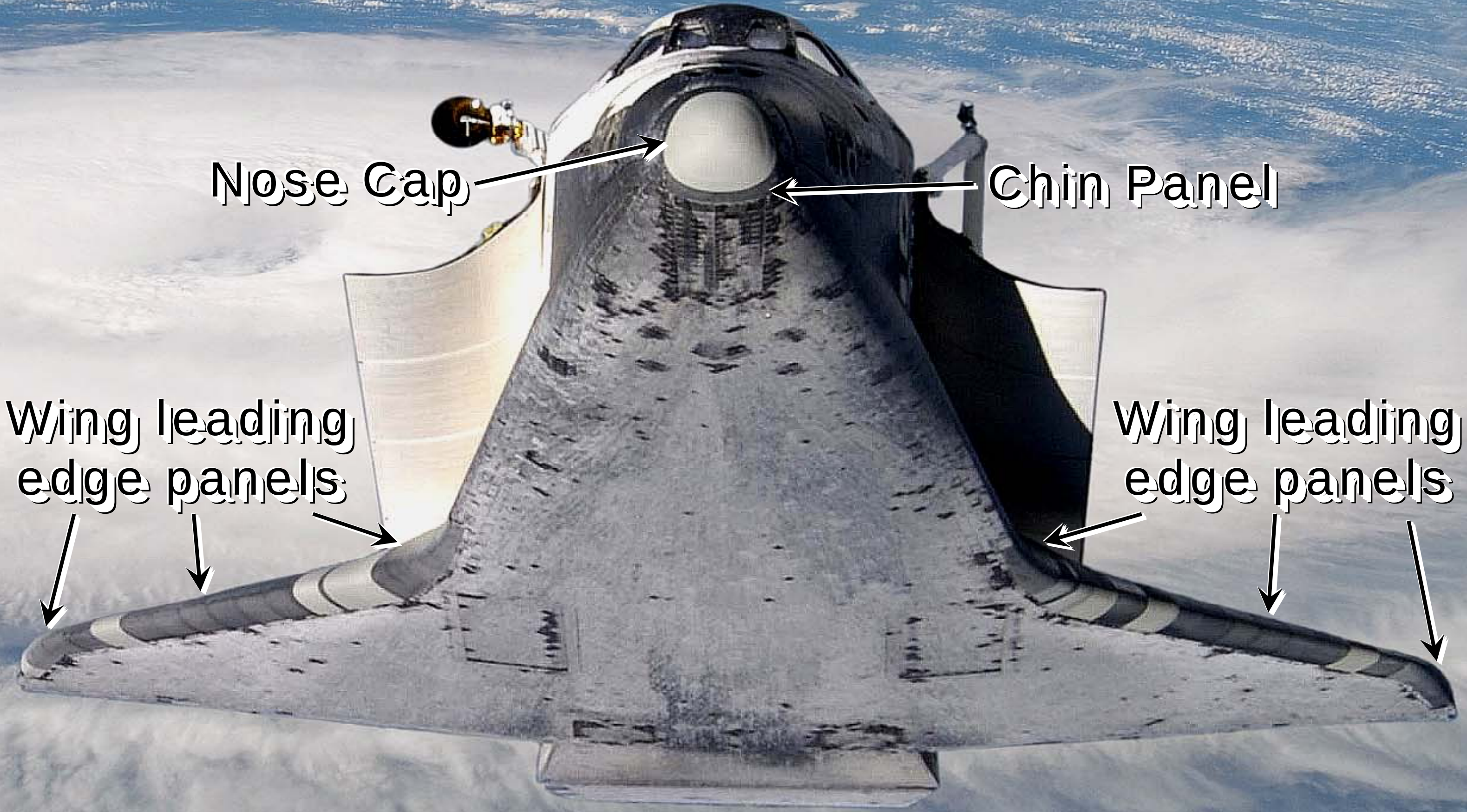
# Reinforced Carbon-Carbon (RCC)



Nose Cap

Chin Panel

Wing leading edge panels

Wing leading edge panels

# Leading Edge Structural Subsystem (LESS)

# RCC History

- A product of scientific minds at LTV Vought Corporation.
- 1960’s: Reinforced Pyrolyzed Plastic (RPP) used for TPS protection on Apollo command module.
- RPP earliest C-C material with real-life applications subsequently designated as ‘RCC’.
- 1970’s; ‘Siliconized’ (ceramic-coated) RCC substrate highly oxidation-resistant; selected for the STS Orbiter.
- 1980’s: Rayon-based RCC refined & improved while PAN-based ACC developed for future application.
- 1990’s: ACC/RCC development ends, only spare LESS articles now made on as-needed basis – Current.

# Manufacturing/Process

- **2-D composite lay-up & autoclave fabrication methods very similar to other laminated systems.**

- **Post-fab processing converts substrate into densified carbon-carbon via several cycles of pyrolysis and polymer impregnation (3 densification cycles to RCC-3).**

- **Outer 30-50mils (3-5 plies) of RCC-3 substrate is converted into β-SiC; Forms a functional gradient ceramic coating which protects the substrate from oxidation.**

- **Due to CTE mistmatch, craze cracks form; Subsequently filled by impregnations with an organosilicate (TEOS) which provides additional oxidation protection.**

- **In the field, Type A (silicate solution) applied periodically.**

# Manufacturing/Process

**Prepreg**
Carbon Cloth / Phenolic Resin

Precision Hand Lay-Up
Autoclave Cure (325°) & Post-Cure (500°)

**Cured Laminate**
(As-Molded State)

**Composite Fabrication Phase**

3 Day Pyrolysis in Coke Particles
(1500°F)

**RCC-0**
(1st Carbon State)

Vacuum/Pressure Resin Impregnation,
Pressure Cure & Post-Cure
(Polyfurfuryl Alcohol)

**RCC-0 BIM**
(1st Bimatrix State)

1500° Pyrolysis

**RCC-1**
(2nd Carbon State)

**Densification Cycle 1**

Resin Impregnation,
Cure & Post-Cure

**RCC-1 BIM**
(2nd Bimatrix State)

1500° Pyrolysis

**RCC-2**
(3rd Carbon State)

**Densification Cycle 2**

Resin Impregnation,
Cure & Post-Cure

**RCC-2 BIM**
(3rd Bimatrix State)

1500° Pyrolysis

**RCC-3**
(4th Carbon State)

**Densification Cycle 3**

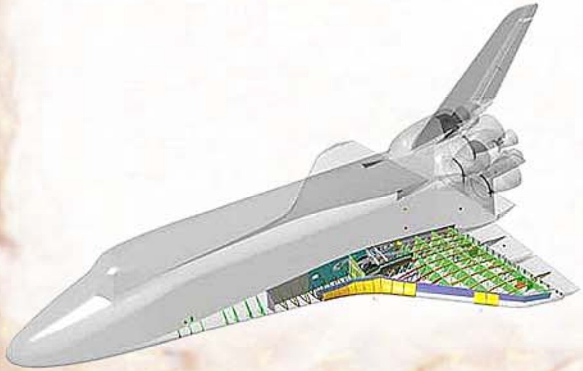
SiC Conversion Coating
via 3000° Solid State Pack Mix

**Coated RCC-3**

Vacuum TEOS Impregnation
Type A Sealant, Cure & Post-Cure

**Sealed RCC-3**

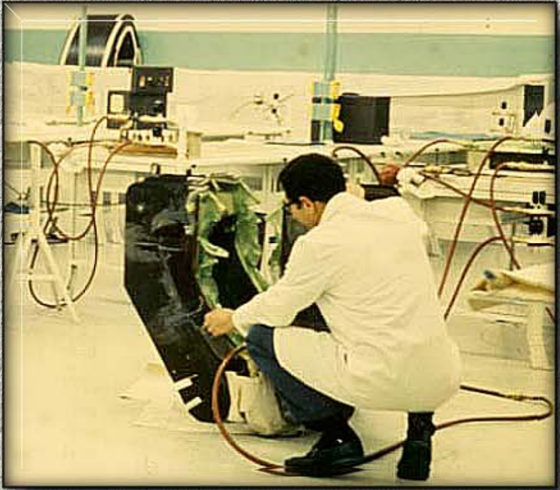
**Coating & Sealing Phase**

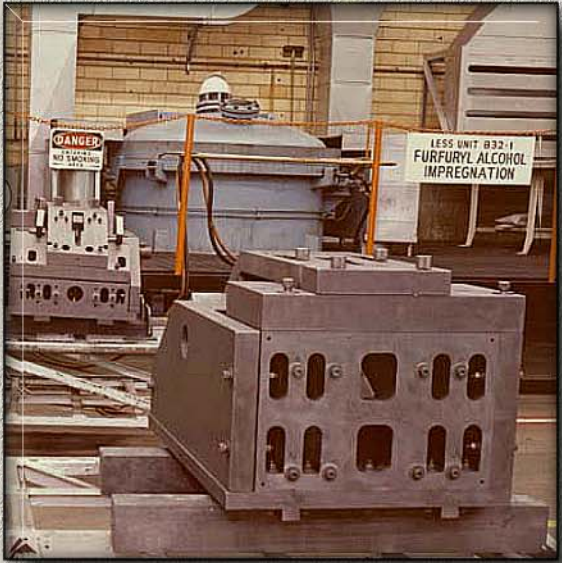


NDE inspections after molding and at RCC-3

1st machining after molding, final machining at RCC-3

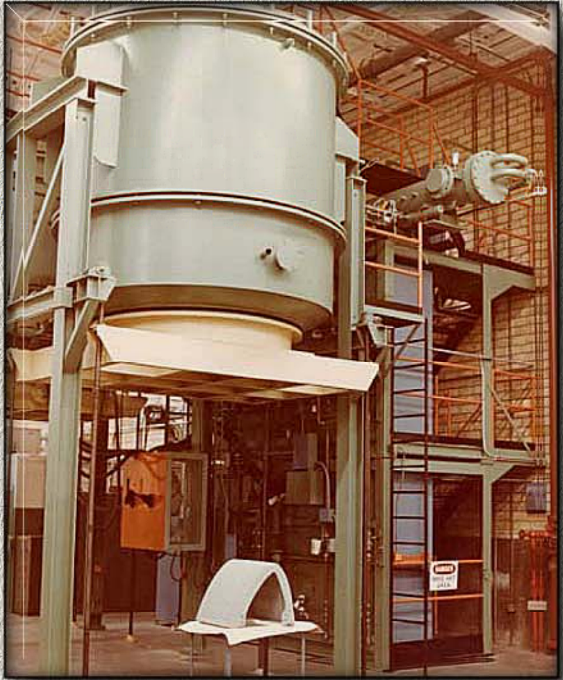
# Manufacturing/Process


Lay-up and debulking operations

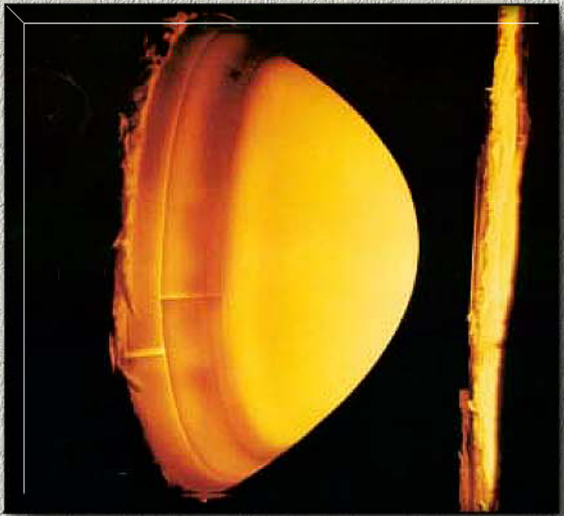


Pyrolysis restraint fixturing;
Impregnation chamber in background

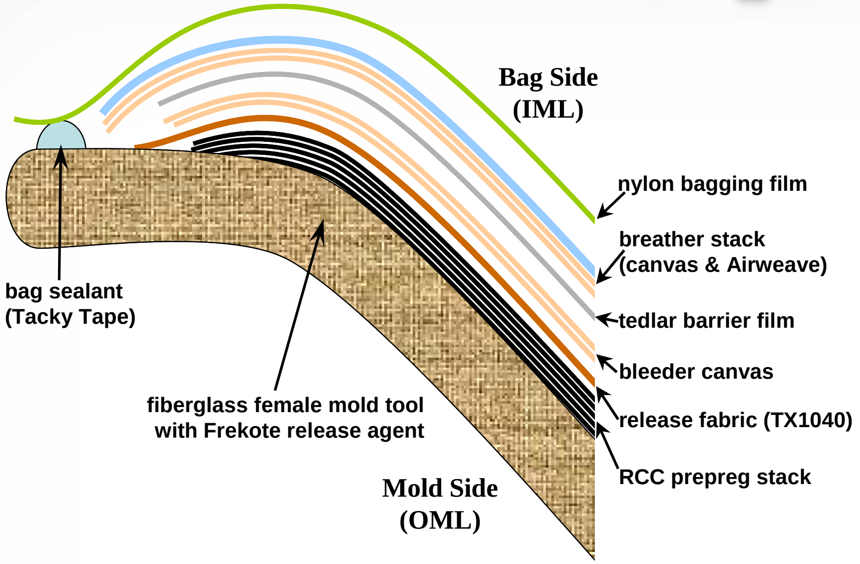

Pyrolysis retort with panels in furnace


72" conversion coating furnace

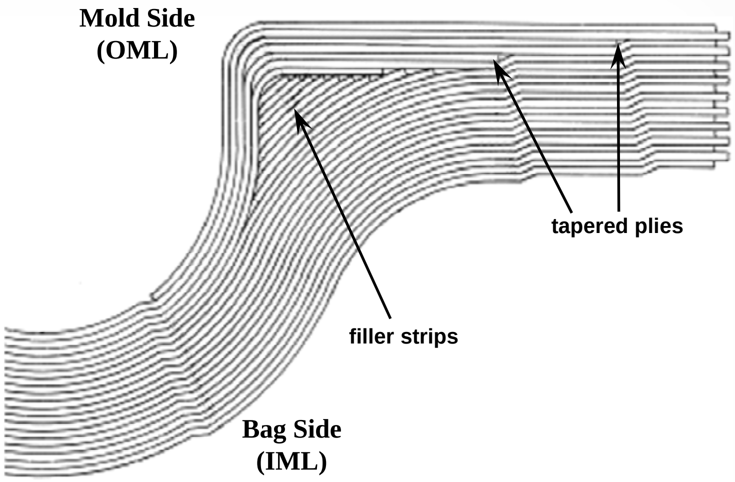

TEOS impregnation underway


Nose cone assembly under test

# RCC Composite Fabrication



Typical lay-up configuration for RCC/ACC



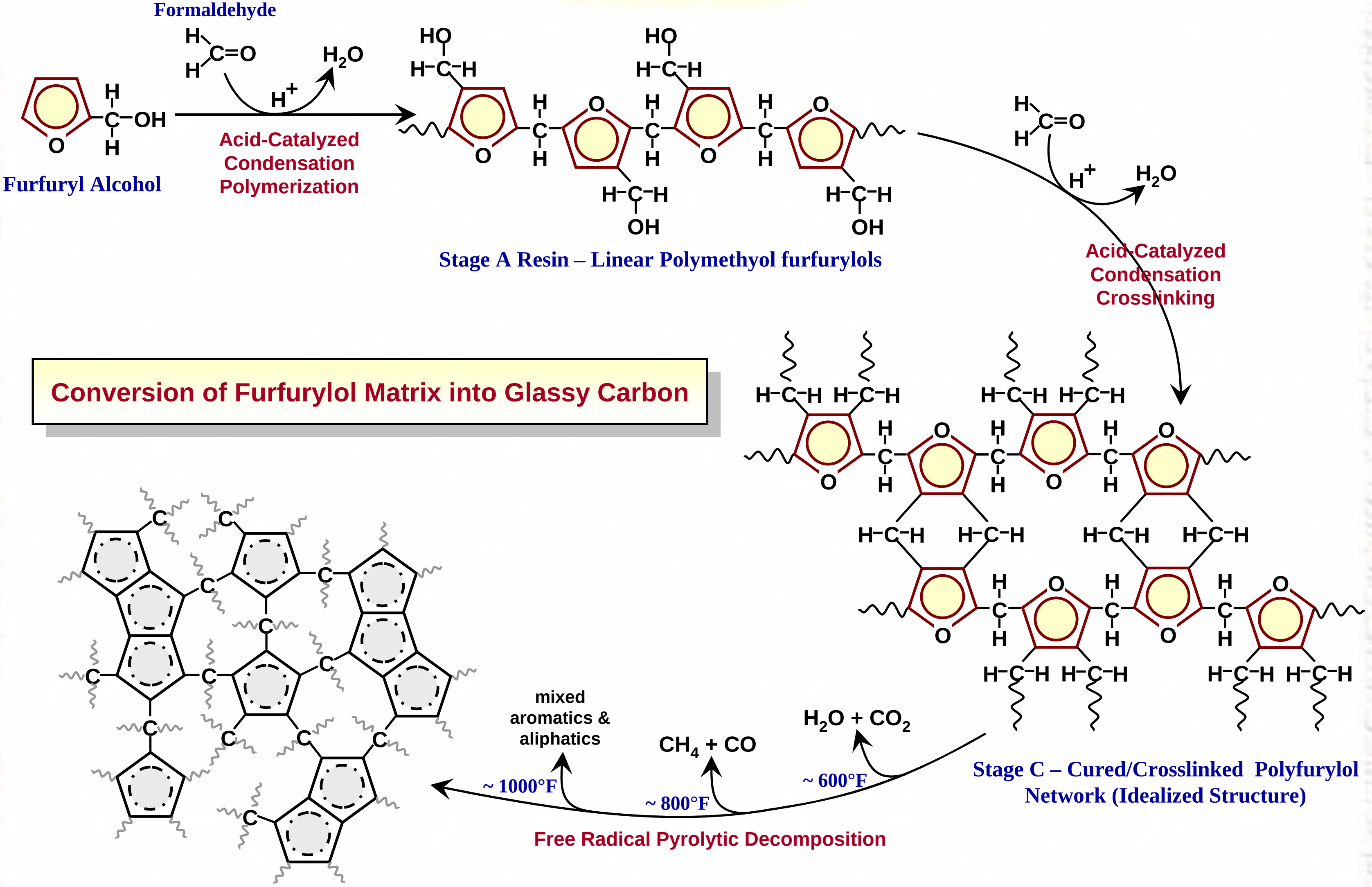
LESS lock side joggle radius lay-up design

- **Specific lay-up & autoclave methods establish substrate properties: Composite fiber volume fraction, Interconnecting porosity network, Ultimate mechanical properties**
- **Open mold, hand lay-up of carbon cloth phenolic prepreg into female tooling; Doubler packs, filler strips & flat acerage regions are tapered, draped, tailored, rollered & precisely crafted into place one ply at a time**
- **Vacuum debulked 1st and every 6 plies; Differential staging to improve resin distribution; Pre-bleed to reduce resin rich radii**

# RCC Chemistry

## Densification

**Conversion of Furfurylol Matrix into Glassy Carbon**



Furfuryl Alcohol

Acid-Catalyzed Condensation Polymerization

Stage A Resin – Linear Polymethyol furfurylols

Acid-Catalyzed Condensation Crosslinking

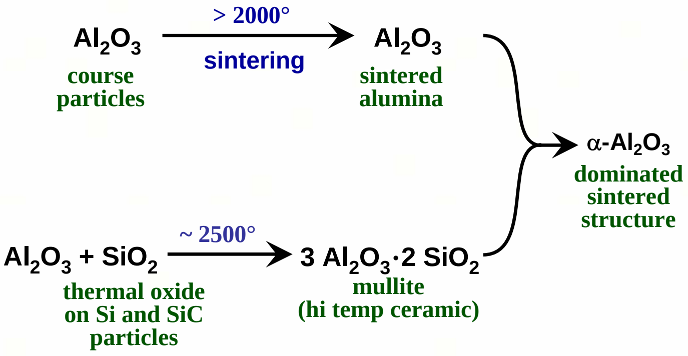
Stage C – Cured/Crosslinked Polyfurylol Network (Idealized Structure)

Free Radical Pyrolytic Decomposition

Charred Furfurylol Carbon Matrix
(Proposed Structure - Idealized)
Inorganic Glassy Carbon

# RCC Chemistry
## Coating & Sealing

### 10% $Al_2O_3$ + 30% Si + 60% SiC Ceramic Pack Mix for Conversion of RCC/ACC Substrates



$Al_2O_3 \xrightarrow[\text{sintering}]{> 2000°} Al_2O_3$

course particles

sintered alumina

$Al_2O_3 + SiO_2 \xrightarrow{\sim 2500°} 3\,Al_2O_3 \cdot 2\,SiO_2$

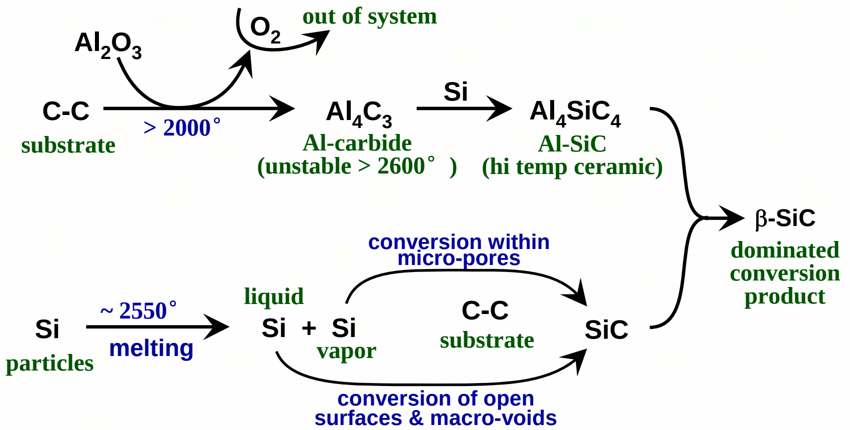
thermal oxide on Si and SiC particles

mullite (hi temp ceramic)

$\rightarrow \alpha\text{-}Al_2O_3$

dominated sintered structure

**Pack Mix Sintering Reactions**



$Al_2O_3$

$O_2$ out of system

$\text{C-C} \xrightarrow{> 2000°} Al_4C_3 \xrightarrow{Si} Al_4SiC_4$

substrate

Al-carbide (unstable > 2600° )

Al-SiC (hi temp ceramic)

$Si \xrightarrow[\text{melting}]{\sim 2550°}$ liquid Si + Si vapor

particles

conversion within micro-pores

C-C substrate

SiC

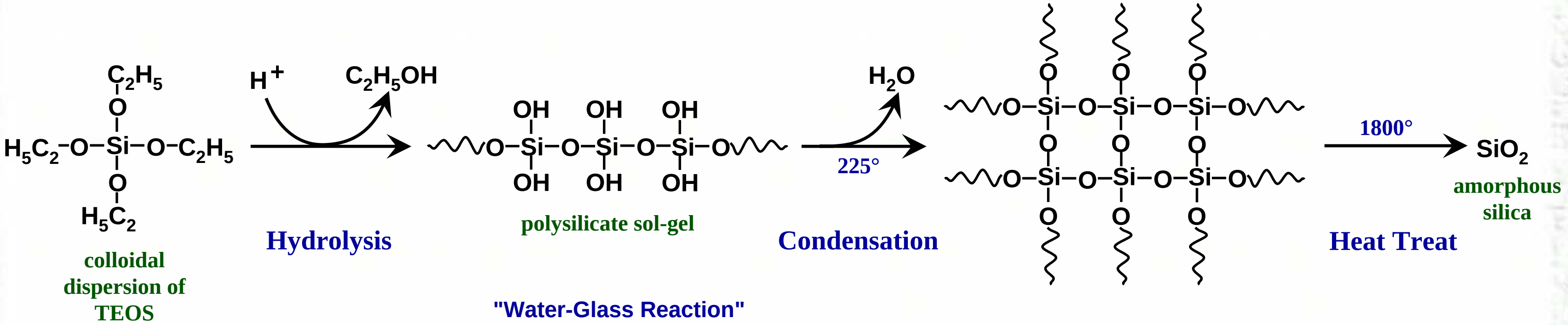
conversion of open surfaces & macro-voids

$\rightarrow \beta\text{-}SiC$

dominated conversion product

**Substrate Conversion Reactions**

### TEOS Sol-Gel Sealing Process for SiC-Coated Substrates



colloidal dispersion of TEOS

Hydrolysis

polysilicate sol-gel

Condensation

Heat Treat

amorphous silica

"Water-Glass Reaction"

# RCC Physical Properties

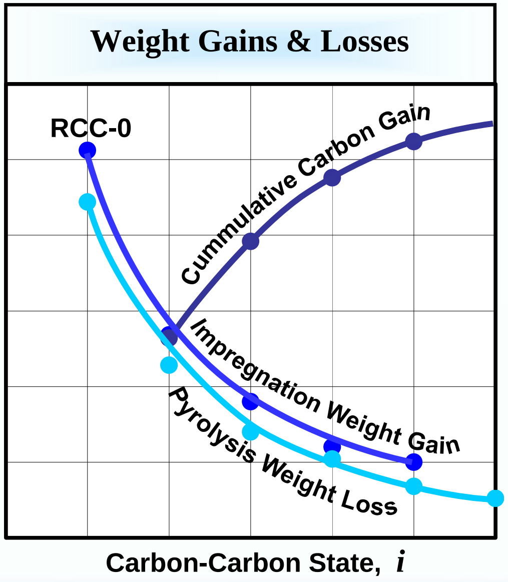
| Uncoated RCC-3 Properties, Typical | |
|---|---|
| Tension (in plane) | 7000 - 10000 psi |
| Flexure (4-point loading) | 15000 - 20000 psi |
| Interlaminar (Flatwise) Tensile | 800 - 1200 psi |
| Interlaminar Shear (via double notch) | 1500 - 2500 psi |
| In-Plane Shear (via double notch) | 6000 - 6500 psi |
| Fiber Volume Fraction | 55 - 60% |
| Bulk Density | 1.30 - 1.40 g/cc |
| Open Porosity | 10 - 15% |

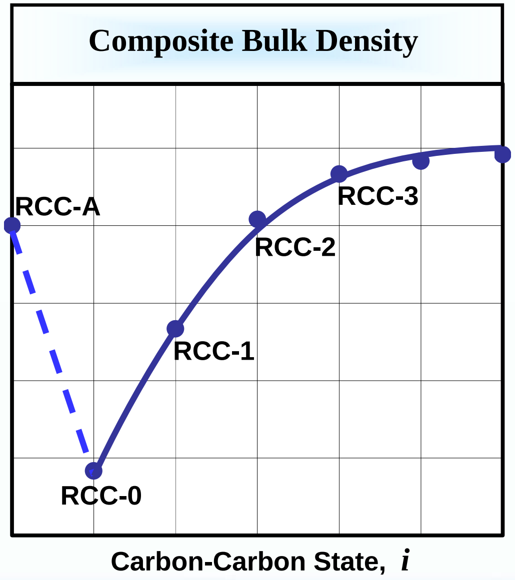
| Coated RCC-3 Properties, Typical | |
|---|---|
| Tension (in plane) | 6000 - 9000 psi |
| Flexure (4-point loading) | 13000 - 17000 psi |
| Interlaminar (Flatwise) Tensile | 600 - 1000 psi |
| Interlaminar Shear (via double notch) | 1200 - 2200 psi |
| In-Plane Shear (via double notch) | 5500 - 6000 psi |
| Coating Weight Gain | 15 - 25% |
| Coating Thickness, Mold Side | 30 - 40 mils |
| Coating Thickness, Bag Side | 40 - 50 mils |

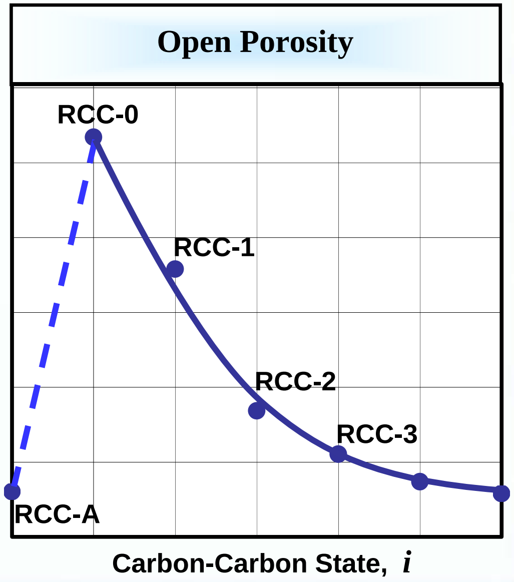
$$W_i = 1-\left(1-W_A\right)\prod_0^i\left(1-\eta_{li}\right)^{-1}\prod_1^i\left(1+\eta_{g(i-1)}\right)^{-1}$$

$$\rho_b = \left(f_w\rho_f^{-1}+m_w\rho_m^{-1}\right)^{-1}\left(1-p\right)$$

$$p = 1-\rho_b\left[\left(1-m_w\right)\rho_f^{-1}+m_w\rho_m^{-1}\right]$$

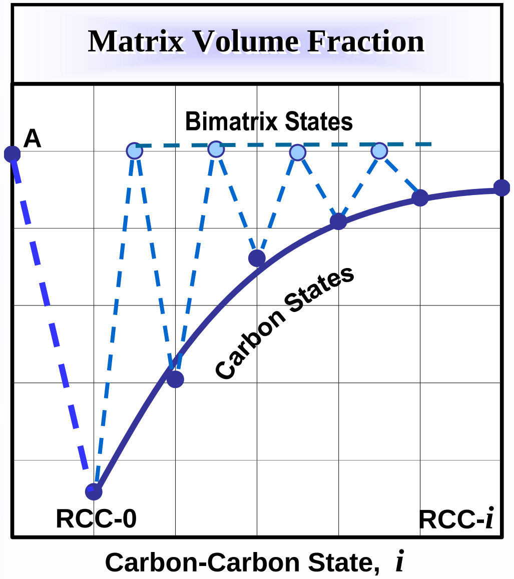

**Weight Gains & Losses**


**Composite Bulk Density**

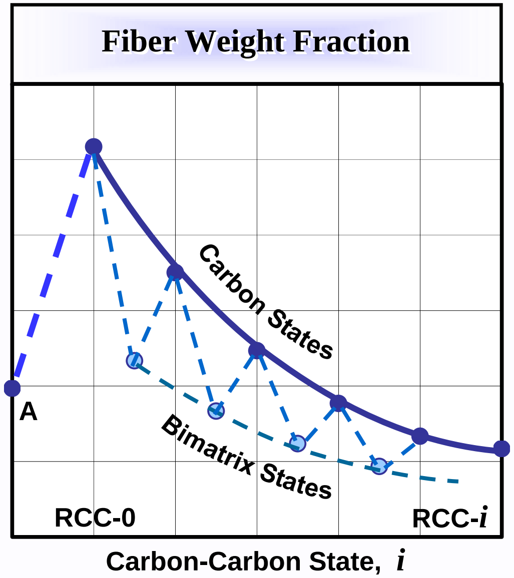

**Open Porosity**

# Process Characterization

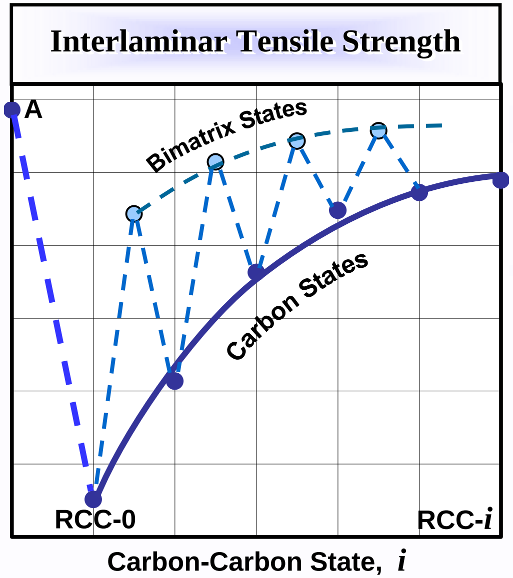
**Substrate Densification = Matrix Densification**



**Matrix Volume Fraction**



**Fiber Weight Fraction**



**Interlaminar Tensile Strength**

**Matrix Content in Terms of Densification Weight Changes:**

At RCC-0 . . . .
$$m_{w0} = 1-\left(1-m_{wA}\right)\left(1-\eta_{l0}\right)^{-1}$$

At RCC-1 . . . .
$$m_{w1} = 1-\left(1-m_{wA}\right)\left(1-\eta_{l0}\right)^{-1}\left(1+\eta_{g0}\right)^{-1}\left(1-\eta_{l1}\right)^{-1}$$

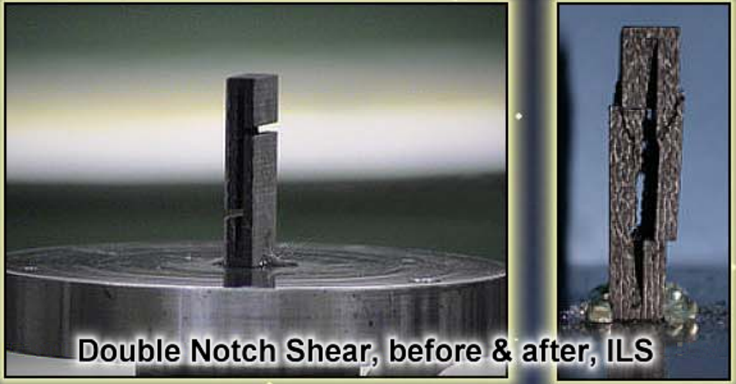
At RCC-*i* . . .
$$m_{wi} = 1-\left(1-m_{wA}\right)\prod_{0}^{i}\left(1-\eta_{li}\right)^{-1}\prod_{1}^{i}\left(1+\eta_{g(i-1)}\right)^{-1}$$

$$I_i = A\left(1-e^{-ki}\right)+C$$

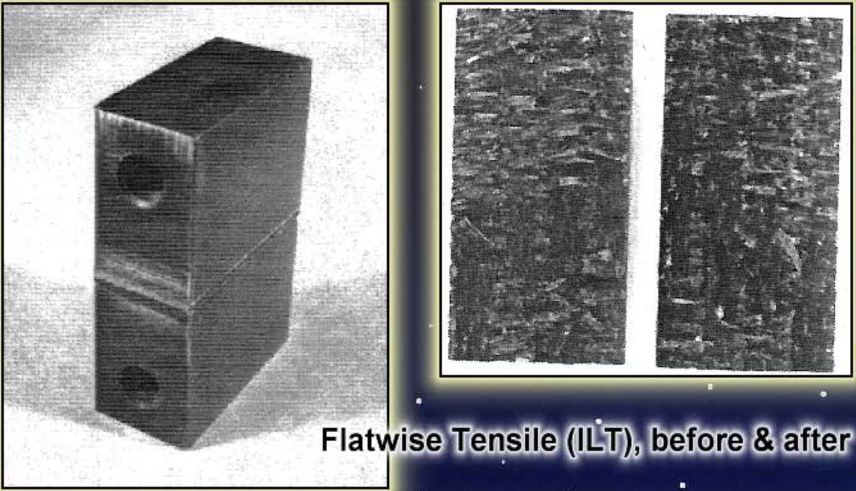
$$I_\infty \to A+C$$

$$I_0 \to C$$

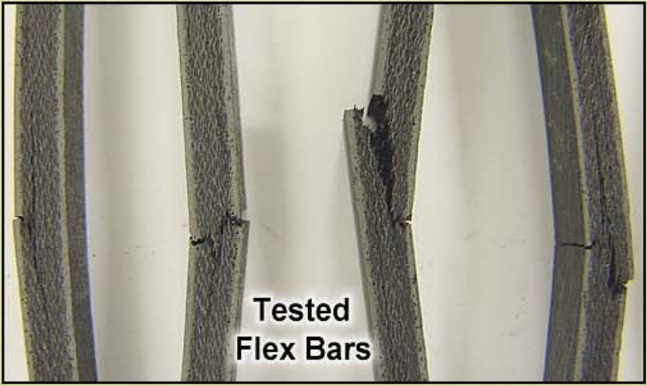
# Mechanical Testing



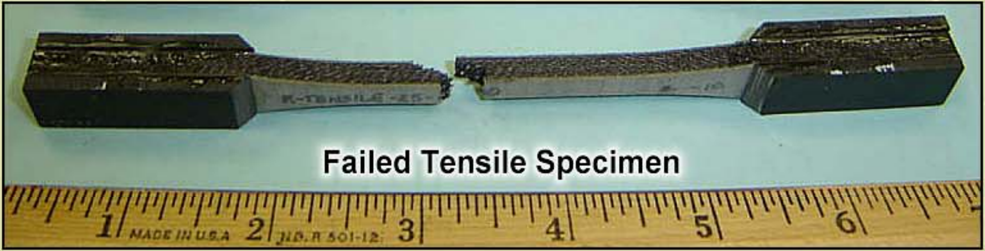
Double Notch Shear, before & after, ILS



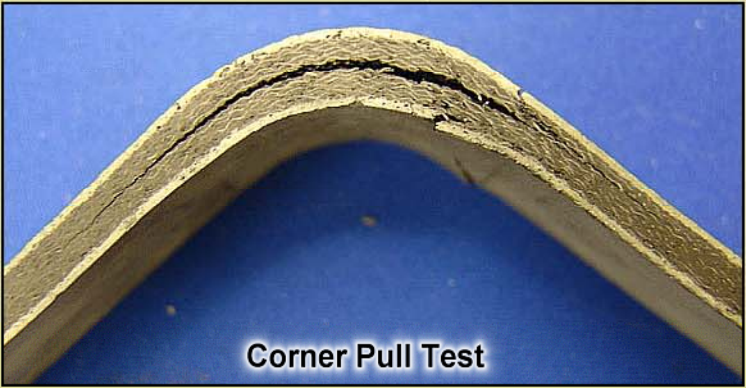
Flatwise Tensile (ILT), before & after



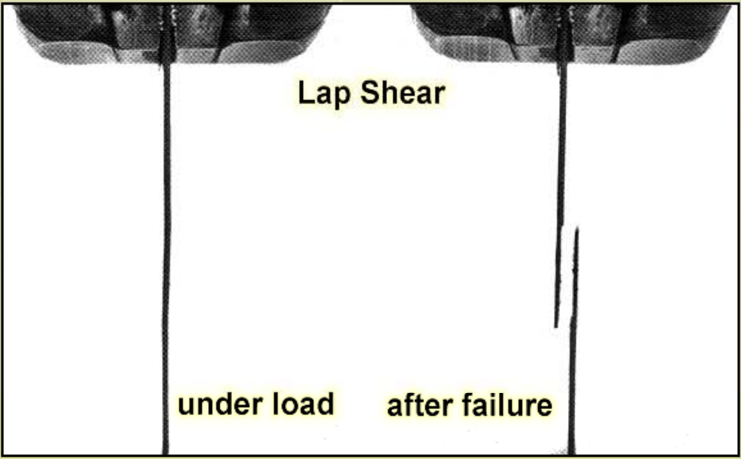
Tested Flex Bars



Failed Tensile Specimen

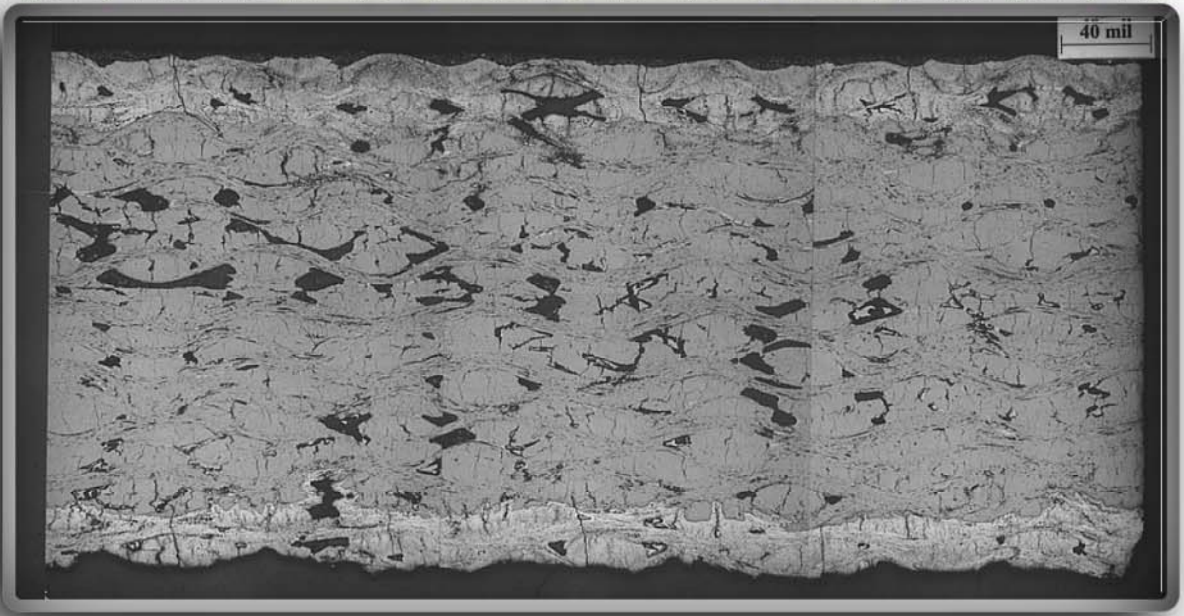


Corner Pull Test



Lap Shear

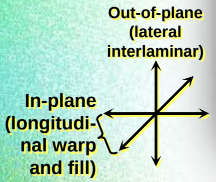
# RCC Cross-Sectional View



SiC ceramic coating phase (IML bag side)

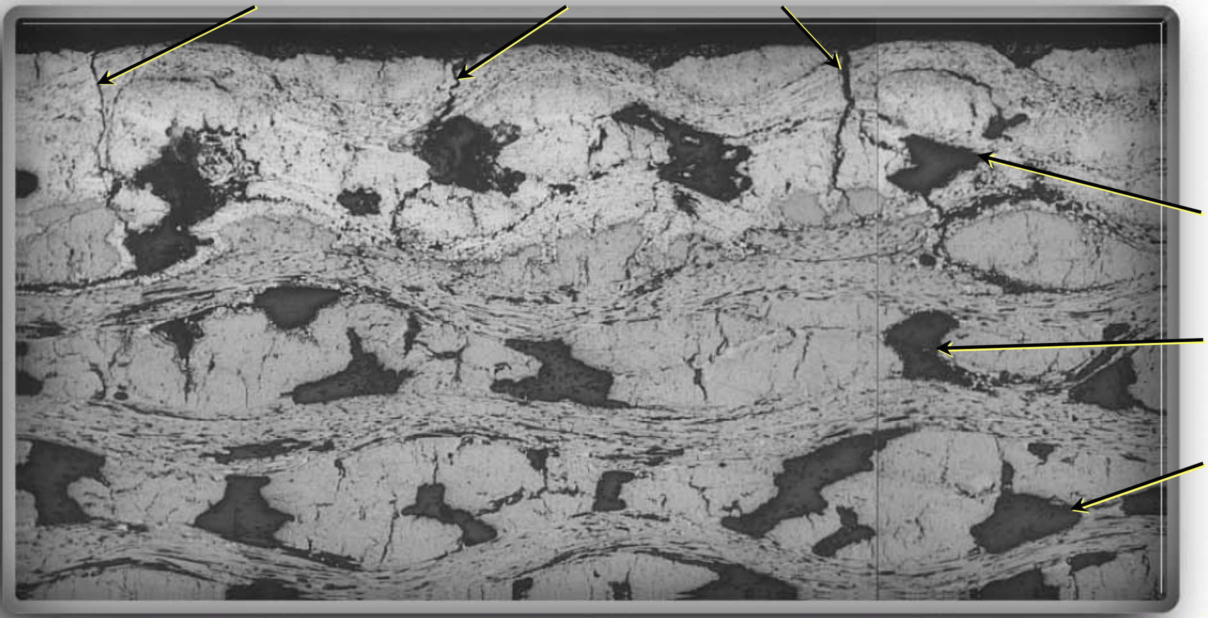
C/C substrate (19 ply flat acerage area)

SiC ceramic coating phase (OML mold side)


Out-of-plane (lateral interlaminar)

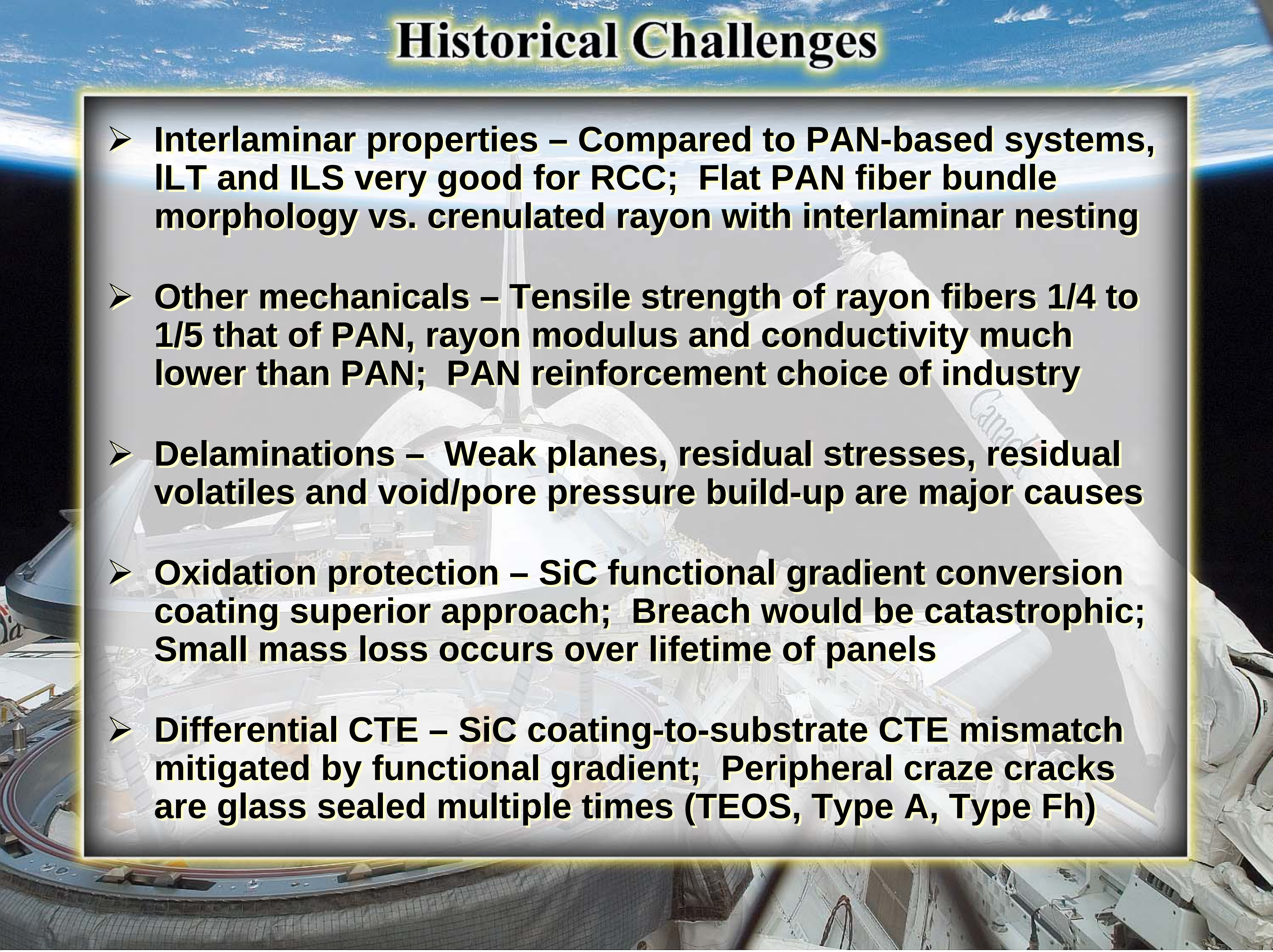
In-plane (longitudinal warp and fill)

Craze cracks due to coating-to-substrate CTE differential



Interface region and gradient conversion zone separating the SiC ceramic phase and RCC-3 carbon substrate

Remnant voids and pores: A combination of closed and open microvoids and macropores which were partially permeable or completely impervious to lateral intrusion fluids



# Historical Challenges

- **Interlaminar properties – Compared to PAN-based systems, ILT and ILS very good for RCC; Flat PAN fiber bundle morphology vs. crenulated rayon with interlaminar nesting**

- **Other mechanicals – Tensile strength of rayon fibers 1/4 to 1/5 that of PAN, rayon modulus and conductivity much lower than PAN; PAN reinforcement choice of industry**

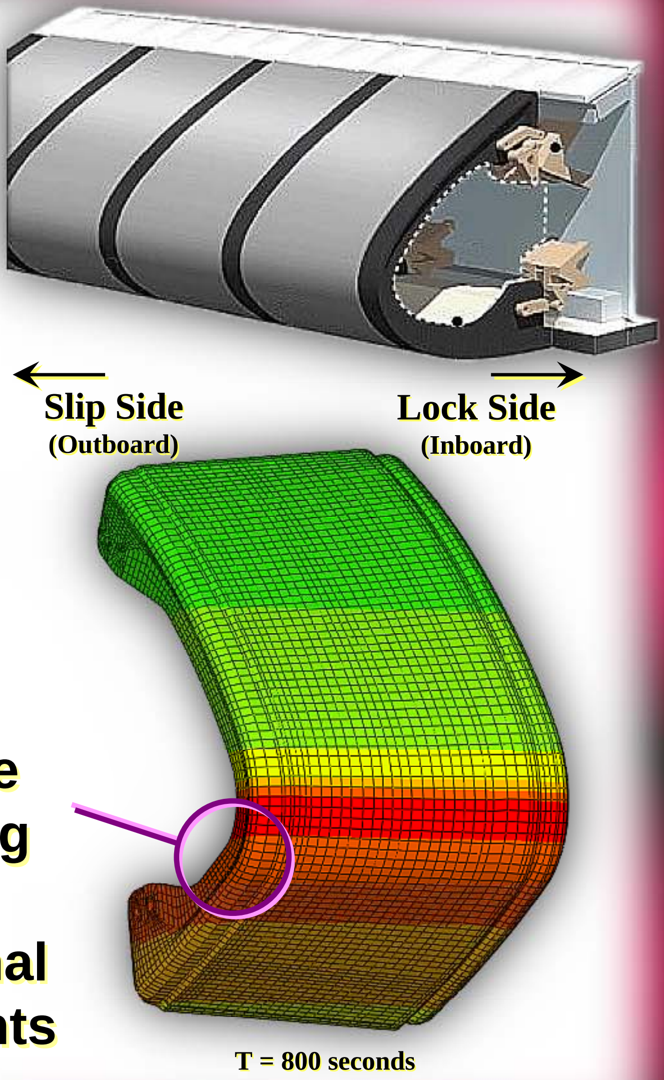
- **Delaminations – Weak planes, residual stresses, residual volatiles and void/pore pressure build-up are major causes**

- **Oxidation protection – SiC functional gradient conversion coating superior approach; Breach would be catastrophic; Small mass loss occurs over lifetime of panels**

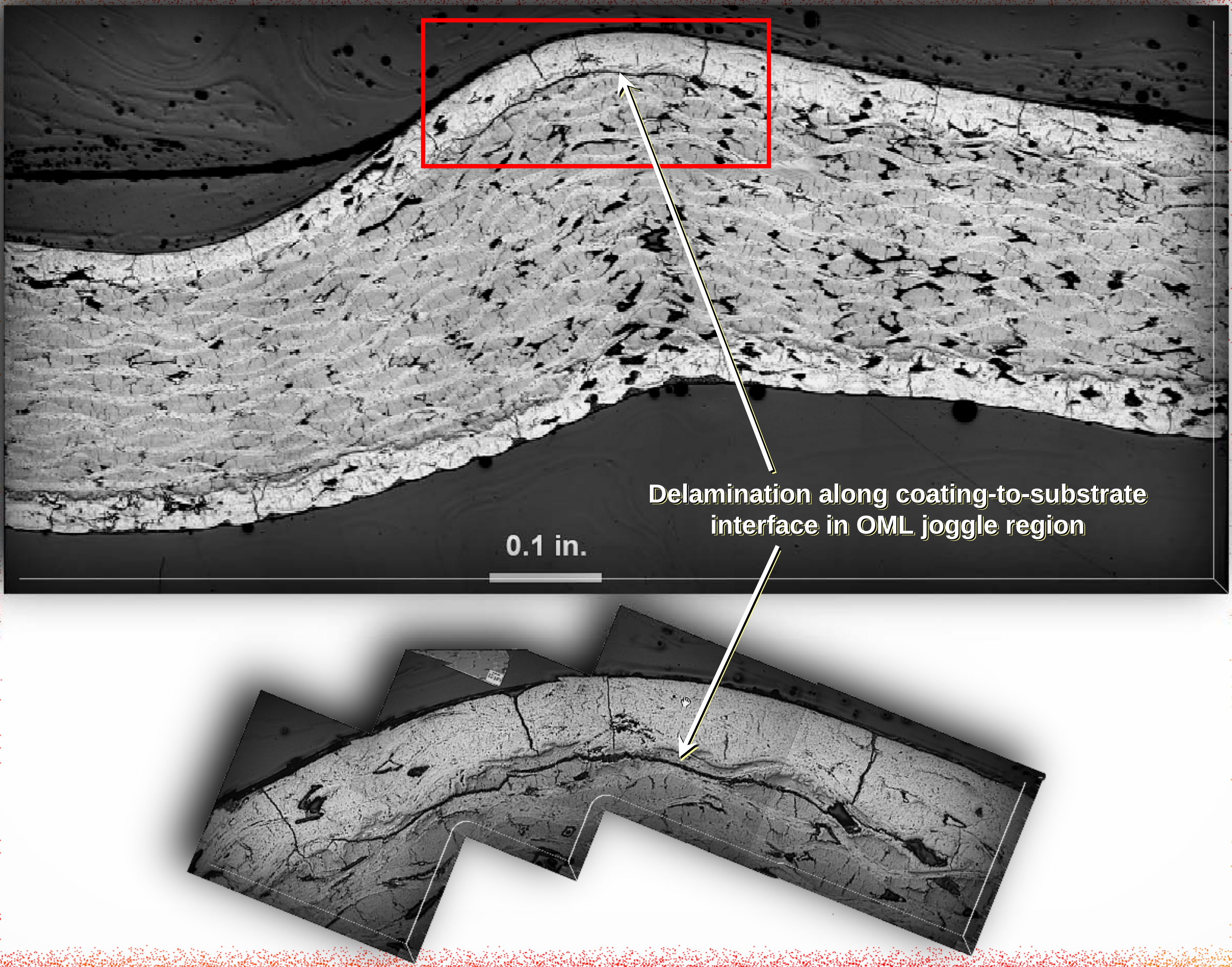
- **Differential CTE – SiC coating-to-substrate CTE mismatch mitigated by functional gradient; Peripheral craze cracks are glass sealed multiple times (TEOS, Type A, Type Fh)**

# Current Problems

- Weakened coating-to-substrate adhesion found on wing panel after STS-114 led to coating spallation
- Other panels/flights have shown indications and sub-coating delams
- Tiger Team formed to identify root cause and pass/fail criteria; 25 - 30 missions before indications appear
- Failures predominant along slip-side OML joggle radius, under the coating
- Thermal models indicate high thermal flux in this area during re-entry events



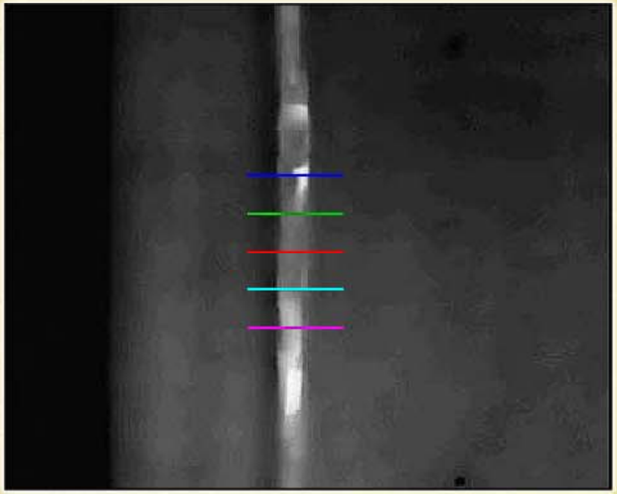
# Current Problems

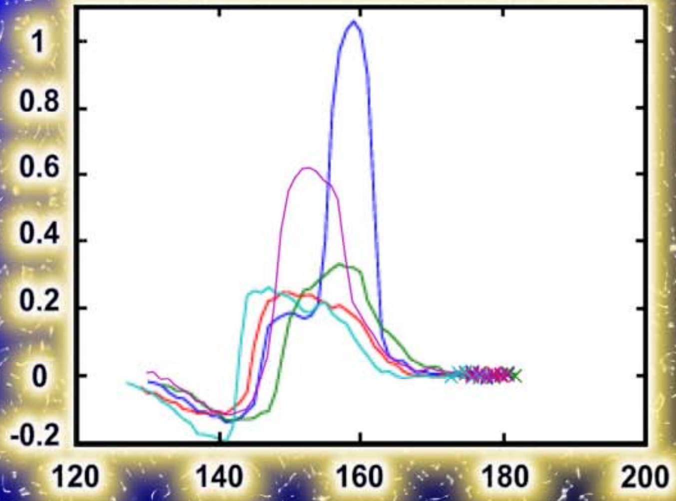


Delamination along coating-to-substrate interface in OML joggle region

# Current Problems

- **Flash IR Thermography NDE technique being refined to identify pass/fail criteria and material property correlations**
- **Minimum 0.2 IR indication proposed by NESC; Tiger Team decisions based on flight-to-flight delta**





# Root Cause Status

- Testing & analysis currently underway at various centers to understand root cause including materials property characterization to re-entry loads to thermal cycling
- Working theories include sealant reactions, refurbishment effects, pore pressure build-up, IML fabric distortions, bag side impressions and thermomechanical fatigue
- Likely cause attributed to thermomechanical fatigue coupled with stresses generated during manufacturing or from repeated re-entry episodes

# The Ultimate Frontier

## Where No Man Has Gone Before