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

![Schematic diagram of turbofan engine](image)

<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, CO$_2$
  - Sulfur oxides (SO$_2$, SO$_3$)
  - 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

NiAl alloy → NiAl alloy

- \( \text{Al}_2\text{O}_3 \) 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
  – \( \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O}(g) + \frac{3}{2} \text{O}_2(g) = 2\text{CrO}_2(\text{OH})_2(g) \)
    • Removes \( \text{Cr}_2\text{O}_3 \), more forms and is removed
    • Part is gradually vaporized!
    • Limits \( \text{Cr}_2\text{O}_3 \) to \(~900\)ºC

• 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 m (sq ft)</th>
<th>Weight, kg (lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRSI - Black</td>
<td>332.7 (3581)</td>
<td>532.1 (1173)</td>
</tr>
<tr>
<td>LRSI - Off White</td>
<td>254.6 (2741)</td>
<td>1014.2 (2236)</td>
</tr>
<tr>
<td>FRSI - White</td>
<td>479.7 (5164)</td>
<td>4412.6 (9729)</td>
</tr>
<tr>
<td>RCC - Light Gray</td>
<td>38.0 (416)</td>
<td>1697.3 (3742)</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>363.0 (3959)</td>
<td>918.5 (2025)</td>
</tr>
<tr>
<td>Total</td>
<td>1105.0 (11895)</td>
<td>8574.7 (18,904)</td>
</tr>
</tbody>
</table>

*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

Amorphous aluminosilicate fibers
Thermal Insulation

Leading Edge Cross-Section

<table>
<thead>
<tr>
<th>LI2200</th>
<th>Inconel 718</th>
<th>RCC</th>
<th>Inconel 601</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI900</td>
<td>A-286 steel</td>
<td>Aluminum 2024</td>
<td></td>
</tr>
</tbody>
</table>

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

- High Strength Carbon Fibers
  - \( \sim 10 \, \mu m \) (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 \( \text{Al}_2\text{O}_3, \text{SiC}, \text{Si} \)
Drawback of SiC coating on Carbon/Carbon

Thermal expansion mismatch \( \Rightarrow \) 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 \( \Rightarrow \) 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
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

Brought to hanger at Kennedy Space Center

*Port Wing RCC Panels 5 to 10*
### Attachment Hardware in Wing Leading Edge Structure

#### Leading Edge Cross-Section

- **Pattern of solidified droplets defined location of breach**

#### Alloy Use and Properties

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Use</th>
<th>Maximum Service Temperature (°C)</th>
<th>~MP (°C)</th>
</tr>
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<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>
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</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...

2.3 μm image from Galileo flyby

What we now know...

- 92 bar
- Primary CO₂, small amount of SO₂, N₂
- Sulfuric acid clouds
- Lots of volcanic activity
Interactions of Venusian Atmosphere with Fresh volcanic Rock

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

- $3\text{FeS}_2 + 16\text{CO}_2(g) = \text{Fe}_3\text{O}_4 + 6\text{SO}_2(g) + 16\text{CO}(g)$
  - Pyrite likely present on Venus surface
  - Reaction may ‘buffer’ SO$_2$(g)
Current studies: Examine a variety of mineral interactions with this environment

Close duplication of Venus atmosphere
92 bar  450ºC
- CO₂
- SO₂
- N₂
- Ar
- Traces of CO, CO₂, HCl, HF
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: SiO₂-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