Microstructural Investigation of High Emittance Glass Coatings on Fibrous Ceramic Insulation

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Sandia National Laboratories
Thermal Protection Materials and Systems Branch
Outline

- Background
  - Space Shuttle Thermal Protection System (TPS)
  - Types of TPS
    - Tiles, Blankets, Leading Edges, and Coatings
- Processing
  - Tiles
  - Coatings
- Properties
  - Mechanical
    - Impact Resistance
- Microstructural Examination of Toughened Uni-Piece Fibrous Insulation (TUF1)
- Summary
- Future Work
Typical Surface Temperatures Experienced During Reentry

LOWER SURFACE VIEW
- 1260°C
- 1095°C
- 1095°C
- 980°C
- 1260°C
- 1500°C
- 1260°C
- 650°C
- 425°C
- 315°C

ENTRY/ASCENT
- 370°C/400°C
- 400°C/445°C
- 455°C/480°C

UPPER SURFACE VIEW
- 315°C
- 650°C
- 425°C
- 650°C

SIDE SURFACE VIEW
- 425°C
- 315°C
- 650°C
- 425°C
- 980°C
- 1095°C
- 420°C
- 405°C

*DENOTES ASCENT TEMPERATURES (MAXIMUM YAW 8 DEG)
Ames Developed Thermal Protection Materials

Adopted to date on Shuttle

AFRSI Blanket
Gap Fillers
AIM-22 Tile
RCG Coating
TUF/AETB Tile
FRG-12 Tile
Rigid Fibrous Ceramic Tile and Coating Systems

Tile Systems
- Pure Silica
- Fibrous Refractory Composite Insulation (FRCI)
  - Silica and Aluminoborosilicate (Nextel 312) Fibers
- Alumina Enhanced Thermal Barrier (AETB)
  - Silica, Nextel 312, and Alumina Fibers

Coating Systems
- Reaction Cured Glass (RCG)
  - Borosilicate Glass and SiB₄ emittance agent
- Toughened Uni-Piece Fibrous Insulation (TUPI)
  - Borosilicate Glass, SiB₆ and MoSi₂
Raw Materials

Fibers
- Silica
  - 1-3 μm diameter
- Nextel 312
  - 62% Al₂O₃-14% B₂O₃-24% SiO₂
  - 8.5 μm diameter
- Alumina
  - 96% Al₂O₃-3% SiO₂
  - 1-3 μm diameter

Coatings
- Borosilicate glass
  - Porous Vycor 7930 w/ added B₂O₃
- Emissivity Agents
  - SiB₄ in RCG
  - MoSi₂ in TUF1
Typical Tile and Coating Processing Steps

- Fibers
- Silicon Carbide Ammonia

V-Blend → Fired ~1275°C → Drying Oven → Casting Tower → Finished Billet
Tile Microstructures

AETB Tile

LI-900 Pure Silica Tile
Typical Coating Process

Reaction Cured Glass (RCG)
Borosilicate Glass
SiB₄ emittance agent

Toughened Uni-Piece Insulation (TUPI)
Borosilicate Glass
MoSi₂ emittance agent
SiB₆ flux

Air
Coating

Spray

Drying Oven

Ball Milling

Firing

Coated Tile

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Schematic of Reaction Cured Glass

INITIAL OXIDATION OF BORON SILICIDE

1 TO 1 1/2 HOURS
1000° TO 1400°C IN AIR

REACTION AND FUSION OF COMPONENTS

FINAL COMPOSITE

- TETRABORON SILICIDE
- BOROSILICATE GLASS
- HIGH SILICA BOROSILICATE GLASS
- PORES

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Reaction Cured Glass (RCG) Coating

- High Emittance $\varepsilon > 0.8$
- 0.38 mm thick
- Compatible with silica tiles
  - no devitrification
  - match tiles CTE
- RCG coating sits on top of tile surface
  - particle size too large to infiltrate
- Dense coating
  - initial moisture barrier
- Poor impact resistance.
Toughened Uni-Piece Fibrous Insulation (TUF1)

- High Emittance $\epsilon > 0.8$
- 2.5 mm thick
- Compatible with tile
  - no devitrification
- Porous coating
- Material penetrates into the tile
  - smaller particle size
- Significantly improved impact resistance
- $\text{MoSi}_2$ act as emissivity agent
  - also increases CTE so it matches that of AETB tiles.
Microstructure of TUFI System

- TUFI is applied as three separate coats.
- Results in a graded coating system that is denser near the surface.
- Two scales of porosity
  - regions that appear deficient in glass
  - denser regions also have a smaller scale porosity
Comparison of Impact Resistance
RCG vs TUF

SHUTTLE TECHNOLOGY, 1978
RCG

CURRENT TECHNOLOGY
TUF

DAMAGE RESISTANCE AS A FUNCTION OF AREAL WEIGHT
IMPACT = 1.8 \times 10^2 \text{ ft-lb}

RELATIVE DAMAGE RESISTANCE

AREAL WEIGHT, \text{ lb/ft}^2

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Shuttle Flight Testing of LI-900/RCG vs AETB-8/TUFI in BaseHeatshield

TUFI/AETB-8 Tiles
Undamaged After Three Flights

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Objective of Microstructural Investigation

- At the time RCG and TUFI were developed, analytical techniques were not available to accurately investigate the reaction mechanisms.
  - Particularly difficult to analyze for Boron.
- Future improvements in tile coatings will require fundamental understandings of these mechanisms.
- Long term consistency in current coatings will also rely on a better understanding of the current process.
  - i.e. if material vendors change, how do slight differences in starting powders affect the final coating?
Automated X-ray Spectral Image Analysis (AXSIA)

- How do you comprehensively survey the chemistry of a large area of a microstructure?

- Point analyses can be subjective—where to take them from and how many.

- 2D distributions of chemical phases are needed but simple mapping alone is not the answer. Mapping has potential artifacts and requires fore-knowledge.

'Phase images' are needed—a spectrum from each phase and an image describing where in the microstructure it's found.
Automated X-ray Spectral Image Analysis (AXSIA)

- Start off with a spectral image—a complete x-ray spectrum from each pixel in a 2D array, sampling the microstructural region of interest (hundreds of microns on a side (SEM) to nanometers on a side (TEM))

- Perform a complete statistical analysis (information extraction) on every spectrum in the spectrum image using the AXSIA software. **Analysis time** on a spectrum image with over 16,000 spectra is only **about a minute**.

- The result is a spectrum from each phase in the microstructure and an image describing that phase’s location in the microstructure: 16000 spectra are reduced to a handful with no loss of chemical information

- Licensed AXSIA to Thermo NORAN, Inc., a U. S. corporation
Evidence of dissolution and reprecipitation of SiB$_x$ and MoSi$_x$ particles.
STEM Images of TUFI Showing Distribution of Small Particles Near Surface
Comparison of Dark and Bright Field STEM Images

Pt layer left from ion milling

Fe, Cu

MoSi$_2$

Mo$_5$Si$_3$

B Rich Region

2 $\mu$m

0.5 $\mu$m

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High Resolution Bright Field Image of MoSi$_2$ Particles

- Evidence of crystalline surface layer on MoSi$_2$ particles.
Elemental Mapping of TUF1 Coating Using AXSIA

Bright Field

Boron Image

SiB_x

Oxygen Image

MoSi_2 + B

Mo_5Si_3 w/o B

Silicon Image

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Elemental Mapping of TUFI Coating Using AXSIA
Summary

- Automated X-ray Spectral Image Analysis shows excellent potential for use in understanding the reactions that occur in tile coatings.
- Images reveal that the reaction mechanisms in TUFI, and presumably RCG, are complex.
- Evidence of dissolution and reprecipitation of MoSi₂.
- Evidence of Fe and Cu solubility in Mo₅Si₃.
- Appears to be some solubility of B in MoSi₂ but not in Mo₅Si₃.
Future Work

- Systematic use elemental mapping to investigate the evolution of RCG and TUF during firing.
- Investigate the influence of SiBx on the coatings
  - SiBx vs SiB?
  - Different vendors
- How trace impurities affect coating formation
- Look for evidence of reactions at the fiber coating interface
- Look at interface between fibers
- Investigate changes in tile microstructure during use.
- Improved our understanding of the reaction mechanisms that occur in tile coatings in order to develop improved coatings for future applications.