Analysis of PICA-NuSil at the Hypersonic Materials Environmental Test System (HyMETS)

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Overview

1. Phenolic Impregnated Carbon Ablator (PICA) and NuSil.

2. Mini Sphere-Cone Architecture and HyMETS Facility.


4. Decomposition Mechanism of NuSil.
**Particulate Shedding Mitigation / PICA – NuSil**

<table>
<thead>
<tr>
<th>Phenolic Impregnated Carbon Ablator (PICA)</th>
<th>NuSil (CV-1144-0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• PICA - created by NASA at Ames Research Center 1995.</td>
<td>• Viscosity: 240 cP</td>
</tr>
<tr>
<td>• Manufactured by impregnating a carbon-fiber preform with phenolic resin.</td>
<td>• Cure time: 7 days</td>
</tr>
<tr>
<td>• PICA gained flight heritage during Stardust and is the baseline material for missions to Mars.</td>
<td>• Cure System: Oxime</td>
</tr>
<tr>
<td>• PICA is friable.</td>
<td>• Refractive index: 1.43</td>
</tr>
<tr>
<td>• Therefore, a coating is applied to the surface of flight material to mitigate particle shedding during assembly, test, and launch operations.</td>
<td>• Specific Gravity: 1</td>
</tr>
</tbody>
</table>

**NuSil**

- CV-1144-0 is a single-component RTV dispersion in VM&P Naphtha.
- Polymerization initiates upon contact with atmospheric moisture.
- Pendant monomers of siloxane polymer strands are functionalized with hydroxyl groups.
- Primary Use: Protection against atomic oxygen in L.E.O.
• The main constituent of NuSil is a siloxane copolymer with monomer units that are functionalized with phenyl and methyl groups. (~974 monomer units / polymer chain)
• The end of the polymer chain is functionalized with hydroxyl groups.
• NuSil contains an oxime crosslinking agent (5 – 10 wt. %) that reacts with pendant hydroxyl groups when exposed to atmospheric moisture.
• The crosslinking agent influences the material properties of NuSil (e.g., thermal stability, mechanical, etc).
NuSil Coating Process and Terminology

- NuSil diluted with Naphtha until a viscosity of 18 seconds is achieved as measured with a #2 Zahn cup.

- Diluted NuSil is applied to the surface of the test article with a Paasche air brush.

- One box coat is equivalent to a pass in one direction and an additional pass in the orthogonal direction.
Mini Sphere-Cone Models

Model Architecture

• Sphere-cone architecture chosen, in-part, to observe viscous flow phenomena.

• PICA plug fitted with two R-type thermocouples (T.C. 1 & 2) and two K-type thermocouples (T.C. 3 & 4) spaced 5 mm apart.

• Mini sphere-cone shell bonded to a graphite sting adapter using RTV-560.
Hypersonic Materials Environmental Test System (HyMETS)

- Plasma generator – segmented arc-heater.

- Arc produced between two electrodes made of multiple stacked copper discs.

- Argon is introduced into anode and cathode to assure sufficient ionization and protect against oxidation.

- Test gases (e.g., Air, N\textsubscript{2}, CO\textsubscript{2}, etc.) are introduced into the constrictor column which is made of water-cooled discs.

- The length of the constrictor column is tailored for desired performance.

- High-temperature plasma introduced into vacuum chamber through convergent-divergent nozzle.
• High-speed cameras were used to observe salient phenomena of the test article surface.

• A two-color pyrometer was used to measure the surface temperature ($T_s$).

• A suite of emission spectrometers were used to analyze species in the post-shock region.

• Data collected in 3 flow compositions (e.g., Air, $N_2$, $CO_2$).

### PICA-N HyMETS I Test Conditions

<table>
<thead>
<tr>
<th>Material</th>
<th>Model Number</th>
<th>Simulated Atmosphere</th>
<th>Heat Flux (W/cm²)</th>
<th>Stagnation Pressure (kPa)</th>
<th>Duration (s)</th>
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</thead>
<tbody>
<tr>
<td>PICA-N</td>
<td>1</td>
<td>Earth</td>
<td>140</td>
<td>5.6</td>
<td>28</td>
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<td>140</td>
<td>5.6</td>
<td>30</td>
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<td>6</td>
<td>$N_2$</td>
<td>131</td>
<td>5.3</td>
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<td>PICA-N</td>
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<td>Mars</td>
<td>127</td>
<td>5.2</td>
<td>33</td>
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<tr>
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<td>$N_2$</td>
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<tr>
<td>PICA-N</td>
<td>12</td>
<td>Mars</td>
<td>170</td>
<td>5.3</td>
<td>31</td>
</tr>
</tbody>
</table>

**HyMETS Facility**

- High Speed Cameras
- Spectrometer
- Arc-Heater
- Pyrometer
Salient Observations

- The coating suppresses the surface temperature relative to virgin PICA in flow compositions primarily composed of air and CO₂.
- The coating suppresses the in-depth temperature response relative to virgin PICA.
- Eventually the coating decomposes and exposes the underlying char layer to the flow.
- The surface temperature of coated models does not reach the same magnitude as the surface temperature of virgin PICA during the test.
The presence of the coating reduces the recession in all environments.
HyMETS Emission Data – Air

- The figure on the left provides a comparison of surface temperature and emission data collected on PICA-N (3 box coats) and the virgin material.

- Red dots on PICA-N surface temperature trace correspond to still images at the top of the figure.

- Si, CN, and NH emission signal collected near post-shock region with spectrometer pointed perpendicular to the flow.

- Ca emission signal collected with the spectrometer pointed at the stagnation surface.

- Pyrometer data collected with the reticle pointed at the intersection of the nose cone and the frustum.
HyMETS Emission Data – Air

- Emission data (Si, CN, NH) collected on the **virgin** test article exhibit an instantaneous rise followed by a slow drop off in intensity.
- Ca emission intensity reaches a steady state within the first few seconds of the test.

- Emission data (CN & NH) collected on the **coated** test articles show an instantaneous rise followed by a rapid drop off in intensity.
- At $t = 6s$, Si, CN, and NH emission intensity rises to a maximum and signal for these species slowly declines for the remainder of the test.
- Ca emission signal begins to rise at $t = 9s$ and slowly rises until reaching a steady state at the end of the test.
- The three second delay between Si and Ca signal intensity is due to the spatial offset between spectrometers.

- The data suggest that the coating survives for at least 6s before it decomposes.
HyMETS Emission Data – CO$_2$

- CN emission collected on the _virgin_ test article exhibit an instantaneous rise followed by a slow drop off in intensity.
  - Emission from NH and Si are weak.
  - Ca emission reaches a steady state within the first three seconds of the test.

- CN emission collected on the _coated_ test article exhibits an instantaneous rise followed by a slow increase in intensity for the remainder of the test.
  - Emission from Si, NH, and Ca are weak.
  - Weak emission signal indicates that the coating remains on the surface.

- Surface temperature stagnates for the duration of the test ($T_{max} = 1500$ °C, $t \sim 30s$).

- A second campaign has been planned to further investigate CO$_2$ environments.
Salient Observations

- The surface temperature of the virgin model reaches a steady state within the first second or two.

- The surface response of the coated model advances according to four stages.

  Stage 1. The surface temperature rises rapidly until it reaches 1500 °C.

  Stage 2. The temperature rise stagnates for several seconds.

  Stage 3. The surface temperature rises again after it reaches 1600 °C.

  Stage 4. The heating rate slows down and approaches the same surface temperature as the virgin model.
Stage 1: Rapid Pyrolysis of NuSil

Time = 2s

$T = ?$
Thermogravimetric analysis (TGA) of NuSil using TA Instruments SDT 650.

- Heating rate = 20 °C min\(^{-1}\).
- Temperature range = ambient to 1500 °C.
- Gas flow rate = 100 ml min\(^{-1}\).

Degradation onset temperature \(T_i = 99\%\) nearly equal between air and nitrogen.

- \(T_i\) (Air) = 420.8 °C.
- \(T_i\) (\(N_2\)) = 420.4 °C.

Decomposition mechanisms change with gas flow composition.

However, the char yield is nearly invariant with respect to flow composition.

- Char yield (Air) = 7.2%.
- Char yield (\(N_2\)) = 7.3%.
Stage 1: Fast Pyrolysis of NuSil

Time < 2s
T > 450 °C

Stage 2: ?

PICA-NuSil HyMETS Campaign

Full Distribution A Statement or Cleared for public release
• Hourlier – pyrolysis and analysis of polysiloxane resins as a function of temperature.

• D (1343 cm\(^{-1}\)) and G (1600 cm\(^{-1}\)) bands appear at 800 °C and indicate the presence of turbostratic glassy carbon.

• Furthermore, the D and G bands narrow at high-temperature indicating increasing structural organization.

• Si-C bonds appear at T > 1400 °C as evidenced by signal between 600 – 1,000 cm\(^{-1}\).

• Scanning electron microscopy image reveals pitting at the surface.

• Panel images D, E, and F show spatial distributions of Si-C, well organized sp\(^2\), and disordered sp\(^2\) carbon.

Full Distribution A Statement or Cleared for public release

Hourlier – Qualitative analysis of siloxane pyrolysis products via T.G.A.-M.S..

- Heating rate = 10 °C min⁻¹ to T_f = 1500 °C.

- Isothermal @ T = 1500 °C for 35 minutes.

- TGA data show mass loss above 1500 °C and m/z = 44, 28, 12.
Stage 2: Phase Separation & Oxidation of SiOC

- Amorphous SiOC phase and domains of disordered sp² carbon.
- Glass ceramic state with increasingly ordered nano domains of silica, highly ordered sp² carbon.
- Domains of silica and carbon may react via carbothermal reduction to form SiC (s) and CO (g).

Stage 3: High-Temperature Decomposition

- $\text{SiO}_2 (s) + 3 \text{C (s)} \rightarrow \text{SiC (s)} + 2 \text{CO (g)}$
- $T \text{ at } \Delta G = 0 \text{ (1515 °C)}$

Time:
- $T > 1,000 \text{ °C}$
- $T > 1,400 \text{ °C}$
- $T > 1,500 \text{ °C}$

Temperature:
- Time < 2s
- $T > 450 \text{ °C}$

PICA-NuSil HyMETS Campaign
Stage 2: Phase Separation & Oxidation of SiOC
Time = ~ 10s
T = 1500 - 1650 °C

Stage 3: High-Temperature Decomposition
Carbothermal Reduction (Overall Reaction)
\[ \text{SiO}_2 (s) + 3\text{C} (s) \rightarrow \text{SiC} (s) + 2\text{CO} (g) \]
\[ T \text{ at } \Delta G = 0 (1515 \degree \text{C}) \]

Stage 4: Steady-State Ablation
The surface temperature rises after SiOC decomposition and subsequent oxidation of the char layer.

The temperatures and time periods:
- Time < 2s, T > 450 °C
- Time = ~ 10s, T = 1500 - 1650 °C
- T > 450 °C

PICA-NuSil HyMETS Campaign
Post-test photo reveals that the nose cone is fully decomposed.

A silica ring separates the PICA char layer from the surrounding silicon oxycarbide coating.

Post-test powder XRD of the surface reveals the presence of SiC, SiO₂, and carbon.

Post-test photo reveals the presence of silica on the nose cone and a frustum that is coated with silicon oxycarbide.

Models subjected to condition B (CO₂ or air) yield similar spectra.
Conclusions

• Mini sphere-cone models were coated with NuSil and subjected to a variety of test conditions (e.g., heating rate, gas composition, etc.).

• The coating depresses the thermal response relative to the virgin material.

• Emission spectra and high-speed video reveal that the coating remains on the surface for several seconds before decomposing.

• Test results suggest that NuSil decomposes rapidly to form a layer of oxidation-resistant silicon oxycarbide.

• The silicon oxycarbide layer is expected to phase separate into domains of SiO$_2$, SiC, and graphitic carbon.

• Post-test surface analysis reveals the presence of SiO$_2$, SiC, and carbon.

• Domains of SiO$_2$ and carbon react through carbothermal reduction to form gaseous products (SiO$_{(g)}$ & CO$_{(g)}$).

• Eventually the coating fully decomposes and exposes the underlying char layer to the flow.
QUESTIONS?

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