillet heating experiment flown on first two Pegasus launches.
- HYFLEX: Working with a multi-agency team to define vehicle. Diboride leading edges and nosetip being evaluated.
- Wave-Rider: Discussions with McDonnell Douglas regarding leading edge design.

NASP

- Responsibility for government work packages #93 and #95 for arc-jet testing and internal TPS insulation design.
- Both have been highly praised by NPO/JPO and Industry Leads (i.e. General Dynamics, Rockwell, Pratt Whitney).

DoD

- Delta Clipper: Cooperative research program being developed with McDonnell Douglas and SDIO. Cooperative efforts proposed in three areas:
  1) TPS design and consultation
  2) Arc-jet testing
  3) Computational studies

Material/TPS Testing Areas

- Arc-Jet Testing
  - Aerodynamic Heating Facility (20 MW)
  - Interactive Heating Facility (60 MW)
  - Panel Test Facility (20 MW)
- Material Characterization
  - SEM, XRF, Optical Microscopes
  - XRD, Large Sample TGA
  - Dilatometer, Instron
  - Infrared & Ultraviolet Spectrometers
  - ICP Mass Spectrometer (inorganic)
- Special Testing
  - Laser Time-of-Flight Mass Spectrometer (SALI)
  - Side Arm Reactor

Material/TPS Analysis Areas

- Computational Surface Thermochemistry
  - Surface heating and catalysis effects (NSCAND, BLIMPK, LAURA, VSL, GASP)
  - Ablation, erosion, and shape change computations (ASC, CMA, ACE)
- Computational Solid Mechanics
  - Multi-dimensional conduction/radiation analyses (SINDA, TRASYS)
  - Multi-dimensional thermal-stress analyses (COSMOS)
- Computational Materials
  - CVD/CVI Processing (GENMIX, NACHOS)
  - Reflective TPS analyses
  - Composite material properties (MATX)

Material/TPS Development Areas

Advanced Material Families

- **Ceramic Matrix Composites**
  - Very-High Temperature Ceramics (HfB_2 +SiC)
  - High Temperature, High Strength Ceramics (C/SiC)
  - Polymer Precursors (Si/C/B fibers, tape casting)
  - Ceramic coatings processing
- **Light Weight Ceramic Insulations**
  - Rigid Tiles (AETB, SMI, UltraLight)
  - TABI and CFBI Flexible Blankets
  - Aerogel Studies
- **Light Weight Ablators**
  - Rigid Ceramic Insulation with a Polymer Filler
- **Surface Coatings**
  - Low Catalytic Efficiency, High Emissivity
  - Reflective

Diboride Materials

- **Manlabs Inc. (Cambridge MA) tested and compiled a data base on a large number of refractory materials in the 60's and early 70's**
- **The diborides of zirconium and hafnium (ZrB_2 and HfB_2) were found to be the most oxidation resistant, high temperature materials in the study, e.g.**

Arc testing of ZrB_2 + 20 v/o SiC
surface temp. 2510 C, stagn. press. 1.0 atm, stagn. enthalpy 11.6 kJ/gm
recession: 0.66 mm/2 hrs equivalent graphite recession: 30 cm ! equivalent SiC recession: 45 cm !

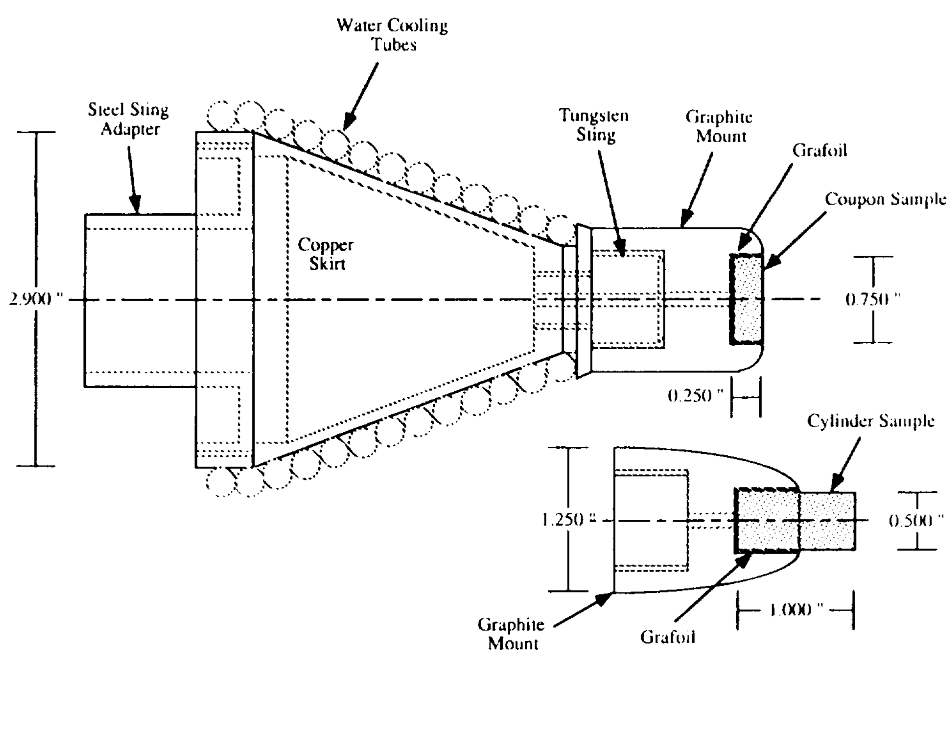
"These results illustrate the reuse capability of the boride composites... This capability is unrivaled by any other material system." - **Quote from Dr. Larry Kaufman, Principal Investigator in the Manlabs Studies**

Research Highlights for FY91

<u>Very-High Temperature Ceramics</u>

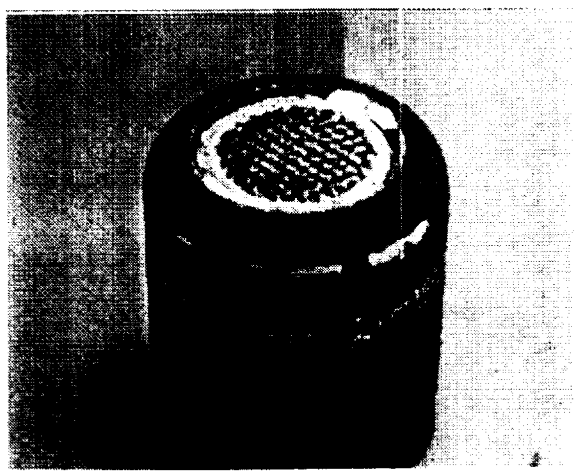
- Phase I arc-jet testing completed
- 19 reinforced Zr and Hf based ceramics tested (from Manlabs, Cerac, Lanxide, SAIC)
- Arc-jet data in good agreement with earlier Manlabs results
- Over 2 times RCC maximum heat flux capability demonstrated
- 2200°C+ (4000°F+) capability demonstrated
- Successfully applied ZrB_2 coatings to RCC using RF sputtering
- Phase II testing of disk samples, nosetip and leading edge components currently in progress

Sample Model Holder



Post-Test Photographs of RCC and ZrB_2 + 20 v/o SiC Samples

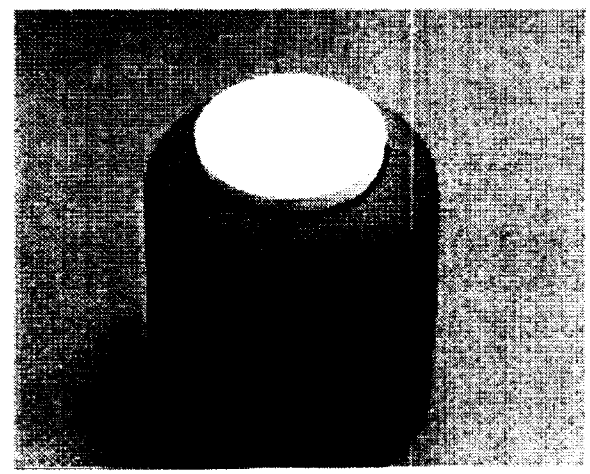
Test Conditions: test time = 3 min, cold wall heat flux = 295 W/cm^2; stag. press. = 0.046 atm, stag. enth. = 25 kJ/gm



LTV-t1n2a
RCC

Recession: 2.0 mm
Weight loss: 1.31 gm
Peak temp.: 2040 C

SiC coating lost after approximately 100 sec.



Cerac-t2n4a
ZrB_2 + 20v/o SiC

Recession: -0.03 mm
Weight loss: 0.01 gm
Peak temp.: 1820 C

Adherent, thin, glassy coating formed on sample

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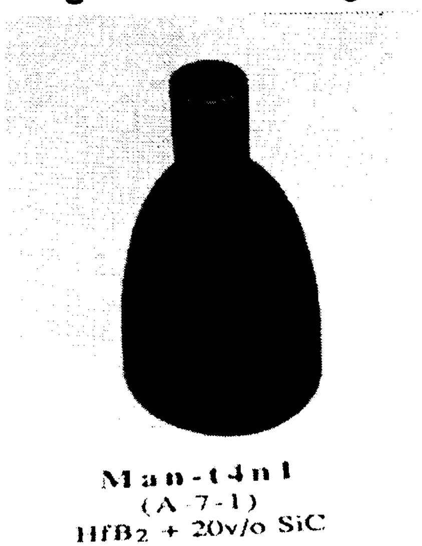
Post-Test Photographs of Two HfB_2 + 20 v/o SiC Samples

Test time = 5 min
Cold wall heat flux = 560 W/cm^2
Stag. press. = 0.075 atm
Stag. enth. = 27 kJ/gm



Recession: -0.05 mm
Weight loss: 0.00 gm
Peak temp.: 1740 C

Clear glassy coating formed on sample

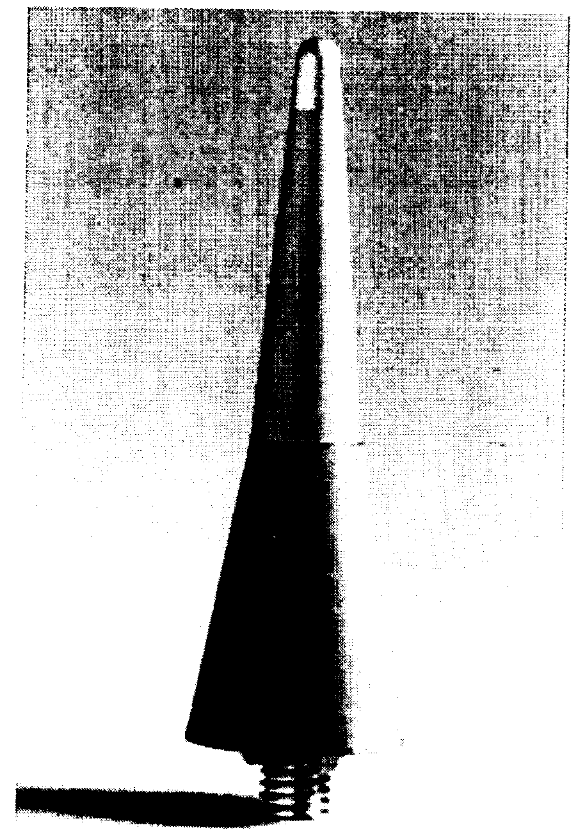
Test time = 3 min
Cold wall heat flux = 730 W/cm^2
Stag. press. = 0.105 atm
Stag. enth. = 27 kJ/gm

Recession: -0.03 mm
Weight loss: 0.08 gm
Peak temp.: 2460 C

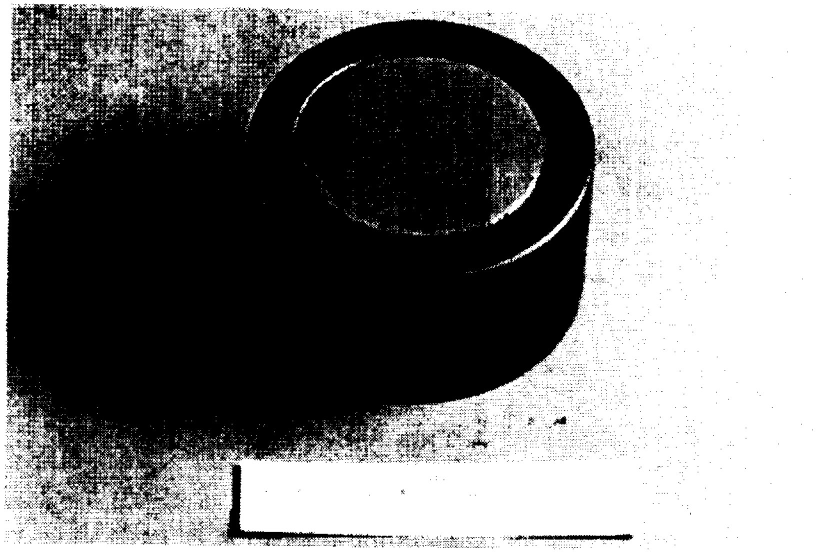
Adherent, thin oxide coating formed on sample

Diboride Components

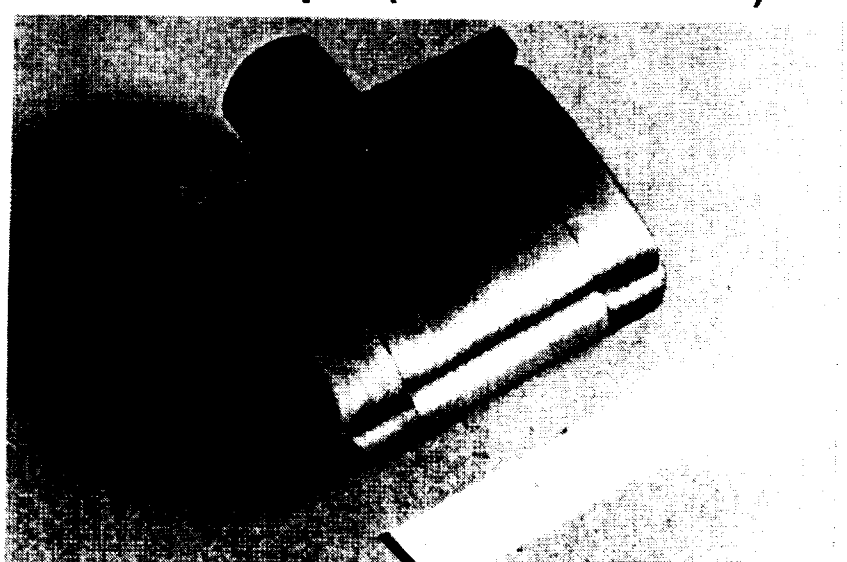
ZrB_2 + 20v/o SiC &
HfB_2 + 20v/o SiC Materials



Hypersonic Vehicle Nosetip
(0.141" nose radius)



Disk Sample (3" diam. x 0.25")



Leading Edge (4.0" x 0.5" diam.)

Table 1: Sample Components Advanced Refractory Composites (Testing Program Phase II) 10/28/91			
Sample Component	Matrix/ Reinforcement	Geometry/Dimension	Quantity
ManLabs-C1	ZrB_2/SiC_p	Coupons/2.8"Dia. x 0.25"	3
ManLabs-C2	ZrB_2/SiC_{pl}	Coupons/2.8"Dia. x 0.25"	3
ManLabs-C3	$ZrB_2/SiC_{pl}+C_{fch}$	Coupons/2.8"Dia. x 0.25"	3
ManLabs-LE	ZrB_2/SiC_{pl}	Leading Edge/0.75"Dia. x 2.75"	2
ManLabs-H1	HfB_2/SiC_{pl}	Hemisphere/0.700"Radius	1
ManLabs-H2	HfB_2/SiC_{pl}	Hemisphere/0.500"Radius	1
ManLabs-H3	HfB_2/SiC_{pl}	Hemisphere/0.125"Radius	1
ManLabs-NT	HfB_2/SiC_{pl}	Nose Tip/0.141"Radius on	3
ManLabs-S	ZrB_2/SiC_p	5.25 Deg. Cone Half Angle Skirt	1
Cerac-S	ZrB_2/SiC_p	5.25 Deg. Cone Half Angle Skirt	2
Cerac-C	ZrB_2/SiC_p	Coupons/2.8"Dia. x 0.25"	3
ACR-C1	ZrB_2/SiC_p+C_{fc}	Coupons/2.8"Dia. x 0.25"	2
ACR-C2	ZrB_2/SiC_p+SiC_{fc}	Coupons/2.8"Dia. x 0.25"	2
ARC-C1	ZrB_2 Coated RCC	Coupons/2.8"Dia. x 0.25"	1
ARC-C2	ZrB_2 Coated RCC	Coupons/2.8"Dia. x 0.25"	1
GA-C1	RS-HfB_2 Coated C/C	Coupons/2"Dia. x 0.25"	2
GA-C2	HfO_2 Coated RS-HfB2 Coated C/C	Coupons/2"Dia. x 0.25"	2
SAIC-C1	$ZrB_2/SiC+C_{fc}$	Coupons/2.8"Dia. x 0.25"	1
SAIC-C2	$ZrB_2/SiC+C_{fc}$	Coupons/2.8"Dia. x 0.25"	1
Total			35

Subscript definitions: p = particulate, pl = platelet, fc = continuous fiber, fch = chopped fiber

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  - TABI and CFBI Flexible Blankets
  - Aerogel Studies
- Light Weight Ablators
  - Polymer Filler + Rigid Ceramic Insulation
- Surface Coatings
  - Low Catalytic Efficiency, High Emissivity
  - Reflective

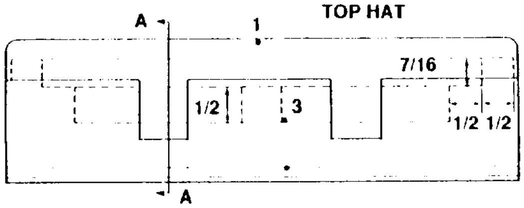
Research Highlights for FY91

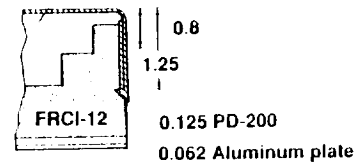
Ceramic Matrix Composites

- DuPont and SEP fabricated Nicalon, Nextel, and carbon fiber reinforced SiC matrix composites evaluated for aerothermal and mechanical performance
- Pre and post-test mechanical property characterization showed that carbon fiber reinforced materials have little degradation after arc-jet exposure to 2700°F for ten cycles of ten minutes each
- DuPont material found to be equivalent or better (particularly in quasi-isotropic configuration) than SEP material.
- Mass loss and mechanical property retention results in very good agreement with radiative heating testing data recently reported by General Dynamics
- New Ames developed "TOP HAT" CMC/rigid tile TPS, using Ames CVD/CVI fabricated C/SiC CMC, shown to survive multiple arc-jet exposures to 3100°F

CERAMIC MATRIX COMPOSITES PROGRAM

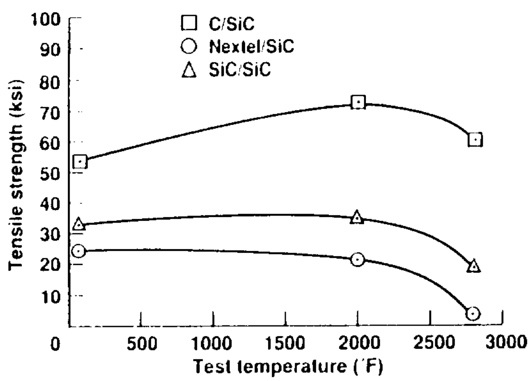
"TOP HAT" Assembly
Edge View



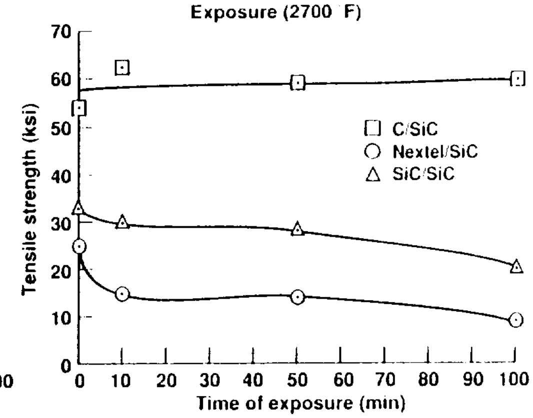


Section A-A

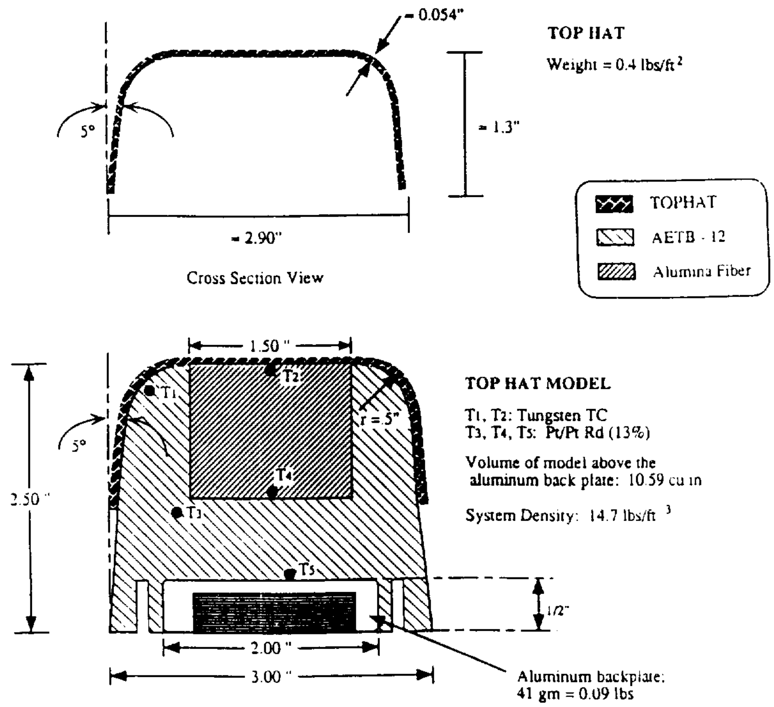
Average Tensile Strength vs. Temperature
Pre-aeroconvective Exposure (U)



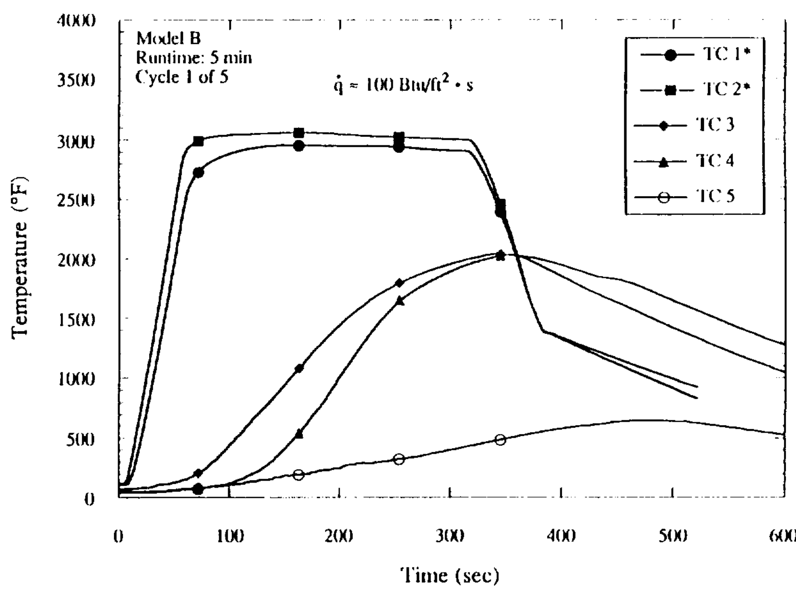
Average Tensile Strength (70 °F, Ar) of Carbon/SiC, Nextel/SiC, and SiC/SiC vs. Time of Aeroconvective Exposure (2700 °F)



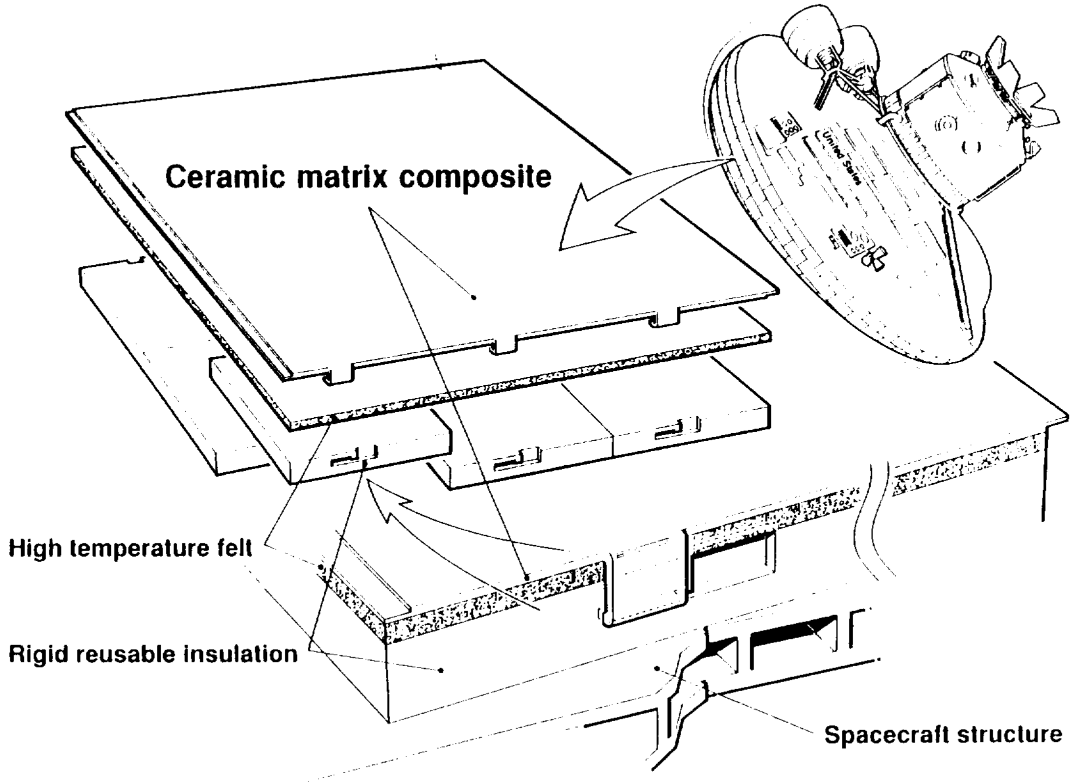
TOPHAT Thermal Protection System
Arc-Jet Model Design



Thermal Response Of TOPHAT Model
In An Aeroconvective Environment



TOP HAT
Thermal Protection System



Material/TPS Development Areas

Advanced Material Families

- Ceramic Matrix Composites
  - Very-High Temperature Ceramics (HfB_2 +SiC)
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  - Ceramic coatings processing
- Light Weight Ceramic Insulations
  - Rigid Tiles (AETB, SMI, UltraLight)
  - TABI and CFBI Flexible Blankets
  - Aerogel Studies
- Light Weight Ablators
  - Polymer Filler + Rigid Ceramic Insulation
- Surface Coatings
  - Low Catalytic Efficiency, High Emissivity
  - Reflective

Research Highlights for FY91

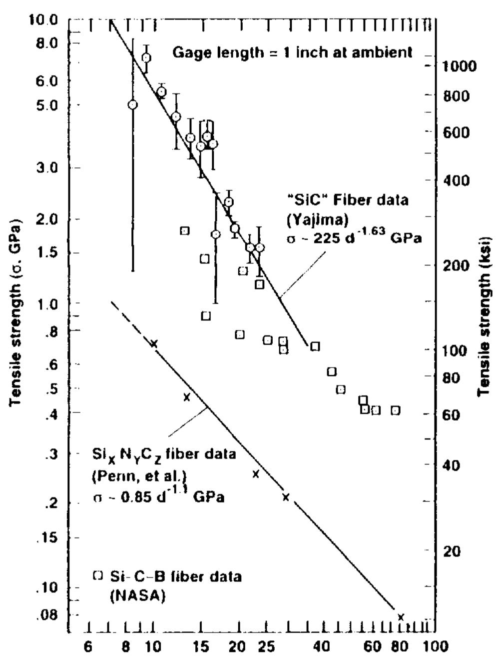
Polymer Precursors

- Low oxygen content Si/C/B polymers synthesized
- UV air and non-oxygen cure procedure demonstrated
- Ceramic fibers show tensile strength retention to 1300°C
- Successfully synthesized Zircon/ZrB_2/SiC 20 mil tapes using a combination of tape casting and sol-gel processing

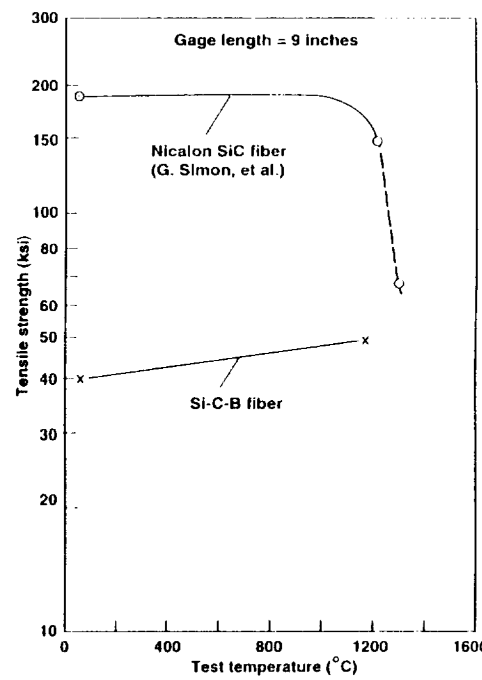
Ceramic Coating Processing

- Successfully applied thin (20 micron) coatings for ZrB_2 to a SiC substrate using RF sputtering
- Planning initial trials for plasma spraying ZrB_2 and ZrB_2/SiC using a constricted arc-jet

TENSILE STRENGTH OF SiC, Si-C-N and Si-C-B FIBERS AS A FUNCTION OF FIBER DIAMETER



TEMPERATURE EFFECTS ON FIBER TENSILE STRENGTH IN AIR



Ref. K.J. Wynne and R.W. Rice, Ann. Rev. Mater. Sci., 14, 297 - 334 (1984).

Maximum Cold Wall Heat Flux Computations

- For one-dimensional, radiative equilibrium, the maximum cold wall heat flux, Q_{cw}, can be computed from the maximum material use temperature, T_{max}, by:

$$Q_{cw} = \varepsilon\sigma T_{max}^4/(1 - H_w/H_r)$$

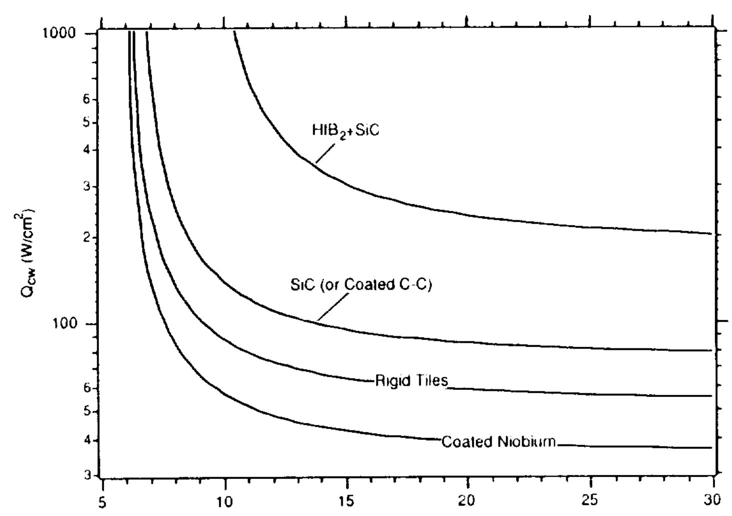
where ε is the emissivity and H_w is the wall gas enthalpy at T_{max}, and H_r is the local recovery enthalpy

- Surface catalytic effects all roll into the value of H_w
- With values for the material maximum use temperature and emissivity, Q_{cw} can be easily computed

Material	Maximum Use Temp. (C)	Emissivity
HfB_2+SiC	2480	0.62
SiC (or Coated C-C)	1760	0.76
Rigid Tiles	1540	0.85
Coated Niobium	1530	0.65

Maximum Cold Wall Heat Flux Computations

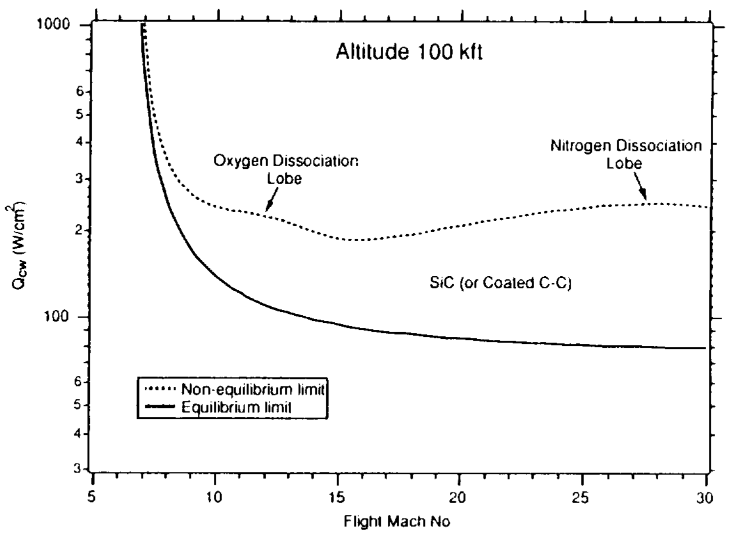
Q_{cw} for a Fully Catalytic Surface*



* H_w evaluated assuming chemical equilibrium

Maximum Cold Wall Heat Flux Computations

Range of Catalytic Effects on Q_{cw} for SiC*



* **Hw evaluated varying from equilibrium to maximum non-equilibrium value**