NASA Conference Publication 2427

Structural Ceramics

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Date for general release May 1988

Proceedings of a workshop sponsored by
NASA Lewis Research Center
Cleveland, Ohio
May 20-21, 1986
Structural Ceramics

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NASA
National Aeronautics
and Space Administration
Scientific and Technical
Information Branch
1986
PREFACE

Welcome to Lewis Research Center and the Materials Division. We are very pleased that you could visit us and hear about all the progress we, our contractors, and grantees have been making in ceramics. We feel ceramics and ceramic matrix composites are an exciting area of tailored structural materials research. NASA has made a strong commitment to advance this technology and we will work with U.S. industry to foster our national position in world markets. In fact, that is the job of the Materials Division in all areas of NASA technology needs.

If any of your organizations are interested in more detailed information on our programs, in joint research efforts, or in sending a research here for some extended on-site studies, feel free to call me and we will discuss it.

Sal Grisaffe
Chief, Materials Division

(216) 433-3193
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CERAMICS FOR TURBINE ENGINES

Stanley R. Levine

NASA Lewis Research Center
Cleveland, Ohio 44135

The Ceramics for Turbine Engines Project is comprised of three main research thrusts with major elements as indicated:

- Materials and Processing
  Monolithics
  Fiber reinforced

- Design Methodology
  Design code
  Tribology

- Life Prediction
  Environmental effects
  Non-destructive evaluation
  Fracture and fatigue
  Time dependent behavior

The overall objective of this program is to provide the ceramics technology base in materials and structures for aerospace propulsion and power applications programs. The effort is complementary to and coordinated with the Department of Energy funded Ceramic Technology for Advanced Heat Engines Project at Oak Ridge National Laboratory. From the NASA perspective an enhanced ceramics technology base directly supports aeronautics initiatives in small engine technology, high-performance turbine engine technology, and hypersonics. The Ceramics for Turbine Engines Project is funded at about $2M per year and involves about 20 researchers in the Materials Division and the Structures Division at Lewis as well as contract and grant research. An overview of the program, which includes the technical objectives and content of each thrust, is provided in the following figures. This workshop reports on research efforts funded mainly by Ceramics for Turbine Engines. A major strength of the program is the increasingly interdisciplinary nature of the research being carried out in-house. Several of the papers presented will illustrate and demonstrate the benefits of such an approach.
CERAMICS FOR TURBINE ENGINES

MATERIALS AND PROCESSING

BRITTLE DESIGN METHODS

PROPERTY EVALUATION

MICROSTRUCTURE EVALUATION

TIME DEPENDENT PROPERTY EVALUATION

GOVERNMENT-SPONSORED TECHNOLOGY PROGRAMS FOR STRUCTURAL CERAMICS

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CD-86-19405

CD-86-19171
DOE/NASA ADVANCED GAS TURBINE TECHNOLOGY DEVELOPMENT PROJECT

OBJECTIVE
• DEVELOP A TECHNOLOGY BASE APPLICABLE TO A COMPETITIVE AUTOMOTIVE GAS TURBINE ENGINE

TECHNOLOGY DEVELOPMENT GOALS
• 30% IMPROVEMENT IN FUEL ECONOMY OVER A CONVENTIONAL (SI) ENGINE IN A 3000 LB VEHICLE
• ADAPTABILITY TO ALTERNATIVE FUELS
• MEET OR EXCEED PRESENT EMISSION STANDARDS
• COMPETITIVE RELIABILITY, LIFE, AND COSTS

APPROACH
• TWO ENGINE/AUTOMOBILE CONTRACTOR TEAMS (GARRETT/FORD AND ALLISON/PONTIAC)
  - DESIGN, FABRICATE, AND TEST ALL-CERAMIC HOT SECTION COMPONENTS
• SUPPORTING RESEARCH AND TECHNOLOGY EFFORT IN CRITICAL AREAS
• INITIATED 1980–PLANNED COMPLETION 1986

AGT101 CERAMIC COMPONENTS
STATUS OF MONOLITHIC CERAMIC MATERIALS

CERAMIC MATERIALS HAVE DEMONSTRATED:

★ GOOD HIGH TEMPERATURE STRENGTH
★ GOOD OXIDATION RESISTANCE
★ GOOD EROSION RESISTANCE
★ NET SHAPE FABRICATION CAPABILITY

BUT

★ LOW RELIABILITY

NUMBER OF PARTS

STRENGTH

UNACCEPTABLE

ACCEPTABLE

REQUIREMENT

4
CERAMIC TECHNOLOGY NEEDS

RELIABILITY
TOUGHNESS
STRENGTH
LUBRICITY
DURABILITY
LIFE PREDICTION
NDE

AEROSPACE
ENGINES

TERRESTRIAL
ENGINES

STATE OF THE
ART

1980'S
1990'S
IMPLEMENTATION
2000

• GRACEFUL
FRACTURE

• NET SHAPE
• LOW COST

STRATEGIC THRUSTS IN AERONAUTICS TO
ESTABLISH TECHNOLOGY FOR 21st CENTURY
ADVANCED AIRCRAFT

NASA OAST/AERONAUTICS - NOVEMBER 1984
PRESIDENTIAL SCIENCE ADVISOR KEYWORTH - APRIL 1985

• DEVELOP ESSENTIAL TECHNOLOGIES FOR HIGH-EFFICIENCY SUBSONIC TRANSPORTS.

• ESTABLISH TECHNOLOGY READINESS FOR EFFICIENT SUPersonic CRUISE TRANSPORT AND FIGHTER/ATTACK AIRCRAFT.

• DEVELOP ESSENTIAL TECHNOLOGIES FOR REALIZATION OF PRACTICAL HYPERSONIC AND TRANSATMOSPHERIC FLIGHT AIRCRAFT.
# FUTURE OPPORTUNITIES IN AEROPROPULSION

## PROPULSION SYSTEMS

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Lewis Research Center

## SMALL ENGINE TECHNOLOGY OPPORTUNITIES

### REGENERATIVE CYCLE

- **ADVANCED CYCLES**
- **ADVANCED COMPONENTS**
- **ADVANCED MATERIALS**

### VERY EFFICIENT ENGINES

- **IFM**
- **ADV. CONCEPTS**

### SUPERIOR TURBOMACHINERY

- **SURFACE TEMPERATURE: °F**
  - CAST
  - SC
  - DS
  - TBC
  - ODS
  - 1500
  - 2000
  - 2500
  - 3000
  - >2600°F TIT UNCOOLED
  - HIGH EFFICIENCY
  - LOW WEIGHT

CD-85-18043

NASA
TECHNOLOGY BENEFITS FROM CERAMICS

TYPICAL-COMMUTER MISSION

- BOTH REGENERATION AND UNCOOLED CERAMICS
- REGENERATION OR UNCOOLED CERAMICS
- IMPROVED COMPRESSOR, TURBINE, AND CYCLE EFFICIENCY
- CURRENT ENGINES

FUEL SAVED, 25 %

CURRENT ENGINES

TECHNOLOGY

Lewis Research Center
NASA
FUTURE HIGH-SPEED AIR TRANSPORTATION
2-HOUR TRIPS

TRANSATMOSPHERIC

HYPersonic

TO AUSTRALIA 12,000 MI

MID-EAST 6000 MI

BRITAIN 3000 MI

N.Y.

AUSTRALIA

NEW YORK

N.Y.

HALF WAY AROUND
CERAMICS FOR TURBINE ENGINES

OBJECTIVE
DEVELOP THE TECHNOLOGY
REQUIRED TO IMPROVE STRUCTURAL
CERAMIC RELIABILITY AND PERMIT
USE OF CERAMICS IN ADVANCED
HEAT ENGINES

APPROACHES
• MATERIALS AND PROCESSING
• DESIGN METHODOLOGY
• LIFE PREDICTION

CERAMICS FOR TURBINE ENGINES

RESEARCH THRUSTS

MATERIALS AND PROCESSING
• RELIABLE, TOUGH MONOLITHICS
• FIBER REINFORCED CERAMICS
• ADVANCED CERAMIC FIBERS
• WEAR RESISTANT & LOW
FRICITION COATINGS

DATA BASE
AND LIFE
PREDICTION
• ENVIRONMENTAL EFFECTS
• NON-DESTRUCTIVE EVALUATION
• FRACTURE & FATIGUE
• TIME DEPENDENT BEHAVIOR

DESIGN METHODOLOGY
• BRITTLE MATERIALS DESIGN CODE
• FRICTION & WEAR DATA

CD-86-19172
8
LEWIS CERAMICS CAPABILITIES

FIBERS
Fiber coating
High temperature fiber testing
Fiber physical/mechanical properties

CERAMIC/CERAMIC COMPOSITE FABRICATION
Fiber/matrix tape fab
Hot press
Reaction bonding
Hot isostatic press (2200 °C, 20 ksi)
High pressure N₂ sintering (2150 °C, 1000 psi)
CVD & CVI fabrication
Sol gel processing/characterization
Polymer processing/characterization
Powder processing/characterization

INTERDISCIPLINARY COLLABORATION
Environmental effects - Burner rigs, H₂/O₂ rig, coatings
NDE - Radiography acoustic microscopy, ultrasonics
Fracture mechanics & fatigue
Structural analysis & design methodology
Surface science - Friction, wear, coatings

CERAMICS FOR TURBINE ENGINES
—MATERIALS AND PROCESSING—

OBJECTIVE:
Improve reliability, strength and toughness of ceramics/ceramic matrix composites

APPROACH:
Powder derived materials
Chemically derived materials

COMPOSITES
Stronger, tougher ceramics
Controlled properties microstructures & models
Fiber reinforced ceramics

IMPROVE RELIABILITY
QUANTIFY PROGRESS & DEFINE NEW OPTIONS
IMPROVE STRENGTH, TOUGHNESS & PROVIDE GRACEFUL FRACTURE

BENEFITS:
Advanced ceramic materials technology for aerospace propulsion and power applications (e.g. advanced small engine technology (ASET), hypersonics)

SCHEDULE:
Identify advanced 1400°C CMC
Demo improved strength & reliability
Potential of advanced CMC assessed
Verify improved strength & reliability

CD-85-19448
APPROACHES TO CERAMIC RELIABILITY

"INSPECT-IN" THE QUALITY

SEPARATE OUT THE UNACCEPTABLE PARTS BY NDE AND PROOF TESTING AND REJECT THEM.

- INEFFICIENT
- COSTLY

IMPROVE THE PROCESS

ELIMINATE
- INCLUSIONS
- VOIDS & CRACKS
- SURFACE FLAWS

QUALITY CONTROL APPROACH
- EFFICIENT
- LOW COST
- RELIABLE

MONOLITHIC CERAMICS

OBJECTIVES:
— UNDERSTAND MICROSTRUCTURE/PROCESSING/PROPERTIES/RELATIONSHIPS
— IMPROVE RELIABILITY

APPROACHES

SINTERING/HIGH $P_{N_2}$

SINTERED $Si_3N_4$ (SSN)

REACTION BONDED $Si_3N_4$ (RBSN)

SINTERED $SiC$ (SSC)

HIP
FIBER REINFORCED CERAMICS APPROACH TO RELIABILITY

INCORPORATE CONTINUOUS CERAMIC FILAMENTS HAVING GREATER STIFFNESS THAN MATRIX

• ADVANTAGES
  - IMPROVED TOUGHNESS IMPARTED BY CRACK DEFLECTION AND CRACK BRIDGING
  - INCREASED MODULUS AND STRESS TO FAILURE
  - "METAL-LIKE" STRESS-STRAIN BEHAVIOR
  - GRACEFUL FAILURE

• DISADVANTAGES
  - PROCESSING MORE DIFFICULT
  - AVAILABLE FIBERS LIMITED
  - CONTROL OF FIBER-MATRIX BOND REQUIRED

CERAMICS FOR TURBINE ENGINES —DESIGN METHODOLOGY—

OBJECTIVES:
• DEVELOP AND VERIFY MECHANICAL DESIGN METHODS FOR CERAMIC AND CERAMIC COMPOSITE COMPONENTS
• UNDERSTAND FRICTION/WEAR INTERACTIONS AND DEVELOP HIGH TEMPERATURE SOLID FILM AND COMPOSITE LUBRICANT TECHNOLOGY

APPROACH:

DESIGN METHODS
RADIAL TURBINE BLADE
DISC SECTOR ANALYSIS
CERAMIC BLADE-DISC
FINITE ELEMENT MODEL

TRIBOLOGY
PLASMA SPRAY & VAPOR DEPOSITION
PRESSURE
NEW SURFACE FILMS AND COATINGS
NEW SELF-LUBRICATING CERAMIC COMPOSITES

BENEFITS:
ENABLING TECHNOLOGY TO PERMIT USE OF CERAMIC MATERIALS IN ADVANCED AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE: AT GL

86  87  88  89  90  91  92
PLASMA SPRAY COATINGS FOR 1000 °C
ESTABLISH BASIC TRIBOLOGY MECHANISMS
2ND GENERATION LUBRICANTS FOR USE TO 1000 °C +
LUBRICANT EVALUATION IN ENGINES
DESIGN CODE FOR COUPLED FLAWS
SURFACE FLAW DESIGN CODE
VOLUME FLAW DESIGN CODE
TIME-DEPENDENT FAILURE CODE
CERAMICS FOR TURBINE ENGINES
—LIFE PREDICTION—

OBJECTIVE:
DEVELOP LIFE PREDICTION AND RELIABILITY ASSESSMENT TOOLS FOR STRUCTURAL CERAMICS

APPROACH:

![Diagram showing furnace and burner rig with temperature and pressure specifications.

CORROSION MECHANISMS
AND CONTROL STRATEGIES

FRACTURE MECHANICS

TIME DEPENDENT
BEHAVIOR

NON-DESTRUCTIVE
EVALUATION AND
PROOF TEST

BENEFITS:
• ENABLING TECHNOLOGY TO PERMIT RELIABLE DESIGN AND USE OF ADVANCED CERAMIC MATERIALS
• GUIDE DEVELOPMENT OF DURABLE CERAMICS FOR AEROSPACE PROPULSION AND POWER SYSTEMS

SCHEDULE:

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<td>* CONSISTENT RT FRACTURE MECHANICS MEASUREMENT TECHNIQUES</td>
<td>* DETERMINE CORROSION MECHANISMS</td>
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<td>* COMPONENT NDE</td>
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FUTURE OPPORTUNITIES FOR CERAMICS

SYSTEMS
• VEHICULAR AND STATIONARY POWER
• ADVANCED SMALL ENGINE TECHNOLOGY (ASET)
• HIGH-THRUST-TO-WEIGHT ENGINES (HPTE)
• AEROSPACEPLANE

MATERIAL NEEDS
• HIGH-TEMPERATURE, NON-STRATEGIC MATERIALS AT LOW COST (2500 °F)
• VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (2700 °F)
• ADVANCED RECUPERATORS/REGENERATORS (2200 °F)
• ASSEMBLY OF CERAMICS INTO A WORKABLE ENGINE SYSTEM
• VERY HIGH RELIABILITY, TOUGHNESS AND STRENGTH-TO-WEIGHT (3000 °F)
• SAME AS HPTE (3000 °F + +)
• DURABLE CERAMICS FOR USE IN 0° AT HIGH HEAT FLUX (EDGE INSERTS) AND IN H2/O2 (ENGINE SEALS)

OPPORTUNITY
• CONTINUE EMPHASIS ON RELIABILITY
• DEVELOP THERMALLY STABLE 10 TO 25 µ DIAMETER CERAMIC FIBER AND APPLY IN CERAMIC MATRIX COMPOSITES
• DEVELOP AND VERIFY POTENTIAL OF ADVANCED MATERIALS
• ADVANCED JOINING, NONJOINING AND CONTACT STRESS CONTROL TECHNOLOGY
• DESIGN AND LIFE PREDICTION
• FIBERS AND COMPOSITES
• FIBERS AND COMPOSITES
• IDENTIFY SUITABLE MATERIALS

CD-86-19169
FRICTION AND WEAR OF CERAMICS

Donald H. Buckley
NASA Lewis Research Center

The adhesion, friction, wear, and lubricated behaviors of both oxide and non-oxide ceramics are reviewed. Ceramics are examined in contact with themselves, other harder materials, and metals. Elastic, plastic, and fracture behavior of ceramics in solid state contact is discussed. The contact load necessary to initiate fracture in ceramics is shown to be appreciably reduced with tangential motion. Both friction and wear of ceramics are anisotropic and relate to crystal structure as with metals. Grit size effects in two- and three-body abrasive wear are observed for ceramics. Both the free energy of oxide formation and the d valence bond character of metals are related to the friction and wear characteristics for metals in contact with ceramics. Surface contaminants affect friction and adhesive wear. For example, carbon on silicon carbide and chlorine on aluminum oxide reduce friction while oxygen on metal surfaces in contact with ceramics increases friction. Lubrication increases the critical load necessary to initiate fracture of ceramics both in indentation and with sliding or rubbing.
Figure 1. - Anisotropies on (0001), (10\overline{1}0), and (11\overline{2}0) surfaces of SIC.
Figure 2. - Effect of temperature on coefficient of friction for silicon carbide (0001) surface sliding against an iron rider. The iron rider was argon ion sputter cleaned before experiments. Normal load, 0.2 N, vacuum, 10 nPa.

Figure 3. - Rate of wear of a rutile single-crystal sphere on a great circle in the plane of the a- and c-axes is normal to plane of sliding at 0 and 180°. Slide direction in plane of the great circle (ref. 8).

Figure 4. - Elemental depth profile of silicon carbide (0001) surface preheated at a temperature of 1500°C for 1 hour.

Figure 5. - Graphitization of silicon carbide surface.
Figure 6. - Representative $S_{1p}$ and $C_{1s}$ XPS peaks on silicon carbide (0001) surface preheated at various temperatures to 1500° C.
Figure 7. - Surface condition of silicon carbide after heating at temperatures above 1200\(^\circ\) C.

Figure 8. - Friction for copper in sliding contact with sapphire in vacuum 30 nPa; load, 100 g; sliding velocity, 0.013 cm/s.
Figure 9. - Coefficient of friction for gold and silver riders sliding on sapphire in vacuum (30 nPa). Sliding velocity, 0.013 cm/s; ambient temperature, 25°C; duration, 1 hr.

Figure 10. - Nature of surface interaction and bonding of metal to $\text{Al}_2\text{O}_3$. 

- $\text{Al}^{+3}$ in first subsurface layer and arranged in octahedral array
- Surface covered by layer of $\text{O}^{-2}$
- Sites for chemical bonding of metals with oxygen when in contact with surface
- Sites for van der Waals interaction with metals sliding on surface

(0001) Plane of Sapphire

Rider --- Metal-to-metal bonding
Interface --- Metal - oxygen chemical and van der Waals forces
Disk --- $\text{Al}_2\text{O}_3$ chemical bonding
Figure 11. - Molecular-orbital energies, as determined by the self-consistent-field X-alpha scattered wave method, for clusters representing bulk sapphire and metal-sapphire interfaces.

Figure 12. - Fe(d) - G(p) molecular-orbital wave-function contour maps for an iron atom supported on sapphire, plotted in the plane of the iron atom and two surface oxygen atoms. The solid and dashed contours represent the positive and negative phases of the wave function.
Figure 13. - Scanning electron photomicrographs of wear tracks on the (0001) surface of single-crystal SiC in contact with rhodium and titanium as a result of ten passes of a rider in vacuum. Sliding direction, \( <10\bar{1}0> \); sliding velocity, 3 mm/min; load, 0.3 N; room temperature; pressure, 30 nPa; metal pin rider, 0.79 mm radius.
SOME DESIGN CONSIDERATIONS FOR CERAMIC COMPONENTS IN HEAT ENGINE APPLICATIONS

John P. Gyekenyesi
NASA Lewis Research Center
Cleveland, Ohio 44135

This presentation reviews the design methodology for brittle material structures which is being developed and used at the Lewis Research Center for sizing ceramic components in heat engine applications. Theoretical aspects of designing with structural ceramics are discussed, and a general purpose reliability program for predicting fast fracture response due to volume distributed flaws is described. Statistical treatment of brittle behavior, based on the Weibull model, is reviewed and its advantages, as well as drawbacks, are listed. A mechanistic statistical fracture theory, proposed by Batdorf to overcome the Weibull model limitations and based on Griffith fracture mechanics, is summarized. Failure probability predictions are made for rotating annular Si₃N₄ disks using various fracture models, and the results are compared to actual failure data. The application of these design methods to Government funded ceramics engine demonstration programs is surveyed. The uncertainty in observed component performance emphasizes the need for proof testing and improved NDE technology to guarantee adequate structural integrity.
POSSIBLE APPROACHES TO CERAMIC DESIGN

A. PROTOTYPE TESTING
   • NO STRESS ANALYSIS REQUIRED
   • POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
   • EVERY DESIGN IS UNIQUE
   • EXPENSIVE

B. SCALE MODEL EVALUATION
   • VOLUME EFFECT MUST BE INCLUDED
   • NO MECHANICAL STRESS ANALYSIS NEEDED
   • POLYAXIAL FRACTURE STRESS THEORY NOT NEEDED
   • THERMAL STRESS PROBLEM CANNOT BE SCALeD
   • EVERY DESIGN IS UNIQUE
   • LESS EXPENSIVE

C. USE OF TEST SPECIMEN TESTING
   • VOLUME EFFECT MUST BE INCLUDED
   • FULL THERMOMECHANICAL ANALYSIS REQUIRED
   • COMBINED FRACTURE STRESS THEORY NEEDED
   • CAN BE APPLIED TO ALL DESIGNS
   • INEXPENSIVE

POTENTIAL FAILURE MODES IN HEAT ENGINES

A. TIME INDEPENDENT FAILURE MODES
   • FAST FRACTURE (TENSION-COMPRESSION)
   • BUCKLING

B. TIME DEPENDENT FAILURE MODES
   • STATIC FATIGUE
   • DYNAMIC FATIGUE
   • CREEP CRACK GROWTH
   • STRESS CORROSION AND OXIDATION
   • IMPACT AND DYNAMIC LOADING
Schematics of strength tests

- Uniaxial tensile strength
- Hydrostatic tensile
- 3-point bending
- 4-point bending
- Uniaxial compressive
- Diametral compression

Brittle material design method

Material brittleness and presence of microcracks requires:
- Allowance for strength dispersion - probabilistic approach
- Consideration of material volume under stress (combination of stress and volume determine integrity)
- Refined thermal and stress analysis - field solutions (examination of critical point is not adequate)

Design practice
- Failure mode is fracture due to crack propagation
- Proof testing and/or NDE required to truncate strength distribution - establish allowable stress
- No design codes and only limited experience available
FRACTURE THEORIES

I. GRIFFITH (1920 AND 1924)
- CRACK SHAPE, SIZE, ORIENTATION SPECIFIED
- IgNORS VOLUME EFFECT
- USES MECHANISTIC FRACTURE CRITERION
- APPROACH IS DETERMINISTIC (BASIS FOR LEFM)

II. WEIBULL (1939)
- CRACK SHAPE, SIZE, ORIENTATION NOT SPECIFIED
- INCLUDES ALLOWANCE FOR STRENGTH DISPERSION
- EXPLAINS VOLUME EFFECT
- USES EMPIRICAL FRACTURE CRITERION
- APPROACH IS PROBABILISTIC

STATISTICAL TREATMENTS
WEAKEST LINK THEORY FOR TENSILE LOADING

- MATERIAL CONTAINS N FLAWS OR LINKS
- EACH FLAW OR LINK HAS A $\sigma_{cr}$
- UPON SINGLE LINK FAILURE, TWO REDISTRIBUTION MECHANISMS ARE POSSIBLE

![Diagram of series-parallel and series models]

- SERIES-PARALLEL MODEL
- SERIES MODEL

- STRUCTURAL CERAMICS ARE ASSUMED TO FOLLOW THE SERIES MODEL
- FAILURE OF SINGLE LINK IMPLIES COMPONENT FAILURE, NO CRACK ARREST MECHANISM EXISTS
Elements of Weibull's Theory (1)

- Testing for required material properties, $m$, $\sigma_0$, $\sigma_U$
- Principle of independent action for polyaxial stress state
- Randomly distributed shear-insensitive cracks
- Survival probability (range limited)
- Assume principal stress is normal to crack plane
- No crack interaction
- WLT
- Volume effect included
- Compression excluded

Weibull Theory

Survival Probability Equation

<table>
<thead>
<tr>
<th>Survival Probability</th>
<th>Equation</th>
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<tbody>
<tr>
<td>In uniaxial tension</td>
<td>$P_S(\sigma) = P_S^V(\sigma) \cdot P_S^A(\sigma)$</td>
</tr>
<tr>
<td>Due to volume cracks</td>
<td>$P_S^V(\sigma) = \exp \left[ -\int_v \left( \frac{\sigma - \sigma^V}{\sigma^V} \right)^{m_V} \right] dv$</td>
</tr>
<tr>
<td>Due to surface cracks</td>
<td>$P_S^A(\sigma) = \exp \left[ -\int_A \left( \frac{\sigma - \sigma^A}{\sigma^A} \right)^{m_A} \right] dA$</td>
</tr>
<tr>
<td>In polyaxial tension</td>
<td>$P_S(\sigma_1, \sigma_2, \sigma_3) = P_S(\sigma_1) \cdot P_S(\sigma_2) \cdot P_S(\sigma_3)$</td>
</tr>
</tbody>
</table>

Where $\sigma = \text{applied stress}$ and $\sigma_1, \sigma_2, \sigma_3 = \text{principal stresses}$. 

Weibull Theory (2) (Continued)
HYPOTHETICAL EXAMPLE OF IMPORTANCE OF HIGH
WEIBULL MODULUS FOR STRUCTURAL CERAMICS

ADVANTAGES OF PROBABILISTIC DESIGN

- PERMITS EFFICIENT MATERIAL UTILIZATION
- INCLUDES TRADE-OFF BETWEEN HIGH STRENGTH AND
  LOW SCATTER
- ACCOUNTS FOR MATERIAL STRENGTH DISPERSION
- INCLUDES COMPONENT SIZE EFFECT
LIMITATIONS OF THE DIRECT STATISTICAL APPROACH

DESIGN STRESS, \( \sigma_d \)

DATA RANGE

PERMISSIBLE, \( \Phi \)

EXTRAPOLATION RANGE

BASIC DATA

SLOW CRACK GROWTH

EFFECTS OF SLOW CRACK GROWTH

SECOND POPULATION (e.g., INCLUSIONS)

MEASURE POPULATION (SURFACE CRACKS)

UNDETECTED FLAW POPULATIONS

BIAXIAL

UNIAXIAL

STRESS STATE EFFECTS

\( \frac{V(S/S_0)^m}{V} \)

TRUNCATION LEVEL

TRUNCATION PROCEDURES

-\ln(1 - \Phi)
ELEMENTS OF BATDORF'S THEORY (1)

TESTING FOR REQUIRED MATERIAL PROPERTIES, \( N(\sigma) - CRACK \) DISTRIBUTION

POLYAXIAL FRACTURE CRITERIA INCLUDED

CRACK CONFIGURATION SPECIFIED
- RANDOMLY ORIENTED CRACKS
- NO CRACK INTERACTION

ADDITION OF SHEAR-SENSITIVE CRACKS

RELIABILITY PREDICTION (RANGE LIMITED)

BATDORF THEORY

BATDORF THEORY (2) (CONTINUED)

\[ P_S(\Sigma) = P_S^V \cdot P_S^A \]

\[ P_S^V = \exp \left( - \int \int_0^{\sigma_1} \frac{\Omega}{4\pi} \frac{dN_1}{d\sigma_{cr}} \ d\sigma_{cr} \ dv \right) \]

\[ P_S^A = \exp \left( - \int \int_0^{\sigma_1} \frac{\omega}{\pi} \frac{dN_2}{d\sigma_{cr}} \ d\sigma_{cr} \ dA \right) \]

\[ N_1 = K_1 \sigma_{cr}^{m_1} \]

\[ N_2 = K_2 \sigma_{cr}^{m_2} \]

\[ \omega = f_1(\sigma_{cr}, \sigma_1, \sigma_2) \]

\[ \Omega = f_2(\sigma_{cr}, \sigma_1, \sigma_2, \sigma_3, a) \]

\[ \sigma_0 = f_3(\sigma_n, \tau), \ f_3 \ DEPENDS \ UPON \ THE \ FRACTURE \ CRITERION \ SELECTED \]

\[ \sigma_n = f_4(\sigma_1, \sigma_2, \sigma_3, a, \beta) \]

\[ \tau = f_5(\sigma_1, \sigma_2, \sigma_3, a, \beta) \]
FLOW CHART FOR RELIABILITY PREDICTION
(VOLUME FLAWS ONLY)

EXAMPLE 1 - ROTATING ANNULAR DISK

DATA:
NC - 132 HOT PRESSED Si₃N₄
m = 7.65
σ₀ = 74.82 MPa m. 3922
k_Β = 16.30
r_i = 6.35 mm (.25 in)
r_o = 41.275 mm (1.625 in)
t = 3.80 mm (.15 in)
RPM RANGE - 70K TO 114K
APPLICATION TO CERAMICS

- Initially only Weibull theory was used (includes CATE, AGT, and DARPA programs)
- Limited success and accuracy obtained
- Battorf bridges gap between fracture theories in 1974 (Graphite nose cones)
- University of Washington (UW) applies Battorf's theory to ceramics (NASA grant)
- LeRC corrects UW publications and develops general purpose design program - SCARE
- SCARE includes Weibull and Battorf theories
- SCARE released to GM, Ford, TRW, Boeing, GE, and NASA and Army for initial evaluation
CONCLUSIONS

1. PROBABILISTIC DESIGN APPROACH AND WLT MUST BE USED FOR CERAMICS

2. FRACTURE MECHANICS MUST BE APPLIED TO IMPROVE MODELING OF:
   - MULTI-AXIALITY EFFECT
   - DELAYED FAILURE

3. PROOF-TESTING AND/OR NDE SHOULD BE USED TO AVOID DATA EXTRAPOLATION

4. MULTIPLE FLAW DISTRIBUTIONS SHOULD BE INCLUDED IN THE ANALYSIS

5. IMPROVED FRACTURE TOUGHNESS AND MATERIAL PROCESSING ARE NEEDED TO INCREASE CERAMIC STRENGTH
A review is presented on research for nondestructive evaluation (NDE) of structural ceramics for heat engine applications. Microfocus radiography and scanning laser acoustic microscopy are the NDE techniques highlighted in this review. The techniques were applied to research samples of sintered silicon nitride and silicon carbide in the form of modulus-of-rupture (MOR) bars. The strengths and limitations of the aforementioned techniques are given in terms of probability of detection for voids in green and sintered MOR bars. Voids for this purpose were introduced by seeding green ceramic bars and characterizing each void in terms of its size, shape, location, and nature before and after sintering. The effects of material density, microstructure, surface finish, thickness, void depth, and size characteristics on detectability are summarized. The review presented here is based on the work of Stanley Klima, Don Roth, George Baaklini, William Sanders, and James Kiser of Lewis Research Center, Cleveland, Ohio.
FABRICATION OF MODULUS-OF-RUPTURE (MOR) BARS CONTAINING SEEDED INTERNAL VOIDS

- 100 MESH α-SIC POWDER
  OR
- 100 MESH Si₃N₄ POWDER

 POWDER PLACED IN DIE

 NOMINALLY 530, 320, 115, 80, OR 50 μm DIAMETER PLASTIC SPHERES PLACED ON POWDER

 MICROSPHERE POSITIONS PHOTOGRAPHICALLY RECORDED

 MICROSPHERES COVERED WITH POWDER AND PRESSED AT 120 MPa TO FORM GREEN TEST BAR

 BAR ISOPRESSED AT 420 MPa

 BAR HEATED 45-60 min
 HOLD AT 550 °C UNDER VACUUM TO BURN OUT MICROSPHERES

 Si₃N₄ SINTERED
 - 2100 °C
 - 2 hr
 - 5 MPa N₂ PRESSURE

 SiC SINTERED
 - 2000 °C
 - 0.5 hr
 - 0.1 MPa Ar PRESSURE

EXPERIMENTAL/ANALYTICAL

• Specially prepared modulus-of-rupture type bars were systematically seeded with critical size voids

• Voids resulted after the styrene divinyl benzene microspheres were decomposed in the green ceramics at 550 °C

• POD statistics were determined using the cumulative probability formula

\[ 1 - G = \sum_{X=S}^{N} \frac{N!}{X!(N-X)!} P_L^X (1-P_L)^{N-X} \]

where \( P_L \) is the lower-bound probability of detection, \( G \) is the confidence level, \( N \) is the number of voids seeded, and \( S \) is the number of void detected
**DIMENSIONAL CHARACTERISTICS OF RESULTING INTERNAL VOIDS IN SINTERED MATERIALS**

<table>
<thead>
<tr>
<th>MATERIALS</th>
<th>SPECIMEN THICKNESS RANGE, µm</th>
<th>SPHERE diam, µm</th>
<th>NUMBER OF SPHERES SEEDED</th>
<th>RESULTING VOID DIMENSION</th>
<th>VOID DEPTH, µm</th>
<th>VOID DIAMETER, µm</th>
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**SCANNING ELECTRON FRACTOGRAPHS SHOWING TYPICAL INTERNAL VOIDS IN GREEN SiC BARS**

[Images of electron fractographs showing typical internal voids in green SiC bars]
SCANNING ELECTRON MICROGRAPHS
OF A TYPICAL VOID IN SINTERED SiC BARS

AS EXPOSED TO SURFACE

TEXTURE OF THE CAVITY-WALL-SURFACE
SCANNING ELECTRON MICROGRAPHS OF TYPE A INTERNAL Voids IN SINTERED Si₃N₄

AS EXPOSED TO SURFACE

CLUSTERS OF GRAINS PROJECTING FROM THE CAVITY WALLS
SCANNING ELECTRON MICROGRAPHS OF TYPE B INTERNAL VOIDS IN SINTERED Si$_3$N$_4$
A SCHEMATIC CONFIGURATION OF MICROFOCUS PROJECTION RADIOGRAPHY

![Diagram showing the schematic configuration of microfocus projection radiography.](image)

MATERIALS | INTERNAL VOIDS | SURFACE VOIDS
--- | --- | ---
SiC GREEN | 2.6 | 1.4
SINTERED | 1.5 | 1.7
Si$_3$N$_4$ GREEN | 2.4 | 1.5
SINTERED | 0.6 | 1.5

- 90/95 POD/CL (PROBABILITY OF DETECTION/CONFIDENCE LEVEL) means that there is a 5% probability that the 90% is an overestimate of the probability of detection.
LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN GREEN ISOPRESSED SiC (GSC) AND Si₃N₄ (GSN) BARS

- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY \% = 100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/ (THICKNESS OF SPECIMEN IN SAME DIRECTION)

LOWER BOUND PROBABILITY OF DETECTION OF SURFACE AND INTERNAL VOIDS IN SINTERED SiC (SSC) AND Si₃N₄ (SSN) BARS

- POD CURVES WERE CALCULATED AT 95 PERCENT CONFIDENCE LEVEL
- THICKNESS SENSITIVITY \% = 100 (VOID DIMENSION IN X-RAY BEAM DIRECTION)/ (THICKNESS OF SPECIMEN IN SAME DIRECTION)
SCHEMATIC ILLUSTRATION OF THE SCANNING LASER ACOUSTIC MICROSCOPE

EFFECT OF SPECIMEN SURFACE CONDITION ON SLAM IMAGE CLARITY

- AS-FIRED SURFACE PRODUCES A HIGHER BACKGROUND NOISE LEVEL

AS-FIRED SURFACE PROFILE.

ACOUSTIC MICROGRAPH OF AS-FIRED SPECIMEN.

HAND-POLISHED SURFACE PROFILE.

ACOUSTIC MICROGRAPH OF HAND-POLISHED SPECIMEN.
EFFECT OF SURFACE FINISH AND SPECIMEN THICKNESS ON DETECTION OF VOIDS IN SSN

(a) SPECIMEN THICKNESS, APPROXIMATELY 4 mm.
(b) SPECIMEN THICKNESS, APPROXIMATELY 3 mm.
(c) SPECIMEN THICKNESS, APPROXIMATELY 2 mm.

EFFECT OF VOID DIAMETER, VOID DEPTH, AND MATRIX MATERIAL ON PROBABILITY OF DETECTION BY SLAM

90% PROBABILITY OF DETECTION AT 95% CONFIDENCE LIMIT

- DEPTH BELOW WHICH A VOID WITH A SPECIFIED DIAMETER CANNOT BE DETECTED AT PDD(CL) = 90%
- DETECTABILITY OF SMALLER, DEEPER VOIDS IN SSN MAY BE ATTRIBUTABLE TO FINER GRAINS AND GREATER DENSITY (SSN AT > 99% VS SSC AT ~ 97% THEORETICAL DENSITY)

44
NDE FOR CHARACTERIZING CERAMIC MICROSTRUCTURES

5 GROUPS OF α-SiC MOR
BARS WITH:
• DIFFERENT DENSITIES
• DIFFERENT MICROSTRUCTURES

SINTERED AND MACHINED
10 BARS/GROUP
• X-RAY
• SLAM

SINTERED AND POLISHED
10 BARS/GROUP
ULTRASONICS:
• INSTRUMENTATION
• HIGH-FREQUENCY
• PROCEDURE DEVELOPMENT
• VELOCITY
• ATTENUATION

SINTERED-HIPPED AND POLISHED
10 BARS/GROUP
• 4-POINT BEND TEST
• FRACTURE TOUGHNESS

INSTRUMENTATION
HIGH-FREQUENCY
PROCEDURE DEVELOPMENT
VELOCITY
ATTENUATION

X-RAY
SLAM

CORRELATIONS
NOC, STRENGTH, FRACTURE TOUGHNESS, MICROSTRUCTURE, DENSITY, SURFACE

ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si3N4

<table>
<thead>
<tr>
<th>Test Temperature</th>
<th>Sub-surface Pore</th>
<th>Surface Pore</th>
<th>Seam</th>
<th>Sub-surface Agglomerate</th>
<th>Columnar Grain</th>
<th>Surface Defect</th>
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*NUMBER EXCLUDES 111, 47, AND 41 BARS FOR R.T., 1200°C, AND 1370°C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.
SUMMARY

SCANNING LASER ACOUSTIC MICROSCOPY

VOID DETECTABILITY WAS AFFECTED BY MATERIAL, MICROSTRUCTURE, SURFACE FINISH, SPECIMEN THICKNESS, VOID DEPTH, AND VOID SIZE.

• VOIDS WERE MORE EASILY DETECTED IN SINTERED SILICON NITRIDE (SSN) THAN IN SINTERED SILICON CARBIDE (SSC). SSN GRAIN SIZE WAS AN ORDER OF MAGNITUDE SMALLER THAN IN SSC.

• VOID DETECTABILITY WAS SIGNIFICANTLY IMPROVED BY SURFACE GRINDING. IN SPECIMENS WITH AS-FIRED SURFACES, 0.90/0.95 POD/CL WAS NOT ACHIEVED FOR ANY VOID SIZE UP TO 160 μm.

• LITTLE OR NO THICKNESS EFFECT ON DETECTABILITY WAS OBSERVED IN SPECIMENS WITH GROUNDED SURFACES. IN SPECIMENS WITH AS-FIRED SURFACES, DETECTABILITY IMPROVED WITH DECREASING THICKNESS.

MICROFOCUS X-RAY RADIOGRAPHY

DETECTABILITY OF VOIDS WAS AFFECTED BY PHOTON ENERGY LEVEL, MATERIAL COMPOSITION IN THE VICINITY OF THE VOID, DENSITY VARIATIONS, SAMPLE THICKNESS AND VOID SIZE.

• LOW PHOTON ENERGY LEVELS (≤20 KeV) PRODUCED BETTER RADIOGRAPHIC FILM CONTRAST AND HENCE BETTER VOID DETECTABILITY THAN HIGHER ENERGY LEVELS.

• YITTRIUM MIGRATING TO THE WALLS OF SEEDED VOIDS AIDED DETECTION OF SOME BUT NOT ALL VOIDS IN SSN. YITTRIA SINTERING AID WAS THE SOURCE.

• DETECTABILITY OF VOIDS DID NOT APPEAR TO BE ADVERSELY AFFECTED BY AS-FIRED SURFACES RELATIVE TO DIAMOND GROUND SURFACES.

• THE THRESHOLD LEVEL OF DETECTION OF VOIDS WAS 1.5 PERCENT OF SPECIMEN THICKNESS OR 50 μm, WHICHER IS GREATER, WHEN THE 0.90/0.95 POD/CL CRITERIA WAS APPLIED.
The application of fracture mechanics to the design of ceramic structures will require the precise measurement of crack growth and fracture resistance of these materials over their entire range of anticipated service temperatures and standardized test methods for making such measurements. The development of a standard test for measuring the plane strain fracture toughness is the initial objective of our ceramics fracture mechanics program.

Current fracture tests make use of a variety of specimen types (single-edge-notched bend, double torsion, double cantilever bend, and surface flawed specimens) having either blunt notches produced by saw cutting, or cracks produced by wedge loading, indenting, or local thermal shock. Specimens with blunt notches can overestimate the fracture toughness. Precracked specimens are difficult to prepare in a reproducible manner, and the initial crack front often cannot be seen on the fracture surface after testing, which makes it impossible to measure the initial crack length. These difficulties can be circumvented by using a specimen containing a chevron notch in which a crack originates at the tip of the triangular ligament during the early stage of specimen loading. Specimens with a chevron notch were first used by Nakayama in fracture studies (ref. 1). Later they were used by Tattersall and Tappin for fracture surface energy measurements (ref. 2) and more recently, by Barker for plane strain fracture toughness measurements (ref. 3). The essential features of the chevron-notch specimen are that (1) a sharp natural crack is produced during the early stage of loading (no precracking is required) and (2) the load passes through a maximum at a constant material-independent crack length-to-width ratio for a specific specimen geometry (no post-test crack length measurement is required). For materials with flat crack growth resistance curves, the plane strain fracture toughness is proportional to the maximum test load and a function of the specimen geometry and elastic compliance.

Stress intensity factor coefficients have been determined for three varieties of chevron-notch specimens, and fracture toughness measurements have been made on silicon nitride, silicon carbide, and aluminum oxide to assess the performance of each specimen variety. It has been determined that silicon nitride and silicon carbide have flat crack growth resistance curves, but aluminum oxide does not. Additionally, batch-to-batch differences have been noticed for the aluminum oxide. Experiments are continuing to explain the rising crack growth resistance and batch-to-batch variations for the aluminum oxide.

REFERENCES


47
PLANE STRAIN ELASTIC STRESS FIELD IN VICINITY OF CRACK TIP

\[ \sigma_x = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left(1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2}\right) + \ldots \]

\[ \sigma_y = \frac{K_I}{(2\pi r)^{1/2}} \cos \frac{\theta}{2} \left(1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2}\right) + \ldots \]

\[ \tau_{xy} = \frac{K_I}{(2\pi r)^{1/2}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2} + \ldots \]

\[ \sigma_z = \nu(\sigma_x + \sigma_y); \quad \tau_{xz} = \tau_{yz} = 0 \]

\( K_I \) IS THE "STRESS INTENSITY FACTOR"

\( K_{IC} \) IS THE "FRACTURE TOUGHNESS"

---

**CHEVRON-NOTCH SPECIMENS**

SHORT BAR

SHORT ROD

FOUR-POINT BEND

CRACK PLANE SECTION
THEORETICAL BASIS FOR CHEVRON-NOTCH SPECIMEN $K_{IC}$ MEASUREMENT

AVAILABLE ENERGY FOR EXTENSION OF CRACK BY $\Delta a$:

$$\Delta U = \frac{p^2}{2W} \cdot \frac{dc}{da} \cdot \Delta a$$

NECESSARY ENERGY FOR EXTENSION OF CRACK BY $\Delta a$:

$$\Delta W = G_{IC} \cdot b \cdot \Delta a = \frac{K_{IC}^2}{E} \cdot b \cdot \Delta a$$

DURING CRACK EXTENSION $\Delta U = \Delta W$, AND:

$$K_{IC} = P \left[ \frac{E}{2bW} \cdot \frac{dc}{da} \right]^{1/2}$$

AND SINCE $b = B \left[ \frac{a - a_0}{a_1 - a_0} \right] = B \left[ \frac{a^2 - a_0^2}{a_1^2 - a_0^2} \right]$

$$K_{IC} = P \left[ \frac{E}{2W} \cdot \frac{dc}{da} \right]^{1/2} = \frac{P}{B/W} \left[ \frac{EB}{2} \cdot \frac{dc}{da} \cdot (a_1 - a_0) \right]^{1/2} = \frac{P}{B/W} \cdot \gamma^*$$

$K_{IC}$ OF $Si_3N_4$

<table>
<thead>
<tr>
<th>$B = 2H$</th>
<th>$W$</th>
<th>$W/2H$</th>
<th>$a_0$</th>
<th>$a_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.9</td>
<td>13.3</td>
<td>1.5</td>
<td>0.20 - 0.51</td>
<td>1.0</td>
</tr>
<tr>
<td>8.9</td>
<td>15.1</td>
<td>1.7</td>
<td>0.20 - 0.51</td>
<td>1.0</td>
</tr>
<tr>
<td>8.9</td>
<td>17.0</td>
<td>2.0</td>
<td>0.20 - 0.50</td>
<td>1.0</td>
</tr>
<tr>
<td>8.9</td>
<td>13.3</td>
<td>1.5</td>
<td>0.17 - 0.38</td>
<td>1.0</td>
</tr>
<tr>
<td>8.8 - 9.6</td>
<td>14.9 - 15.4</td>
<td>1.7</td>
<td>0.17 - 0.48</td>
<td>0.45 - 1.0</td>
</tr>
</tbody>
</table>

All dimensions in mm.
CHEVRON-NOTCH SPECIMEN $K_{lc}$ FROM $P_{\text{max}}$ AND $Y_m^*$

\[ K_{lc} = \frac{P_{\text{max}}}{Y_m^*} \]

CHEVRON-NOTCH SPECIMEN $K$ CALIBRATION SETUP
CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

[Image of calibration setup]

CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP

[Image of calibration setup]
CHEVRON-NOTCH SPECIMEN K CALIBRATION SETUP
CHEVRON-NOTCH SHORT BAR SPECIMEN
DIMENSIONLESS COMPLIANCE

\[ C'_{cr}, C' \]

\[ W/H = 4 \]
\[ a_1 = 1 \]
CHEVRON-NOTCH SHORT BAR SPECIMEN
STRESS INTENSITY FACTOR COEFFICIENTS
VARIATION IN $K_{IC}$ WITH CRACK EXTENSION TO $P_{MAX}$

$\text{AL}_2\text{O}_3$

- $a_1 = 1, a_0$ VARIED
- $a_0 = 0.2, a_1$ VARIED

<table>
<thead>
<tr>
<th>$B$ - mm</th>
<th>$W/2H$</th>
<th>$a_1$</th>
<th>$a_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.4</td>
<td>2.0</td>
<td>1.0</td>
<td>0.21-0.43</td>
</tr>
<tr>
<td>25.4</td>
<td>1.5</td>
<td>1.0</td>
<td>0.22-0.44</td>
</tr>
<tr>
<td>12.7</td>
<td>2.0</td>
<td>1.0</td>
<td>0.19-0.44</td>
</tr>
<tr>
<td>12.7</td>
<td>1.5</td>
<td>1.0</td>
<td>0.09-0.37</td>
</tr>
<tr>
<td>12.7</td>
<td>2.0</td>
<td>0.40-1.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$K_{IC}$ - MN m$^{-3/2}$

$(a_m - a_0)$ - mm
$AL_2O_3$ R-CURVES

![Graph showing R-curves for $AL_2O_3$.](image)

<table>
<thead>
<tr>
<th>$B$ (mm)</th>
<th>$W/2H$</th>
<th>$\alpha_1$</th>
<th>$\alpha_0$</th>
<th>BATCH</th>
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<tbody>
<tr>
<td>25.4</td>
<td>2.0</td>
<td>1.0</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>25.4</td>
<td>2.0</td>
<td>1.0</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
<td>25.4</td>
<td>2.0</td>
<td>1.0</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>25.4</td>
<td>2.0</td>
<td>0.4</td>
<td>0.2</td>
<td>2</td>
</tr>
</tbody>
</table>
STRUCTURAL CERAMICS RESEARCH

J.I. Mueller, R.J.H. Bollard, and R.C. Bradt
University of Washington
Seattle, Washington

OUTLINE

CERAMIC RESEARCH AT U. OF W.

BRITTLE MATERIALS DESIGN PROGRAM

NASA PROGRAM RESEARCH AT U. OF W.
STRUCTURAL CERAMIC RESEARCH at U. of W.

AKSAY, I. MSE powder processing, sintering
BERG, J. ChE colloidal studies
BJORKSTAM, J. EE NDE/NDT
DOLLARD, R.J.H. AA evaluation, design
BRADT, R. MSE mechanical properties
DASH, G. PHY thermal conditions
EMERY, A. ME thermal stresses
FISCHBACH, D. MSE fiber composite, carbon
HARTZ, B. CE design
KIKUCHI, R. MSE theoretical modeling
KOBAYASHI, A. ME mechanical prop., dynamic fracture
LIN, K. AA elast. mechanical comp.
MILLER, A. MSE processing, environ. effects
RAMULU, M. ME dynamic fracture, machining
RAO, Y. MSE nitridation Si
REED, D. CE design
SARIKAYA, M. MSE characterization
SCOTT, W. MSE oxidation
STOEBE, T. MSE nitridation, defects
TAGGART, R. ME design
TAYA, M. ME comp., mechanics
WHITTEMORE, O MSE processing

BRITTLE MATERIALS DESIGN PROGRAM (COURSE)

BRITTLE MATERIALS

PROCESSING of CERAMICS

ELASTICITY

MECHANICAL CHARACTERIZATION

MICROSTRUCTURE/MECHANICAL PROPERTIES

ENGINEERING PROPERTIES of CERAMICS

STRENGTH and FAILURE THEORIES

NDE/NDT

DESIGN of COMPONENTS

LABORATORY (PP) COMPONENT MANUFACTURE

60
CURRENT NASA RESEARCH PROGRAM AT UW

I. PROCESSING AND CHARACTERIZATION

STOEBE - Lattice Defects in $\text{Si}_3\text{N}_4$

RAO - Nitridation of Si

AKSAY - Powder Consolidation by Injection Molding

SCOTT - Oxidation Resistance of $\text{Si}_3\text{N}_4$

II. MECHANICAL PROPERTIES

MILLER - Environmental Effects on $\text{Si}_3\text{N}_4$ :SiC

EMERY - Thermal Fracture

KOBAYASHI - Impact, Erosion, Dynamic Fracture

BOLLARD - Evaluation of Mechanical Tests

BRADT/REED - Micromechanical Stresses

PROPOSED 86/87 CERAMIC/COMPOSITES RESEARCH TOPICS

AKSAY - POWDER PROCESSING

RAO - NITRIDATION

MILLER - COMPOSITE NITRIDATION

BERG - COLLOIDAL PROCESSING OF COMPOSITES

EMERY - THERMAL PROPERTIES

KOBAYASHI - DYNAMIC MECHANICAL PROPERTIES

TAYA - THERMAL CYCLING FATIGUE

BRADT/REED - ANISOTROPIC RESIDUAL STRESSES

BOLLARD - MECHANICAL CHARACTERIZATION
COMPOSITE CHARACTERIZATION

Material

Microstructure Evaluation

Mathematical Modelling

Experimental Evaluation

Design & Interpretation of Tests

Prediction of Behavior Constants and Failure

Elastic Anisotropic Behavior Constants

Failure

Design of Materials and Structures with Performance Prediction Up to Failure
This report describes work performed in the first year of the program conducted for NASA to develop silicon carbide materials of high strength and to form components of complex shape and high reliability. The approach has been to adapt a beta-SiC powder and binder system to the injection molding process and to develop procedures and process parameters capable of providing a sintered silicon carbide material with improved properties.

The initial effort has been to characterize the baseline precursor materials (beta silicon carbide powder and boron and carbon sintering aids), develop mixing and injection molding procedures for fabricating test bars, and characterize the properties of the sintered materials. Parallel studies of various mixing, dewaxing, and sintering procedures have been performed in order to distinguish process routes for improving material properties.

A total of 276 MOR bars of the baseline material have been molded, and 122 bars have been fully processed to a sinter density of approximately 95 percent. The material has a mean MOR room temperature strength of 43.3 ksi (299 MPa), a Weibull characteristic strength of 45.8 ksi (315 MPa) and a Weibull modulus of 8.0. Mean values of the MOR strengths at 1000 °C, 1200 °C and 1400 °C are 41.4 ksi, 43.2 ksi and 47.2 ksi, respectively. Strength controlling flaws in this material were found to consist of regions of high porosity and were attributed to agglomerates originating in the initial mixing procedures.

New fluid mixing techniques have been developed which significantly reduce flaw size and improve the strength of the material. Initial MOR tests indicate the strength of the fluid-mixed material exceeds the baseline property by more than 33 percent.

Plans for the development of the fluid-mixing process to reduce flaw size and increase density and the optimization of sinter-body microstructure to increase toughness of the silicon carbide materials will be reviewed.

Contributions to this program were made by the following.


**NASA:** S. Levine and N. Shaw

---

*Work performed under NASA Contract No. NAS3-24384*
FIRST YEAR REVIEW

T. J. Whalen
J. A. Mangels

May 21, 1986

OBJECTIVE:
Develop High Strength, High Reliability Silicon Carbide Parts Having Complex Shapes by a Method Adaptable to Mass Production on an Economically Sound Basis.

APPROACH:
Adapt Powder and Binder System to Injection Molding Process and Develop Procedures and Optimize Process Parameters Leading to a Sintered Silicon Carbide Material with Improved Properties.

BENEFITS:
Silicon Carbide Parts for Advanced Gas Turbines and Other Heat Engines Would Permit Higher Temperature Operation with Resulting Fuel Efficiencies.

START / FINISH:
February, 1985 to February, 1988
**OUTLINE**

**TASK I**

T. J. WHALEN

* Baseline Powders Characterization
* Baseline Composition Selection
* Baseline Results

**TASK VII AND PLANS**

J. A. MANGELS

* Processing and Composition Improvements
* Planning
TASK I

BASELINE CHARACTERIZATION

POWERS

CHEMICAL ANALYSIS - BASELINE MATERIAL

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>UF-SiC</th>
<th>BORON</th>
<th>CARBON</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>30.4</td>
<td>0.36</td>
<td>98.6</td>
</tr>
<tr>
<td>O</td>
<td>0.85</td>
<td>1.71</td>
<td>1.12</td>
</tr>
<tr>
<td>Al</td>
<td>0.046</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.043</td>
<td>0.17</td>
<td>0.005</td>
</tr>
<tr>
<td>Ca</td>
<td>0.019</td>
<td>0.046</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.015</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.005</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td>0.25</td>
</tr>
</tbody>
</table>

* Weight Percent

B.E.T. SURFACE AREA

As Received Powders for Baseline Bars

<table>
<thead>
<tr>
<th></th>
<th>Lot</th>
<th>Material</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibiden UF</td>
<td>0166</td>
<td>SiC</td>
<td>21.5 m²/g</td>
</tr>
<tr>
<td>Starck</td>
<td>S-3506</td>
<td>B</td>
<td>12.1 m²/g</td>
</tr>
<tr>
<td>Monsanto</td>
<td>TL-246</td>
<td>C</td>
<td>53.1 m²/g</td>
</tr>
</tbody>
</table>
PARTICLE DIAMETER, SPECIFIC GRAVITY, PACK DENSITY,
AND POLYPHASE ANALYSIS OF SiC POWDER FOR BASELINE BARS

<table>
<thead>
<tr>
<th>Particle Diameter</th>
<th>Volume Dist.</th>
<th>Frequency Dist</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Lot 0166</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
<td>1.05</td>
<td>0.61</td>
</tr>
<tr>
<td>Mode</td>
<td>1.16</td>
<td>0.64</td>
</tr>
<tr>
<td>Geometric Mean</td>
<td>1.04</td>
<td>0.59</td>
</tr>
<tr>
<td>Arithmetic Mean</td>
<td>1.18</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Specific Gravity 3.161 g/cm³
Pack Density 0.787 g/cm³
X-ray Polyphase Analysis

<table>
<thead>
<tr>
<th>Phase</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C Phase</td>
<td>84.0 %</td>
</tr>
<tr>
<td>Disordered Phase</td>
<td>16.0 %</td>
</tr>
</tbody>
</table>

Sample: RNW-PARAFFIN CARNUBA LQ
Size: 13.50 mg
Rate: SC/MIN 100ML/MIN ARG
Program: TGA Analysis v2.0

Data: 26-Aug-85 Time: 8:11:08
File: TGA.DI TGA, BAUG.1985
Operator: L. SKEWES
Plotted: 26-Aug-85 10:56:43
TGA

Sample: RMW-PARAFFIN LOW CARNUBA
Size: 13.41 mg
Rate: 5C/MIN 8mm Hg
Program: TGA Analysis V2.6

Date: 5-Aug-85  Time: 13:56:50
File: TGA.13 TGA.7JULY.1985
Operator: L. SKEWES
Plotted: 5-Aug-85  15:44:12

[Graph showing thermal analysis data with temperature and weight changes.]

DSC

Sample: RMW-PARAFFIN LOW CARNUBA
Size: 1.873mg
Rate: 5C/MIN 9mg
Program: Interactive DSC 3.0

Date: 30-Jul-85  Time: 13:23:47
File: DSC.03 DSC.3JUL.85
Operator: L. SKEWES
Plotted: 31-Jul-85  15:35:29

[Graph showing differential scanning calorimetry data with temperature and heat flow changes.]
TASK I

BASELINE CHARACTERIZATION

PROCESS

BEGIN WITH PROCESS

1. TASK I
2. BASELINE CHARACTERIZATION

PROCESS

STARTING POWDERS

MIXING

INJECTION HOLDING

DEMAKING

SAMPLES

Chemical Analysis

Part Size Distribution

Surface Area

Fractography

Agglomerate Size

Visual Inspection

X-ray

Fracture Surface Inspection

Mass

Density

SINTERING

CHARACTERIZATION

ANALYSIS

STATISTICAL EFFECTS AND INTERACTIONS

Time

Dryness

Pressure

Temperature

Position in Die

Visual

X-ray

Shrinkage

Mass

Density

Mean Strength

Standard Dev.

Mean Density

Weibull Strength

Weibull Modulus

Fracture Orig.

Flaw Size-SEM

Correlation of Properties with Process & Material Parameters

Main Effects

2-factor Interactions

Level of Significance

Planning Next Matrix

Recommendations to NASA

69
**2³ EXPERIMENT TO**

**DETERMINE BASELINE COMPOSITION**

![Graph showing composition vs solids loading with levels for Resin, C-Black, and Powder.]

**2³ BASELINE EXPERIMENT**

<table>
<thead>
<tr>
<th>NASA #</th>
<th>SOLIDS LOADING LEVEL</th>
<th>CARBON SOURCE</th>
<th>81C SOURCE</th>
<th>XT.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>55.5</td>
<td>C-BLACK</td>
<td>UF</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>58.5</td>
<td></td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>55.5</td>
<td>C-BLACK</td>
<td>SF</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>58.5</td>
<td></td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>55.5</td>
<td>RESIN</td>
<td>UF</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>58.5</td>
<td></td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>55.5</td>
<td>RESIN</td>
<td>SF</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>58.5</td>
<td></td>
<td></td>
<td>88</td>
</tr>
</tbody>
</table>
BASELINE COMPOSITION

(From 2³ Experiment)

2% C - 1% B - 97% SiC
55.5% Solids Loading
SPC CHART OF BASELINE MOLDING PROCESS

SPC CHART SINTERING

OBSERVATIONS (FOUR-GROUP MEANS)

OBSERVATIONS

SPC C

H

ART OF BAS

E

OLD IN

M

PROCESS

2.15

2.13

2.11

UCL

2.85

LCL

2.85

2.80

2.75

2.70

2.65

2.60

0.5

5

10

15

MOLDED DENSITY (G/CC)

DENSITY (G/CC)

UCL

3.86

3.86

3.82

3.78

3.74

3.70

3.66

3.62

3.58

3.54

3.50

3.46

3.42

3.38

3.34

3.30

3.26

3.22

3.18

3.14

3.10

3.06

3.02

2.98

2.94

2.90

2.86

2.82

2.78

2.74

2.70

2.66

2.62

2.58

2.54

2.50

2.46

2.42

2.38

2.34

2.30

2.26

2.22

2.18

2.14

2.10

2.06

2.02

1.98

1.94

1.90

1.86

1.82

1.78

1.74

1.70

1.66

1.62

1.58

1.54

1.50

1.46

1.42

1.38

1.34

1.30

1.26

1.22

1.18

1.14

1.10

1.06

1.02

0.98

0.94

0.90

0.86

0.82

0.78

0.74

0.70

0.66

0.62

0.58

0.54

0.50

0.46

0.42

0.38

0.34

0.30

0.26

0.22

0.18

0.14

0.10

0.06

0.02

-0.04

-0.08

-0.14

-0.20

-0.26

-0.32
# NASA 4B Baseline

## Fractography and X-ray

<table>
<thead>
<tr>
<th>M.O.R. Bars</th>
<th>Fracture Origin</th>
<th>X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 5           | 39.9 ± 6.2      | 3 - Sub Surface Porosity   
              | 2 - Surface Porosity    | Large inclusions,  
                          |                        | Comp. Surface          |
| 5           | 41.1 ± 5.3      | 4 - Sub Surface Porosity   
              | 1 - Surface Porosity    | Large inclusions,  
                          |                        | Center Line            |
| 5           | 37.3 ± 6.7      | 3 - Sub Surface Porosity   
              | 2 - Surface Porosity    | Clean                  |
| 5           | 42.3 ± 3.9      | 3 - Sub Surface Porosity   
              | 2 - Surface Porosity    | Small inclusions       |

## M.O.R. Baseline Summary

- Molded: 276
- X-ray acceptable: 210
- Dewaxed (1 run): 127
- Sintered (3 runs): 122
- Room Temp. M.O.R.: 30
- 1000°C: FF 6 (est), SR 6 (est)
- 1200°C: FF 6 (est), SR 6 (est)
- 1400°C: FF 6 (est), SR 6 (est)

* Number of M.O.R. Bars
FF Fast Fracture Test
SR Stress Rupture Test
**Task I**

**Baseline Characterization**

**M.O.R. Results**

<table>
<thead>
<tr>
<th>RT (°C)</th>
<th>1000°C</th>
<th>1200°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>43.3</td>
<td>41.4</td>
<td>43.2</td>
</tr>
<tr>
<td>mPa</td>
<td>(299)</td>
<td>(285)</td>
<td>(298)</td>
</tr>
<tr>
<td>n</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

**M.O.R. Baseline Results**

- $\bar{X} = 43.3$ mPa (299)
- $\theta = 45.8$ mPa (315) WEIBULL SAMPLES TOO SMALL FOR ACCEPTABLE ACCURACY

<table>
<thead>
<tr>
<th>MOR KSI</th>
<th>PROB. OF FAILURE</th>
<th>EXPECTED VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>25.72</td>
<td>34.55</td>
</tr>
<tr>
<td>10.00</td>
<td>43.76</td>
<td></td>
</tr>
<tr>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>90.00</td>
<td>50.00</td>
<td>50.00</td>
</tr>
<tr>
<td>95.00</td>
<td>53.59</td>
<td></td>
</tr>
<tr>
<td>99.00</td>
<td>55.51</td>
<td>58.41</td>
</tr>
<tr>
<td>99.90</td>
<td>55.51</td>
<td></td>
</tr>
</tbody>
</table>

**NASA Base Line RT 3’20’86**

[Graph showing Weibull probability plot with MOR KSI on the x-axis and percent failure on the y-axis.]
FRACTURE SURFACE
FLAW ORIGIN—IRON RICH

FRACTURE ORIGIN

LT= 300 SECS

X-ray overall spectrum

ENERGY (keV)
FRACTURE SURFACE
FLAW ORIGIN - SULFUR RICH

LT = 300 SECS

FRACTURE ORIGIN

ENERGY (keV)

COUNTS

0.000 5.000 10.000

ENERGY (keV)
TASK VII

OBJECTIVE:
CONTINUOUS THROUGHOUT THE PROGRAM

"ADVANCE THE STATE OF THE ART OF SiC TECHNOLOGY"

PROVIDE INPUT TO TASKS I AND II
WAYS TO IMPROVE THE STRENGTH OF A CERAMIC...

\[ \sigma \propto K_I E / c^{1/2} \]

INCREASE THE FRACTURE TOUGHNESS (MICROSTRUCTURE)

INCREASE THE ELASTIC MODULUS (DENSITY) **

REDUCE THE FLAW SIZE **

** ADDRESSED IN TASK VII

INJECTION MOLDED SiC PROCESS FLOW SHEET

POWDER PREPARATION

BLEND SINTERING ADDITIVES WITH SiC **

MIX SOLIDS WITH INJECTION MOLDING BINDERS **

INJECTION MOLD **

BINDER REMOVAL **

SINTER **

MACHINE

STRENGTH EVALUATION

** ADDRESSED IN TASK VII
DEVELOPMENT OF IMPROVED MIXING TECHNIQUES

FRActure OrigIns IDENTIFIED AS PROCESSING FlAWS

FlAWS IDENTIFIED AS AGGLOMERATES IN THE INJECTION MOLDING BATCH

AGGLOMERATES WERE DETECTED IN THE "MIXING" STAGE OF THE PROCESS

"GREEN" INJECTION MOLDED TEST BARS

STRENGTH CONTROLLING AGGLOMERATES (UF POWDER)

NO AGGLOMERATES OBSERVED (SF POWDER)
DRY MIXING PROCESS
(METHOD 1)

POWDER PREPARATION

DRY BLEND SINTERING ADDITIVES WITH SiC

MIX SOLIDS WITH INJECTION MOLDING BINDER USING DOUBLE PLANETARY MIXER **

INJECTION MOLD **

** AGGLOMERATES OBSERVED

DRY MIXING PROCESS
(METHOD 2)

POWDER PREPARATION

DRY BLEND SINTERING ADDITIVES WITH SiC

MIX SOLIDS WITH INJECTION MOLDING BINDER USING DOUBLE PLANETARY MIXER **

RE-MIX MOLDING BATCH IN HIGH SHEAR HAAKE MIXER **

INJECTION MOLD **

** AGGLOMERATES OBSERVED
HIGH SHEAR MIXING WAS FOUND TO REDUCE THE AGGLOMERATE SIZE

FLUID MIXING WAS INVESTIGATED TO REDUCE AGGLOMERATE SIZE

FLUID MIXING PROCESS (METHOD 1)

POWDER PREPARATION

FLUID BLEND SINTERING ADDITIVES WITH SiC

FLUID BLEND SOLIDS WITH INJECTION MOLDING BINDERS (BINDERS DISSOLVED IN FLUID)

REMOVE FLUID BY DRYING

ADD ADDITIONAL WAX USING DOUBLE PLANETARY MIXER **

INJECTION MOLD **

** AGGLOMERATES OBSERVED
FLUID MIXING WAS FOUND TO FURTHER REDUCE THE AGGLOMERATE SIZE

REGRESSION MODEL ILLUSTRATES THE RELATION BETWEEN STRENGTH AND AGGLOMERATE SIZE
FLUID MIXING PROCESS WILL BE USED IN THE REMAINDER OF THE PROGRAM (TASK II)

INJECTION MOLDING

INJECTION MOLDING PROCESSING WINDOW WAS IDENTIFIED

INJECTION MOLDING BEHAVIOR OF ALL SILICON BASED CERAMIC POWDERS IS A FUNCTION OF SURFACE AREA
INJECTION MOLDING PROCESS YIELDS WERE IMPROVED THROUGH EQUIPMENT MODIFICATION

COMPOSITION: 12A - 60.0 VOL % SOLIDS

ORIGINAL SYSTEM:

332 BARS MOLDED
221 BARS VOID FREE

66.6 % YIELD

IMPROVED VACUUM SYSTEM:

24 BARS MOLDED
23 BARS VOID FREE

95.8 % YIELD

BINDER REMOVAL - SINTERING

CURRENT PROCESS USES VACUUM FOR BINDER REMOVAL VACUUM FOR SINTERING

VACUUM PROCESSING RESULTS IN CRACK FREE TEST BARS HAVING GOOD DENSITY

PROBLEMS ARE ANTICIPATED WITH VACUUM PROCESSING:

CRACKING IN THICK CROSS SECTION COMPONENTS

LOW DENSITY AREAS ON AS SINTERED SURFACES
EXPERIMENTS WERE INITIATED TO INVESTIGATE ALTERNATIVES TO VACUUM PROCESSING DURING BINDER REMOVAL AND SINTERING.

BINDERS REMOVAL

2² EXPERIMENTAL DESIGN

VARIABLES:
- HEATING RATE
- PRESSURE

<table>
<thead>
<tr>
<th>EXP.</th>
<th>BINDER REMOVAL</th>
<th>VACUUM DENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>-</td>
<td>91.7</td>
</tr>
<tr>
<td>2)</td>
<td>+</td>
<td>91.4</td>
</tr>
<tr>
<td>3)</td>
<td>-</td>
<td>95.8</td>
</tr>
<tr>
<td>4)</td>
<td>+</td>
<td>96.4</td>
</tr>
</tbody>
</table>

EXP. 1 USED FOR BASELINE PROCESSING

EXP. 3 OFFERS POTENTIAL FOR PROCESSING LARGE COMPONENTS

SINTERING

ARGON SINTERING POTENTIAL DEMONSTRATED

SINTERED DENSITY VS SINTERING VARIABLES

![Graph showing sintered density vs sintering temperature]
FUTURE PLANS

TASK II

\[ \sigma \propto \frac{K_I E}{c^{1/2}} \]

FIRST ITERATION:

REDUCE PROCESSING FLAW SIZE (AGGLOMERATES)

SECOND ITERATION:

INCREASE DENSITY (ELASTIC MODULUS)

OPTIMIZE MICROSTRUCTURE (INCREASE FRACTURE TOUGHNESS)

FUTURE PLANS

TASK VII

CONTINUE TO STUDY WAYS TO REDUCE AGGLOMERATE SIZE

CONTINUE TO INVESTIGATE BINDER REMOVAL TECHNIQUES

CONTINUE TO STUDY THE INTERRELATION BETWEEN BINDER REMOVAL AND SINTERING

INITIATE WORK TO INCREASE SINTERED DENSITY AND IMPROVE SINTERED MICROSTRUCTURE
### Program Timing Chart

#### Phase I

<table>
<thead>
<tr>
<th>Task</th>
<th>1986</th>
<th>1987</th>
<th>1988</th>
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<tbody>
<tr>
<td>I Baseline</td>
<td>Complete</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II MOR Matrix</td>
<td>Iter. 1</td>
<td>Iter. 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduce &quot;c&quot;</td>
<td>Inc. K_i, E</td>
<td></td>
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<tr>
<td>III Opt. MOR</td>
<td></td>
<td></td>
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<tr>
<td>VII Tech.</td>
<td>Reduce &quot;c&quot;</td>
<td>Inc. K_i, E</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixing</td>
<td>Comp. &amp; Sinter</td>
<td></td>
</tr>
<tr>
<td>VIII Turbo. Mold.</td>
<td></td>
<td></td>
<td></td>
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</table>
Silicon carbide is of great interest for structural use in aircraft and automobile engines. This ceramic combines high thermal conductivity and low coefficient of thermal expansion, and consequently has good thermal shock resistance. However, like other ceramics, silicon carbide shows strength variability due to processing flaws such as large voids, shrinkage cracks, inclusions, etc. Agglomerates in the starting powder seem to be the predominant cause for such defects. Improved processing techniques such as slurry pressing and hot isostatic pressing were employed to minimize these defects and to improve strength and reliability in the fabricated material. For this purpose 2-inch diameter discs were fabricated by various consolidation techniques. These include: (1) dry pressing and sintering, (2) slurry pressing and sintering, and (3) slurry pressing and HIPing. High density (>96 percent of theoretical) was produced by sintering at 2150 - 2200 °C. By contrast, a much lower temperature (1850-1900 °C) was required by HIPing to achieve high final density specimens. Dry pressing and sintering yielded an average flexure strength (4-point bend) of 350 MPa (50 ksi), while slurry pressing and sintering produced an average strength of 430 MPa (62 ksi), a 30 percent improvement in strength. Further, slurry pressing and HIPing yielded an average strength of 580 MPa (84 ksi). This strength value is 60 percent higher than the dry-pressed/sintered strength, and 30 percent higher than the slurry-pressed/sintered strength. The HIP silicon carbide exhibited an ultrafine grained microstructure (0.3-3 μm) as compared to 1-30 μm produced by sintering. Process related defects such as large isolated voids, shrinkage cracks, etc. were not observed in HIPed silicon carbide.
### Table 1: Analysis of As-Received α-SiC Powders

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>TYPE 1</th>
<th>TYPE 2</th>
<th>TYPE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-SiC (100%)</td>
<td>α-SiC (B, C)</td>
<td>α-SiC (Al, C)</td>
</tr>
<tr>
<td>Al</td>
<td>50</td>
<td>140</td>
<td>1.2°</td>
</tr>
<tr>
<td>Ca</td>
<td>70</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Fe</td>
<td>10</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>V</td>
<td>20</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>0.60°</td>
<td>-</td>
</tr>
<tr>
<td>FREE C</td>
<td>1.66°</td>
<td>7.31°</td>
<td>6.30°</td>
</tr>
<tr>
<td>SURFACE AREA (BET)</td>
<td>31.47</td>
<td>4.19</td>
<td>11.38</td>
</tr>
</tbody>
</table>

% WT PERCENT

### Relative Density of Three Types of Starck α-SiC Powder Sintered for 30 min at Different Temperatures

![Graph showing relative density of three types of Starck α-SiC powder sintered at different temperatures]
### PROCESSING AND PROPERTIES OF TYPE 2 (AS-RECEIVED) α-SiC (B, C) MATERIAL

<table>
<thead>
<tr>
<th>Type</th>
<th>Sintered Temperature, °C</th>
<th>Time, min</th>
<th>Density, g/cm³</th>
<th>MOR/Test Temperature, °C</th>
<th>Number of Specimen</th>
<th>Mean MOR/δ-D., MPa</th>
<th>Weibull/R², m</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2150</td>
<td>30</td>
<td>95</td>
<td>RT</td>
<td>23</td>
<td>353</td>
<td>11/95</td>
</tr>
<tr>
<td>2</td>
<td>2150</td>
<td>60</td>
<td>96</td>
<td>RT</td>
<td>28</td>
<td>306/32</td>
<td>12/97</td>
</tr>
<tr>
<td>2</td>
<td>2200</td>
<td>30</td>
<td>97</td>
<td>RT</td>
<td>30</td>
<td>404/40</td>
<td>12/89</td>
</tr>
<tr>
<td>2</td>
<td>2150</td>
<td>30</td>
<td>95</td>
<td>1370</td>
<td>20</td>
<td>312</td>
<td>7/97</td>
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<tr>
<td>2</td>
<td>2150</td>
<td>60</td>
<td>96</td>
<td>1370</td>
<td>24</td>
<td>265/32</td>
<td>10/94</td>
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<tr>
<td>2</td>
<td>2200</td>
<td>30</td>
<td>97</td>
<td>1370</td>
<td>30</td>
<td>316/53</td>
<td>7/80</td>
</tr>
</tbody>
</table>

**CD-86-19202**

### WEIBULL PROBABILITY CHART FOR ROOM TEMPERATURE FRACTURE OF STARCK TYPE 2 α - SiC (B, C)

[Weibull probability chart image]

**Legend:**
- □ 11 350 2150 °C / 30 min
- △ 12 308 2150 °C / 60 min
- □ 12 404 2200 °C / 30 min

**CD-85-15097**
WEIBULL PROBABILITY CHART FOR 1370°C FRACTURE OF STARCK TYPE 2 α-SiC (B, C)

CUMULATIVE PERCENT FAILURE

FOUR POINT FLEXURE STRENGTH, MPa

STRENGTH, SINTERED TEMP/TIME

- 8 305 2150°C/30 MIN.
- 9 273 2150°C/60 MIN.
- 7 316 2200°C/30 MIN.

ROOM TEMPERATURE FRACTURE OF DRY-PRESSED/SINTERED α-SiC

αf - 227 MPa

αf - 225 MPa

CD-85-16178

CD-86-19188
SLURRY-PRESSING FLOW DIAGRAM

1. SIC POWDER (-100 MESH)
2. MIX WITH NH₄OH/H₂O (PH ~ 11) FOR 48 hr
3. SLURRY PRESS AT 14 MPa
4. DRY AT ROOM TEMP. FOR 48 hr
5. ISO-STATIC PRESS AT 413 MPa
6. SINTER AT 1900 - 2200 °C
7. MACHINE TO TEST BAR
8. CHARACTERIZATION DENSITY, MOR, FRACTURE

SCHEMATIC OF SLURRY PRESSING APPARATUS

- VACUUM EXHAUST
- TOP PLUNGER
- DIE
- PREFORMED BULK FILTER PAPER
- POROUS STAINLESS STEEL
- FILTER PAPER
- POROUS STAINLESS STEEL
- PREFORMED BULK FILTER PAPER
- BOTTOM PLUNGER
### Properties of Sintered vs Hot Isostatic Pressed α-SiC

<table>
<thead>
<tr>
<th>α-SiC Type</th>
<th>Processing Method</th>
<th>Densification Temperature, °C</th>
<th>Time, min</th>
<th>Density (% of Theoretical)</th>
<th>Mean MOR/6-D, MPa</th>
<th>No. of Specimen</th>
<th>Weibull/R², m</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>DRY PRESS/SINTERED</td>
<td>2200</td>
<td>30</td>
<td>97.4</td>
<td>342±52.8 (49.6±5.7 ksi)</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>SLURRY PRESS/SINTERED</td>
<td>2200</td>
<td>30</td>
<td>96.5</td>
<td>416±53.3 (60.3±7.7 ksi)</td>
<td>22</td>
<td>9.3</td>
</tr>
<tr>
<td>2</td>
<td>SLURRY PRESS/HiPed</td>
<td>1900</td>
<td>30</td>
<td>95.3</td>
<td>580±77</td>
<td>15</td>
<td>8.8</td>
</tr>
<tr>
<td>2</td>
<td>SLURRY PRESS/HiPed</td>
<td>1800</td>
<td>30</td>
<td>80.5</td>
<td>N.D.</td>
<td>8</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

**Effect of Dry Pressing vs Slurry Pressing on Sintered Microstructures of α-SiC**

![Microstructures](image1)

**Dry Press/Sintered 2200 °C/1/2 hr/RT σf = 345 MPa**

![Microstructures](image2)

**Slurry Press/Sintered 2200 °C/1/2 hr/RT σf = 480 MPa**

CD-86-19187
ROOM TEMPERATURE FRACTURE OF SLURRY-PRESSED/SINTERED $\alpha$-SiC

$\sigma_f = 340$ MPa

$\sigma_f = 260$ MPa

HIPing OF STRUCTURAL CERAMICS

ADVANTAGES:

HOT ISOSTATIC PRESSING (HIPing) OF STRUCTURAL CERAMICS, e.g., $\text{Si}_3\text{N}_4$ AND SiC.

- ENHANCES DENSITY (APPROACHES TD)
- IMPROVES MICROSTRUCTURE
- SIGNIFICANTLY INCREASES STRENGTH
- IMPROVES RELIABILITY
HOT ISOSTATIC PRESSING - GENERAL FLOW CHART

SIC + ADDITIVES (B, AI, C) GREEN PART

SINTER PARTS TO CLOSE POROSITY

VACUUM SEAL IN TA OR GLASS CAN

HIP

STRENGTH AND MICROSTRUCTURE CHARACTERIZATION

OPTIMIZATION OF COMPOSITION AND PROCESSING

RELIABLE CERAMIC PARTS

SELECTED INTERACTIONS

MICROSTRUCTURE DEVELOPMENT IN SINTERED AND HOT ISOSTATIC PRESSED α-SiC

DRY-PRESSED/SINTERED 2200 C / 1/2 hr

SLURRY-PRESSED/SINTERED 2200 C / 1/2 hr

SLURRY-PRESSED/HIPed 1900 C / 1/2 hr
REPLICA PHOTOMICROGRAPHS OF SINTERED AND HOT ISOSTATIC Pressed α-SiC

Dry-Pressed/Sintered

Slurry-Pressed/Sintered

Slurry-Pressed/HIPed

ROOM TEMPERATURE FLEXURE STRENGTH OF SINTERED VS HIPed SILICON CARBIDE

FLEXURE STRENGTH, ksi

(a) 40 60 80 100

Dry Press Sintered

2200 °C 1/2 hr

Slurry Press Sintered

2200 °C 1/2 hr

Slurry Press HIPed

1900 °C 1/2 hr

CD-86-19196
ROOM TEMPERATURE FRACTURE OF HOT ISOSTATIC PRESSED $\alpha$-SiC

CONCLUSIONS

- DRY PRESSING / SINTERING OF STARCK ALPHA SILICON CARBIDE PRODUCED HIGH DENSITY BODIES WITH AN AVERAGE FLEXURE STRENGTH (4-POINT BEND) OF 350 MPa (50 ksi).
- IN CONTRAST, SLURRY PRESSING / SINTERING PRODUCED AN AVERAGE STRENGTH OF 430 MPa (62 ksi), A 30% IMPROVEMENT IN STRENGTH.
- FURTHER, SLURRY PRESSING / HOT ISOSTATIC PRESSING (HIPing) PRODUCED HIGH DENSITY BODIES AT 1850 - 1900 °C, WITH AN AVERAGE STRENGTH OF 580 MPa (84 ksi). THIS STRENGTH VALUE IS 60% HIGHER THAN THE DRY-PRESSED / SINTERED STRENGTH, AND 30% HIGHER THAN THE SLURRY-PRESSED / SINTERED STRENGTH.
- THE SLURRY-PRESSED / HIPed MATERIAL EXHIBITED AN ULTRAFINE GRAINED (0.3 - 3.0 μm) MICROSTRUCTURE AS COMPARED TO 1 - 30 μm PRODUCED BY SINTERING.
- PROCESS RELATED DEFECTS SUCH AS LARGE VOIDS, AND SHRINKAGE CRACKS WERE NOT OBSERVED IN HIPed SILICON CARBIDE.
IMPROVED SILICON NITRIDE FOR ADVANCED HEAT ENGINES

H.C. Yeh
A1Research Casting Company
Torrance, CA 90509

and

J.M. Wimmer.
Garrett Turbine Engine Company
Phoenix, AZ

Silicon nitride is a high temperature material currently under consideration for heat engine and other applications. This presentation describes the progress made in the first 1-1/2 years of a NASA funded, 5 year program on improved Si3N4. The objective of this program is to improve the net shape fabrication technology of Si3N4 by injection molding. This is to be accomplished by optimizing the process through a series of statistically designed matrix experiments. To provide input to the matrix experiments, a wide range of alternate materials and processing parameters were investigated throughout the whole program.

The improvement in the processing is to be demonstrated by a 20 percent increase in strength and a 100 percent increase in the Weibull modulus over that of the ACC baseline material. A full characterization of the baseline material/process was completed. The room temperature MOR and Weibull modulus of the as-processed test bars were established as 79.3 ksi and 7.9, respectively. In the first iteration of the MOR matrix experiments, a material with a room temperature MOR of 97 ksi and a Weibull modulus of 14 has been developed.

Material properties were found to be highly dependent on each step of the process. Several important parameters identified thus far are the starting raw materials, sinter/HIP cycle, powder bed, mixing methods, and sintering aid levels.
OBJECTIVES

- DEVELOP FABRICATION TECHNOLOGY BASE
- INCREASE THE AS PROCESSED TEST BAR STRENGTH BY 20% (RT THRU 2550°F)
- INCREASE WEIBULL MODULUS BY 100%
- ACHIEVE INJECTION MOLDING CAPABILITY FOR LARGE COMPONENTS

NASA WORK STATEMENT: SCHEDULE AND EFFORT

<table>
<thead>
<tr>
<th>TASK NO.</th>
<th>DESCRIPTION</th>
<th>PERCENT EFFORT</th>
<th>YEARS FROM CONTRACT INITIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>BASELINE CHARACTERIZATION</td>
<td>5</td>
<td>1 PHASE I</td>
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<tr>
<td>II.</td>
<td>MOR MATRIX</td>
<td>25</td>
<td>2 PHASE I</td>
</tr>
<tr>
<td>III.</td>
<td>OPTIMIZED MOR</td>
<td>5</td>
<td>3 PHASE II</td>
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<tr>
<td>IV.</td>
<td>BASELINE LARGE SHAPE</td>
<td>10</td>
<td>4 PHASE II</td>
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<tr>
<td>V.</td>
<td>LARGE SHAPE MATRIX</td>
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<tr>
<td>VI.</td>
<td>OPTIMIZED LARGE SHAPE</td>
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<tr>
<td>VII.</td>
<td>MATERIAL/PROCESS IMPROVEMENT</td>
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<td></td>
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<tr>
<td>VIII.</td>
<td>REPORTS/PROJECT MANAGEMENT</td>
<td>5</td>
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</tbody>
</table>
INJECTION MOLDING PROCESS

ITERATIVE APPROACH FOR IMPROVING CERAMIC MATERIAL PROPERTIES AND PROCESS CONTROLS
PROCESSING VARIABLES

STARTING POWDER
- ALTERNATE Si₃N₄
- ALTERNATE ADDITIVES
- LOT VARIATIONS

COMPOSITION
- % Al₂O₃, Y₂O₃
- ZrO₂
- Y₂O₃-SiO₂

POWDER PROCESSING
- ALTERNATE MILLING
- CLASSIFICATION
- ELUTION/WASHING
- MILLING AIDS
- TIME

TOOLING
- GATE SIZE
- GATE ORIENTATION
- SEPARATION DESIGN
- TEST BARS PER SHOT

ADDITIVES
- ALTERNATE BINDERS
- % BINDER
- PLASTICIZER
- WETTING AGENT
- LUBRICANT
- DISPERSANT
- ACID-BASE CONTROL

INJECTION MOLDING
- MACHINE
- TEMPERATURES
- PRESSURE
- RAM SPEED
- VACUUM

DEWAX
- TEMPERATURE
- PRESSURE
- CYCLE
- APPROACH
- TIME
- EQUIPMENT
- CYCLE

MIXING
- MIXER
- TIME
- TEMPERATURE
- SHEAR RATE
- SOLVENT
- VACUUM

SINTERING
- TIME
- TEMPERATURE
- OVERPRESSURE
- CYCLE
- EQUIPMENT
- FIXTURING

PHASE I DIRECTED TOWARDS TEST BARS

TASK I BASELINE MATERIAL CHARACTERIZATION
PRIOR EXPERIENCE

DESIGN MOR MATRIX

MAJOR MATRIX TO SCREEN KEY VARIABLES AND DETERMINE INTERACTIONS

OPTIMIZATION EXPERIMENTS

TASK II MOR MATRIX

STATISTICAL AND FRACTURE ANALYSES

MAJOR MATRIX ITERATION

TASK III FABRICATION AND MOR CHARACTERIZATION OF 3 LOTS OF OPTIMIZED MOR BARS

CONTINUE ADVANCED MATERIALS AND PROCESSING EXPERIMENTS

TASK VII SEQUENCE OF EXPLORATORY PROCESS PARAMETER EVALUATIONS
NASA IMPROVED Si₃N₄

Baseline Test Bar Injection Molding Task I
452 Bars

Non-destructive and Destructive Evaluation

Baseline Reference Task III, Matrix I
24 Bars

Randomization

Binder Removal

Binder Removal

Binder Removal

Binder Removal

Load 1
88 Bars

Load 2
80 Bars

Load 3
80 Bars

Load 4
80 Bars

Evaluation

Evaluation

Evaluation

Evaluation

Sintering

Sintering

Sintering

Sintering

Load 1
70 Bars

Load 2
70 Bars

Load 3
70 Bars

Load 4
70 Bars + 6 Exp. Bars

Baseline Characterization

SPA 8597-4B
TEST BAR SINTERING SUPPORT

WEIBULL ANALYSIS OF BASELINE ROOM TEMPERATURE DATA

MOR (MPa)

FAILURE PROBABILITY (PERCENT)

TEST BAR SERIAL NUMBER

SURFACE QUALITY (VISUAL INSPECTION) GRADE

INITIAL 66 BASELINE BARS / IMPROVED 313N4 / NAS3-24385

AVERAGE STRENGTH 79.3 ksi

STD. DEV. 10.2 ksi

WEIBULL MODULUS 4.21 ± .5

CHAR. STRENGTH 84.1 ksi

AVERAGE STRENGTH 79.3 ksi

WEIBULL MODULUS 7.9
BASLINE STRENGTH

WEIBULL DISTRIBUTION FOR HIGH TEMPERATURE DATA

BASELINE MATERIAL AT 2250°F
WEIBULL MODULUS = 8.6
CHARACTERISTIC STRENGTH = 49.5
AVERAGE STRENGTH = 47.27
STD. DEV. = 5.2
NO. OF BARS = 28

BASELINE MATERIAL AT 1950°F
WEIBULL MODULUS = 8.6
CHARACTERISTIC STRENGTH = 61.74
AVERAGE STRENGTH = 58.38
STD. DEV. = 8.1
NO. OF BARS = 13

BASELINE MATERIAL AT 2550°F
WEIBULL MODULUS = 5.1
CHARACTERISTIC STRENGTH = 22.57
AVERAGE STRENGTH = 20.76
STD. DEV. = 4.6
NO. OF BARS = 12
BASELINE STRESS RUPTURE

PRELIMINARY TEST CONDITIONS

<table>
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<tr>
<th></th>
<th>1800°F</th>
<th>2200°F</th>
<th>2500°F</th>
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</thead>
<tbody>
<tr>
<td>10 KSI — 24 HR</td>
<td>10 KSI — 24 HR</td>
<td>10 KSI — 9 HR, 42 MIN</td>
<td></td>
</tr>
<tr>
<td>20 KSI — 24 HR</td>
<td>20 KSI — 24 HR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 KSI — 24 HR</td>
<td>30 KSI — 24 HR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 KSI — 1 MIN</td>
<td>40 KSI — 24 HR</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 KSI — 0</td>
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</tbody>
</table>

FINAL TEST RESULTS

<table>
<thead>
<tr>
<th></th>
<th>1800°F</th>
<th>2200°F</th>
<th>2500°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 KSI — 7 HR, 22 MIN</td>
<td>40 KSI — 0</td>
<td></td>
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<tr>
<td>40 KSI — 17 HR, 19 MIN</td>
<td>30 KSI — 1 MIN</td>
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<tr>
<td>30 KSI — 100 HR (SURVIVED)</td>
<td>30 KSI — 3 HR, 38 MIN</td>
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<td></td>
<td>30 KSI — 4 HR, 55 MIN</td>
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</table>

TASK VII EXPERIMENTAL MATRIXES

<table>
<thead>
<tr>
<th>PROCESS VARIABLE</th>
<th>EXPERIMENTAL MATRIX NUMBER</th>
<th>1</th>
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<th>3</th>
<th>4</th>
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<th>7</th>
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<td>BINDER</td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>BINDER EXTRACTION</td>
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<td>X</td>
<td>X</td>
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<td>INJECTION MOLDING</td>
<td>X</td>
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<tr>
<td>POWDER PREPARATION (MILLING)</td>
<td>X</td>
<td></td>
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<td>COMPOSITION</td>
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<td>X</td>
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<td>SINTERING</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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</tbody>
</table>
MIXING BEHAVIOR COMPARISON ON TORQUE RHEOMETER

![Graph showing mixing behavior comparison on torque rheometer]

GTE SN502 Si₃N₄ + 6% Y₂O₃ + 2% Al₂O₃ AT 15.5% BINDER

AS INJECTED TEST BAR SURFACES

A. 8 HR. MILLING 99°C (210°F) MOLDING  
B. 8 HR. MILLING 77°C (170°F) MOLDING  
C. 24 HR. MILLING 77°C (170°F) MOLDING

GTE SN502 Si₃N₄ + 6% Y₂O₃ + 2% Al₂O₃ AT 15.5% BINDER
FLOW CHARACTERISTICS OF INJECTION MOLDING

MOLDING TEMPERATURE, °F

EXCESS FLUIDITY

GOOD INJECTION

INSUFFICIENT FLUIDITY

MOLDING TEMPERATURE, °C

MILLING TIME, HOURS

NASA IMPROVED Si$_3$N$_4$

SURFACE CHANGE DURING DEWAX – 96 HOUR MILLED POWDER

AS INJECTED

DEWAXED
DEWAX EFFECT

[Graph showing the relationship between molding temperature and milling time, highlighting the tendency to develop defects due to excess binder.

GTE SN502 +6% Y_2O_3 + 2% Al_2O_3 AT 15% BINDER

NASA IMPROVED Si_3N_4

TASK II EXPERIMENTAL MATRIX
1/2 REPLICATE OF A 2^5 FRACTIONAL FACTORIAL DESIGN

<table>
<thead>
<tr>
<th></th>
<th>C+</th>
<th>C-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D+</td>
<td>D-</td>
</tr>
<tr>
<td></td>
<td>E+</td>
<td>E-</td>
</tr>
<tr>
<td>A+</td>
<td>B+</td>
<td>abcde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>abce</td>
</tr>
<tr>
<td>B-</td>
<td>acde</td>
<td></td>
</tr>
<tr>
<td>A-</td>
<td>B+</td>
<td>bcde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cd</td>
</tr>
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A = CONSOLIDATION METHODS — SINTER/HP CYCLE (A-) VS CYCLE (A+)
B = CONSOLIDATION ENVIRONMENT — WITHOUT POWDER BED (B-) VS WITH POWDER BED (B+)
C = MIXING — SIGMA MIXER (C-) VS SIGMA MIXER PLUS EXTRUDER (C+)
D = SINTERING AIDS — (6% Y_2O_3 + 2% Al_2O_3) (D-) VS (6% Y_2O_3 + 1% Al_2O_3) (D+)
E = BINDER CONTENT — 15.5% (E-) VS 14.5% (E+)

SPA BN6237A
NASA IMPROVED $\text{Si}_3\text{N}_4$

EXPERIMENTAL MATRIX PROCESS FLOW CHART

MILLING — SINTERING AIDS

- D- (6% $\text{Y}_2\text{O}_3 + 2% \text{Al}_2\text{O}_3$)
- D+ (6% $\text{Y}_2\text{O}_3 + 1% \text{Al}_2\text{O}_3$)

MIXING — BINDER CONTENT

- E- (15.5%)  E+ (14.5%)
- E- (15.5%)  E+ (14.5%)

EXTRUSION

MOLDING AND BINDER REMOVAL

SINTER/HIP CYCLES

- a
- b
- c
- d

POWDER BED

- e
- f
- g
- h

TASK II — MOR BAR MATRIX STUDY

MONTHS 1 THROUGH 7

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<thead>
<tr>
<th>TASK II FIRST ITERATION</th>
<th>1985</th>
<th>1986</th>
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<td>AUG</td>
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<td>1 Characterize as</td>
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<td>2 Powder preparation</td>
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<tr>
<td>3 Re-evaluate after</td>
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<td>powder preparation</td>
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<td>4 Binder addition</td>
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<td>and mixing</td>
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<td></td>
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<tr>
<td>5 Injection molding</td>
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<td>and in-process</td>
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<tr>
<td>evaluation</td>
<td></td>
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<td>6 Binder removal</td>
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<tr>
<td>and evaluation</td>
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<tr>
<td>8 Post-process</td>
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<td>characterization</td>
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<td>9 Statistical and</td>
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<td>photographic</td>
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<tr>
<td>analysis</td>
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<td>10 Develop statistical</td>
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<td>improvement plan</td>
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<tr>
<td>11 Submit to NASA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>for co-head plan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>for months</td>
<td></td>
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</tr>
<tr>
<td>0-14</td>
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</table>
**TASK II TORQUE CHARACTERIZATION**

<table>
<thead>
<tr>
<th>MIXING VARIATION</th>
<th>D- (6% Y₂O₃ + 2% Al₂O₃)</th>
<th>D+ (6% Y₂O₃ + 1% Al₂O₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E- (15.5% BINDER)</td>
<td>1450 1500 1386 1544</td>
<td></td>
</tr>
<tr>
<td>E+ (14.5% BINDER)</td>
<td>1100 1452 762 1290</td>
<td></td>
</tr>
<tr>
<td>C-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C+ (EXTRUDED)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**MATRIX II-1 INJECTION MOLDING BATCHES**

**MATRIX II-2 INJECTION MOLDING BATCHES**

<table>
<thead>
<tr>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VALUES ARE FROM SINGLE MIXER RUNS</td>
</tr>
<tr>
<td>2. MIXER COOLING RATE WAS 1°C (1.8°F) PER MINUTE</td>
</tr>
<tr>
<td>3. m·g = meter·gram</td>
</tr>
</tbody>
</table>

**MATRIX II-1 TORQUE CHARACTERIZATION**

**EFFECT OF BINDER CONTENT ON RHEOLOGY**

15.5% BINDER  
14.5% BINDER
### MATRIX II-1 AND II-2 X-RADIOGRAPHIC YIELD

#### AS-INJECTED BARS

<table>
<thead>
<tr>
<th>MIXING PROCEDURE</th>
<th>YIELD IN PERCENT</th>
<th>D-[ (6% Y$_2$O$_3$ + 2% Al$_2$O$_3$)</th>
<th>D+[ (6% Y$_2$O$_3$ + 1% Al$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E- (15.5% BINDER)</td>
<td>E+ (14.5% BINDER)</td>
<td>E- (15.5% BINDER)</td>
</tr>
<tr>
<td>MATRIX II-1, STARCK H-1 Si$_3$N$_4$, 200 BARS INJECTED FOR EACH CONDITION</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-</td>
<td>77</td>
<td>77</td>
<td>69</td>
</tr>
<tr>
<td>C+ (EXTRUDED)</td>
<td>87</td>
<td>92</td>
<td>68</td>
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<tr>
<td>MATRIX II-2, DENKA 9FW Si$_3$N$_4$, 160 BARS INJECTED FOR EACH CONDITION</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C-</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>C+ (EXTRUDED)</td>
<td>96</td>
<td>96</td>
<td>98</td>
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#### ROOM TEMPERATURE MOR AND WEIBULL SLOPE (MATRIX II-2)

<table>
<thead>
<tr>
<th>PROCESSING CONDITION</th>
<th>AVERAGE STRENGTH,* ksi</th>
<th>WEIBULL SLOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82.90</td>
<td>6.97</td>
</tr>
<tr>
<td>ab</td>
<td>97.25</td>
<td>13.63</td>
</tr>
<tr>
<td>bc</td>
<td>91.96</td>
<td>7.66</td>
</tr>
<tr>
<td>ac</td>
<td>95.58</td>
<td>12.73</td>
</tr>
<tr>
<td>be</td>
<td>92.18</td>
<td>10.15</td>
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<tr>
<td>ae</td>
<td>91.56</td>
<td>10.13</td>
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<tr>
<td>bd</td>
<td>76.20</td>
<td>12.84</td>
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<tr>
<td>de</td>
<td>82.84</td>
<td>7.01</td>
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<td>7.94</td>
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<td>abcd</td>
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<td>84.84</td>
<td>19.93</td>
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<td>bcde</td>
<td>77.73</td>
<td>9.74</td>
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<tr>
<td>acde</td>
<td>78.95</td>
<td>5.32</td>
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<tr>
<td>ad</td>
<td>89.30</td>
<td>12.18</td>
</tr>
<tr>
<td>cd</td>
<td>74.40</td>
<td>5.64</td>
</tr>
</tbody>
</table>

*30 SAMPLES TESTED FOR EACH CONDITION
STATISTICAL ANALYSIS

MATRIX II-2

- PROCESSING FACTORS HAVING SIGNIFICANT EFFECTS ON MOR
  A, B AND D

- TWO FACTOR INTERACTIONS HAVING SIGNIFICANT EFFECTS ON MOR
  B × C, B × D AND C × D

NOTE: A — SINTERED/HP
  B — POWER BED
  C — MIXING
  D — SINTERING AID
### SINTER/HIP CYCLE EFFECT

#### MATRIX II-2

<table>
<thead>
<tr>
<th>SINTERING/HIP 2 HRS</th>
<th>SINTERING/HIP 4 HRS</th>
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<tbody>
<tr>
<td>83.2 ksi</td>
<td>89.8 ksi</td>
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</tbody>
</table>

**DIFFERENCE = 6.6 ksi**

### POWDER BED AND SINTERING AIDS EFFECTS

#### MATRIX II-2

<table>
<thead>
<tr>
<th></th>
<th>(B+) PB*</th>
<th>(B-) NO PB*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D+) 6% Y₂O₃ + 2% Al₂O₃</td>
<td>81.0 Ksi</td>
<td>81.6 Ksi</td>
</tr>
<tr>
<td>(D-) 6% Y₂O₃ + 1% Al₂O₃</td>
<td>94.3 Ksi</td>
<td>89.1 Ksi</td>
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</table>

*PB: POWDER BED*
POWDER BED AND MIXING METHOD EFFECTS

MATRIX II-2

<table>
<thead>
<tr>
<th></th>
<th>(B+) PB*</th>
<th>(B-) NO PB*</th>
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</thead>
<tbody>
<tr>
<td>(C+) SIGMA MIXER AND EXTRUDER</td>
<td>87.7 Ksi</td>
<td>83.9 Ksi</td>
</tr>
<tr>
<td>(C-) SIGMA MIXER</td>
<td>87.6 Ksi</td>
<td>86.8 Ksi</td>
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</table>

*PB: POWDER BED

SUMMARY

• AVERAGE STRENGTH AND WEIBULL MODULUS OF BASELINE AS-PROCESSED, RANDOMLY SELECTED INJECTION MOLDED, SINTERED Si3N4 SAMPLES ARE 547 MPa (79.3 ksi) AND 7.9 RESPECTIVELY

• STRENGTH AND AS-PROCESSED SURFACE QUALITY ARE CLOSELY RELATED

• TORQUE RHEOMETRY HAS THE POTENTIAL TO PREDICT INJECTION MOLDING BEHAVIOR

• GOOD QUALITY AS-INJECTED BARS CAN DEGRADE DURING DEWAX IF THEY ARE PROCESSED WITH EXCESS BINDER

• FINAL TEST BAR PROPERTIES STRONGLY DEPEND ON EACH PROCESSING STEP

(CONTINUED)
A material with a mean strength of 97 Ksi and a Weibull modulus of 14 has been developed by a statistically designed matrix experiment.

Statistical analysis can identify key processing parameters and processing variations.
A sintered $\text{Si}_3\text{N}_4$-$\text{SiO}_2$-$\text{Y}_2\text{O}_3$ composition, NASA 6Y, was developed that reached four-point flexural average strength/standard deviation values of 857/36, 544/33, and 462/59 MPa at room temperature, 1200 and 1370 °C respectively. These strengths represented improvements of 56, 38, and 21 percent over baseline properties at the three test temperatures. At room temperature the standard deviation was reduced by more than a factor of three. These accomplishments were realized by the iterative utilization of conventional x-radiography to characterize structural (density) uniformity as affected by systematic changes in powder processing and sintering parameters. Accompanying the improvement in mechanical properties was a change in the type of flaw causing failure from a pore to a large columnar $\text{Si}_3\text{N}_4$ grain typically 40-80 μm long, 10-30 μm wide, and with an aspect ratio of 5:1.
IMPROVED PROCESSING OF Si₃N₄

OBJECTIVE

TO IMPROVE THE STRENGTH AND UNIFORMITY OF SINTERED SILICON NITRIDE BY A SYSTEMATIC INVESTIGATION OF POWDER PROCESSING AND SINTERING VARIABLES AS THEY AFFECT RADIOGRAPHICALLY CHARACTERIZED DENSITY GRADIENTS, AND CONSEQUENTLY THE STRENGTH LEVEL AND SCATTER OF SILICON NITRIDE

CHARACTERIZATION OF SILICON NITRIDE AND OXIDE POWDERS

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>SOURCE</th>
<th>MANUFACTURERS DESIGNATION</th>
<th>PURITY, %</th>
<th>SPECIFIC SURFACE AREA, m². g⁻¹</th>
<th>X-RAY DIFFRACTION ANALYSIS, %</th>
<th>CHEMICAL ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄</td>
<td>KBI-AME</td>
<td>HIGH PURITY</td>
<td>99.5</td>
<td>4.7</td>
<td>83.7 15.7 0.6</td>
<td>0.89 0.18</td>
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<tr>
<td>SiO₂</td>
<td>APACHE CHEMICALS</td>
<td>6846</td>
<td>99.99</td>
<td>166</td>
<td>---- ---- ----</td>
<td>---- .16</td>
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<tr>
<td>Y₂O₃</td>
<td>MOLYCORP</td>
<td>5600</td>
<td>99.9</td>
<td>7.5</td>
<td>---- ---- ----</td>
<td>---- .11</td>
</tr>
</tbody>
</table>

CHEMICAL ANALYSIS

- Oxygen, wt %
- Carbon, wt %
- Spectrographic Analysis, ppm
- Chemicals: 240A1, 60Ca, 20Co, 50Cr, 1280Fe, 20Mg, 30Mn, 40Ti, 40V, 590Y, 30Zr, 10Zr
- Oxides: 220A1, 150Ca, 30Cr, 50Cu, 50Fe, 130Mg, 90Mn, 340Na, 40Ti
POWDER PROCESSING OF NASA 6Y Si₃N₄

HPSN MEDIA

MILL CHARGE

Si₃N₄
SiO₂
Y₂O₃

Si₃N₄ + ETHANOL SIEVED,
20 µm SCREEN

RBSN MILL

ETHANOL

SLURRY

SLURRY SIEVED,
10 µm SCREEN

ETHANOL REMOVAL
(HEAT + VACUUM)

VACUUM OVEN DRY

CRUSH SOFT AGGLOMERATES
(HPSN HARDWARE)

149 µm SCREEN

DIE PRESS TEST BARS

ISOPRESS TEST BARS

EVALUATION OF NASA 6Y Si₃N₄

FEEDBACK TO:

POWDER PROCESSING

SINTERING PROCEDURES

ISOPRESSED TEST BARS

X-RADIOGRAPHY

SINTER TEST BARS

X-RADIOGRAPHY

MACHINE TEST BARS

X-RADIOGRAPHY

FLEXURE TESTING
R. T., 1200 °C, 1370 °C

FRACOGRAPHY -SEM
METALLOGRAPHY - LIGHT, TEM

CORRELATIONS OF:

DENSITY GRADIENTS

STRENGTH

FLAW CLASSIFICATION
MICROSTRUCTURE
Si$_3$N$_4$ BAR/BN SETTER ARRANGEMENT IN W SINTER CUP

CONVENTIONAL RADIOGRAPHY OF NASA 6Y Si$_3$N$_4$ TEST BARS

(W, L) RADIOGRAPHIC IMAGE

(T, L) RADIOGRAPHIC IMAGE

CS-86-0235

CS-85-4207
RADIOGRAPHS OF 15-BAR SINTER-GROUPS OF NASA 6Y Si₃N₄

TOP LAYER OF BARS

SINTER HT. ADJUSTED

SINTER HT. NOT ADJUSTED

CASE-CORE STRUCTURE COMPARISON FOR BASELINE AND IMPROVED NASA 6Y Si₃N₄

BASELINE

IMPROVED

CS-85-4205

CS-85-4197

123
TEM MICROSTRUCTURES OF NASA 6Y Si₃N₄ EFFECT OF GRINDING TIME

tg = 24 hr
0.3 - 4.0 μm EQUIAX
0.35 - 3.5 μm COLIM. WIDTH
1:2 TO 1:6 ASPECT RATIO
70 VOL. % COLIM.

tg = 100 hr
0.2 - 3.5 μm EQUIAX
0.4 - 2.0 μm COLIM. WIDTH
1:2 TO 1:14 ASPECT RATIO
40 VOL. % COLIM.

tg = 300 hr
0.2 - 3.0 μm EQUIAX
0.25 - 2.0 μm COLIM. WIDTH
1:2 TO 1:8 ASPECT RATIO
20 VOL. % COLIM.

CS-85-4209

SINTERING CONDITIONS AND RESULTS FOR Si₃N₄-SiO₂-Y₂O₃
COMPOSITION NASA 6Y SINTERED AT 2140 °C

<table>
<thead>
<tr>
<th>NASA 6Y BATCH NUMBER</th>
<th>MILLING TIME, hr</th>
<th>SINTERING CONDITIONS</th>
<th>SINTERING RESULTSᵃ</th>
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<tbody>
<tr>
<td></td>
<td>TIME, hr</td>
<td>PN, MPa</td>
<td>BN SETTER CONTACT</td>
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<tr>
<td>BASELINE</td>
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<td>MAX</td>
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<tr>
<td>11</td>
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<td>15</td>
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<td>16</td>
<td>24</td>
<td>2</td>
<td>MAX</td>
</tr>
<tr>
<td>17</td>
<td>100</td>
<td></td>
<td>MIN</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td></td>
<td>MAX</td>
</tr>
<tr>
<td>25</td>
<td>300</td>
<td></td>
<td>MAX</td>
</tr>
<tr>
<td>26ᵇ</td>
<td>100</td>
<td></td>
<td>MIN</td>
</tr>
<tr>
<td>29ᵇ, c</td>
<td>100</td>
<td></td>
<td>MAX</td>
</tr>
<tr>
<td>31ᵇ, c</td>
<td>300</td>
<td></td>
<td>MIN</td>
</tr>
<tr>
<td>21 (2500 °C)</td>
<td>100</td>
<td></td>
<td>MAX</td>
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</tbody>
</table>

ᵃAVERAGE FOR EACH COMPOSITION REPRESENT 30 BARS EXCEPT FOR BASELINE WHICH REPRESENTS 150 BARS AND BATCH 28 WHICH REPRESENTS 15 BARS.
bSINTER CUP RAISED 3.8 cm.
cSi₃N₄ POWDER WET SIEVED BEFORE AND AFTER MILLING.

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COMBINED EFFECT OF MODIFIED PROCESSING/SINTERING PROCEDURES ON THE FLEXURAL STRENGTH OF NASA 6Y Si₃N₄

<table>
<thead>
<tr>
<th>FLEXURAL STRENGTH, MPa</th>
<th>R.T.</th>
<th>1200 °C</th>
<th>1370 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE LINE</td>
<td>117</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>STANDARD DEVIATION</td>
<td>3.12</td>
<td>3.21</td>
<td>3.29</td>
</tr>
<tr>
<td>DENSITY, g/cm³</td>
<td>108</td>
<td>36</td>
<td>34</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>tₜₜ, h</th>
<th>tₛₜₜ, h</th>
<th>Pₙₜ, MPa</th>
<th>Bₙₜ,</th>
<th>SINTER HT. ADJ.</th>
<th>POWDER WET SIEVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>100</td>
<td>100</td>
<td>300</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
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</tr>
<tr>
<td>2.5</td>
<td>5.0</td>
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<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>max</td>
<td>min</td>
<td>max</td>
<td>min</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

ASSESSMENT OF FRACTURE ORIGINS FOR NASA 6Y SINTERED Si₃N₄

<table>
<thead>
<tr>
<th>R.T. FLEXURE TEST</th>
<th>TOTAL FRACTURE ORIGINS IDENTIFIED</th>
<th>PERCENT OF TOTAL</th>
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<tbody>
<tr>
<td></td>
<td>192</td>
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<td></td>
<td>56</td>
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<tr>
<td></td>
<td>44</td>
<td>23</td>
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<td>17</td>
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<td></td>
<td>13</td>
<td>5</td>
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</table>

<table>
<thead>
<tr>
<th>1200 °C FLEXURE TEST</th>
<th>TOTAL FRACTURE ORIGINS IDENTIFIED</th>
<th>PERCENT OF TOTAL</th>
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<tbody>
<tr>
<td></td>
<td>90</td>
<td>100</td>
</tr>
<tr>
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<td>23</td>
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<td></td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>15</td>
</tr>
<tr>
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<td>0</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>20</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>1370 °C FLEXURE TEST</th>
<th>TOTAL FRACTURE ORIGINS IDENTIFIED</th>
<th>PERCENT OF TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>127</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>17</td>
</tr>
</tbody>
</table>

aNUMBER EXCLUDES 111, 47, AND 41 BARS FOR R.T., 1200 °C, AND 1370 °C, RESPECTIVELY, WHERE FLAW REGION OR FLAW TYPE COULD NOT BE DETERMINED.
CRITICAL FLAWS IN R. T. FRACTURE OF NASA 6Y Si₃N₄

SURFACE PORE, $\sigma_F = 620$ MPa

AGGLOMERATE, $\sigma_F = 470$ MPa

CS-85-4199

COLUMNAR Si₃N₄ GRAIN CRITICAL FLAW IN R. T. FRACTURE OF IMPROVED NASA 6Y Si₃N₄

$\sigma_F = 905$ MPa

CS-85-4201

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SUMMARY

APPLICATION OF CONVENTIONAL RADIOGRAPHY VERY BENEFICIAL IN GUIDING POWDER PROCESSING AND SINTERING PARAMETER CHANGES FOR IMPROVED Si₃N₄

INCREASED $t_{\text{GRIND}}$ + INCREASED $t_{\text{SINTERED}}$ + MINIMUM BN SETTER CONTACT + SINTER HEIGHT ADJUSTMENT + POWDER WET SIEVING

HIGHER DENSITY

LESS DENSITY GRADIENT

BAR-TO-BAR UNIFORMITY

IMPROVED STRENGTH

LESS STRENGTH SCATTER

LESS CRITICAL DOMINANT FLAW
The colloidal behavior of aqueous ceramic slips strongly affects the forming and sintering behavior and the ultimate mechanical strength of the final ceramic product. The colloidal behavior of these materials, which is dominated by electrical interactions between the particles, is complex due to the strong interaction of the solids with the processing fluids. A surface titration methodology, modified to account for this interaction, has been developed and used to provide fundamental insights into the interfacial chemistry of these systems. Various powder pretreatment strategies were explored to differentiate between true surface chemistry and artifacts due to exposure history. The colloidal behavior of both silicon nitride and carbide is dominated by silanol groups on the powder surfaces. However, the colloid chemistry of silicon nitride is apparently influenced by an additional amine group. With the proper powder treatments, silicon nitride and carbide powder can be made to appear colloidally equivalent. The impact of these results on processing control will be discussed.

*Work done under NASA Grant NAG3-468.
WHY?

* SINTERING OF COVALENT SOLIDS REQUIRES SUBMICRON PARTICLES (PROCESSING COLLOIDAL DISPERSIONS)

-- CERAMIC POWDERS ACQUIRE SURFACE CHARGE AND INTERACT WITH IONS IN PROCESSING FLUID

-- STABILITY AND RHEOLOGY DOMINATED BY ELECTROSTATIC EFFECTS

* STRONG CORRELATION BETWEEN DISPERSION QUALITY AND FINAL PROPERTIES OF SINTERED CERAMIC

TECHNIQUES - SPECTROSCOPIC CHARACTERIZATION FTIR, ESCA, SIMS, AUGER

- ELECTROPHORETIC CHARACTERIZATION ZETA POTENTIAL

- TITRATION OF SURFACE GROUPS SURFACE CHARGE

- RHEOLOGICAL CHARACTERISTICS VISCOMETRY

- STABILITY CHARACTERIZATION SEDIMENTATION
RELATIONSHIP BETWEEN SURFACE POTENTIAL AND SURFACE CHARGE

Development of Surface Charge and Surface Potential

Adsorption of Potential Determining Ions:

\[ \equiv Si-OH + OH^- \rightleftharpoons Si-O^- + H_2O \]

\[ \equiv Si-OH + H^+ \rightleftharpoons Si-OH_2^+ \]
ORIGIN OF SURFACE POTENTIAL

REVERSIBLE ELECTRODE --

NERNST EQUATION RELATES SURFACE POTENTIAL ($\Psi$) TO CONCENTRATION OF POTENTIAL DETERMINING IONS:

$$\Psi = \frac{2.303 R T}{Z_F} \log \left( \frac{C}{C_p} \right)$$

AMPHOTERIC OXIDE --

ASSUMING $H^+$ AND $OH^-$ ARE POTENTIAL DETERMINING AND EXHIBIT NERNSTIAN BEHAVIOR:

$$\Psi = 59.7 (pH_{ZS} - pH)$$

ORIGIN OF SURFACE SPECIES --

THERMODYNAMICS OF THE DOUBLE LAYER

SITE MODEL OF SOLID/LIQUID INTERFACE:

$$\text{MH}^+_{eq} \rightleftharpoons \text{MH} + H^+$$
$$\text{MH} \rightleftharpoons M^- + H^+$$

EQUATE CHEMICAL POTENTIALS:

BULK COMPONENTS--

$$\mu_j = \mu_j^{eq} + RT \ln a_j$$

SURFACE SITES--

$$\mu_j = \mu_j^{eq} + RT \ln n_j + ZF \Psi$$
EXPERIMENTAL APPROACH

-- IDENTIFY PRETREATMENT METHOD TO YIELD REPRODUCIBLE, PRISTINE SURFACE

-- INVESTIGATE EFFECT OF MANUFACTURING HISTORY, SUBSTRATE ON ADSORPTION

-- COMPARE SILICON NITRIDE, SILICON CARBIDE AND SILICA

-- EXPLORE THE ROLE OF ELECTROLYTE

-- COMPARE TITRATION RESULTS WITH RESULTS FROM OTHER METHODS

POTEN TI OMETRIC TITRATION

\[
\sigma_e = F \left( \Gamma^{++} - \Gamma^{+} \right)
\]

WHERE \( F = \) FARADAY'S CONSTANT

\( \Gamma^{+}, \Gamma^{++} \) = EQUIVALENTS OF H⁺ OR OH⁻ BOUND TO SURFACE
HANDLING AND PRETREATMENT:

* NONE (AS RECEIVED)
* FIRE 500°C IN ARGON
* FIRE 300°C IN OXYGEN
* WASH IN DI WATER, THEN:
  -- NO DRY
  -- DRY, MILD CONDITIONS
  -- DRY RAPIDLY
* WASH IN ACIDIC ELECTROLYTE
* EXPOSE TO MODERATE VACUUM

EFFECT OF PRETREATMENT ON TITRATION RESULTS

H+ ADSORPTION (SITES/NM2)

pH

KEY:
- AS RECEIVED
- DI WASHED
- VACUUM
- VACUUM, ACID WASH

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EFFECT OF PRETREATMENT ON TITRATION RESULTS

SUMMARY OF RESULTS

* **PHYSISORBED SPECIES REMOVED**
  - BAKE IN DRY ENVIRONMENT
  - EXPOSE TO MODERATE VACUUM

* **CHEMISORBED SPECIES DESORB RAPIDLY**
  IN ACIDIC ELECTROLYTE

* **SILICON NITRIDE REACTS WITH AQUEOUS**
  SOLUTION TO RE-FORM ORIGINAL ADSORBED SPECIES

* **WASHING IN ACIDIFIED SOLUTION REMOVES**
  ALL ADSORBATE, BUT LEAVES SURFACE UNALTERED FROM "AS RECEIVED" STATE
COMPARISON OF UBE AND TOYA SODA SILICON NITRIDE

![Graph comparing H⁺ adsorption of UBE and TOYA SODA silicon nitride with pH on the x-axis and H⁺ adsorption (sites/nm²) on the y-axis.]

KEY:
- (a) UBE SIN in .001M KNO₃
- (b) GTE SIN in .001M KNO₃
- (c) DENKA SIN in .001M KNO₃
- (d) TOSHIBA SIN in .001M KNO₃
HYPOTHESES

* TITRATABLE SURFACE SPECIES IS SILICA

* SPECIES ADSORBED ON SILICON NITRIDE IS AMMONIA
  - MOST PHYSIOSORBED, SOME CHEMISORBED
  - SIMILAR TO REPORTED ADSORPTION OF AMMONIA ON SILICA

* AMMONIA IS FORMED BY HYDROLYSIS OF SILICON NITRIDE:

\[ 6 \text{H}_2\text{O} + \text{Si}_3\text{N}_4 \rightarrow 3 \text{SiO}_2 + 4 \text{NH}_3 \]

COMPARISON OF SILICON NITRIDE AND SILICON CARBIDE

![Graph comparing H+ adsorption on silicon nitride and silicon carbide vs pH]
SUMMARY OF SURFACE TITRATION DATA

* SUGGEST PZC < pH 3 FOR BOTH SILICA AND SILICON CARBIDE

* SUGGEST PZC > pH 6 FOR MOST SILICON NITRIDES

* LITTLE DIFFERENCE AMONG VARIOUS MANUFACTURERS OF SILICON NITRIDE

* LITTLE DIFFERENCE BETWEEN SILICON NITRIDE AND SILICON CARBIDE Si-OH SITE DENSITY

* WITH CAREFUL PRETREATMENT, DATA IS REPRESENTATIVE OF NATIVE SURFACE AND IS REPRODUCIBLE
Photoacoustic microscopy (PAM) has been utilized to detect surface and subsurface defects in structural ceramic materials. A computerized PAM data acquisition, color imaging and analysis system has been developed and used under this program. Subsurface simulated cylindrical holes can be detected to about 1 mm below the interrogating surface. Simulated tight surface cracks of 96 μm length and 48 μm depth can be detected in these materials under optimum conditions.
OBJECTIVES

- Develop computerized capability to digitally acquire/retrieve and image PAM signals
- Develop capability to detect 250μm size voids/inclusions 1mm below interrogating surface
- Develop capability to detect surface connected cracks
- Demonstrate ability of NDE to predict failure site on MOR bar containing natural flaws

NDE OF STRUCTURAL CERAMICS BY PHOTOACOUSTIC MICROSCOPY

[Diagram showing the process flow of the program from supply of reference materials to mechanical testing.]
PAM FLAW DETECTION
DATA ACQUISITION AND IMAGING SYSTEM

FEATURES
- SCANNER
  - PROGRAMMABLE X-Y RASTER SCAN
  - 2µm AXIS RESOLUTION
- DATA ACQUISITION/IMAGING
  - MENU DRIVEN ALGORITHMS
  - ACQUIRES AND STORES DATA
  - 12 BIT A/D RESOLUTION
  - MONOCROME AND COLOR DISPLAY
  - 8 COLOR PLOTTER
  - EXPERIMENTAL STATISTICS
  - MAGNIFICATION/ZOOM
  - PAN
  - THRESHOLDING
  - FLAW/PAM SIGNAL SIZING
  - HISTOROGRAM OF PAM SIGNALS

DATE 4/10/86
CHART NO. PKK
PAM FLAW DETECTION
BATCH—A AS—FIRED Si₃N₄

HOLE LOCATION FROM TOP SURFACE µm

<table>
<thead>
<tr>
<th>HOLE #</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OPEN TO SURFACE</td>
</tr>
<tr>
<td>2</td>
<td>VERY NEAR TO SURFACE BUT NOT OPEN</td>
</tr>
<tr>
<td>3</td>
<td>156</td>
</tr>
<tr>
<td>4</td>
<td>390</td>
</tr>
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<td>547</td>
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<td>6</td>
<td>665</td>
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<tr>
<td>7</td>
<td>825</td>
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<td>8</td>
<td>1015</td>
</tr>
</tbody>
</table>

NOMINAL DIAMETER = 375 µm
NOMINAL DISTANCE BETWEEN HOLES = 2.5 mm
APPROXIMATE DEPTH = 3.125 mm

PAM SUBSURFACE FLAW DETECTION
AS—FIRED SILICON NITRIDE

MAGNITUDE

f = 40 Hz
PAM DIGITAL IMAGING - SUBSURFACE FLAWS
BATCH-A AS-FIRED Si₃N₄

PAM SUBSURFACE FLAW DETECTION
AS FIRED SINTERED SILICON CARBIDE
### PHOTOACOUSTIC MICROSCOPY
### SURFACE CRACK DETECTION

#### Chart

<table>
<thead>
<tr>
<th>Crack #</th>
<th>Load (Kg)</th>
<th>Length (2c) [µm]</th>
<th>Depth* (a) [µm]</th>
<th>Signal-to-Noise Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>401</td>
<td>200</td>
<td></td>
<td>40 Hz 250µm/sec. 200 µV</td>
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<tr>
<td>1</td>
<td>12</td>
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<td>Saturated</td>
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<td>2</td>
<td>10</td>
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<td>9.0</td>
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<td>6</td>
<td>1</td>
<td>96</td>
<td>48</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

*Assuming semicircular flaw, a = c

N.D. - Signal-to-noise ratio of 1
Difficult to separate the flaw signal from the background

---

### PHOTOACOUSTIC MICROSCOPY
### SURFACE CRACK DETECTION

#### Diagrams

40 Hz

300 Hz
PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION

1 2 3 4 5 6
OPTICAL

40Hz

300Hz
DIGITAL IMAGE

PHOTOACOUSTIC MICROSCOPY
SURFACE CRACK DETECTION

2C=96μm
a=48μm

HPSi₃N₄
t=40Hz

50μm/SEC

250μm/SEC

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MOLTEN SALT CORROSION OF SIC AND SI₃N₄

N. S. Jacobson, J. L. Smialek, and D. S. Fox
NASA Lewis Research Center
Cleveland, Ohio

The most severe type of corrosion encountered in heat engines is corrosion by molten sodium sulfate, which is formed by the reaction of ingested sodium chloride and sulfur impurities in the fuel. This problem has been studied extensively for superalloys, but only recently examined for ceramics. Our program at Lewis addresses this problem with laboratory studies to understand the fundamental reaction mechanisms and with burner studies to provide a more realistic simulation of the conditions encountered in a heat engine. In addition we are assessing the effect of corrosion on the strengths of these materials. Each of these aspects will be reviewed and some ideas toward possible solutions will be discussed.
THE HOT CORROSION PROBLEM

• FORMATION OF \( \text{Na}_2\text{SO}_4 \)
  \[ 2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HCl} \]

• DEPOSITION OF MOLTEN \( \text{Na}_2\text{SO}_4 \) ON ENGINE PARTS
  FUNCTION OF \( T, P, [\text{SALT}] \)

• POTENTIALLY CATASTROPHIC ATTACK

CS-86-1388

TURBINE VANE HOT CORROSION

CS-73740
BASIC AND ACIDIC MOLTEN SALTS

• \( \text{Na}_2\text{SO}_4 = \text{Na}_2\text{O} + \text{SO}_3 = 2\text{Na}^+ + \text{O}^2- + \text{SO}_3 \)  
  \[ K = 4.6 \times 10^{16} \text{ AT 1000 °C} \]

  LOW \( P_{\text{SO}_3} \) - HIGH \( a_0 \) = - BASIC

  HIGH \( P_{\text{SO}_3} \) - LOW \( a_0 \) = - ACIDIC

• \( \text{Na}_2\text{CO}_3 = \text{Na}_2\text{O} + \text{CO}_2 = 2\text{Na}^+ + \text{O}^2- + \text{CO}_2 \)  
  \[ K = 9.7 \times 10^{-7} \text{ AT 1000 °C} \]

MODEL BASIC SALT

CS-86-1383

REATIONS WITH MOLTEN SALTS

• DISSOLUTION OF PROTECTIVE OXIDE (MO) BY MOLTEN SALT

• UNPROTECTED METAL OR CERAMIC SUSCEPTIBLE TO ATTACK

• TYPES OF DISSOLUTION
  • ACIDIC \( \text{MO} = \text{M}^{++} + \text{O}^2- \)
  • BASIC \( \text{MO} + \text{O}^2- = \text{MO}_2^2- \)

• \( \text{SiO}_2 \) IS AN ACIDIC OXIDE
  • EXPECT REACTION WITH BASIC SALT

• \( \text{SiO}_2 + \text{O}^2- = \text{SiO}_3^3- \)

• SILICATES LIQUID T 780 °C

CS-86-1384

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EXPERIMENTAL TECHNIQUES

- LABORATORY
  - AIRBRUSH SAMPLE WITH SALT; HEAT
  - PRECISELY CONTROL PARAMETERS
  - MONITOR KINETICS, MICROSTRUCTURAL CHANGES
  - ONE TIME DEPOSITION OF SALT

- BURNER
  - JET FUEL SEEDED WITH NaCl
  - CONTINUOUS DEPOSITION OF SALT; CLOSER TO ENGINE CONDITIONS
  - DIFFICULT TO CONTROL PARAMETERS

CS-86-1382

LEWIS CORROSION STUDIES OF SiC AND Si$_3$N$_4$

LABORATORY STUDIES
CHEMICAL MECHANISMS

BURNER RIG STUDIES

CHARACTERIZE ATTACK

PITTING STUDIES OF SiC

STRENGTH MEASUREMENTS
FRACTOGRAPHY

CONTROL STRATEGIES
MATERIALS STUDIED

- **SINTERED \( \alpha \)-SiC (B, C)**
  HP SiC, CVD SiC, SC SiC

- **SINTERED Si\(_3\)N\(_4\) (Al\(_2\)O\(_3\), Y\(_2\)O\(_3\))**

  SINTERED Si\(_3\)N\(_4\) (Y\(_2\)O\(_3\)), HIP'd RB Si\(_3\)N\(_4\)

CS-86-1386

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*TGA - SINTERED \( \alpha \)-SiC+Na\(_2\)CO\(_3\)/.1CO\(_2\)/O\(_2\)-1000 °C*

![TGA graph: curve labeled III]
MECHANISM OF CORROSION BY Na$_2$CO$_3$

I. DECOMPOSITION OF SALT AND SILICATE FORMATION

\[ \text{SiC} + \frac{3}{2} \text{O}_2 = \text{SiO}_2 + \text{CO} \]

\[ \text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{O} \cdot (\text{SiO}_2) + \text{CO}_2 \]

II. MOVE TOWARD LIQUIDUS

\[ \text{SiC} + \frac{3}{2} \text{O}_2 = \text{SiO}_2 + \text{CO} \]

\[ \text{Na}_2\text{O} \cdot (\text{SiO}_2) + 2.65(\text{SiO}_2) = \text{Na}_2\text{O} \cdot 3.65(\text{SiO}_2) \]

III. GROWTH OF PROTECTIVE SiO$_2$ LAYER-SLOWING OF REACTION

\[
\begin{align*}
\text{GAS} & \\
\text{Na}_2\text{O} \cdot x(\text{SiO}_2) & \\
\text{SiO}_2 & \\
\text{SiC} & 
\end{align*}
\]

Na$_2$CO$_3$ VERSUS Na$_2$SO$_4$/O$_2$

- \( \text{Na}_2\text{SO}_4 = \text{Na}_2\text{O} + \text{SO}_3 \uparrow \) BASIC MOLten SALT
- SiC - SIMILAR BEHAVIOR
- Si$_3$N$_4$ - Na$_2$SO$_4$/O$_2$ CORROSION IS SLOWER THAN Na$_2$CO$_3$/O$_2$
- IMPORTANT SYSTEM - CLOSE TO BURNER RIG
Na$_2$SO$_4$ / SO$_3$ CASE

Na$_2$SO$_4$ + SiO$_2$ = Na$_2$SiO$_3$ + SO$_3$ \hspace{1cm} \Delta G = + 35 \text{ kcal/mol}

- $P_{SO_3} > 10^{-6}$ atm -- NO REACTION
- Na$_2$SO$_4$/10$^{-4}$ SO$_3$-O$_2$ DOES NOT ATTACK
  - QUARTZ
  - HOT PRESSSED (Al$_2$O$_3$) SiC
  - SINGLE CRYSTAL SiC
  - PREOXIDIZED (1400°C - 23 h) SINTERED SiC
- Na$_2$SO$_4$/10$^{-4}$ SO$_3$ - O$_2$ DRAMATICALLY ATTACKS AS-GROUND SINTERED SiC

BASIC/ACIDIC CHARACTER OF MELT

ACIDIC

SO$_3$-O$_2$

BASIC

MELT

EXCESS CARBON

Na$_2$SiO$_3$ + SO$_3$ = SiO$_2$ + Na$_2$SO$_4$

\begin{align*}
\{ \text{Na}_2\text{SO}_4 + \text{C} + \frac{1}{2} \text{O}_2 = \text{Na}_2\text{CO}_3 + \text{SO}_2} \\
\text{Na}_2\text{CO}_3 + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{CO}_2
\end{align*}

ESTABLISHES FLUXING CONDITION

CS-85-2266
ATTACK OF CERAMIC SUBSTRATE

• HF REMOVES GLASSY PRODUCT LAYERS
  (CAUTION WITH Si₃N₄)

• ATTACK DOES NOT OCCUR BY EVEN RECESSION

• SiC - SEVERE PITTING ATTACK
  \[ \text{Na}_2\text{CO}_3 < \text{Na}_2\text{SO}_4/\text{O}_2 < \text{Na}_2\text{SO}_4/\text{SO}_3 \]

• Si₃N₄ - SEVERE GRAIN BOUNDARY ATTACK

CS-86-1385

CORROSION PITTING

SINTERED α-SiC BEFORE CORROSION

SIC AFTER CORROSION

\[ \text{Na}_2\text{CO}_3/\text{CO}_2 \text{ - 48 hrs - 1000 °C} \]

PRODUCTS REMOVED WITH HF

CS-85-3407
PITTING ATTACK MORPHOLOGY AFTER Na$_2$SO$_4$/SO$_3$ CORROSION

SCALE REMOVED BY HF DISSOLUTION

UNIFORM PITTING OBSERVED OVER LARGE AREAS

DETAIL OF (a) SHOWING HONEYCOMB PIT STRUCTURE

CS-85-2307

STRENGTH DEGRADATION OF $\alpha$-SiC AFTER FURNACE CORROSION TESTING

FRACTURE STRESS, $\sigma_f$ MPa

AS-RECEIVED $-49\%$
Na$_2$SO$_4$/SO$_3$ $-13\%$
Na$_2$CO$_3$/CO$_2$ $-38\%$
Na$_2$SO$_4$/AIR

CS-85-2336
FRACTURE ORIGIN, PITTING, AND GRAIN BOUNDARY ATTACK AFTER Na₂SO₄/SO₃ CORROSION

SCALE REMOVED BY HF

\( \sigma_f = 188 \text{ MPa} \)

PIT DEPTH = 113 \( \mu \text{m} \)

CORROSION PIT FRACTURE ORIGIN AFTER Na₂SO₄/AIR CORROSION

SCALE REMOVED BY HF DISSOLUTION; \( \sigma_f = 373 \text{ MPa}, \) PIT DEPTH = 40 \( \mu \text{m} \)

RADIAL CRACK LINES POINTING TO CORROSION PIT

INTERSECTION OF DEEPLY PITTED REGION WITH FRACTURE SURFACE

GRANULAR ATTACK MORPHOLOGY IN PIT

CS-85-2305
• PARALLEL TO Na₂SO₄/O₂ FURNACE STUDY
• CONTINUOUS SOURCE OF Na₂O
  -- CONTINUOUS Na₂O • x(SiO₂) FORMATION

OPERATING PARAMETERS
- T = 990 ± 10 °C
- JET A FUEL - 0.05% S
- 4 ppm Na AS NaCl
- FLOW VELOCITY - 310 ft/sec

CS-86-1374

BURNER RIG TESTS OF \(\alpha\)-SiC AT 1000 °C

![Burner rig test images]

NO SALT
46 hr

4 ppm Na
13.5 hr

AIR FLOW ↔

CS-85-1205

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EXTENSIVE BUBBLE FORMATION IN BURNER RIG SAMPLES

MECHANICAL SCALE REMOVAL

α-SiC PITTING MORPHOLOGY CAUSED BY BURNER RIG CORROSION

SCALE REMOVED BY HF DISSOLUTION
EFFECT OF BURNER RIG HOT CORROSION ON ROOM TEMPERATURE $\alpha$-SiC STRENGTH

![Graph showing MOR fracture strength](image)

- **AS-RECEIVED**
- **BURNER RIG CORROSION (1000 °C/13.5 hr)**
- **FURNACE CORROSION (1000 °C/48 hr)**

- **RA 330 METAL LINER**
- **$\text{Al}_2\text{O}_3$ CERAMIC LINER**

FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN

- **MATING HALVES OF FrACTURE ORIGIN**
- **CORROSION PRODUCT IN FrACTURE ORIGIN**
- **PITTING REVEALED BY HF DISSOLUTION**

CS-85-1210
FRACTURE ORIGIN OF BURNER RIG CORROSION SPECIMEN

CRACK LINES RADIATE FROM CORNER CORROSION PIT

BUBBLE FORMATION AT INTERFACE

PITTING REVEALED BY HF DISSOLUTION

CS-85-1204

SUMMARY

LABORATORY STUDIES

• BASIC MOLTEN SALTS
  SiO₂ FORMATION AND DISSOLUTION TO LIQUIDUS
• ACIDIC MOLTEN SALTS
  NO ATTACK, UNLESS BASIC CONDITIONS AT MELT BOTTOM

BURNER RIG

• PARALLEL TO Na₂SO₄/O₂ - BASIC SALT ATTACK
• CONTINUOUS Na₂O ⋅ x(SiO₂) FORMATION

ATTACK OF CERAMICS

• SiC -- SEVERE PITTING -- UP TO 50% STRENGTH REDUCTION
• Si₃N₄ - SEVERE GRAIN BOUNDARY ATTACK -- WORK IN PROGRESS
SUMMARY AND CONTROL STRATEGIES

• MOLTEN SALT CORROSION
  • CAN BE CATASTROPHIC
  • ENGINEERS MUST BE AWARE CERAMICS, LIKE SUPERALLOYS, ARE SUSCEPTIBLE

• CONTROL STRATEGIES
  • WORK OUTSIDE SALT DEPOSITION REGIME
  • MAKE SALTS ACIDIC
  • COATINGS; MODIFY SiO₂ LAYER

CS-86-1390
THERMAL CYCLIC DURABILITY TESTING OF CERAMIC MATERIALS FOR TURBINE ENGINES

L.J. Lindberg
Garrett Turbine Engine Company
Phoenix, Arizona 85010

The thermal cyclic durability of commercial ceramic materials for turbine engines has been under evaluation since 1978. Ceramic materials are exposed to cyclic diesel-fired burner exhaust at either 1204 or 1371C (2200 or 2500F) for up to 3500 hours. The test conditions are selected to simulate the environment experienced by the hot flow path components in an automotive gas turbine engine. The silicon nitride and silicon carbide materials tested are the same ceramic materials currently used on the AGT100 and AGT101 ceramic turbine engine programs.

This work was performed under the NASA funded program, 3500-Hour Durability Testing of Commercial Ceramic Materials, Contract DEN3-27.
THERMAL CYCLIC DURABILITY TESTING OF CERAMIC MATERIALS FOR TURBINE ENGINES

3500-HOUR DURABILITY TESTING OF COMMERCIAL CERAMIC MATERIALS

- OBJECTIVE
  - DETERMINE LONG-TERM DURABILITY OF CERAMIC GAS TURBINE ENGINE MATERIALS

- APPROACH
  - CYCLE CERAMIC TEST BARS FROM HIGH TEMPERATURE BURNER EXHAUST TO COLD AIR
  - MONITOR CHANGES IN STRENGTH, WEIGHT, AND DIMENSIONS WITH EXPOSURE TIME AND COMPARE TO BASELINE PROPERTIES
  - TESTING IS TERMINATED WHEN THE STRENGTH IS REDUCED TO 50 PERCENT OF THE BASELINE STRENGTH

- BENEFITS
  - IDENTIFIES CERAMIC MATERIALS CAPABLE OF LONG-TERM USE IN GAS TURBINE ENGINE
  - PROVIDES DIRECT COMPARISON OF NEW CERAMICS WITH MATERIALS PREVIOUSLY TESTED IN THIS CONTINUING PROGRAM
NASA/GARRETT FACILITY DEVELOPED FOR 1371C (2500F) CYCLIC DURABILITY TESTING

A VARIETY OF CERAMICS HAVE BEEN DURABILITY TESTED

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>TEMP. C (F)</th>
<th>DURABILITY, HOURS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOHIO SINTERED ALPHA SILICON CARBIDE (SASC)</td>
<td>1204 (2200)</td>
<td>3500</td>
</tr>
<tr>
<td>SOHIO REACTION SINTERED SILICON CARBIDE (RSSC)</td>
<td>1204 (2200)</td>
<td>3500</td>
</tr>
<tr>
<td>ACC RBN 101 REACTION BONDED SILICON NITRIDE (RBSN)</td>
<td>1204 (2200)</td>
<td>2100</td>
</tr>
<tr>
<td>REFEL SILICONIZED SILICON CARBIDE (SISC)</td>
<td>1204 (2200)</td>
<td>2100</td>
</tr>
<tr>
<td>NGK SN-50 SINTERED SILICON NITRIDE (SSN)</td>
<td>1204 (2200)</td>
<td>&lt;350</td>
</tr>
<tr>
<td>GTE AY6 SSN</td>
<td>1204 (2200)</td>
<td>&lt;350</td>
</tr>
<tr>
<td>TOSHIBA SSN</td>
<td>1204 (2200)</td>
<td>&lt;350</td>
</tr>
<tr>
<td>ACC SSN</td>
<td>1204 (2200)</td>
<td>&lt;350</td>
</tr>
<tr>
<td>NORTON NCX 34 HOT PRESSLED SILICON NITRIDE (HPSN)</td>
<td>1204 (2200)</td>
<td>&lt;100</td>
</tr>
<tr>
<td>SOHIO SASC</td>
<td>1371 (2500)</td>
<td>3500</td>
</tr>
<tr>
<td>ACC RBSN</td>
<td>1371 (2500)</td>
<td>2100</td>
</tr>
<tr>
<td>REFEL SISC</td>
<td>1371 (2500)</td>
<td>&lt;350</td>
</tr>
</tbody>
</table>
SEVERAL CERAMIC MATERIALS DEMONSTRATE ACCEPTABLE PERFORMANCE AT 1204C (2200F)

TEST RESULTS SHOW CERAMIC DURABILITY AT 1371C (2500F)
NEW MATERIALS ARE TESTED AS THEY BECOME AVAILABLE

- KYOCERA SC201 SINTERED SILICON CARBIDE (SSC) — DURABILITY TESTING IN PROGRESS
- SOHIO SASC (INJECTION MOLDED, AS-FIRED SURFACES) — DURABILITY TESTING IN PROGRESS
- GE $\beta$ SSC — BASELINE TESTING COMPLETE
- CORNING LAS — BASELINE TESTING COMPLETE
- NGK SN-82 SSN — BASELINE TESTING COMPLETE
- ACC CODE 2 SSN — TO BE PROCURED
- KYOCERA SN 250M OR 270M SSN — TO BE PROCURED

BASELINE STRENGTH OF KYOCERA SINTERED SILICON CARBIDE HAS BEEN DETERMINED

MATERIAL: KYOCERA SC201
CONDITION: AS-FIRED TEST BARS

<table>
<thead>
<tr>
<th></th>
<th>ROOM TEMPERATURE</th>
<th>1204C (2200F)</th>
<th>1371C (2500F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAN STRENGTH, KSI (12 DATA POINTS)</td>
<td>61.9</td>
<td>66.2</td>
<td>71.3</td>
</tr>
<tr>
<td>STANDARD DEVIATION, KSI</td>
<td>11.4</td>
<td>8.2</td>
<td>8.8</td>
</tr>
</tbody>
</table>

CYCLIC EXPOSURE TESTING IS BEING CONDUCTED AT 1371C (2500F)
KYOCERA SC201 HAS UNDERGONE 1050 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)

Baseline strength of Sohio injection molded sintered SiC has been determined

**Material:** Sohio SASC  
**Condition:** As-fired test bars

<table>
<thead>
<tr>
<th></th>
<th>Room Temperature</th>
<th>1204C (2200F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean strength, KSI</td>
<td>63.5</td>
<td>60.7</td>
</tr>
<tr>
<td>(12 data points)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard deviation, KSI</td>
<td>9.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Cyclic exposure testing is being conducted at 1371C (2500F)
SOHIO INJECTION MOLDED SASC HAS UNDERGONE 350 HOURS OF CYCLIC EXPOSURE TO 1371C (2500F)

FLEXURAL TEST TEMPERATURE

- ROOM TEMPERATURE
- 1371C (2500F)

EXPOSURE TIME, HOURS

FLEXURE STRENGTH, KSI

BASELINE STRENGTH OF GE β SILICON CARBIDE HAS BEEN DETERMINED

MATERIAL: GE β SiC
CONDITION: AS-FIRED TEST BARS

<table>
<thead>
<tr>
<th></th>
<th>ROOM TEMPERATURE</th>
<th>1371C (2500F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAN STRENGTH, KSI</td>
<td>61.4</td>
<td>61.2</td>
</tr>
<tr>
<td>(12 DATA POINTS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STANDARD DEVIATION, KSI</td>
<td>4.6</td>
<td>8.9</td>
</tr>
</tbody>
</table>

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1371C (2500F)
BASELINE STRENGTH OF NGK SINTERED SILICON NITRIDE HAS BEEN DETERMINED

MATERIAL: NGK SN-82
CONDITION: AS-FIRED TEST BARS

<table>
<thead>
<tr>
<th></th>
<th>982C (1800F)</th>
<th>1204C (2200F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROOM TEMPERATURE</td>
<td>120.4</td>
<td>103.9</td>
</tr>
<tr>
<td>MEAN STRENGTH, KSI (12 DATA POINTS)</td>
<td>14.0</td>
<td>97.3</td>
</tr>
<tr>
<td>STANDARD DEVIATION, KSI</td>
<td>9.2</td>
<td>5.5</td>
</tr>
</tbody>
</table>

CYCLIC EXPOSURE TESTING TO BE CONDUCTED AT 1204C (2200F)

RESULTS

- SOHIO SASC (ISOPRESSED, MACHINED SURFACES) EXPERIENCES NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1371C (2500F)
- SOHIO RSSC EXPERIENCES NO STRENGTH DEGRADATION AFTER 3500 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)
- ACC RBSN EXPERIENCES A 20-PERCENT STRENGTH REDUCTION AT 1204C (2200F) AFTER 2100 HOURS OF EXPOSURE AND A 20-PERCENT STRENGTH REDUCTION AFTER 350 HOURS AT 1371C (2500F)
- ALL SSN MATERIALS TESTED TO DATE (NGK SN-50, ACC CODE 2, CTE AY6, TOSHIBA SSN) EITHER EXHIBITED LOW BASELINE FLEXURE STRENGTHS AND/OR SHOWED >50-PERCENT STRENGTH DEGRADATION DURING THE FIRST 350 HOURS OF CYCLIC EXPOSURE AT 1204C (2200F)
BASELINE FLEXURE STRENGTH AND CYCLIC DURABILITY TESTING IS SCHEDULED FOR 1986-1987

- CYCLIC EXPOSURE TESTING IS CURRENTLY BEING CONDUCTED ON INJECTION MOLDED SOHIO SASC WITH AS-FIRED SURFACES AND KYOCERA SSC WITH AS-FIRED SURFACES AT 1371°C (2500°F)

- CYCLIC EXPOSURE TESTING OF GE β SSC, CORNING LAS, NGK SN-82 SSN AND ACC CODE 2 SSN WILL BE CONDUCTED DURING 1986-1987

- KYOCERA SN-250M OR 270M WILL BE PROCURED FOR BASELINE AND EXPOSURE TESTING DURING 1986-1987
FRACTOGRAPHIC AND MICROSTRUCTURAL EVALUATION OF 3500-HOUR DURABILITY SPECIMENS

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NASA Lewis Research Center has since 1978 contracted with Garrett Turbine Engine Company to conduct long-term durability testing of candidate ceramic materials for advanced gas turbine applications. Specimens of the materials are exposed to combustion atmospheres under temperature cyclic conditions for times up to 3500 hours and at peak temperatures of 1200 and 1370 C. The specimen strengths after exposure are measured at room temperature and at 1200 C. In addition, a number of physical measurements are taken, however no provision is made in the contract for microstructural examination of the specimens.

The work under this project covers examination of three materials, (1) sintered alpha silicon carbide manufactured by Carborundum Co., (2) sintered silicon nitride, manufactured by Toshiba, and (3) reaction bonded silicon nitride, grade RBN-104, manufactured by Airresearch Casting Company. The work required the development of sample preparation techniques to provide high quality thin-section specimens which can be examined by transmitted light or thinned using an ion mill for subsequent TEM examination.

Specimen preparation techniques and the results of optical and electron microscopic examination of the reaction interfaces of the selected specimens are presented and discussed.
Figure 1. - Baseline SASC; crossed Nichols. 95X

Figure 2. - Baseline SASC; crossed Nichols. 240X.
Figure 3. - Same field as fig.2; crossed Nichols, rotated 45°. 240X.

Figure 4. - SASC; 2100-hr exposure at 1370 °C; crossed Nichols. 95X.
Figure 5. - Same field as fig. 4. 240X.

Figure 6. - SASC; 3500-hr exposure at 1370 °C; crossed Nichols. 240X.
Figure 7. - Baseline Toshiba SSN; crossed Nichols. 95X.

Figure 8. - Toshiba SSN; 350-hr exposure at 1205 °C; crossed Nichols. 95X.
Figure 9. - Same specimen as fig. 8; field near interface; crossed Nichols. 240X

Figure 10. - Same specimen as fig 8; field far from interface; crossed Nichols. 240X.
Figure 11. - Toshiba SSN; 700-hr exposure; crossed Nichols. 95X.
An overview is presented covering NASA Lewis research efforts aimed at materials and processing development for structurally reliable fiber-reinforced ceramic matrix composites (FRC). With the primary goal of developing technology for strong, tough Si-based FRC with use-temperatures above 1400°C, guidelines for optimum material properties and current problems in achieving these properties are discussed. Brief descriptions of particular research projects directed toward solving these problems are presented. Particular emphasis is placed on those efforts addressing the critical need of developing high performance SiC fibers with stability above 1400°C and with proper coatings for optimum composite structural performance. Based on current results for fiber and matrix development, concluding remarks are made concerning future directions for NASA Lewis FRC studies.
OBJECTIVE: TECHNOLOGY DEVELOPMENT FOR FABRICATION OF STRONG, TOUGH, AND RELIABLE CERAMIC COMPOSITES FOR AEROSPACE STRUCTURAL APPLICATIONS TO 1400 °C AND ABOVE

PRIMARY APPROACH: FIBER REINFORCED CERAMICS (FRC) - REINFORCEMENT OF Si-BASED CERAMIC MATRICES WITH CONTINUOUS HIGH PERFORMANCE CERAMIC FIBERS

FRC DEFORMATION AND FRACTURE

FIBER BRIDGING OF MATRIX CRACKS
STRUCTURAL ADVANTAGES OF FIBER-
REINFORCED CERAMICS

• IMPROVED STIFFNESS
  • MATRIX FRACTURE STRENGTH
  • MATRIX FRACTURE STRAIN
  • FRACTURE TOUGHNESS
  • THERMAL SHOCK

• METAL-LIKE STRESS-STRAIN BEHAVIOR

• ULTIMATE FAILURE INDEPENDENT OF MATRIX FRACTURE

• NONCATASTROPHIC MATERIAL FAILURE

• AVAILABLE ONLY FOR HIGH ASPECT RATIO REINFORCEMENT

FRC - KEY TECHNICAL ISSUES

I. FABRICATION APPROACH FOR HIGH FRC STRENGTH
  • PREPARATION OF OPTIMUM MATRIX PRECURSORS
  • UNIFORM PRECURSOR INFILTRATION INTO FIBER ARRAY
  • MATRIX CONSOLIDATION AND DENSIFICATION WITHOUT
    • FIBER STRENGTH DEGRADATION
    • LARGE SHRINKAGE CRACKS OR POROSITY
    • NONUNIFORM FIBER DISTRIBUTION

II. AVAILABILITY OF HIGH PERFORMANCE CERAMIC FIBERS
  • HIGH STRENGTH AND STIFFNESS
  • THERMAL STABILITY ABOVE 1200 °C
  • SMALL DIAMETER

III. FIBER COATINGS
  • FIBER STRENGTH RETENTION UNDER FRC PROCESSING AND USE
  • OPTIMUM FOR COMPOSITE TOUGHNESS AND OFF-AXIS STRENGTH
I. COMPOSITE FABRICATION

<table>
<thead>
<tr>
<th>PROCESSING APPROACH</th>
<th>PRIMARY SYSTEM</th>
<th>KEY ISSUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>REACTION-BONDED Si$_3$N$_4$ WITH CVD SiC FIBERS</td>
<td>SiC/RBSN</td>
<td>- STRENGTH AND TOUGHNESS GREATER THAN RBSN - THERMAL STABILITY TO 1400 °C</td>
</tr>
<tr>
<td>CARBON MATRICES REACTION BONDED WITH SILICON</td>
<td>SiC/RBSC</td>
<td>- MATRIX MORPHOLOGY AND SILICONIZATION - FIBER DEGRADATION</td>
</tr>
<tr>
<td>POLYMER-DERIVED PRECURSORS TO SiC AND Si$_3$N$_4$ MATRICES</td>
<td></td>
<td>- HIGH CHAR YIELD - INFILTRATION RHEOLOGY WITH CERAMIC FILLERS</td>
</tr>
</tbody>
</table>

II. HIGH PERFORMANCE SiC FIBERS

- HIGH TEMPERATURE PROPERTIES OF COMMERCIAL SiC FIBERS - FIBER PROCESSING APPROACH BEST SUITED FOR HIGH TEMPERATURE FRC
- POST PROCESSING OF NICALON FIBERS AT HIGH PRESSURE - POTENTIAL OF HIPPING FOR IMPROVING NICALON THERMAL STABILITY

III. FIBER COATINGS

- OXYGEN EFFECTS ON COMMERCIAL COATINGS FOR CVD SiC FIBERS - COATING DESIGN FOR OXIDATION RESISTANCE
- FIBER-MATRIX LOAD TRANSFER IN SiC/RBSN COMPOSITES - COATING DESIGN FOR COMPOSITE TOUGHNESS AND STRENGTH
PROPERTY COMPARISON - COMMERCIAL SiC FIBERS

<table>
<thead>
<tr>
<th>TYPE</th>
<th>NiCAlON (NIPPON CO.)</th>
<th>SCS (AVCO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRODUCTION</td>
<td>POLYMER SPUN,</td>
<td>CVD ONTO CARBON</td>
</tr>
<tr>
<td>METHOD</td>
<td>CURED, PYROLYZED</td>
<td>FILAMENT (1300 °C)</td>
</tr>
<tr>
<td>FORM</td>
<td>MULTIFILAMENT YARN</td>
<td>MONOFILAMENT</td>
</tr>
<tr>
<td>(500 PER TOW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIAMETER, µm</td>
<td>10 TO 20</td>
<td>142</td>
</tr>
<tr>
<td>MODULUS, GPa</td>
<td>180</td>
<td>390</td>
</tr>
<tr>
<td>STRENGTH, GPa</td>
<td>2.0</td>
<td>&gt;3.5</td>
</tr>
<tr>
<td>20 °C</td>
<td>2.0</td>
<td>&gt;3.5</td>
</tr>
<tr>
<td>1400 °C</td>
<td>&lt;1.0</td>
<td>&gt;2.5</td>
</tr>
</tbody>
</table>

CVD SiC FIBERS PROVIDE CREEP RESISTANCE TO RBSN MATRICES
ADVANTAGES OF FIBER COATINGS FOR CERAMIC MATRIX COMPOSITES

PHYSICAL - CHEMICAL:

• CAN SERVE AS A DIFFUSION BARRIER INHIBITING INTERDIFFUSION AND REACTIONS WITH MATRIX AND AGGRESSIVE GASES, SUCH AS, OXYGEN

• MINIMIZE DEGRADATION OF FIBER STRENGTH AND FIBER-MATRIX INTERFACIAL BONDING

STRUCTURAL:

• REDUCE MECHANICAL DEGRADATION DURING HANDLING AND COMPOSITE PROCESSING

• REDUCE INTERNAL DEGRADATION BY TRAPPING EVOLVING GASES

• HEAL FIBER SURFACE FLAWS AND INCREASE FIBER STRENGTH

• PROVIDE WEAK FIBER-MATRIX BONDING FOR CRACK DEFLECTION AND TOUGH COMPOSITES

CS-85-0274

CVD SiC FIBER CROSS SECTION AND COATINGS

β-SiC SHEATH
(142 μm DIAM.)

GRAPHITE-COATED CARBON CORE
(~37 μm DIAM.)

TRANSITION IN GRAIN STRUCTURE
(~80 μm DIAM.)

CARBON-RICH COATING

(a) AVCO SiC 

% Si

50

β-SiC

~ 1 μm

(b) AVCO SCS-6

% Si

50

β-SiC

~ 2 μm

CS-84-0419
CERAMIC COMPOSITES - FUTURE DIRECTIONS

I. FRC FABRICATION
- SiC/RBSN OPTIMIZATION
- CVD-CVI PROCESSING
- COMBINED PROCESSING APPROACHES
- TOUGHENING ADDITIONS TO MATRIX
- MULTITYPE FIBERS AND FIBER WEAVES
- HYBRID MATRICES

II. HIGH PERFORMANCE CERAMIC FIBERS
- MULTIFILAMENT TOW OF SMALL DIAMETER CVD SiC FIBERS
- SINGLE CRYSTAL SiC AND OXIDE FIBERS
- NEW INNOVATIVE PROCESSING

III. FIBER COATINGS
- STABLE AND OPTIMIZED CVD SiC-C COATINGS
- OTHER CERAMIC COATINGS BY CVD, SOL-GEL, ETC
Polymer Precursors for SiC Ceramic Materials

by

Morton H. Litt
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

We have worked on precursor polymers to SiC, concentrating on polymers made from decamethyl cyclohexasilyene units. Our initial approach was to synthesize mixed diphenyl decamethyl cyclohexasilane, dephenylate and polymerize. This produced polymers which had yields of up to 50% SiC. [Theoretical yield is 75%.] Our present approach is to make polymer through the intermediate trans-1,4-diphenyl decamethyl cyclohexasilane. This should produce a crystalline polymer and high strength fibers. These will be thermally decomposed to SiC fibers. This requires new chemistry which we are studying now.
(CH₃)₂SiCl₂ $\xrightarrow{\text{Na, sealed tube}}$ \(\begin{array}{c}
\text{CH₃} \\
\text{-Si-} \\
\text{CH₃}
\end{array}\) \(\xrightarrow{\Delta}\)

\[
\text{PhMeSiCl₂ + 2Me₂SiCl₂} \xrightarrow{\text{Na-K, THF}} \text{Me}_{12-x}\text{Ph}_x\text{Si}_6 + \text{MCl}
\]

\((x = 0-6) \quad (M = \text{Na,K})\)
<table>
<thead>
<tr>
<th>$\text{Me}_{12-x}\text{Ph}_x\text{Si}_6$</th>
<th>Yield</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt(%)</td>
<td>mol(%)</td>
<td>mol(%) (theoretical)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>8</td>
<td>11</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>27</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>32</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>30</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

**FIG 1. NMR OF DIPHENYLDECAMETHYLCYCLOHEXASILANE**
<table>
<thead>
<tr>
<th>$^1$H (No. of Methyl Groups) (δ ppm)$^a$</th>
<th>$^{13}$C (No. of Carbon) (δ ppm)$^b$</th>
<th>$^{29}$Si (No. of Silicon) (δ ppm)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.530 (2)</td>
<td>-4.32 (4)</td>
<td>-41.08 (4)</td>
</tr>
<tr>
<td>0.330 (4)</td>
<td>-6.49 (2)</td>
<td>-41.40 (2)</td>
</tr>
<tr>
<td>0.198 (4)</td>
<td>-6.71 (4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>134.68 (o,4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127.86 (p,2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>127.71 (m,4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>146.98 (1,2)</td>
<td></td>
</tr>
</tbody>
</table>

$a$ - CH$_2$Cl$_2$ (δ 5.35) was used as an internal reference.

$b$ - CDCl$_3$ (δ 77.0) was used as an internal reference.

$c$ - TMS (δ 0.0) was used as an internal reference.

\[
\begin{array}{cc}
\text{Ph} & \text{NH}_4\text{Cl/H}_2\text{SO}_4 \\
\text{Benzene} & \text{Cl} \\
\rightarrow & \text{Na} \\
\rightarrow & \text{toluene} \\
\end{array}
\]

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### TABLE 1 ELEMENTAL ANALYSIS OF POLYMER25 AND POLYMER27

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Analytical</th>
<th>% C</th>
<th>% H</th>
<th>% Si</th>
<th>% O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polym25</td>
<td>Calcd.</td>
<td>37.74</td>
<td>9.43</td>
<td>52.83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>33.52</td>
<td>8.69</td>
<td>48.22</td>
<td>9.57 (by difference)</td>
</tr>
<tr>
<td>Repeat</td>
<td>Found</td>
<td>34.40</td>
<td>8.51</td>
<td>-----</td>
<td>None or Trace</td>
</tr>
<tr>
<td>Polym27</td>
<td>Calcd.</td>
<td>37.74</td>
<td>9.43</td>
<td>52.83</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>38.10</td>
<td>9.65</td>
<td>48.70</td>
<td>3.55 (by difference)</td>
</tr>
<tr>
<td>Repeat</td>
<td>Found</td>
<td>40.14</td>
<td>9.23</td>
<td>-----</td>
<td>0.16</td>
</tr>
</tbody>
</table>

**FIG. 6. IR OF POLYMER25**
FIG 7. IR OF POLYMER27

TABLE 2 THERMOGRAVIMETRIC ANALYSIS OF POLYMER25 CURED AT VARIOUS TEMPERATURES

<table>
<thead>
<tr>
<th>Temperature/Time</th>
<th>Char Yield %</th>
<th>Heating Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer25</td>
<td>27.39</td>
<td>1.5°C/min</td>
</tr>
<tr>
<td>124° ± 4°C/4 hrs</td>
<td>18.75</td>
<td>10°C/min</td>
</tr>
<tr>
<td>200° ± 1°C/5 min</td>
<td>20.85</td>
<td>10°C/min</td>
</tr>
<tr>
<td>250° ± 5°C/15 min</td>
<td>(a) 20.80</td>
<td>10°C/min</td>
</tr>
<tr>
<td></td>
<td>(b) 48.27</td>
<td>10°C/min</td>
</tr>
<tr>
<td>200° ± 1°C/5 hrs</td>
<td>(c) 51.52</td>
<td>10°C/min</td>
</tr>
<tr>
<td></td>
<td>17.74</td>
<td>10°C/min</td>
</tr>
<tr>
<td></td>
<td>36.47</td>
<td>10°C/min</td>
</tr>
<tr>
<td></td>
<td>25.71</td>
<td>15°C/min</td>
</tr>
<tr>
<td></td>
<td>19.64</td>
<td>1.5°C/min</td>
</tr>
</tbody>
</table>

(a) Hexane soluble fraction (59.8% of total polymer).
(b) Gel (12.67% of the total polymer).
(c) A piece of polymer was used, rather than ground powder.
New Work

Trans-1,4-diphenyl decamethyl cyclohexasilane

mp = 169.5-170°C, yield = 0.2%

Poly(trans 1,4'-decamethyl cyclohexasilane)

1. Crystallizable polymer.
2. Should be spinnable from solvent in nematic form.
3. Strong, stable fiber
4. Could retain strength to some degree during pyrolysis to SiC.
5. Higher yield and easier processing than present materials.
TlSi(CH₃)₂Cl + CH₃SiCl₂ → TlSi(CH₃)₂Cl + CH₃SiCl₂

Na/K, THF → TlSi(CH₃)₂Cl + CH₃SiCl₂ → TlSi(CH₃)₂Cl + CH₃SiCl₂

Tl = p-Tolyl, n = 0 → ?

Theory - highest yield = 27% of n=1

Best yield so far = 20%, n=0,1,2,3,4 isolated

CH₃ CH₃ CH₃ CH₂Cl₂ CH₃ SO₃H CH₃ CH₃ CH₃
TlSi - Si - Si - Si - Si - Si - Si - Si - Si - Si - Si - Si - Si
CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ CH₃

Na → Toluene
The fiber composite approach to reinforced ceramics provides the possibility
of achieving ceramics with high fracture toughness relative to monolithics.
Fabrication of ceramic composites, however, demands low processing
temperatures to avoid fiber degradation. Formation of complex shapes further
requires small diameter fibers as well as techniques for infiltrating the
matrix between fibers.

Polymers offer low temperature processability, control of rheology not
available with ceramic powders, and could serve as precursors to fibers of
matrix. In recent years, a number of polysilanes and polysilezanes have been
investigated as potential precursors. A review of candidate polymers will be
presented, including recent studies of silsesquioxanes underway at LeRc.
NEEDS

- SMALL DIAMETER CERAMIC FIBER
- HIGH TEMPERATURE, ENVIRONMENTALLY RESISTANT MATRIX

PROBLEMS

- LOW CHAR YIELD
- HIGH SHRINKAGES - VOIDS
- NEED FOR REPEATED IMPREGNATION
- DEVIATION FROM STOICHIOMETRY - CHEMICAL INSTABILITY AT HIGH TEMPERATURES

POLYMER + CERAMIC PARTICULATE + CONTINUOUS FILAMENT $\rightarrow_{\text{hot press}}$ HIGH TEMPERATURE COMPOSITE $\rightarrow_{\text{pyrolyze}}$
MONOMERS

DEDPM
diethynylidiphenylmethane

DEDPE
diethynylidiphenylethane

TETPB
triethynyltriphenylbenzene

TETPM
triethynyltriphenylmethane

CROSSTLINKED HOMOPOLYMER OR COPOLYMER
**Si Containing Polymers**

- $(\text{CH}_3)_x\text{Si}_y$ **Methylpolysilane**
- $((\text{CH}_3)_2\text{SiCH}_2\text{SiCH}_3)_x$ **Polycarbosilane**
- $(\text{C}_6\text{H}_5\text{CH}_3\text{Si})_x((\text{CH}_3)_2\text{Si})_y$ **Polysilastrene**
- $(\text{CH}_3\text{Si})_x(\text{CH}_2\text{CHSiCH}_3)_y$ **Vinylsilane**
- $(\text{CH}_3\text{HSiN})_x$ **Polymethylsilazane**
- $(\text{CH}_3\text{Si})_x(\text{NCH}_3)_y(\text{NHCH}_3)_z$ **Polycarbosilazane**
- $(\text{Si}--\text{Si})_x(\text{Si}--\text{Si})_y$ **Poly (cyclohexamethylsilane)**

**Silsesquioxanes**

$\text{RSiO}_{1.5}$

$R = \text{methyl, propyl, vinyl, phenyl}$

**T Resin**

**Ladder Polymer**

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Polymer derived Nicalon SiC fibers are known to be thermally unstable at temperatures beyond 1200°C. In an effort to further understand the mechanisms of fiber degradation, Nicalon fibers were heat treated at temperatures up to 2200°C and argon gas pressures varying from 0 to 1360 atm. The effects of gas pressure on the thermal stability of the fibers were determined through property comparisons between the pressure-treated fibers and vacuum-treated fibers. Investigation of the thermal stability included studies of the fiber microstructure and mechanical and physical properties before and after treatments.
Nicalon Fiber Thermal Stability

Problem:
• Polymer derived Nicalon SiC fibers degrade significantly in tensile strength above 1200 °C in inert environments

Probable Mechanisms:
• Creation of increased internal porosity and flaw growth caused by reactions between SiC, SiO₂, C, and Si₃N₄ in the as-produced fiber
• Grain growth of microcrystalline SiC

Objectives

• To determine the effects of heat treatment in high pressure argon on the tensile strength and physical properties of commercially available Nicalon SiC fibers

• To determine whether Hot Isostatic Pressing can offer a viable approach to improving the thermal stability of Nicalon fibers
Experimental Parameters

Nicalon Fibers: Ceramic Grade \( \sim 40 \) 50 8 2 at%
Standard Grade \( \sim 37 \) 46 15 2 at%

Treatment Conditions: Pressure: 10, 1, 1360 atm Argon
Temperature: 1000 - 2200°C
Time: 1 hour

Properties: Weight Loss
Tensile Strength
Grain Size
Microstructure
Crystalline Phases

Pressure and Temperature Effects on the Weight Loss of Treated Nicalon Fibers
Pressure and Temperature Effects on the Grain Growth of Treated Nicalon Fibers

Pressure and Temperature Effects on the Tensile Strength of Treated Nicalon Fibers
Fracture Surfaces of As-Received Nicalon Fibers

Standard Grade
250 ksi

Ceramic Grade
231 ksi

Ceramic Grade Nicalon Heated to 1000°C

1 atm
0.8 % wt loss
235 ksi

10^-8 atm
0.8 % wt loss
154 ksi

1360 atm
0.6 % wt loss
240 ksi
Ceramic Grade Nicalon Heated to 1400°C

1360 atm
1.0 % wt loss
208 ksi

1 atm
22 % wt loss
85 ksi

10^(-8) atm
27 % wt loss
— ksi

Ceramic Grade Nicalon Fibers Heated to 1600°C

1360 atm
0.8 % wt loss
90 ksi

1 atm
28 % wt loss
— ksi
Nicalon Fibers Heated to 2200°C

Standard Grade
1360 atm
25% wt loss
— ksi

Ceramic Grade
1360 atm
28% wt loss
— ksi

Correlation Between Weight Loss and Grain Growth of Heat Treated Nicalon Fibers
Effect of Weight Loss on the Tensile Strength of Heat Treated Nicalon Fibers

Results of Additional Heat Treatment Tests on High Pressure Treated Nicalon Fibers

<table>
<thead>
<tr>
<th>Heat Treatment Conditions</th>
<th>% Weight Loss (CG / SG)</th>
<th>Tensile Strength (ksi) (CG / SG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200 C - 1 hr 1360 atm Ar</td>
<td>0.8 / 0.7</td>
<td>236 / 271</td>
</tr>
<tr>
<td>1200 C - 1 hr 1360 atm Ar</td>
<td>28 / 24</td>
<td>-- / --</td>
</tr>
<tr>
<td>1400 C - 1 hr 1 atm Ar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600 C - 1 hr 1360 atm Ar</td>
<td>0.8 / 2.0</td>
<td>90 / 78</td>
</tr>
<tr>
<td>1600 C - 1 hr 1360 atm Ar</td>
<td>23 / 26</td>
<td>-- / --</td>
</tr>
<tr>
<td>1400 C - 1 hr 1 atm Ar</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Approximate Weight Loss due to Sizing Removal
Pressure Effects on Nicalon Thermal Stability

Summary:

• High pressure treatments in Argon suppress fiber weight loss to temperatures above 1500 C

• Strength degradation and grain growth can be correlated with weight loss and thus are also inhibited by high pressure treatments

• Strength degradation occurs rapidly within the first 1% weight loss (beyond the sizing removal) whereas grain growth does not proceed as rapidly until ~20% weight is reached

• Fibers retreated at 1400 C in 1 atm Ar after high pressure treatment show no improvement in strength over as received fibers treated at 1400 C

Pressure Effects on Nicalon Thermal Stability

Conclusions:

• Increased external pressure creates a diffusion barrier which inhibits CO gas evolution from internal SiO₂ – Carbon reactions thus suppressing fiber weight loss

• Suppression of CO gas evolution may also delay exaggerated grain growth due to the tendency of excess carbon in SiC to act as a grain growth inhibitor

• Initial and major strength degradation mechanism is most likely due to the rapid growth of pre-existing flaws near the surface

• In general, high pressure treatment of commercial Nicalon fibers offers no improvement in thermal stability unless pressure can be maintained throughout composite fabrication and fiber use

• Because of initial porosity and/or creep resistance in the as-produced Nicalon fibers Hot Isostatic Pressing does not appear to be an effective post-fabrication method for improving fiber thermal stability
Fiber Development – Future Directions

Based on potential SiC Properties:

- High modulus (>400 GPa)
- High strength (>4 GPa)
- Creep resistance
- Environmental resistance
- Low density
- High thermal conductivity
- Property retention to above 1400 C

Efforts will continue to develop processing approaches for producing

- Continuous
- Small diameter
- High performance
- Multifilament tows of SiC fibers

Current results indicate CVD Processing as the optimum approach for the base fibers and for required fiber coatings
SiC FIBER REINFORCED REACTION-BONDED Si$_3$N$_4$ COMPOSITES

Ramakrishna T. Bhatt
NASA Lewis Research Center
Cleveland, Ohio 44135

A technique for fabricating strong and tough SiC fiber reinforced reaction bonded Si$_3$N$_4$ matrix composites (SiC/RBSN) has been developed. Using this technique, composites containing ~23, 30, and 40 volume fractions of aligned 140 µm diameter, chemically vapor deposited SiC fibers have been fabricated. The room temperature physical and mechanical properties have been evaluated. The results for composite tensile strength, bend strength, and fracture strain indicate that the composite displays excellent properties when compared with the unreinforced matrix of comparable porosity. The composite stress at which the matrix first cracks and the ultimate composite fracture strength increase with increasing volume fraction of fibers, and the composite fails gracefully.

Measurements of room temperature tensile strength of SiC/RBSN composites after 100 hr exposure in flowing air at 1200°C and at 1400°C, and measurements of bend strength at temperatures up to 1300°C did not show any appreciable strength loss from the strength values of as-fabricated composites. The mechanical property data of this ceramic composite are compared with similar data for unreinforced commercially-available Si$_3$N$_4$ materials and for SEP SiC/SiC composites.
SiC Fiber Reinforced Reaction-Bonded Si$_3$N$_4$

by

R. T. Bhatt

NASA-LEWIS RESEARCH CENTER
CLEVELAND, OHIO 44135

OBJECTIVE:
- To fabricate and evaluate properties of fiber reinforced Si$_3$N$_4$ matrix composites for advanced heat engine applications

RATIONALE:
- Si$_3$N$_4$ is a light, oxidation resistant, thermal shock resistant, nonstrategic material but lacks ductility (toughness) and strength reproducibility

APPROACH:
- Reinforcement of Si$_3$N$_4$ by high strength, high modulus ceramic fiber should
  - Improve toughness by crack deflection at the interface
  - Increase first matrix failure stress due to increase in stiffness of material

PROPERTIES:
- First matrix crack stress
- Ultimate strength
- Interfacial shear strength
- Thermal shock resistance
- Thermal stability

TESTS:
- Tensile strength - (Room temperature)
- Flexure strength - (Room temperature to 1400 °C)

Materials for Si$_3$N$_4$ Composite

Fibers
- AVCO CVD Silicon Carbide Fibers
- High modulus - 390 GPa (57x10$^6$ psi)
- High strength - 3.5 GPa (500 ksi)
- High purity
- Creep resistant
- Compatible with Si$_3$N$_4$

Matrix
- Reaction-Bonded Silicon Nitride
- Low modulus - 100-200 GPa (15-30x10$^6$ psi)
- Low temperature fabrication
- Net shape processing
AVCO SiC FIBER COMPOSITION

β-SiC SHEATH (142 μm DIAM) - GRAPHITE COATED CARBON CORE

CARBON-RICH COATING

COATING (SCS-6)

DEPTH BELOW SURFACE

SiC/RBSN COMPOSITE FABRICATION

FIBER MAT BONDED BY Si POWDER + BINDER

SiC/Si PREFORM

SILICON TAPE CONTAINING Si POWDER, ORGANIC BINDER ADDITIVES

HEATED TO 500 °C IN VAC FURNACE FOR BINDER REMOVAL

HOT PRESSED IN VACUUM OR ARGON AT 1000 °C

NITRIDED BETWEEN 1200 - 1350 °C IN N₂/H₂ MIXTURE FOR 30-75 hr

COMPOSITE PANEL
CROSS SECTION OF 39 VOL% SiC/RBSN COMPOSITE

INTERFACIAL REGION IN SiC/RBSN COMPOSITE

SCS-0 FIBER

SCS-6 (DOUBLE COATED) FIBER
### DENSITY AND POROSITY DATA FOR SiC/RBSN COMPOSITES

<table>
<thead>
<tr>
<th>VOLUME FRACTION OF FIBERS</th>
<th>BEFORE NITRIDATION</th>
<th>AFTER NITRIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DENSITY gm/cc</td>
<td>MATRIX POROSITY, %</td>
</tr>
<tr>
<td>0</td>
<td>1.56</td>
<td>35</td>
</tr>
<tr>
<td>23 ± 3</td>
<td>1.70</td>
<td>54</td>
</tr>
<tr>
<td>40 ± 2</td>
<td>1.90</td>
<td>51</td>
</tr>
</tbody>
</table>

---

**THE LOAD-DISPLACEMENT BEHAVIOR FOR 20 vol % SiC/RBSN COMPOSITE IN 3-POINT BENDING**

![Graph showing load-displacement behavior](image-url)
THE AXIAL STRESS-STRAIN BEHAVIOR FOR 20 vol % SiC/RBSN COMPOSITE

AXIAL STRESS, $\sigma$ MPa

AXIAL STRAIN, %

FIRST MATRIX CRACKING

NON-LINEAR RANGE

LINEAR RANGE

FRACTURED TENSILE SPECIMEN OF SiC/RBSN COMPOSITE
### Room Temperature Strengths of SiC/RBSN Composite

<table>
<thead>
<tr>
<th>Test</th>
<th>Axial Strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% Fiber</td>
</tr>
<tr>
<td>4 Point Bend ( \frac{L}{h} = 15 )^a</td>
<td>107 ± 26</td>
</tr>
<tr>
<td>4 Point Bend ( \frac{L}{h} = 45 )</td>
<td>−−−−−</td>
</tr>
<tr>
<td>3 Point Bend ( \frac{L}{h} = 35 )</td>
<td>−−−−−</td>
</tr>
<tr>
<td>Tensile(^b)</td>
<td>−−−−−</td>
</tr>
</tbody>
</table>

\(^a\) Test specimen height ≈ 1.25 mm

\(^b\) Test gauge length 50 mm

### SiC/RBSN Fracture Parameters

<table>
<thead>
<tr>
<th>Fiber Fraction, %</th>
<th>Matrix Crack Spacing, mm</th>
<th>Interfacial Shear Stress(^a), MPa</th>
<th>Composite Stress at Which Matrix First Cracked, MPa</th>
<th>Matrix Fracture Strain(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 ± 3</td>
<td>2.0 ± 0.3</td>
<td>10.91(^1)</td>
<td>237 ± 25</td>
<td>0.0015</td>
</tr>
<tr>
<td>40 ± 2</td>
<td>0.9 ± 0.2</td>
<td>10.23</td>
<td>293 ± 15</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from ACK theory

\(^b\) Calculated from estimated composite modulus
FRACTURE SURFACE OF SiC/RBSN IN TRANSVERSE FLEXURE

SiC FIBERS STRENGTHEN AND TOUGHEN REACTION-BONDED Si$_3$N$_4$

---

Silicon Slurry → SiC Preform → Hot Press → Nitride → SiC/RBSN Composite

Ultimate Strength | Matrix Cracking Strength | Composite, 40% Fiber

Bend Stress, MPa

Typical Monolithic RBSN | Unreinforced RBSN Matrix | Composite, 23% Fiber

Density, gm/cc

---

Microstructure

---

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THERMAL STABILITY DATA FOR SiC/RBSN AND SiC/SiC COMPOSITES

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>ROOM TEMPERATURE AXIAL ULTIMATE STRENGTH, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 vol % SiC/RBSN</td>
</tr>
<tr>
<td>AS-FABRICATED 1200 °C, 100 hr, AIR</td>
<td>350\textsuperscript{a}</td>
</tr>
<tr>
<td>1400 °C, 100 hr, AIR</td>
<td>316\textsuperscript{a}</td>
</tr>
<tr>
<td></td>
<td>323\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} TENSILE STRENGTH.
\textsuperscript{b} 4-POINT BEND STRENGTH. (NO TENSILE DATA REPORTED. TENSILE STRENGTHS WOULD BE MUCH LOWER THAN 4-POINT BEND STRENGTH.)

ELEVATED TEMPERATURE STRENGTH (4-POINT BEND) FOR SiC/RBSN COMPOSITE, MONOLITHIC SILICON-BASED CERAMICS, AND SEP SiC/SiC COMPOSITE

![Graph showing 4-point bend strength at different conditions and materials]
SUMMARY OF RESULTS

- A STRONG AND TOUGH CERAMIC MATRIX COMPOSITE CAN BE FABRICATED BY REINFORCING RBSN BY HIGH MODULUS, HIGH STRENGTH CONTINUOUS LENGTH CVD SiC FIBER

- REINFORCEMENT OF RBSN BY CVD SiC FIBERS ALSO MEASURABLY INCREASES COMPOSITE MODULUS AND THE COMPOSITE STRESS AT WHICH MATRIX CRACKS

- WEAK FIBER-MATRIX BONDING ALLOWS MULTIPLE CRACKING AND GRACEFUL FAILURE

- COMPOSITE IS THERMALLY STABLE AND HAS BETTER ELEVATED TEMPERATURE STRENGTH THAN MANY COMMERCIALLY AVAILABLE MONOLITHIC CERAMICS

- FURTHER IMPROVEMENTS IN COMPOSITE PROPERTIES ARE POSSIBLE WITH
  - INCREASE IN MATRIX STRENGTH (DECREASE IN POROSITY)
  - SMALL DIAMETER FIBERS
  - FIBER COATING

CURRENT AND FUTURE STUDIES

CURRENT:
- OPTIMIZATION OF PROCESSING VARIABLES
- POST FABRICATION TREATMENTS
- LAMINATE PROPERTIES (0°/90°, 0°/90°/45°)
- INTERFACIAL REACTION KINETICS

FUTURE:
- MEASUREMENT OF ELEVATED TEMPERATURE TENSILE STRENGTH AND STRESS RUPTURE DATA
- THERMAL PROPERTIES
- OXIDATION
This publication is a compilation of abstracts and slides of papers presented at the NASA Lewis Structural Ceramics Workshop held at the Sheraton Hopkins Hotel, Cleveland, Ohio, on May 20 and 21, 1986. Collectively, these papers depict the scope of NASA Lewis' structural ceramics program. Each paper provides a brief overview of a technical area in which NASA Lewis Research Center has a significant research focus. The technical areas include monolithic SiC and Si$_3$N$_4$ development, ceramic matrix composites, tribology, design methodology, nondestructive evaluation (NDE), fracture mechanics, and corrosion.