High Temperature Chemistry at NASA: Hot Topics

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Outline of Presentation

I. High Temperature issues in aircraft engines
   A. Hot section: Ni and Co based Superalloys
   B. Oxidation and Corrosion (Durability) at high temperatures

II. Thermal protection system (TPS) and RCC (Reinforced Carbon-Carbon) on the Space Shuttle Orbiter

III. High temperatures in other worlds: Planets close to their stars

IV. Summary and Questions
Gas turbine engine

Turbine inlet temperatures in the gas path of modern high-performance jet engines can exceed 1650°C
Gas Turbine Materials

• Higher temperature, light weight, strong

• Need to understand every aspect of material
  – Mechanical behavior
  – Chemical behavior

• Materials
  – Colder sections: Ti alloys, Fe alloys
  – Hot sections: Ni- and Co- based superalloys, ceramics
    (some day!)
Issues in Each Stage of a Modern Turbine

<table>
<thead>
<tr>
<th>Component</th>
<th>Typical operating conditions</th>
<th>Critical problems</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Stress (MPa)</td>
</tr>
<tr>
<td>Blades</td>
<td>900 – 1050</td>
<td>140 – 210</td>
</tr>
<tr>
<td>Vanes</td>
<td>950 – 1100</td>
<td>35 – 70</td>
</tr>
<tr>
<td>Disks</td>
<td>400 – 650</td>
<td>420 – 1050</td>
</tr>
<tr>
<td>Combustors</td>
<td>850 – 1100</td>
<td>20 – 35</td>
</tr>
</tbody>
</table>
Environmental Effects and Coatings Branch

- Chemical interactions of engine materials with the combustion environment
  - Oxygen: Oxidation
  - Water vapor, CO₂
  - Sulfur oxides (SO₂, SO₃)
  - Deposits: Salts, volcanic ash, desert sands

- Chemical reactions at high temperatures
  - Thermodynamics
  - Kinetics
Tools: 1. Burner Rig--Realistically Simulates Turbine Engine and uses Less Fuel

Fuels: Aircraft fuel (high purity kerosene), Diesel Fuel
Inject: Sea salt, particulates
Burner Rig
Tools: 2) Thermogravimetric Apparatus (TGA)

Continuous weight change measurements without removing sample and controlled environment

- Flow velocity
- Temperature
- Gas composition

Sensitivity to 100 μg
Oxidation of Metals and Ceramics

- Thermodynamics tells us oxides are the most stable

  - $\text{Al}_2\text{O}_3$ forms as a thin film around metal

- Formation or “growth” rate (kinetics) $\propto t^{1/2}$
  - As film grows, the rate slows
  - Proportionality constant is the parabolic rate constant

- Want thermodynamically stable oxide, low growth rate, not sensitive to other impurities
Primary protective oxides at high temperatures: \( \text{Cr}_2\text{O}_3, \text{SiO}_2, \text{Al}_2\text{O}_3 \)
What about other Effects?

• Water Vapor
  – $\text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O}(g) + 3/2 \text{O}_2(g) = 2\text{CrO}_2(\text{OH})_2(g)$
    • Removes $\text{Cr}_2\text{O}_3$, more forms and is removed
    • Part is gradually vaporized!
    • Limits $\text{Cr}_2\text{O}_3$ to ~900°C

• Na impurities (marine environment)
  – Opens $\text{SiO}_2$—more oxygen transport

• Fluxing by molten salts, volcanic ash
  – $\text{Na}_2\text{O} + \text{SiO}_2(s) = \text{Na}_2\text{SiO}_3(l)$
    – Important area of research!
Re-entry Heat Shields:

Heating for Short Times
Atmosphere of Dissociated Gases—N, O
Re-entry Heating: Why the Orbiter gets so Hot

• Orbiter begins re-entry at Mach 25 (18,000 mph) in upper atmosphere
• Must slow down on re-entry, tremendous energy must be dissipated
• “Shock waves”: Pile-up of gas molecules as vehicle slows
Re-entry Heating: Why the Orbiter gets so Hot

• Blunt body: Shock spreads out and dissipates a lot of heat

• Nose cap and wing leading edges take most the heat: up to 1600°C for short periods (~5 min)
Thermal Protection on the Orbiter: Highest Temperature Materials on Nose Cap and Wing Leading Edges

Thermal Protection System, Orbiter 102

<table>
<thead>
<tr>
<th>Coloring</th>
<th>Area, sq ft</th>
<th>Weight, lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRSI - Black</td>
<td>332.7</td>
<td>532.1</td>
</tr>
<tr>
<td>LRSI - Off White</td>
<td>254.6</td>
<td>1014.2</td>
</tr>
<tr>
<td>FRSI - White</td>
<td>479.7</td>
<td>4412.6</td>
</tr>
<tr>
<td>RCC - Light Gray</td>
<td>38.0</td>
<td>1689.3</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>918.5</td>
<td>918.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1105.0</strong></td>
<td><strong>18936.1</strong></td>
</tr>
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*Includes bulk insulation, thermal barriers, and closeouts
Reinforced Carbon/Carbon (RCC) in the Shuttle

- Composite of Carbon Fibers in a Carbon Matrix → “Carbon/Carbon”
- Remarkably effective > 130 flights
Wing Panels Attached with Complex Metal Attachment Hardware
Allows for Thermal Expansion and Contraction

Leading Edge Cross-Section

Amorphous aluminosilicate fibers
Thermal Insulation

- LI2200
- Inconel 718
- RCC
- Inconel 601
- LI900
- A-286 steel
- Aluminum 2024

1 cm
Wing Panels Protect Aluminum Wing Structure
Fabrication of Carbon/Carbon Composites
Lockheed-Martin

• High Strength Carbon Fibers
  – ~10 µm (0.01 mm) diameter
  – 4000 MPa strength
  – Graphite (crystalline carbon)

• Woven into cloth
Coated with a ‘pre-preg’ and pressed into molds

Then a liquid carbon precursor is added to fill porosity: makes carbon matrix
Cross Sectional Views of Carbon/Carbon

• 25X Showing bundles (‘tows’) of fibers in longitudinal and transverse directions

• Porosity due to incomplete compaction

• Important to distinguish this porosity from oxidation

• SEM Photo shows fibers and matrix

• Rayon Fibers—first generation carbon fibers Perform well in this application

• ‘Crenulations’ or grooves in fibers: important in oxidation
Carbon/Carbon: The Ideal Aerospace Material

• Lightweight

• Strong: Carbon Fibers even become stronger as temperature is increased

• Drawback?
  – Oxidizes!
Oxidation Protection of Carbon/Carbon

- Oxidation is the major barrier to widespread application of carbon/carbon
- Need to select adherent, oxidation resistant coating material that does not react with carbon
- Many years of research and development
  - Oxides
  - Metals/alloys
  - SiC
- SiC: the best choice
Oxidation Protection of Carbon/Carbon

- Chemical reaction: “Conversion Coating”

- $\text{Si(vapor)} + \text{C} = \text{SiC}$ Controlled exposure in powder pack leads to 1 mm thick coating. In pack of $\text{Al}_2\text{O}_3$, SiC, Si
**Drawback of SiC coating on Carbon/Carbon**

**Thermal expansion mismatch ⇒ Cracking**

- On cooling from processing temperature, SiC (CTE = 5 x 10^{-6} /K) shrinks faster than C/C (CTE = 1 x 10^{-6}/K)
  - Tensile stresses develop in SiC ⇒ SiC fractures/cracks
  - Cracks may serve as pathways for oxidation

- High temperature glasses are applied, which flow at higher temperatures and seal cracks
  - Silica and sodium silicate with SiC particles
  - Surprisingly effective for the short duration of re-entry
Coated Reinforced Carbon/Carbon Composite

- Cracks - some through thickness
- Sodium Silicate Glass
- Short SiC fibers, particles
- SiC (~1.5 mm)
- Vacuum infiltrate with Tetra Ethyl Orthosilicate (TEOS)
- Fills cracks with SiO₂

Carbon/Carbon - 2 dimensional lay-up

Sealant

SiC

Carbon/carbon
The Columbia Tragedy:
Damaged RCC
The Columbia Disaster: February 1, 2003

Shedding from External Fuel Tank Damaged Left Wing

_Tragically Showed How Important RCC is to the Orbiter_
The Columbia Disaster

• Many large teams at NASA and other organizations involved in determining cause of accident
• Impact damage of RCC panel led to entry of hot re-entry gases, melted wing structure, and brought vehicle down
Recovered Pieces of RCC Provided Clues to Cause of Accident

Port Wing RCC Panels 5 to 10

Brought to hanger at Kennedy Space Center
### Attachment Hardware in Wing Leading Edge Structure

![Leading Edge Cross-Section](image)

Pattern of solidified droplets defined location of breach

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Use</th>
<th>Maximum Service Temperature (°C)</th>
<th>~MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 2024</td>
<td>Wing spar</td>
<td>NA</td>
<td>650</td>
</tr>
<tr>
<td>A286</td>
<td>Spar attachment fitting</td>
<td>815</td>
<td>1370</td>
</tr>
<tr>
<td>IN718</td>
<td>Clevis, spanner beam</td>
<td>980</td>
<td>1370</td>
</tr>
<tr>
<td>IN601</td>
<td>Spar insulation foil</td>
<td>1090</td>
<td>1370</td>
</tr>
</tbody>
</table>
Proposed Breach Location and Plasma Flow Based on Results of Deposit Analysis

Flow Exiting through RCC 8 lower on to Carrier Panel 9 tiles
Oxidation Morphology helped with interpretation of fragments
Unique appearance of remaining Fibers

- Laboratory oxidation of uncoated carbon/carbon
- Oxidation Morphology: Fibers thinner and pointed

- Edge of recovered fragment from Columbia
- Pointed fibers indicated burning when vehicle broke-up
- Flat fracture surfaces indicated fracture on impact with ground
Oxidation Pattern: Tells which fragments formed on Impact with Ground and which Burned During Break-up

Port Wing RCC Panels 5 to 10
In Memoriam . . .
Dramatic Changes in Implemented for Shuttle Operation after the Accident

• Careful examination of RCC immediately after lift-off. Camera extends on boom to photograph regions of each panel

• Careful examination of RCC before re-entry

• Extensive NDE (Non-Destructive Evaluation) examination of RCC panels on ground—before installation and on-vehicle
  – Development of novel thermography techniques (relates changes in thermal conductivity to structure) for on-vehicle examination of RCC

• Development of repair methods

• Successful missions through the last flight of the fleet
Chemistry on Other Worlds

Venus

Exoplanets
What is the atmosphere of Venus like?

What we once thought...

What we now know...

- 92 bar
- Primary CO$_2$, small amount of SO$_2$, N$_2$
- Sulfuric acid clouds
- Lots of volcanic activity

2.3 μm image from Galileo flyby
Interactions of Venusian Atmosphere with Fresh volcanic Rock

• $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2(\text{g})$
  – Can create large $\text{CO}_2(\text{g})$ pressure
  – Thought to ‘buffer’ $\text{CO}_2(\text{g})$ pressure at surface of Venus
  – Now unlikely as not a true ‘buffer’

• $3\text{FeS}_2 + 16\text{CO}_2(\text{g}) = \text{Fe}_3\text{O}_4 + 6\text{SO}_2(\text{g}) + 16\text{CO}(\text{g})$
  – Pyrite likely present on Venus surface
  – Reaction may ‘buffer’ $\text{SO}_2(\text{g})$
Close duplication of Venus atmosphere
92 bar  450ºC
- CO$_2$
- SO$_2$
- N$_2$
- Ar
- Traces of CO, CO$_2$, HCl, HF

Current studies: Examine a variety of mineral interactions with this environment
Exoplanets: Planets outside our Solar System

- Confirmed discoveries:
  - 1988—First discovery, confirmed 2002
  - 2009—300
  - 2010—453
  - exoplanets.org (2014)—1516

- Most commonly found by transit method

- Hot, rocky Exoplanets
  - Short orbital periods
  - Tidally locked/strongly irradiated
  - CoRot-7b, Kepler 10b, 55 Cnc e
  - Very hot!
Atmospheres of Hot, Rocky Exoplanets
CoRoT-7b, Kepler 10b, 55 Cnc e (55 Cancri)

• Estimated densities suggest BSE (basic silicate earth: SiO$_2$-MgO-FeO-CaO) or moon-like compositions

• Inorganic vapors above lava oceans—molten silicates (Fegley)

• Major species are Na(g), SiO(g), Mg(g)
  – Fractionating as they move to the cold side
  – Can also form silicate ‘clouds’

• Grant with MSU (Reed, Cornelison), Wash U (Fegley), and NASA (Jacobson, Costa).
Simulate these atmospheres in a Knudsen Cell

- Typically 1 cm diameter x 1 cm high with a 1 mm orifice
- Near equilibrium established in cell
- Vapor effusing from orifice forms a molecular beam which can be analyzed with a mass spectrometer (standard method from high temperature chemistry)
Vapors above Olivine: (Mg, Fe) silicate

- Primary constituent of the earth’s mantle—may be a major part of exoplanets as well
- Vapor species are Fe(g), SiO(g), Mg(g), O(g), O_2(g)
- Vapor pressure vs T

Atmosphere of Fe(g), SiO(g), MgO(g)! Need specialized spectroscopic methods to confirm or refute this…
Conclusions: Hot Topics at NASA

• Hot section of Aircraft turbines

• Re-entry shields of the Space Shuttle Orbiter

• High temperature chemistry and physics on Venus and planets beyond our solar system