ORNL/TM-13219

**OAK RIDGE
NATIONAL
LABORATORY**

**Propulsion System Materials
Program Semiannual Progress
Report for April 1995 Through
September 1995**

Prepared for
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Office of Transportation Technologies

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

UCRL-13219 (26 6-95)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Metals and Ceramics Division

**PROPULSION SYSTEM MATERIALS PROGRAM
SEMIANNUAL PROGRESS REPORT FOR
APRIL 1995 THROUGH SEPTEMBER 1995**

**D. R. Johnson
Program Manager**

Date Published: April 1996

NOTICE:

**This document contains information
of a preliminary nature. It is subject to revision
or correction and therefore does not represent
a final report.**

**Prepared for
U.S. Department of Energy
Assistant Secretary for Energy Efficiency and Renewable Energy
Office of Transportation Technologies
EE 51 05 00 0**

**Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under Contract DE-AC05-96OR22464**

REPORTS PREVIOUSLY ISSUED

ORNL/TM-9325	Period March 1983-September 1983
ORNL/TM-9466	Period October 1983-March 1984
ORNL/TM-9497	Period April 1984-September 1984
ORNL/TM-9673	Period October 1984-March 1985
ORNL/IM-9947	Period April 1985-September 1985
ORNL/TM-10079	Period October 1985-March 1986
ORNL/TM-10308	Period April 1986-September 1986
ORNL/TM-10469	Period October 1986-March 1987
ORNL/TM-10705	Period April 1987-September 1987
ORNL/TM-10838	Period October 1987-March 1988
ORNL/TM-11116	Period April 1988-September 1988
ORNL/TM-11239	Period October 1988-March 1989
ORNL/TM-11489	Period April 1989-September 1989
ORNL/TM-11586	Period October 1989-March 1990
ORNL/TM-11719	Period April 1990-September 1990
ORNL/TM-11859	Period October 1990-March 1991
ORNL/TM-11984	Period April 1991-September 1991
ORNL/TM-12133	Period October 1991-March 1992
ORNL/TM-12363	Period April 1992-September 1992
ORNL/TM-12428	Period October 1992-March 1993
ORNL/TM-12674	Period April 1993-September 1993
ORNL/TM-12778	Period October 1993-March 1994
ORNL/TM-12924	Period April 1994-September 1994
ORNL/TM-13046	Period October 1994-March 1995

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Propulsion System Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

SUMMARY	1
0.0 PROGRAM MANAGEMENT AND COORDINATION	3
1.0 MATERIALS AND PROCESSING	5
INTRODUCTION	5
1.1 MONOLITHICS.....	7
1.1.2 Silicon Nitride	7
<i>Characterization of Attrition Milled Silicon Nitride Powder (NIST)</i>	7
<i>Microwave Sintering of Silicon Nitride (ORNL)</i>	10
<i>Development of a Low Cost Silicon Nitride Powder (The Dow Chemical Company)</i>	28
<i>Cost Effective Sintering of Silicon Nitride Ceramics (SIU-C)</i>	40
1.1.4 Processing of Monolithics	48
<i>Improved Processing (ORNL)</i>	48
1.2 CERAMIC COMPOSITES	54
1.2.2 Silicon Nitride Matrix	54
<i>Optimization of Mechanical Properties of Silicon Nitride Ceramics (University of Michigan)</i>	54
<i>Microstructure Optimization of SRBSN (University of Michigan)</i>	57
<i>Characterization of Grain Boundary Phases in Silicon Nitride Ceramics (University of Michigan)</i>	63
<i>Microstructure Design of Si₃N₄ (University of Michigan)</i>	66

	<i>Development of Silicon Nitride Ceramic Materials with Elongated Grain Microstructures Exhibiting High Fracture Toughness Phase II (AlliedSignal Inc.)</i>	69
1.2.3	Oxide Matrix	74
	<i>Dispersion-Toughened Ceramic Composite (ORNL)</i>	74
1.2.4	Low Expansion Materials	87
	<i>Characterization and Testing of Low-Expansion Ceramic Materials (ORNL)</i>	87
	<i>Development of NZP Ceramic-Based "Cast-In-Place" Diesel Engine Port Liners (LoTEC, Inc.)</i>	92
1.3	THERMAL AND WEAR COATINGS	111
	<i>Fabrication and Testing of Corrosion-Resistant Coatings (ORNL)</i>	111
	<i>Development of Adherent Coatings to Reduce Contact Stress Damage of Ceramics (Boston University)</i>	120
1.4	JOINING	126
1.4.1	Ceramic-Metal Joints	126
	<i>Joining of Ceramics for Heat Engine Applications (ORNL)</i>	126
1.5	CERAMIC MACHINING	129
	<i>Cost-Effective Ceramic Machining (ORNL)</i>	129
	<i>Cost-Effective Method for Determining the Grindability of Ceramics (Chand Kare Technical Ceramics, Inc.)</i>	134
	<i>High-Speed, Low-Damage Grinding of Advanced Ceramics (Eaton Manufacturing Technologies Center)</i>	146

<i>Grinding Optimization for Advanced Ceramics</i> (NIST)	162
<i>Chemically Assisted Machining of Ceramics</i> (NIST)	175
<i>Laser Scatter Methods for Detection of</i> <i>Subsurface Machining Damage in Ceramics</i> (Argonne National Laboratory)	188
1.5.2 Advanced Ceramic Manufacturing Technology	199
<i>Advanced Manufacturing Technology for</i> <i>Ceramic Heavy Duty Diesel Turborotors</i> (Kyocera Industrial Ceramics Corp.)	199
<i>Development of Advanced Ceramic Manufacturing</i> <i>Technology</i> (Norton)	207
2.0 MATERIALS DESIGN METHODOLOGY	219
INTRODUCTION	219
2.2 CONTACT INTERFACES	221
2.2.2 Dynamic Interfaces	221
Development of Standard Test Methods for Evaluating the Wear Performance of Ceramics (ORNL)	221
3.0 DATA BASE AND LIFE PREDICTION	223
INTRODUCTION	223
3.1 STRUCTURAL QUALIFICATION	225
<i>Microstructural Analysis of Structural</i> <i>Ceramics</i> (NIST)	225
<i>Mechanical Properties and Microstructural</i> <i>Characterization of Si₃N₄ Ceramics</i> (ORNL)	234
<i>Project Data Base</i> (ORNL)	237

3.2	TIME-DEPENDENT BEHAVIOR	242
	<i>Fracture Behavior of Toughened Ceramics</i> (ORNL)	242
	<i>Cyclic Fatigue of Toughened Ceramics</i> (ORNL)	247
	<i>Life Prediction Verification</i> (ORNL)	272
	<i>Toughened Ceramics Life Prediction</i> (NASA Lewis Research Center)	292
	<i>Life Prediction Methodology</i> (AlliedSignal Engines)	304
3.3	ENVIRONMENTAL EFFECTS	344
	<i>Environmental Effects in Toughened Ceramics</i> (University of Dayton)	344
3.4	FRACTURE MECHANICS	356
	<i>Testing and Evaluation of Advanced Ceramics</i> <i>at High Temperature in Uniaxial Tension</i> (North Carolina A&T State University)	356
	<i>Standard Tensile Test Development</i> (NIST)	364
3.5	NONDESTRUCTIVE EVALUATION DEVELOPMENT	371
	<i>Nondestructive Characterization</i> (ORNL)	371
	<i>NDE Standards for Advanced Ceramics</i> (ORNL)	381
	<i>X-ray Computed Tomographic Imaging</i> (ANL)	383
	<i>Nuclear Magnetic Resonance Imaging</i> (ANL)	400
4.0	TECHNOLOGY TRANSFER	403
4.1	TECHNOLOGY TRANSFER	403
4.1.1	Technology Transfer	403
	<i>Technology Transfer</i> (ORNL)	403

<i>IEA ANNEX II Management (ORNL)</i>	404
<i>Characterization of Ceramic Powders (NIST)</i>	410
<i>Ceramic Mechanical Property Test Method Development (NIST)</i>	413

PROPULSION SYSTEM MATERIALS PROGRAM
SEMIANNUAL PROGRESS REPORT
FOR APRIL 1995 THROUGH SEPTEMBER 1995

SUMMARY

The Propulsion System Materials Program was originally developed by the Department of Energy's Office of Transportation Systems (OTS) in Energy Efficiency and Renewable Energy. This program, part of the OTS's Materials Development Program, was developed to meet the ceramic technology requirements of the OTS's automotive technology programs.

Significant accomplishments in fabricating ceramic components for the Department of Energy (DOE), National Aeronautics and Space Administration (NASA), and Department of Defense (DoD) advanced heat engine programs have provided evidence that the operation of ceramic parts in high-temperature engine environments is feasible. However, these programs have also demonstrated that additional research is needed in materials and processing development, design methodology, and data base and life prediction before industry will have a sufficient technology base from which to produce reliable cost-effective ceramic engine components commercially.

An assessment of needs was completed, and a five-year program plan was developed with extensive input from private industry. In July 1990, the original plan was updated through the estimated completion of development in 1993. The original objective of the program was to develop the industrial technology base required for reliable ceramics for application in advanced automotive heat engines.

During the course of the Propulsion System Materials Program, remarkable progress has been made in the development of reliable structural ceramics. However, further work is needed to reduce the cost of ceramics to facilitate their commercial introduction, especially in the highly cost-sensitive automotive market. To this end, the direction of the Propulsion System Materials Program is now shifting toward reducing the cost of ceramics to facilitate commercial introduction of ceramic components for near-term engine applications. In response to extensive input from industry, the plan is to extend the engine types which were previously supported (advanced gas turbine and low-heat-rejection diesel engines) to include near-term (5-10 years) applications in conventional automobile and diesel truck engines. To facilitate the rapid transfer of this technology to U.S. industry, the major portion of the work is being done in the ceramic industry, with technological support from government laboratories, other industrial laboratories, and universities.

A systematic approach to reducing the cost of components is envisioned. The work elements are as follows: economic cost modeling, ceramic machining, powder synthesis, alternative forming and densification processes, yield improvement, system design studies, standards development, low-expansion ceramics, and testing and data base development.

This program is managed by ORNL for the Office of Transportation Technologies and is closely coordinated with complementary ceramics tasks funded by other DOE offices, NASA, DoD, and industry. A joint DOE and NASA technical plan has been established, with DOE focus on automotive applications and NASA focus on aerospace applications. A common work breakdown structure (WBS) was developed to facilitate coordination. The work described in this report is organized according to the following WBS project elements:

0.0 Program Management and Coordination

1.0 Materials and Processing

- 1.1 Monolithics
- 1.2 Ceramic Composites
- 1.3 Thermal and Wear Coatings
- 1.4 Joining
- 1.5 Ceramic Machining

2.0 Materials Design Methodology

- 2.1 Modeling
- 2.2 Contact Interfaces
- 2.3 New Concepts

3.0 Data Base and Life Prediction

- 3.1 Structural Qualification
- 3.2 Time-Dependent Behavior
- 3.3 Environmental Effects
- 3.4 Fracture Mechanics
- 3.5 Nondestructive Evaluation Development

4.0 Technology Transfer

4.1 Technology Transfer

This report includes contributions from all currently active program participants. The contributions are arranged according to the work breakdown structure outline.

0.0 PROGRAM MANAGEMENT AND COORDINATION

D. R. Johnson
Oak Ridge National Laboratory

Objective/scope

This task includes the technical management of the program in accordance with the program plans and management plan approved by the Department of Energy (DOE) Oak Ridge Operations Office, and the Office of Transportation Technologies. This task includes preparation of annual field work proposals, initiation and management of subcontracts and interagency agreements, and management of ORNL technical tasks. Monthly management reports and bimonthly reports are provided to DOE; highlights and semiannual technical reports are provided to DOE and program participants. In addition, the program is coordinated with interfacing programs sponsored by other DOE offices and federal agencies, including the National Aeronautics and Space Administration (NASA) and the Department of Defense (DoD). This coordination is accomplished by participation in DOE and NASA joint management meetings, annual interagency heat engine ceramics coordination meetings, DOE contractor coordination meetings, and DOE Energy Materials Coordinating Committee (EMaCC) meetings, as well as special coordination meetings.

1.0 MATERIALS AND PROCESSING

INTRODUCTION

This portion of the program is identified as program element 1.0 within the work breakdown structure (WBS). It contains five subelements: (1) Monolithics, (2) Ceramic Composites, (3) Thermal and Wear Coatings, (4) Joining, and (5) Ceramic Machining. Ceramic research conducted within the Monolithics subelement currently includes work activities on low cost Si_3N_4 powder, green state ceramic fabrication, characterization, and densification, and on structural, mechanical, and physical properties of these ceramics. Research conducted within the Ceramic Composites subelement currently includes silicon nitride and oxide-based composites, and low expansion materials. Research conducted in the Thermal and Wear Coatings subelement is currently limited to oxide-based coatings and involves coating synthesis, characterization, and determination of the mechanical and physical properties of the coatings. Research conducted in the Joining subelement currently includes studies of processes to produce strong, stable joints between zirconia ceramics and iron-base alloys. As part of an expanded effort to reduce the cost of ceramic components, a new initiative in cost effective machining has been started.

A major objective of the research in the Materials and Processing program element is to systematically advance the understanding of the relationships between ceramic raw materials such as powders and reactant gases, the processing variables involved in producing the ceramic materials, and the resultant microstructures and physical and mechanical properties of the ceramic materials. Success in meeting this objective will provide U.S. companies with new or improved ways for producing economical, highly reliable ceramic components for advanced heat engines.

1.1 MONOLITHICS

1.1.2 Silicon Nitride

Characterization of Attrition Milled Silicon Nitride Powder

S. G. Malghan, P. T. Pei and D. B. Minor

(National Institute of Standards and Technology)

Objective/Scope

Currently, the starting materials in the manufacture of silicon nitride ceramic components are fine powders. These fine sized powders tend to form agglomerates due to the Van der Waals attractive forces. For improved reliability in the manufacture of ceramic components, the agglomerates in the powders should be eliminated since they form defects. In addition, the powders should have an appropriate range of size distribution and specific surface area for achieving a near-theoretical density of the ceramic after densification. These factors necessitate the use of powder milling as one of the major powder processing unit operations. Therefore, milling of powders is an integral unit operation in the manufacture of silicon nitride components for advanced energy applications. The production and use of these powders require the use of efficient milling techniques and understanding of characteristics of the milled powders in a given environment. High energy attrition milling appears to offer significant advantages over conventional tumbling and vibratory mills.

The major objectives of this project are: 1. establish repeatability of particle size distribution and other relevant characteristics of slurries milled in a high energy agitation mill (HEAM); 2. determine processing and densification characteristics of powders milled in HEAM; and 3. compare properties of powder, and resulting ceramic obtained by milling in the HEAM vs. vibratory ball mill in a collaborative project with Norton Company.

Technical Progress

The primary activity during this period was completion of repair of the milling system, and conduct a milling tests on Dow's silicon nitride powder.

We milled the silicon nitride powder from Dow Chemical Company with a goal to establish the behavior of this powder in the high energy agitation ball mill (HEAM). It appears that the mill had developed a leak in the mechanical seal system during the last test. However, we were unaware of the leak. It became clear during the samples analysis time that the slurry was diluted by leakage of water from the mechanical seal of the cooling system. As a result, not only the slurry density but also its particle size distribution was affected. Therefore, we decided to discard the data of the first test.

In the next test, dispersion and milling parameters were kept at the same level as for the Ube powder. Electroacoustic data has shown that the pH_{zpc} of this powder is in the range of pH 2 to 3, and it was not significantly affected by the presence of Daxad-32, polymethacrylate, as a dispersant. Concentration of Daxad-32 was maintained at 650 ppm based on the total weight of powder. The initial solids concentration, before beginning of the milling test was 62% by weight and increased to

76% when the milling was terminated at 80 min. Yttria (4% by weight) was added between the 20th and 32nd min of milling time. The mill was operated at 2800 rpm and the slurry flow rate was maintained at 250 cm³/min. The resulting samples were analyzed for particle size distribution and specific surface area by laser light scattering and BET gas adsorption, respectively. Overall, the data showed that the final particle size distribution was too small, resulting in the final specific surface area of 19.5 m²/g.

The particle size distribution and specific surface area data showed the following:

- * Bimodal size distribution of the initial powder gradually became monomodal.
- * Most of the size reduction took place in the first 20 min during which period the coarsest particles in the 2 micrometers range were size reduced. This type of size reduction behavior has been observed with other powders.
- * Excessive quantity of very small size daughter fragments, finer than 0.5 micrometer, produced by the size reduction of coarse particles appears to be the reason for larger than desired surface area of the 80 min milled powder.
- * The rate of increase of the surface area was linear with the milling time.

The major difference between the two powders--Ube and Dow--is their behavior in water. The Ube powder exhibited a significant shift in the pH_{zpc}. In addition, the concentration of Daxad had no effect on the level of dispersion. These data lead us to conclude that the adsorption of Daxad on this silicon nitride powder was negligible. Therefore, another dispersant containing an ammonium alcohol was experimented. The adsorption data on ube powder of this dispersant showed that though a small amount was adsorbed, the pH of the slurry was in excess of 10.8. The probable reason for this dispersant's effectiveness was the enhanced electrostatic interactions between the particles at high pH.

For some powders, we have observed improved dispersion when using the ammonium alcohol-based dispersant. In this test, we observed no significant differences during milling, except a strong odor of ammonia in the initial period. The ammonia odor is expected because at pH greater than 10.0, the solubility of ammonia in silicon nitride slurries is severely limited. Therefore, the combination of ammonia from silicon nitride slurries and that from the dispersant is the cause of this increased odor of ammonia. The milling kinetics data and the resulting solids loading in the final slurry showed very little differences from those using ammonium methacrylate as a dispersant. One significant difference was in the final green body density and strength. Both were comparatively low, though the starting density of the slurry had 75% weight solids. Additional tests are planned to provide improved dispersion and resultant improvements in green density.

Status of Milestones

On schedule

Communications/Visits

Dr. Naito, JFCC, Japan, visited NIST to discuss IEA Subtask 8 data.

Publications

1. Reports on Data Compilation and Data Comments to Subtask 8 Technical Leaders, September 1995.

W.B.S. ELEMENT 1.1.2.4
 MICROWAVE SINTERING OF SILICON NITRIDE
 J. O. Kiggans, T. N. Tiegs, C. C. Davisson, J. M. Snodgrass, and D. L. Barker
 Oak Ridge National Laboratory
 Oak Ridge, TN 37831
 Stan Morrow and Stan Forrester
 Y-12 Development Division
 Oak Ridge, TN 37831

Objective/Scope

The objective of this research element is to identify those aspects of microwave processing of silicon nitride that might (1) accelerate densification, (2) permit sintering to high density with much lower levels of sintering aids, (3) lower the sintering temperature, or (4) produce unique microstructures. The investigation of microstructure development is being performed on dense silicon nitride materials annealed in the microwave furnace. The sintering of silicon nitride involves two approaches. The first approach comprises heating of silicon nitride and sialon powder compositions in the 2.45- or 28-GHz units. The second approach uses reaction-bonded silicon nitride as the starting material and is done entirely in the 2.45-GHz microwave furnace.

Technical Highlights

Golden Technologies CRADA

This work is being performed as part of a CRADA arrangement with Golden Technologies. The objective of this CRADA is to investigate the use of microwave heating for the nitridation of silicon clevis pin preforms fabricated by Golden Technologies, Inc. More specifically, a larger goal has been established of demonstrating the microwave nitridation of 100 to 200 parts. Several activities have been undertaken during this time period to achieve this goal: TGA analysis of clevis pin preforms were performed to determine their nitridation behavior in nitrogen; weight gain experiments involving silicon preforms were done in a graphite furnace to determine their nitridation behavior in $N_2 - 4 \text{ vol. } \% H_2$; microwave nitridation trials were performed; and x-ray diffraction analysis was performed on clevis pin RBSN processed by microwave and conventional heating.

The TGA study of clevis pin samples was undertaken in order to establish the temperature versus weight gain relationship for nitridation. The TGA study was performed using a TA Instruments SDT 2960 Simultaneous DTA-TGA. Data was collected for clevis pin and for comparison, bucket tappet and TM-145 silicon preforms. Flowing nitrogen was used for nitridation, since $N_2 - 4 \text{ vol. } \% H_2$, the preferred gas, could not be used with the Type "S" thermocouples (reaction problem). Fig. 1 is a graph showing the measured conversion of silicon to silicon nitride, as a function of temperature. The data in this graph is interpreted by drawing a vertical line between the data point on the percent conversion curve to the corresponding temperature (dotted line). The data indicate that the clevis pin material started nitriding at between 1000 to 1100°C and nitridation was complete at approximately 1400°C. The TM-145 sample and bucket tappet sample did not show significant nitridation until around 1250°C and were nitrided to approximately 95 % completion at 1450°C. The large difference in the nitridation behavior of the clevis pin and the other two sample types was due to the higher iron content of the clevis pin samples and possibly other compositional differences. The effect of various chemicals on silicon nitridation has been cited in the literature.

A series of nitridation runs were performed in a graphite furnace, in order to obtain the percent silicon conversion for the clevis pin and other comparison samples in N_2 - 4 vol. % H_2 . The nitridation setup has been described in previous bimonthly reports. Fig. 2 shows that the percent conversion as a function of temperature for the clevis pin, TM-145, and bucket tappet samples. The nitridation of the clevis pins in N_2 - 4 vol. % H_2 was approximately 40 % complete at 1200°C and was 95% complete by 1275°C. The nitridation of the TM-145 and bucket tappet samples was just starting at 1200°C, and was near completion at 1400°C. The absence of data points for the temperatures below 1200°C makes a comparison with TGA data at the start of the nitridation difficult, however this data does indicate that the addition of H_2 appeared to lower the temperature at which conversion was complete for all samples. The effect of H_2 additions on nitridation has been cited in the literature.

X-ray diffraction analysis was performed on selected samples to compare the α -silicon nitride content of materials produced by conventional and microwave heating. Table 1 is a compilation of the data. High α -silicon nitride values were obtained for clevis pin samples which were nitrided by microwave heating to a final temperature of 1300°C in nitrogen and in N_2 - 4 vol. % H_2 . The slightly higher α -silicon nitride content obtained for the sample processed in hydrogen was expected, based on previous work on the effect of H_2 on nitridation. A comparable α -silicon nitride content was obtained from a clevis pin preform processed to 1350°C in a graphite furnace in N_2 - 4 vol. % H_2 . This appears to support belief that conventional and microwave processing follow the same nitridation routes. Clevis pin samples processed in a graphite furnace to 1450°C in N_2 and in N_2 - 4 vol. % H_2 showed much lower α -silicon nitride contents, since the α silicon nitride is converted to β -silicon nitride as the sintering aids are converted to liquid phase at a temperature between 1350 and 1450°C.

In the previous semiannual period, several microwave insulation packaging setups were tested for the nitridation of clevis pins provided by Golden Technologies. The most promising setup for microwave processing of the clevis pins was a Si_3N_4 -SiC crucible surrounded by a 2.5 cm thick rigid alumina fiberboard box. Two groups of 36 clevis pins were successfully nitrided using very fast heating cycles (<10 h) in this insulation arrangement. During the present semiannual period several experiments were done to test several factors concerning microwave nitridation of clevis pin preforms: effect of sample number; the effect of sample spacing, touching versus spaced; the effect of alternative crucible construction; and the effect of lower H_2 content in the nitriding gas.

A summary of the results from various test runs made during this reporting period are presented in Table 2. Test 1 was a scaleup run to 100 test parts using the same insulation arrangement which had shown success in previous tests with 36 samples. In test 1 some sample melting occurred. Fig. 3 shows the temperature profile of test 1 including the thermal runaway which occurred. The same experiment was repeated, test 2, with the same results. The reason for the uneven processing in tests 1 and 2 is believed due to the much larger amount of heat released for 100 versus 36 samples. An alternative insulation setup, to the one used for test 1 and 2, was then built (Fig. 4) as a possible solution to the problem. This crucible arrangement consisted of Si_3N_4 -SiC side panels for the side walls of the crucible and microwave-transparent hot-pressed BN setter plates for the top and bottom of the inner crucible. The BN top and bottom were added to absorb the excess heat released during nitridation. Tests 3 and 4 were performed to test this new crucible. Results of these tests in Table 2 show that both the exterior samples (samples 1-20, Fig. 4) and the interior samples (samples 21-36, Fig. 4) showed comparable nitridation. There was very minor distortion in a few of the exterior samples due to the fact that the crucible wall was cooler than the interior samples. Also, there was a problem with poor temperature control by the "Micristar" controller. Test 5 was performed to test the effect of

reducing the amount of hydrogen on nitridation cycle. Good weight gain results were obtained in this test, indicating that lower amounts of hydrogen can be used, however the temperature oscillation still persisted. Test 6 was performed to test the effect of lowering the peak nitridation temperature to 1200°C, to avoid the controller problem. A lower average weight gain and a larger statistical deviation of weight gain values was obtained when the 1200 °C endpoint was used. It appears that a peak temperature above 1200 °C is necessary for complete nitridation of all samples. It is possible that a longer hold at 1200°C might dampen the sudden nitridation that occurs above 1200°C. Figure 5 is a plot of the temperature profile for test 6, which shows that the temperature of the exterior samples (1-20), as measured by a two-color pyrometer, initially lagged the temperature of the interior samples (21-36), as measured by a thermocouple, by up to 100 °C at 1100 °C and then moved closer as the temperature rose to 1200 °C. As with conventional nitrogen studies have shown, a peak temperature of 1300 °C is necessary for complete nitridation of all samples to occur. Test 7 was a scale-up to 100 clevis pins using microwave heating in a larger Si₃N₄-SiC-BN crucible, with the sample, edge to edge spacing at 0.5 cm, as was used in tests 3 and 4. Very good weight values and statistical deviation were obtained in this test, however as in previous tests, there was a problem with power control and also a slight warping of a few exterior samples. A photo of the RBSN clevis pins produced in this run is shown in Fig. 6. Test 8 was performed to see if increasing the packing density of samples (samples touching) would lead to better temperature control. Table 2 shows that a much better statistical deviation was obtained for this tight pack arrangement, but unfortunately there was partial sintering of some interior samples, as well as the problems with temperature control.

The results from the 8 tests have been used to determine the proper composition of sample crucibles, the proper spacing of samples, and the proper nitriding gas for microwave nitridation. Crucible containing 60 wt % and 80 wt % SiC have been prepared for future nitridation tests. Gas containing at least 1 vol. % H₂ will be used, and sample spacing will be held at least 0.7 cm. The problem of inadequate microwave power control, which was experienced in some runs, will be addressed through the use of a state-of-the-art "Yokagawa" PID controller.

Scaleup Microwave Nitridation - Sintering Studies

Four microwave nitridation and sintering scaleup experiments were completed during the reporting period, two in the 500 liter ORNL microwave furnace, and two in the Y-12 furnace. These experiments included several sub-tasks: the fabrication of new crucible materials; the preparation of large numbers of silicon preforms; completion of the nitridation and sintering runs; and the characterization of the final SRBSN products.

Three groups of samples were used for the scaleup trials at ORNL and Y-12: gelcast TM-150 silicon preforms (same composition as TM-141), gelcast TM-145 preforms, and bucket tappet samples. The methods for gelcasting silicon preforms using the isopropanol solvent system have been discussed in the previous semiannual report, 1995. The compositions of the gelcast preforms are noted in Table 3. Milled TM-145 powder was gelcast in a 25 cm by 10 cm by 1.25 cm aluminum mold (Fig. 7). Milled TM-150 powder was cast in plastic culture dishes, which were 3 cm in diameter. The gelcast silicon preforms were then isopressed at 138 MPa pressure, heated in air to 550 °C for binder removal. The TM-145 gelcast slabs were then cut into 1.25 cm by 1.25 cm by 3.3 cm rectangular samples. Approximately 375 gelcast samples, having a density of 1.60 g/cm³, were produced for the scaleup experiments. Bucket tappets were purchased from the Cremer Forschungsinstitut of Germany and were used as received.

Two microwave scaleup experiments involving the nitridation and sintering of silicon preforms were performed in the 500 liter ORNL furnace. In experiment 1, 72 TM-150 gelcast silicon preforms, 3 cm diameter by 1 cm thick, were processed in a microwave insulation setup similar to ones described in previous reports (Aug.-Sept., 1994). In experiment 2, 108, TM-145 silicon preforms, 3 cm tall by 1.25 cm thick by 1.25 cm width, were processed using a microwave package described in the June - July, 1995 bimonthly (double fiberboard box). Both crucibles utilized hot-pressed BN setter plates and a 17 cm by 17 cm by 17 cm, inner crucible composed of sintered plates of the composition, Si_3N_4 - 4.2 wt % - Y_2O_3 - 0.8 wt % SiO_2 . The final sintering condition for both runs was 1775°C for 2 h. Two additional microwave scaleup experiments involving the nitridation and sintering of silicon preforms were performed in the 4000 L, Y-12 microwave furnace. A hybrid-heating crucible was used for these nitridation and sintering trials. The top and bottom of the crucible was constructed of gelcast sintered plates of the composition, Si_3N_4 - 4.2 wt % - Y_2O_3 - 0.8 wt % SiO_2 , the side walls of the crucible were composed of sintered plates of the composition Si_3N_4 - 4.2 wt % Y_2O_3 - 0.8 wt % SiO_2 - 5 wt % SiC , and 25 cm wide by 30 cm long by 0.7 cm thick, BN setter plates were utilized. The overall interior dimensions of the sample crucible were 25 cm by 31 cm by 18 cm. Insulation of the samples and crucible were accomplished via the standard Si_3N_4 - BN powder bed and and fiberboard box setup. A new fiber board product, Rath type KVS144 (rated to 1400°C) was used for the construction of the outer box. In the first experiment, experiment 3, 90 silicon bucket tappets were processed. In the second experiment, experiment 4, 230 rectangular gelcast silicon bars were processed. Fig. 8 shows the silicon preforms as placed in each of the three sample layers in experiments 3 and 4. The final sintering condition for both runs was 1765°C for 2 h. A slightly lower sintering temperature was chosen (normally 1800°C) because of the uncertainty of the temperature measurement in the large package. Densities for all samples in these two scaleup runs were determined using the alcohol immersion density technique. Three sintered samples were removed from each of the three layers of the samples in experiment 2. These samples were sliced into three equal parts, which were ground and polished. The polished samples were tested for hardness and indent toughness.

A summary of the average densities and statistical deviations for the 4 experiments are shown in Table 3, along with data from nitridation and sintering runs done in previous studies. An examination of the samples from experiments 1 and 2 indicated that the microwave heating uniformity appeared to be quite good, however the data in Table 3 indicates that the standard deviations were higher than scaleup experiments involving fewer samples. Since no large scale conventional experiments could be performed (lack of available samples) it is difficult to make statements as to whether microwave heating is more or less uniform than conventional heating. However, in the experiments where similar numbers of samples were processed, the standard deviations between the microwave and conventional heated materials were similar. Table 4 gives an additional breakdown of the densities of three sample layers of experiment 2, as well as the hardness and toughness values. These data show that there was good uniformity in the densities, hardness values, and toughness values for samples in all three layers of samples in experiment 2. Analysis of the data for experiments 3 and 4 performed at the larger microwave furnace at Y-12 shows that the statistical deviations of the 90 sample bucket tappet (experiment 3) and 230 sample gelcast pieces (experiment 4) were very comparable to the 72 sample run made at ORNL. It is possible that if the samples had been processed at 1800°C, higher densities and a lower standard deviation might have been achieved. There was slight warping in few of the thin bucket tappet samples of experiment 3, which were located along the outer periphery of the sample crucible. The warping of some buckets was probably due to a slightly lower temperature along the inner edge of the crucible. There was no sample warping of samples in the second Y-12 experiment. It was interesting to note that although the sample crucible used in experiments 3 and 4 was about

2 times that of the largest experiments performed at ORNL, the peak power used was similar, approximately 6 kW. Fig. 9 shows the microwave power - temperature curves for experiment 4. The low power use in the Y-12 experiment was due to the higher efficiency of microwave absorption at higher loads, and due to the thicker exterior fiberboard casket. The final run of 230 silicon parts met the milestone of 200 parts to be processed at the Y-12 facility. Fig. 10 and 11 are photos of the groups of SRBSN parts fabricated in experiments 3 and 4, respectively.

Semi-annual summary statements

Several statements are in order to summarize what has been learned to date from the Golden CRADA on the scaleup of the nitridation of silicon preforms and from the Ceramic Technology Milestone 112408 involving the scaleup of the nitridation and sintering of silicon preforms using microwave heating: Microwave heating shows promise for scaleup. Both silicon and RBSN do not suffer from "dielectric runaway," which plagues other ceramic-microwave systems. Microwave heating is attractive because it is one of the few ways to sinter SRBSN in a non-carbon environment. Microwave nitridation is a more attractive process than microwave sintering, because of the much more simple sample packaging used for nitridation (no powder insulation), and because the power required is less than half that required sintering. Microwave sintering of SRBSN is not viable for materials containing large amounts of contaminants, which may volatilize and migrate into the surrounding microwave insulation (rendering them useless) at temperatures above 1400°C. For both microwave nitridation and sintering processes, either special "hybrid-heating" crucibles must be used, or supplemental conventional heat must be provided to achieve uniform temperatures.

Status of Milestones

Milestone 112408 completed Oct. 4, 1995, and the results have been reported in the Aug. - Sept., 1995 bimonthly.

Problems Encountered

None

Publications

Kiggans, J. O., Nunn, S. D., Tiegs, T. N., Davisson, C. C., Coffey, D. W., and Maria, J.-P., "Gelcasting of Preforms for the Production of Sintered Reaction-Bonded Silicon Nitride" to be published in MPIF 4th International Conference on Powder Metallurgy in Aerospace, Defense, and Demanding Applications Proceedings (1995).

Kiggans, J. O., Tiegs, T. N., Lin, H. T., and Holcombe, C. E., "The Utilization of Microwave Heating for the Fabrication of Sintered Reaction-Bonded Silicon Nitride," pp. 59-63 in 30th Microwave Power Symposium Proceedings, International Microwave Power Institute, Manassas, VA, 1995.

Nunn, S. D., Kiggans, J. O. Jr., Simpson, R. E., and Maria, J. P., "Gelcasting of Silicon Compositions for SRBSN," to be published in the proceedings of the annual meeting of the American Ceramics Society, 1995.

Maria, J-P., Kiggans, J. O., Tiegs, T. N., and Nunn, S. D., "Gelcasting of Reaction-Bonded Silicon Nitride To Improve Mechanical Properties," to be published in the proceedings of 19th Annual Cocoa Beach Conference (1995).

Communications/Visits/Travel

Travel by J. O. Kiggans for the presentation of a paper, "Gelcasting of Preforms for the Production of Sintered Reaction-Bonded Silicon Nitride" at the 4th International Conference on Powder Metallurgy in Aerospace, Defense, and Demanding Applications, May 8-10, 1995, in Anaheim, California.

Travel by J. O. Kiggans for the presentation of a paper, "The Utilization of Microwave Heating for the Fabrication of Sintered-Reaction Bonded Silicon Nitride" at the 30th Microwave Power Symposium, July 9-12, 1995, in Denver, Colorado.

Travel to Golden Technologies in Golden, Colo. on July 13, 1995. The visit included a tour of the facility where SRBSN clevis pins are manufactured. Techniques for preparation of silicon powders and green bodies were discussed, as well as methods used for nitridation and sintering of these silicon parts.

Visit by T. N. Tiegs to Golden Technologies in Golden, Colo. on Sept. 14-15, 1995. The visit included a tour of the facility where SRBSN clevis pins are manufactured, and discussions on the progress of the CRADA with Golden Technologies. Clevis pin samples which had previously nitrided by microwave heating at ORNL were given to Gary Garvey for sintering at their facility.

Table 1. α - Si_3N_4 content of clevis pin samples nitrided by microwave and conventional heating.

Temp. ($^{\circ}\text{C}$)	Furnace	Atmosphere	α - Si_3N_4 Content (%)
1300	microwave	N_2 -4 H_2	90
1300	microwave	N_2	87
1350	graphite	N_2 -4 H_2	87
1450	graphite	N_2 -4 H_2	58
1450	graphite	N_2	9

Table 2. Summary of experimental test conditions and results for nitridation of clevis pins using microwave heating.

Test #	Sample Total	Crucible Type	Nitriding Gas	Run Time (h) / Temp. ($^{\circ}\text{C}$)	Avg. % Wt. Gain Total Samples	Avg. % Wt. Gain Exterior Samples	Avg. % Wt. Gain Interior Samples	Standard Deviation of Total Avg. Wt. Gain
1	100	Si_3N_4 -SiC	N_2 -4 vol % H_2	8 / 1300	ND	ND	ND	ND
2	100	Si_3N_4 -SiC	N_2 -4 vol % H_2	8 / 1300	ND	ND	ND	ND
3	36	Si_3N_4 -SiC-BN	N_2 -4 vol % H_2	11 / 1300	43.33	43.26	43.43	0.23
4	36	Si_3N_4 -SiC-BN	N_2 -4 vol % H_2	11 / 1300	42.98	43.02	42.93	0.26
5	36	Si_3N_4 -SiC-BN	N_2 -0.8 vol % H_2	11 / 1300	43.49	43.50	43.49	0.14
6	36	Si_3N_4 -SiC-BN	N_2 -0.8 vol % H_2	10 / 1200	41.75	41.69	41.83	1.29
7	100	Si_3N_4 -SiC-BN	N_2 -0.8 vol % H_2	18 / 1300	44.18	44.18	43.74	0.32
8	60	Si_3N_4 -SiC-BN	N_2 -0.8 vol % H_2	16 / 1300	43.85	43.91	43.80	0.08

Table 3. Summary Data for SRBSN Fabrication

Furnace-Exp #	Location	# Samples	Avg. Density g/cm ³	St. Dev. Densities g/cm ³
Graphite	ORNL	9*	3.26	0.003
MW	ORNL	8*	3.27	0.005
MW	ORNL	21*	3.23	0.002
MW-Exp 1	ORNL	72**	3.30	0.018
MW-Exp 2	ORNL	108***	3.25	0.008
MW-Exp 3	Y-12	90*	3.18	0.020
MW-Exp 4	Y-12	230***	3.19 ^a	0.019 ^a

* bucket tappets

** Si₃N₄ - 9% La₂O₃ - 3% Al₂O₃*** Si₃N₄ - 9% Y₂O₃ - 3% Al₂O₃^a values based on density measurement made on every fourth sample

Table 4. Analysis of microwave SRBSN experiment 2

Sample Layer	Avg. Density g/cm ³	Std. Dev. Dens. g/cm ³	Avg. Hardness kg/mm ²	Avg. Toughness MPa m ^{1/2}
Top	3.25	0.009	1221	6.23
Middle	3.25	0.007	1240	6.64
Bottom	3.25	0.009	1253	6.60

Figure 1. TGA analysis of silicon preforms.

Figure 2. Percent Si-Si₃N₄ conversion for samples nitrided in a graphite furnace in N₂ - 4 vol. % H₂.

Figure 3. Temperature profile obtained for test 1.

Figure 4. Alternate microwave package for processing silicon clevis pins

Figure 5. Temperature profile for test 6

Fig. 6. Insulation package and 100 RBSN clevis pins following nitridation using microwave heating.

Fig. 7. Gelcast TM-145 silicon preform and mold used for casting it.

(a)

(b)

Fig. 8. Microwave insulation packages (a) and (b) showing layers of silicon preforms, as loaded for microwave heating experiments 3 and 4, respectively.

Fig. 9. Microwave power - temperature curves for experiment 4 in the scaleup of SRBSN using microwave heating.

Fig. 10. 90 SRBSN bucket tappets fabricated using microwave heating in experiment 3.

Fig. 11. 230 SRBSN parts fabricated using microwave heating in experiment 4.

**W.B.S. Element 1.1.2.5
Development of a Low Cost Silicon Nitride Powder**

D.F. Carroll, C.L. Conner, and G.A. Eisman,

**The Dow Chemical Company
Midland, MI 48667**

SEMI-ANNUAL REPORT: April - September - 1995

OBJECTIVE/SCOPE

The objective of this program is to further advance the carbothermal nitridation process for producing silicon nitride powder developed during Phase I of the contract. This phase of the effort is focusing on identifying and demonstrating issues relating to the overall cost of manufacturing the powder. Specifically, the process which was demonstrated at the pilot plant level for the production of a high quality silicon nitride powder will be evaluated, modified, and refined as appropriate in order to reduce the overall costs. The tasks of this program are designed to: 1) determine the feasibility of using low cost raw materials and their impact on the final product quality; 2) reduce the processing costs; and 3) characterize, process, fabricate MOR test specimens, and evaluate the mechanical properties of the lower cost powder. Results of the sintering studies will be used to modify the sintering model developed under Phase I.

OVERVIEW

In order to meet the objectives of the program, the period from April through September focused on synthesis trials utilizing low cost raw materials, reformulated feeds, and a modified precursor preparation process. During this reporting period a total of 45 synthesis trials were performed. Although a large number of runs were carried out during this period, reactor power supply electrical problems developed and resulted in significant downtime. The unit was repaired and became fully operational by the end of August. During the period when synthesis trials were disrupted, the effort focused on feed preparation and analysis of the product produced prior to the shutdown. In addition to powder synthesis, a significant effort was also put forth in determining and modifying powder processing procedures which were developed in Phase I for densification of the powder. As a result, the sintering package developed during Phase I has been modified so as to incorporate the new powder.

TECHNICAL PROGRESS

Task 1.0 Low Cost Raw Materials

The first attempts to synthesize silicon nitride with alternative raw materials by the carbothermal process developed during Phase I were initiated at the onset of this reporting period. At first, the effort focused on an alternative for the silica used during Phase I while latter efforts investigated the synthesis of silicon nitride prepared with both the newly identified lower cost silica source and an alternative for one of the proprietary additives. Due to the fact that different raw materials will exhibit different handling properties, at the beginning of this period the feed preparation procedures had to be revisited from what had been developed under Phase I. Therefore, a number of precursors were prepared, analyzed, and evaluated to determine how well the feed components would mix and perform in the Dow process.

In addition to powder handling differences, the reactivity of the new starting material components had to be evaluated. Once it was determined that the feed components were intimately and randomly mixed in the precursor granule, a series of reactor runs had to be carried out whereby the reaction conditions had to be reconfirmed. Although it was anticipated that differences in reactor temperature would not be significant, some refinement of the heat schedule had to be made. This was addressed in a short series of synthesis runs. In addition to temperature, reaction time and flow rate also had to be re-evaluated. The analysis of the product carried out to determine the effect of the reaction conditions on the powder included the determination of residual oxygen and carbon concentrations (via combustion analysis methods), the measurement of the surface area (via BET), particle size and particle size distribution (laser light scattering), and by observing the morphology of the crystallites via scanning and transmission electron microscopy (SEM & TEM). As a natural consequence of using TEM, the silicon carbide produced in the Dow process could also be analyzed. Once the reaction conditions were fine tuned and the properties found to be desirable, the powder was further evaluated by how it performed in greenware fabrication, sintering, and mechanical property testing (see below under Tasks 3 & 4).

Another aspect of the development of a powder utilizing new raw materials is the effect of reactor charge, or sample quantity, on both the time to complete the reaction as well as the effect on product quality. In order to assess the effect of the size of the reactor charge on the product, a number of runs were carried out whereby the precursor quantity was varied. Another critical aspect of this task was to determine the degree of reactivity as a function of location within the reactor core. In this evaluation, key properties such as residual oxygen and carbon were mapped within the reactor sample assembly itself. The results of the trials used to evaluate the reactor charge size are reported below in Table I. As above, it was determined that the best way to evaluate this effect was by looking at residual oxygen and carbon. During this test, the reactor conditions such as temperature, time, and flow rate were fixed. As can be seen from the results presented in Table I, all reaction charges of sizes up to 900 grams were completely converted. Further increases in reaction charge were not attempted.

Table I
Reactor Charge vs. Residual Oxygen & Carbon

Trial #	Reactor Charge (grams)	Residual Oxygen (wt%)	Residual Carbon (wt%)
1	227	1.53	1.12
2	454	1.58	0.94
3	563	1.43	0.81
4	681	1.57	0.98
5	794	1.55	0.78
6	908	1.51	0.79

Reactor Modifications

During this period, a minor (proprietary) modification was made to the reactor internals in an effort to improve the distribution of feed gases through the sample assembly and therefore the charge. By making this change, the new gas flow pattern would ensure a more evenly distributed source of fresh nitrogen to the reacting precursor and therefore impact the ratio of nitrogen to carbon monoxide.

Powder Synthesis Trials

The powder properties generated in the program within this period are reported below in Table II along with the 2 kg delivered to MMES, the final powder deliverable under Phase I, and the powder specifications of the contract. Due to the large number of runs carried out during this period, only selected trials are listed. As is evident from the data, the synthesis results are fairly reproducible and similar (in properties) to the powder developed in Phase I. Although not reported in Table II, the metal impurity level was measured on selected synthesis products. In general, the iron level was measured to be approximately 250 ppm whereas the Al was measured at 450 -550 ppm. Both numbers are consistent with starting material purity. During the period though, it became evident that the Al content had increased to approximately 1100 ppm. After an investigation, it was determined that the higher Al content was a result of a mixing arm coming in contact with its container. Once corrected, the aluminum content returned to expected levels. Except for the aluminum and a slightly higher carbon level, the Phase II powder properties for material produced to date falls well within the specifications of the contract. The carbon specification is based on free carbon, not the carbon of silicon carbide as is produced in this process.

Differences do exist between the Phase I and II powders. Such differences include a lower surface area, larger particle size, as well as the previously mentioned higher metallic impurities. Even though this powder is not milled to reduce the agglomerates, the overall size of the fundamental crystallite is slightly larger in the Phase II powder. This is evident from the SEM presented in Figure 1 below. This increase in particle size would also

explain the drop in surface area of the unmilled powder. The drop from approximately 8 - 9 m²/g for the unmilled Phase I powder to ~ 6 m²/g for the larger Phase II powder is not unexpected considering the raw materials in use. It is anticipated that further optimization of the process will impact some of these properties.

Table II
Characteristics of Silicon Nitride Powder
From Phase II Feed

Run Property	30	35	45	51	55	60	66	70	75	80	85	2 kg Deliverable	Phase I Powder	Phase I Goals
Oxygen (wt.%)	1.28	1.39	1.54	1.55	1.60	1.43	1.37	1.50	1.53	1.61	1.57	1.5	1.91	< 2.5
Carbon (wt.%)	0.85	0.87	1.15	1.19	0.83	0.81	0.78	0.74	0.84	--	0.75	0.75	0.47	< 0.6
Surface Area (m ² /g) ⁺	5.60	5.64	6.14	6.15			5.80	5.68	5.86	5.98	5.80	5.85	9.6	5 - 10
% Alpha	>95	>95	>95	>95	>95	>95	>95	>95	>95	>95	>95	>95	> 95	> 90

+ Powder was not de-agglomerated

% alpha: estimated by x-ray diffraction

Reactor Power Supply Failure

As mentioned above, during the month of June, the reactor power supply failed and resulted in considerable downtime. The failure was the result of a series of blown power transistors which had to be replaced. Once corrected the unit ran for a number of runs until the problem resurfaced. The unit was sent back to the manufacturer for refurbishing and testing. Since its reinstallation, the unit has been fully operational.

Task 2.0 Reduction of Processing Costs

The focus of this task is to evaluate the process to produce silicon nitride developed during Phase I with the ultimate objective being to reduce the processing costs. As reported in previous bimonthlies, the first attempts focused on the pre-processing unit operations during which the feed composition is blended, mixed, and granulated. The second aspect of this effort is to reduce the carbon levels determined during Phase I. To date, experiments have been initiated to address both concepts. For the former, precursor preparation unit operations continue to be evaluated with the principal emphasis on the pre-mixing of the raw materials. Rather than utilizing a ball mill for the initial mixing, the material is processed by dry mixing in a Hobart mill. The material is then processed in a similar fashion to that developed earlier. The overall product mix and homogeneity of the precursor has been evaluated and shown not to be affected.

The second aspect of this task is to evaluate the effect of carbon content in the feed on reactivity as well as on the product. By lowering the carbon content in the feed, significant gains can be realized in cost reduction as well as throughput of the process. Tests have been carried out whereby the carbon level in the feed has been controlled. Although not detailed in the list of runs (Table II), the trials tabulated include two different carbon levels. As mentioned previously, the overall results are consistent and little direct evidence exists to suggest the powder is impacted negatively by the above changes.

Task 3.0 Powder Evaluation and Part Fabrication

The main objective of this task is to characterize the low cost powders produced in Tasks 1.0 and 2.0 and provide feedback on the powders' ability to be pressureless sintered into components with good mechanical properties. A second aspect of Task 3.0 is to make adjustments to the sintering composition and schedule so that the low cost powder developed in Phase II can be pressureless sintered into components with maximum density, strength and fracture toughness.

Reactor Qualification

During the first month of Phase II, a new reactor facility was brought on line to produce the low cost silicon nitride powder. The initial reactor experiments were carried out with the raw materials used in Phase I so that the operating conditions could be defined for making high quality silicon nitride powder. Once the operating conditions were developed, the silicon nitride powder was evaluated using the sintering package developed in Phase I of this program. The results of this evaluation were compared to the sintered properties of components made with the same sintering package and Phase I powder. Using the recommended Y_2O_3/Al_2O_3 sintering composition, the silicon nitride powder was attrited in water and then slip cast into greenware approximately 2" x 2" in size. No noticeable differences were observed in the slip casting behavior of the silicon nitride powder produced in the new reactor. The slip cast greenware was then pressureless sintered to an average density of 98.9% of theoretical density using a two-step sintering cycle. This sintered density was found to equal the densities of components made with Phase I powder. These sintered components were submitted to Task 4.0 for mechanical property evaluation. With the new reactor on-line and capable of making high quality powder, the effort focus on the production of a lower cost silicon nitride powder as defined by Tasks 1.0 and 2.0 of this program.

Powder Evaluation

One of the first low cost silicon nitride powders produced in Task 1.0 was evaluated with the sintering package defined in Phase I to determine how the densification behavior varied from Phase I powder. This particular powder was made with low cost raw material silica A, additive 4B and excess carbon level Q2. The oxygen content, carbon content and surface area of this powder was measured to be 1.47 wt.%, 0.67 wt.% and ~5-6 m²/g, respectively. The powder was evaluated using the following sintering composition: 87.93

vol.% Si₃N₄, 4.77 vol.% Y₂O₃, 2.55 vol.% Al₂O₃ and 4.78 vol.% SiO₂. The powder was first attritted in water, slip cast into greenware and pressureless sintered in a batch type furnace using a schedule that contained a 1600°C soak followed by a 1700°C soak for 10 hours. The sintered density of the component fabricated with Phase II powder was measured to be ~96% of theoretical density. In comparison, a component made with Phase I powder was sintered to ~99.0% of theoretical density. The lower sinterability of the Phase II powder is most likely due to the lower surface area and/or higher residual carbon (i.e., SiC) of the powder.

Sintering Package Development

One of the goals of Task 3.0 was to develop a sintering package for our carbothermal silicon nitride powder that would be amenable to "fast" sintering cycles using a batch type furnace. The information gained from this study should provide a baseline for those who would like to pressureless sinter the low cost silicon nitride powder in a continuous furnace environment. The definition of a "fast" sintering cycle is a schedule where the total time under heat-up and soak is limited to ~3 to 5 hrs. The length of the cool down cycle is limited by natural cool down of the furnace (~2-3 hours in length). The initial work under this task was to examine the best Y₂O₃/Al₂O₃ ratio and glass content for a "fast" sintering schedule that utilized a 1675°C, 1.5 hr soak. This evaluation was conducted on Phase I carbothermal powder to first establish a baseline while the production of Phase II silicon nitride powder was brought on line. The results indicated that with this short sintering cycle, Phase I powder could be easily sintered to ~96% density when the Y₂O₃/Al₂O₃ ratio was between 2.5 and 3.6. For Y₂O₃/Al₂O₃ ratios within this range, the highest densities for this sintering cycle were obtained when the glass content was ~11.4 volume %. This initial composition and glass content will be used as a starting point for developing a sintering package for Phase II powder.

A lot of Phase II silicon nitride powder was produced so that the "fast" sintering cycle could be developed. This particular powder was made with low cost raw material silica A, additive 4B and excess carbon level Q2 and had an oxygen and carbon content of 1.52 wt.% and 0.70 wt.%, respectively. Greenware was slip-cast with this powder using a sintering composition of 88.65 wt.% Si₃N₄, 8.11 wt.% Y₂O₃ and 3.25 wt. % Al₂O₃. Initial temperature/time profiles were conducted to determine which conditions would achieve densification and provide maximum α to β transformation for a total heatup and soak time of 3-5 hrs. The greenware plates were sintered in a BN crucible under flowing nitrogen gas without the use of a surrounding powder bed. Figure 2 summarizes the initial density results for the various temperature and time profiles. The results indicated that the highest density was obtained at 1675°C after a 1 hour hold. Higher sintering temperatures or longer sintering times resulted in a slight decrease in the final sintered density. This result suggests a maximum in the sintered density as a function of temperature and time.

When using a "fast" sintering cycle at relatively low temperatures, it is necessary to ensure that full alpha to beta transformation has occurred in the densified part in order to obtain maximum mechanical performance. In Figure 2, the weight percentage of beta silicon nitride as a function of the sintering conditions is also shown for the densified components.

For the component sintered at 1675°C for 1 hour, a beta silicon nitride content of ~57% was measured. Higher sintering temperatures and longer sintering times were needed to complete the α to β transformation. Since these conditions are detrimental to density, the following sintering schedule was developed as a compromise to reach maximum density and beta silicon nitride content. Figure 3 is a schematic representation of the suggested sintering cycle. This sintering cycle contains an initial soak at a high temperature to achieve initial densification followed by a lower temperature soak to maximize the alpha to beta transformation. The second lower soak is at a temperature that is not detrimental to densification.

In order to develop the proposed sintering format described in Figure 3, carbothermal silicon nitride plates (2" x 2") were cast using Phase II powder and a formulation of 88.71 wt.% Si₃N₄, 7.76 wt.% Y₂O₃ and 3.53 wt.% Al₂O₃. These plates were then sintered using the conditions shown in Figure 4. The density of these sintered plates were measured to be 97.7% of theoretical with a beta silicon nitride content of 70 wt.%. These densified plates were then machined into test specimens to characterize the mechanical properties. The results of the mechanical property measurements are summarized in Task 4.

In order to try and improve the sintered density of our Phase II powder, the "fast" sintering cycle was further investigated to determine the conditions which would yield maximum density and beta silicon nitride content. The results of this study indicated that, within the limits specified by the "fast" sintering cycle, the highest densities and beta silicon nitride contents that were obtained in a sintered component made with Phase II powder were ~97% and 80 wt.%, respectively. Current work is underway to determine the maximum density and beta silicon content which can be achieved at longer sintering times and higher temperatures using a conventional batch sintering cycle. It appears from this work that it may be very difficult to achieve greater than 99% density with Phase II powder using pressureless sintering conditions. With a surface area of ~5-6 m²/g, overpressure sintering conditions may be required to fully densify our current Phase II powder. This result is not surprising since most commercial silicon nitride powders with similar surface areas also require pressure-assisted densification methods to achieve full density.

To determine if an increase in glass content could improve the pressureless sintered density of components made with Phase II powder, a study was initiated where the amount of glass in the sintering formulation was varied from a total of 10.5 to 12.3 volume%. The oxygen content from the silicon nitride powder was assumed to be in the form of SiO₂ and taken into consideration during calculation of the glass content. This study also varied the Y₂O₃/Al₂O₃ ratio in the sintering formulation so that the effect of glass content and composition on the sintered density and alpha/beta transformation of Phase II powder could be determined. The Y₂O₃/Al₂O₃ weight ratio was varied from 1.5 to 3.0. The Phase II silicon nitride powder used for this evaluation had an oxygen and carbon content of 1.46 and 0.80 wt.%, respectively. These formulations were slip cast to produce greenware with green densities ranging from 58 to 60%. The components were sintered at 1610 and 1640°C with a soak time of 2.5 and 4.5 hours. Higher sintered

temperatures were not investigated since they yielded a decrease in density. The results of this study are summarized in Figure 5. The increase in glass content was found to improved the sintered density slightly but not above 97-97.5% of theoretical density. Unless the glass contents is increased further to excessive levels, it appears that the maximum sintered density for our current Phase II powder has been achieved for this rapid sintering schedule and Y_2O_3/Al_2O_3 formulation. It is expected that an increase in the surface area of the Phase II powder would improve the densification behavior under these conditions. Other trends which were observed in this study and summarized in Figure 5 are as follows:

- an increase in glass content had a minimal an effect on the degree of alpha to beta transformation.
- the degree of alpha to beta transformation was higher for glass compositions with a lower Y_2O_3/Al_2O_3 ratio.
- the degree of alpha to beta transformation increased at the higher sintering temperature and time (1640°C, 4.5 hrs).
- the lower Y_2O_3/Al_2O_3 ratio yielded higher sintered densities at sintering conditions of 1610°C, 2hrs.
- at 1640°C, 4.5 hrs, the Y_2O_3/Al_2O_3 ratio of 3.0 yielded the highest sintered densities.

Task 4.0 Part Fabrication and Mechanical Property Characterization

The effort under this task is directed toward the production of slip cast greenware and sintered parts to meet our deliverables (25 MOR specimens) to MMES at the end of 7 and 12 month of the contract. This task will also characterize the mechanical property specimens fabricated in Task 3.0 in order to determine the average fracture strength and Weibull modulus.

The mechanical properties of the material made during qualification of the new reactor were characterized by measuring the 4 point bend room temperature strength. This material was made from carbothermal silicon nitride powder produced in our new reactor facility using raw material precursor leftover from Phase I. The results of the mechanical property measurements showed that the average strength and Weibull modulus of the component was 535 ± 95 MPa and 5, respectively. These mechanical property results were significantly lower than components fabricated during Phase I. Fractography analysis indicated that the main fracture origin were due to inhomogeneous greenware. Even though there was no major difference in slip properties with this powder, the characteristics of the greenware were obviously different from Phase I. A program was initiated to eliminate this type of defect from our greenware when using Phase II powder.

The first part deliverable during Phase II required 25 MOR bars to be sent to MMES at the end of the 7 month of the contract. The specimens used for this deliverable were machined from sintered plates with a density of 97.7%. These plates were sintered with the fast schedule describe in Task 3. A total of 32 four-point bend flexure specimens were

machined from the material. Seven of these specimens were broken in-house to determine the average room temperature fracture strength. The remaining twenty-five specimens were delivered to MMBS as part of our 7 month deliverable. The average fracture stress of this material was measured to be 730 ± 80 MPa. Fracture surface analysis revealed the major flaw to be localized porosity. It is believed that improvements in sintered density would minimize this defect and increase the overall fracture strength of the material.

Figure 1. Scanning Electron Micrograph of Phase II Powder

Figure 2. Percent of theoretical density and beta silicon nitride content for components sintered at different temperatures and times.

Figure 3. Schematic representation showing recommended sintering schedule for Phase II carbothermal silicon nitride powder. The recommended sintering schedule simulates a "fast" sintering cycle.

Figure 4. Sintering schedule utilized for a 88.71 wt.% Si_3N_4 , 7.76 wt.% Y_2O_3 and 3.53 wt.% Al_2O_3 formulation.

Figure 5. The % theoretical density and the % beta-silicon nitride for sintered components made with Phase II powder as a function of the $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio in the sintering package. The results are shown for components made with a total glass content of 10.5 vol.% (solid lines) and 12.3 vol.% (dashed lines). The components were sintered at 1610 and 1640°C for 2.5 and 4.5 hours, respectively.

STATUS OF MILESTONES

All milestones are on schedule. During this period 2 kg of powder and 25 MOR test specimens were sent to MMES as dictated by the deliverable schedule.

PUBLICATIONS

A presentation was made at the 1995 Annual American Ceramic Society Meeting held in Cincinnati, Ohio in April.

COMMUNICATION/TRAVEL/OTHER

Dr. C.L. Conner visited AlliedSignal Ceramic Components in May.

Drs. G.A. Eisman, D. F. Carroll, and C.L. Conner attended the 1995 Annual American Ceramic Society Meeting held in Cincinnati, Ohio (April).

Professor Stephan Danforth of Rutgers University was sent 1 kg of Phase I powder.

Dr. Michael Hoffmann of the University of Karlsruhe (formerly of the Max Planck Institute) was sent a kilogram of Phase I powder.

AlliedSignal was supplied 20 kg of Phase I powder for further assessment.

Cost Effective Sintering of Silicon Nitride Ceramics (SIU-C)-

D. E. Wittmer, Southern Illinois University, Carbondale, IL 62901

Objective/Scope

The purpose of this work is to investigate the potential of cost effective sintering of Si_3N_4 through the development of continuous sintering techniques and the use of lower cost Si_3N_4 powders and sintering aids.

Technical Highlights

Task 1. Refine Economic Model and Design for Chosen Furnace Configuration

This task was completed as reported in a previous semiannual report.

Task 2. Continue evaluation of sintering parameters on properties of selected Si_3N_4 compositions

Continuous Sintering

A total of 66 billets (approximately 100 g each) were continuously sintered at Centorr/Vacuum Industries in the Model 44-BF prototype furnace at 1775°C for 90 min. These sintering trials served the purpose of proof testing the tungsten hot zone prior to shipment of the furnace to SIU-C. Si_3N_4 test bars representing the A2Y6, A4Y6 and A2Y8 formulations, prepared with both Ube E-10 and Dow Chemical Co. silicon nitride powders, were machined from these billets. Room temperature four-point flexural strength and fracture toughness, oxidation resistance, and elevated temperature four-point flexural (fast fracture) strength were measured. The results of this work form the basis of a Master's thesis and will be discussed in more detail as part of Task 3.

After installation of the Model 44-BF belt furnace at SIU-C, 60 additional billets were continuously sintered to both qualify the furnace after delivery and installation were completed and to observe the effects of turbomilling and sintering parameters on the sinterability of the Dow Chemical Co., Shin-Etsu, and Ube E-10 Si_3N_4 powders. The details of the turbomilling time and sintering conditions, along with the bulk density results will also be presented and discussed in more detail in Task 3.

Continuous sintering of H. C. Starck M-11 powder (a gratis sample provided by H. C. Starck) in the A4Y6 formulation is presently being completed. Variables for these milling runs were milling media type (silicon nitride or YTZ) and dispersion technique (pH control or dispersant with pH control).

Improved Processing

Four lots of H. C. Starck M-11 powder (a gratis sample provided by H. C. Starck) in the A2Y8 formulation were processed by turbomilling and pressure filtration. Variables for these milling runs were milling media type (silicon nitride or YTZ) and dispersion technique (pH control or dispersant with pH control). The dispersant utilized was Rohm and Haas-Duramax D-3007 which is an acrylic copolymer with low sodium content. Disks have been pressure cast, dried and isopressed and are currently being continuously sintered in the Model 44-BF belt furnace. Density, four-point flexural strength, elevated temperature strength and microstructure will be compared with the same formulation using the other silicon nitride powders.

Elevated temperature, four-point flexural strength, and fracture toughness continue to be measured for A2Y6, A2Y8 and A4Y6 processed using Ube E-10 powder. For the A4Y6, solids loading (30 and 40 vol.%) and turbomilling processing temperature (10 and 20°C) were the variables investigated. For the A2Y6 and A2Y8 formulations, processing was completed at 30 vol.% and 10°C. The properties of all formulations continue to be measured as test bars are generated from the continuous sintering runs.

In general, processing at the lower solids content and the lower processing temperature has produced stronger material at room temperature and elevated temperature. Also, the A2Y8 formulation has consistently displayed the greatest high-temperature flexural strength (730 MPa at 1000°C and 330 MPa at 1350°C), compared with the A2Y6 and the A4Y6 formulations.

Fracture toughness by the strength method was also completed for the A4Y6-E10 formulations; solids loading (30 and 40 vol.%) and turbomilling processing temperature (10 and 20°C). The lower solids content and the lower processing temperature appeared to produce marginally higher fracture toughness; however additional testing is planned to produce more statistically significant data.

Task 3. Continue Evaluation of Low Cost Si_3N_4 Powder

The goal of this task is to evaluate silicon nitride powders which are potentially more cost effective than Ube E-10, but which can be processed to produce properties similar to those obtained for Ube E-10 or used in applications which are not as demanding. To this end, we have been evaluating the Dow powder produced by carbothermal reduction, the Shin-Etsu SN10-DW powder produced by nitridation of Si, and the H.C. Starck M-11 powder, also produced by nitridation of Si.

In previously reported work, A2Y6, A2Y8 and A4Y6 formulations were prepared from the Dow Chemical Co. silicon nitride powders. The same formulations were prepared, using Ube E-10 silicon nitride powder, for comparison of the room temperature and high temperature properties. As reported in Task 2, billets of all formulations were sintered continuously at 1750°C for 90 min in the same sintering runs to produce consistent sintering conditions for each test billet. Table I is a summary of the room

temperature and elevated temperature properties measured as an average of 3 test bars per test condition.

Table I. Results for Ube and Dow Si_3N_4 formulations that were continuously sintered at 1750°C for 90 min.

Comp.- Powder *	Density % of TD	Four-Point Flexural Strength					K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)
		Room T	850°C	1000°C	1200°C	1350°C	
A2Y6-U	96.4	1068	792	707	622	253	6.5
A2Y6-D	87.7	698	622	476	478	253	5.8
A4Y6-U	99.3	881	755	578	551	251	6.2
A4Y6-D	90.3	712	709	506	437	187	5.7
A2Y8-U	96.1	1088	747	730	641	329	6.7
A2Y8-D	92.7	889	821	689	633	390	6.2

* The -U and -D extensions to the compositions indicate the use of either Ube or Dow Si_3N_4 powder, respectively, in the formulations.

The following conclusions were made with regard to the observed results:

- Billets prepared from Ube E-10 had significantly higher density for all formulations. Because equivalent density was not obtained for formulations prepared with both Ube and Dow powders, the direct comparison of properties is not justified.
- Room temperature strength and fracture toughness values were higher for formulations prepared with Ube E-10, with the A2Y8 formulation having higher strength and fracture toughness.
- Elevated temperature strength was higher for formulations prepared with Ube E-10, except for the A2Y8 formulation at 1350°C .

It is expected that the properties of the formulations prepared from the Dow powder can be improved significantly if densification can be improved. The primary differences between Ube and Dow powders are: surface area, carbon content and oxygen content (amount and location). It was believed that with more intensive turbomilling and the use of a thermal pretreatment that the densification behavior of formulations prepared with the Dow powder could be improved.

To determine the effect of increased milling time of the sinterability of the Dow powder in the A4Y6 formulation turbomilling was conducted for 2, 4, 6 and 8 hours. The billets were continuously sintered in the belt furnace for several times and temperatures to observe the effect of turbomilling time on sinterability. The results of density as a function of turbomilling time and sintering conditions are given in Table II. These results show that increasing the turbomilling time did not lead to enhanced densification as hoped, with the densities being significantly lower than obtained for the other two powders for the same sintering conditions. Also, the Dow formulations had higher density at lower sintering temperature and time (1700°C and 60 min) and the density did not increase with temperature and/or time as is usually observed for other Si_3N_4 's. The use of low sintering temperatures, presintering and/or seeding will be investigated to determine if the densification can be improved.

The gratis sample of Shin-Etsu Si_3N_4 (a potential low cost powder) in the A4Y6 formulation was continuously sintered during this reporting period for three time/temperatures. The results are also given in Table II. This powder in the A4Y6 formulation has similar sinterability to the results previously obtained for Ube E-10, but it has much higher green density (67% compared with 59%). Additional sintering trials are currently taking place and billets will be machined into test bars to measure the room temperature and elevated temperature properties.

The densities obtained for the Ube E-10 formulations were also significantly lower than obtained in previous work. There is some indication that these differences are caused by this being a "new" lot of powder purchased from Ube recently. Some additional milling and sintering trials are underway to determine if these differences are due to the powder or processing. This should be completed during the next reporting period.

Task 4. Design and Construct Prototype Belt Furnace

Construction of the prototype belt furnace by Centorr/Vacuum Industries, Inc. (CVI), Nashua, NH was completed and the furnace was proof tested at CVI prior to delivery and installation at STU-C. Since installation, the Model 44-BF belt furnace (with the tungsten hot zone installed) has been in operation for a total of 172 hours of high-temperature operation (35 sintering runs) without any problems with the furnace. Potential problems which may arise due to power outages have been corrected by the installation of a gas bypass line and an additional cooling water/drain line. Discussions are underway with gas vendors for the installation of a bulk liquid nitrogen supply.

Addition of bulk supply will eliminate delivery and quality issues and reduce the cost of process gas.

In addition to the materials formulated and processed at SIU-C, materials have been received from Golden Technologies Company (GTC), Norton Advanced Ceramics (NAC) and Allied Signal Inc. (ASI) for continuous sintering in the new belt furnace.

Several continuous sintering runs have been completed on GTC SRBSN. Many of the specimens of SRBSN from GTC were sintered to full density under a range of continuous sintering conditions. Based on these preliminary results, SIU-C and GTC will continue to investigate continuous sintering of GTC silicon nitride under a Memorandum of Agreement. The goal of this work will be to determine the economics of continuous sintering for pilot production scale quantities of silicon nitride parts and will provide the basis of Master thesis.

As part of the NAC ACMT contract, the belt furnace has been used successfully to continuously sinter several silicon nitride parts. Additional materials are expected shortly for sintering in the belt furnace under a collaborative program with NAC. The details are presently being discussed.

The results for the ASI materials were encouraging and additional materials have been requested to complete sufficient validation of continuous sintering for ASI silicon nitride. Following validation, the intent is to develop a collaborative program with ASI through a Memorandum of Agreement or a Memorandum of Understanding for sintering a much larger number of parts.

Status of Milestones

1.	Refine Economic Model and Design for Chosen Furnace Configuration	Completed
2.	Continue Evaluation of Sintering Parameters on Properties of Selected Si_3N_4 Compositions	On Schedule
Continuing
3.	Continue Evaluation of Low Cost Si_3N_4 Powders	On Schedule
Continuing
4.	Design and construct prototype belt furnace	Completed

Communications/Visits/Travel

D. E. Wittmer to Annual American Ceramic Society Conference and Exposition Cincinnati, OH May 1-4, 1995.

C. W. Miller, Jr. to SIU-C to finalize furnace installation, June 5-8, 1995.

D. E. Wittmer to Golden Technologies Company, Inc. to discuss results of continuous sintering of SRBSN and future collaborative efforts between GTC and SIU-C.

D. E. Wittmer completed and signed a Memorandum of Understanding with GTC and is awaiting approval and signature of GTC.

Problems Encountered

Isopress was down for 3 weeks waiting for repair parts which has delayed final processing of M-11 compositions. The isopress has been repaired and work is continuing.

Publications

B. E. Rodely, "Effect of Powder Source on Properties of Si_3N_4 at Ambient and Elevated Temperatures," Master of Science Thesis, Southern Illinois University at Carbondale, College of Engineering, August, 1995.

D. E. Wittmer*, B. E. Rodely, V. A. Knapp, and S. P. Etherton, Southern Illinois University, Carbondale, IL and C. W. Miller, Jr., Centorr/Vacuum Industries, Inc., Nashua, NH, "Comparison of Properties for Formulations Prepared From Two Silicon Nitride Powders," Abstract of paper to be presented at the 1996 Conference on Composites and Advanced Materials, Cocoa Beach, FL, January, 1996. To be published in Ceramic Engineering and Science Proceedings.

Presentations

None

Table II. Continuous Sintering Results for Dow, Ube and Shin-Etsu Silicon Nitride

Composition	Sintering Conditions (temp/time)	Bulk Density (g/cc)	Percent Theoretical Density
Dow A2Y6 2h milling	1750/90	2.85	87.7
	1700/60	2.92	89.5
Dow A4Y6 2h milling	1750/90	2.94	90.3
	1700/60	3.12	95.8
Dow A4Y6 4h milling	1800/90	2.98	91.3
	1750/120	2.99	91.6
	1750/90	2.99	91.6
	1750/30	3.05	93.6
	1700/60	3.09	94.8
Dow A4Y6 6h milling	1800/90	3.01	92.1
	1750/120	3.02	92.7
	1750/90	3.01	92.1
	1750/30	3.05	93.4
	1700/60	3.10	95.0
Dow A4Y6 8h milling	1750/120	3.01	92.3
	1700/60	3.11	95.8

Table II. Continuous Sintering Results for Dow, Ube and Shin-Etsu Silicon Nitride (continued).

Ube A2Y6 2h milling	1750/90	3.13	96.4
	1750/30	2.88	88.5
	1700/60	2.84	87.2
Ube A4Y6 2h milling	1750/90	3.17	97.3
	1750/30	3.09	94.7
	1700/60	3.08	94.4
Ube A2Y8 2h milling	1800/90	3.17	96.8
	1750/120	3.06	93.4
	1750/90	3.03	92.3
	1750/30	3.04	92.8
	1700/60	3.04	92.9
Shin-Etsu A4Y6	1800/90	3.23	99.1
2 h milling	1750/90	3.16	97.1
	1750/30	3.08	94.4

1.1.4 Processing of Monolithics

W.B.S. ELEMENT 1.1.4.2 IMPROVED PROCESSING

S. D. Nunn, O. O. Omatete, and C. A. Walls
Oak Ridge National Laboratory

Objective/Scope

To determine and develop the reliability of selected advanced ceramic processing methods. This program is to be conducted on a scale that will permit the potential for manufacturing use of candidate processes to be evaluated. The emphasis is on silicon nitride. Issues of practicality; safety, hygiene, and environmental issues; and in-process testing methods are to be addressed in addition to technical feasibility. The methodology includes selection of candidate processes and evaluation of their range of applicability to various kinds of commercially available ceramic powders.

Technical Highlights

I. Silicon Nitride Gelcasting - Dow Powder (C. A. Walls)

Dow Chemical Co. is developing a low-cost silicon nitride powder under W. B. S. Element 1.1.2.5 of the Ceramic Technology Project. As part of the evaluation of this powder, we will be conducting experiments to characterize its behavior in gelcasting.

Continued sintering studies with gelcast Dow phase 1 materials to improve density and sintering characteristics has yielded some success. Four samples fired in separate runs utilizing two 1800° C sintering schedules gave parts with fired densities in the range of 96 percent of theoretical density. Both of the firing schedules incorporated low temperature soaks as recommended by Dow and density improvements were seen (Table 1) for both of the low temperature soak levels we tried. All parts survived with no warpage, cracking, or distortion. As with previous firings we noted no improvement in properties between the gelcast parts and the gelcast/isopressed parts. In all of this material five weight percent yttrium oxide and five weight percent aluminum oxide were used as the sintering aids.

Table 1. Gelcast phase 1 sintered densities				
Sample #	Part History	Green Bulk g/cc	Fired Immersion g/cc	% of Theoretical %
1790°C. 2hr #2	as gelcast	1.60	3.02	91.50
#4	gelcast/isopressed	1.74	2.93	88.60
1700°C. 2hr #2	as gelcast	1.60	3.03	92.00
#4	gelcast/isopressed	1.74	3.05	92.40
1700°C. 4hr #2	as gelcast	1.60	3.12	94.40
#4	gelcast/isopressed	1.74	3.11	94.30
1750°C. 4hr #2	as gelcast	1.60	3.05	92.30
#4	gelcast/isopressed	1.74	2.97	90.00
1800°C. 2hr #1	as gelcast	1.61	3.15	96.40
#3	gelcast/isopressed	1.78	3.14	96.20
1800°C. 2hr #1	as gelcast	1.61	3.14	96.30
#3	gelcast/isopressed	1.78	3.13	96.00

Study of dispersants continues in efforts to increase the solids loading of the aqueous gelcast suspension of the Dow phase 1 material. In parallel to this work phase 2 material will be tested against the best dispersants found for the phase 1 powder. Initial evaluation of phase 2 material distribution shows higher mean particle size and higher maximum particle size as shown in figure 1. Milling studies were conducted to determine the basic particle size and the level of agglomeration of the phase 2 powder; figure 2 shows the results of milling. After 30 hours of milling phase 1 powder has a mean of 0.63 microns and phase 2 powder has a mean of 0.7 microns. Both powders show no material remaining above 2 microns.

Planned experimentation will focus on dispersing the milled powder and on altering the milling techniques in slurry preparation to yield a more highly loaded gelcasting slurry.

Figure 1. Particle size distribution of as received phase 1 and phase 2 Dow low cost silicon nitride powder.

Figure 2. Dow phase 1 and phase 2 powders milled to basic particle size.

II. SRBSN Gelcasting (S. D. Nunn)

Evaluation was begun on the preparation of large SRBSN gelcasting batches (1 kg) using ball milling instead of attrition milling. The SRBSN compositions were prepared using the alcohol-based gelcasting system. It was found that batches containing 50 vol. % solids could be readily prepared by this method. Castings from the slurries include plates of varying thickness (0.2, 0.25, and 1.0 in.) for determination of the effect of green density and sample thickness on the degree of nitridation under constant processing conditions.

Samples were isopressed to vary the green density of the silicon compact before the nitriding heat treatment. Green density can have a significant effect on the nitridation kinetics if the volume expansion of the silicon near the surface of the sample limits the nitrogen from access to the unreacted silicon at the interior of the sample. The results of comparison testing are shown in Table 2.

The effect of sample thickness on the degree of nitridation was also compared. Samples having thicknesses of 0.2, 0.5, and 1.0 in. were gelcast and nitrided. The results, shown in Table 3, indicate only a slight decrease in nitridation rate for the thickest samples. This lack of dependence on thickness is believed to be due to the uniform open pore structure which exists in the gelcast materials allowing easy diffusion of the nitrogen gas to the interior of the samples.

With the completion of these tests and the physical property measurement tests reported in the previous semiannual report, the requirements for Milestone 114212 have been completed on schedule.

Table 2. Comparison of the effect of isostatic on nitridation of silicon compacts.

Sample Number	Isostatic Pressing Pressure (psi)	Percent Nitridation (%)
1	0	87
2	5,000	85
3	10,000	83
4	20,000	79

Table 3. Comparison of the effect of sample thickness on nitridation of silicon compacts.

Sample Number	Sample Thickness (in.)	Percent Nitridation (%)
1	0.2	87
2	0.5	89
3	1.0	83

III. Drying of Gelcast Green Bodies (O. O. Omatete)

It was reported earlier that "the data indicated very little loss of moisture from the plates held at 50°C and 92 % relative humidity for 10 h." The cause of this anomaly has been found. At 50°C and 92 % relative humidity, there was condensation on top of the chamber and around the plate protecting the balance on top of the chamber. This condensate dropped back onto the plates and formed a pool of water there. Thus, the moisture was re-adsorbed and there was no loss at those conditions. Three modifications of the schedule have been designed to overcome this condensation problem. These are shown in Table 4. In addition, the chamber was modified.

Table 4: Three Schedules for Drying Gelcast Parts

Schedule I

Segment	1	2	3	4	5	6	7
Rel Humidity	92	92	75	75	50	50	50
Temp. °C	25	25	25	25	25	25	25
Time, h	0.5	10	1	10	1	10	1
Next Segment	2	3	4	5	6	7	7

Schedule II

Segment	10	11	12	13	14	15	16	17	18
Rel Humidity	92	92	92	75	75	50	50	50	50
Temp. °C	25	35	35	35	35	35	35	25	25
Time, h	0.5	1	10	1	10	1	10	1	1
Next Segment	11	12	13	14	15	16	17	18	18

Schedule III

Segment	20	21	22	23	24	25	26	27	28	29
Rel Humidity	92	92	92	75	75	50	50	50	50	50
Temp. °C	25	35	35	35	35	35	50	50	25	25
Time, h	0.5	1	10	1	10	1	1	10	1	1
Next Segment	21	22	23	24	25	26	27	28	29	29

Thirteen runs have been completed on the drying of two thicknesses of alumina plates. Table 5 shows the details of the runs. It shows the premix solution used, the age of the slurry and the mass of water lost. More importantly, it shows the drying program schedule used in the runs: schedule I at 25°C, schedule II at 35°C and schedule III at 35°C and 50°C, respectively.

Table 5: Details of the Drying of Gelcast Alumina Plates

Run Number	Program Schedule	Size of plate	Premix	Age of slurry [days]	Wet Mass [g]	Dry Mass [g]	% of H ₂ O Lost
1	I	.5" x 4" x 4"	MAM/MBAM	4 days	330.0	283.1	98.0
5	I	.5" x 4" x 4"	MAM/PEG	7 days	336.7	290.7	94.1
3	II	.5" x 4" x 4"	MAM/MBAM	15 days	332.5	285.6	97.3
7	II	.5" x 4" x 4"	MAM/MBAM	1 day	331.9	284.2	98.9
6	II	.5" x 4" x 4"	MAM/PEG	10 days	336.5	294.9	85.2-cond
11	III	.5" x 4" x 4"	MAM/MBAM	4 days	331.1	283.7	98.8
9	III	.5" x 4" x 4"	MAM/PEG	5 days	329.0	285.4	91.4
2	I	1" x 4" x 4"	MAM/MBAM	8 days	683.8	583.2	101.4
10	I	1" x 4" x 4"	MAM/PEG	8 days	662.0	593.5	71.3
8	II	1" x 4" x 4"	MAM/MBAM	5 days	675.7	579.5	98.3
13	II	1" x 4" x 4"	MAM/PEG	2 days	666.5	594.2	74.8-crack
12	III	1" x 4" x 4"	MAM/MBAM	11 days	685.9	584.0	84.9

The 0.5" thick plates were all dried, losing over 90 % of the initial water content irrespective of the drying schedule except for run #6 where there was some condensation on the plate. At the 1.0" thick, plates gelcast in the MAM/PEG system only lost about 75% of their water content; one plate even cracked. The plates in the MAM/MBAM premix lost higher percentage of their water, although this has to be confirmed as the experimentation continues. The effect of the different schedules is yet to be seen.

The 0.5" plates from runs 1, 3, 5 and 7 were dried successfully without any cracking. However, their strengths have not been measured.

IV. Golden Technologies CRADA (S. D. Nunn)

A CRADA has been signed with Golden Technologies to evaluate the gelcasting of aluminum titanate to form exhaust port liners. The work plan includes development of an appropriate gelcasting slurry, casting of simple test shapes for firing and characterization, and casting of a more complex shape to demonstrate the process for the intended application.

With the determination of milling and firing conditions for obtaining high density aluminum titanate material completed, the final requirement for this project was the preparation of tubular gelcast samples for evaluation by Golden Technologies. After discussion with the principal investigator at Golden, it was determined that the most desirable tube dimensions would be about 1.25 in. outer diameter, 0.125 in. wall thickness, and 6.0 in. long. An appropriate mold was prepared and the aluminum titanate tubes were gelcast. After drying, five tubes were shipped to Golden for final evaluation of the use of the gelcasting process for fabricating these components.

V. Green Machining of Gelcast Ceramics (S. D. Nunn)

A new project has been initiated to study the green machining characteristics of gelcast ceramics. The machinable nature of gelcast materials was demonstrated more than two years ago, however, limited facilities were available for an in-depth evaluation. Recently, a computer controlled, 3-axis milling machine was acquired for the purpose of studying green machining and rapid prototyping. A CAD system on the computer is used to define part geometry. The file generated by the CAD system is then converted to code to drive the milling machine and produce the component. The software is also capable of recognizing certain file formats generated by other CAD systems and utilizing these files to generate the machine control code.

Preliminary evaluation runs have shown that the gelcast materials can be machined at very rapid speeds without damaging the ceramic green body. In tests of a gelcast alumina plate, a 0.25 in. diameter carbide tool was able to cut a 0.125 in. deep groove at speeds ranging from 20 to 150 in./min. without chipping or cracking the plate. In other tests, complex shapes have been machined with excellent surface finishes. Additional hardware components to rotate the workpiece while it is being milled have been received and are presently being installed on the system. These components will allow the use of simplified machining methods for producing axially symmetric parts. They will also give added capabilities for machining screw threads and forming complex 3-dimensional shapes. Evaluation of the capabilities and limitations of the milling machine and the green ceramics are in progress.

Tests are also underway to assess the capability of the CAM software to convert CAD files prepared using AutoCAD to machine code to drive the milling machine. New software has been received to convert scanned file formats to the necessary machine driver code on the 3-axis milling machine. File conversion will greatly enhance the flexibility of the system and eliminate the need to redraw files.

Status of Milestones

Milestone 114212 was completed on schedule.

Publications and Presentations

J-P. Maria, J. O. Kiggans, Jr., T. N. Tiegs, and S. D. Nunn, "Gelcasting of Sintered Reaction-Bonded Silicon Nitride for Improved Mechanical Properties," *Ceram. Eng. Sci. Proc.*, **16** [5] 1071-76 (1995).

S. D. Nunn, J. O. Kiggans, Jr., R. E. Simpson, II, and J-P. Maria, "Gelcasting of Silicon Compositions for SRBSN," Paper SXIX-62-95, presented at the 97th Annual Meeting of the American Ceramic Society, Cincinnati, OH, April 30 - May 3, 1995.

C. A. Walls, D. L. Barker, M. A. Janney, S. D. Nunn, and O. O. Omatete, "Gelcasting: A Net Shape Forming Process," Poster SXIXP-16-95, presented at the 97th Annual Meeting of the American Ceramic Society, Cincinnati, OH, April 30 - May 3, 1995.

D. L. Barker, M. A. Janney, S. D. Nunn, O. O. Omatete, and C. A. Walls, "Green Body Strength and Machining Characteristics of Gelcast Alumina," Poster SXIXP-18-95, presented at the 97th Annual Meeting of the American Ceramic Society, Cincinnati, OH, April 30 - May 3, 1995.

1.2.2 Silicon Nitride Matrix**Optimization of Silicon Nitride Ceramics**

K. J. Lee and T. Y. Tien

Objective/Scope

Silicon nitride ceramics with fiber-like β - Si_3N_4 grains will have higher fracture strength and toughness and better creep resistance. The fiber-like structure can be obtained by sintering the silicon nitride ceramics at high temperature under a nitrogen over-pressure. The mechanical properties can further be improved by controlling the size and the aspect ratio of the fiber like β - Si_3N_4 grains and the composition and nature of the grain boundary phase(s). In order to develop processing methods to optimize strength, toughness and creep resistance of monolithic silicon nitride ceramics, it is first necessary to have an accurate and reliable method to access the microstructure of the acicular β - Si_3N_4 grains. The major goal of this project is to evaluate and then assure the way of measuring grain sizes by comparing two different methods used by the group in Max-Planck-Institut of Materials Research in Germany and by the group in Michigan.

Technical Highlights

Samples were obtained from the group in Max-Planck-Institut. Compositions of all the samples are 85.81 wt% Si_3N_4 , 10.64 wt% Y_2O_3 , and 3.55 wt% Al_2O_3 . Samples were sintered at 1900°C under 10 MPa N_2 pressure for 10 min, 1 hr, 3 hr, and 6 hr. There are two series of samples with only difference being their starting powders. One is Ube-series which has a high α - Si_3N_4 content (Ube E10), and the other is Denka-series with high β - Si_3N_4 content (Denka SP). They are designated as sample ID: MP1-0, MP1-1, MP1-3, and MP1-6, respectively for Ube-series. Samples using Denka-series powders were designated as sample ID: MP2-0, MP2-1, MP2-3, and MP2-6, respectively.

The major goal of this investigation is to compare and evaluate the methods for measuring the size of the silicon nitride grains: Method 1 using SEM micrographs of individually disintegrated grains to measure grain sizes directly. Method 2 using SEM micrographs of polished section and then applying the statistical interpretation of 2-dimensional pictures to obtain final grain sizes and aspect ratio.

Method 1 has been carried out following usual procedure. Samples were chemically etched in KOH:NaOH and then they were ultrasonically vibrated to disintegrate the grains. Loose grains were collected on the filter paper for microscopic examination. Digital tablet was used for measuring the size of grains in SEM micrographs. Approximately near 1000 individual grains for each sample were measured. All the results were shown in Table 1. A typical size distribution in length direction is given in Figure 1 for both series. Log normal distribution was observed for all sintered specimens.

It was observed that the size (length) distribution became flat and broader as sintering time increased for the samples from Denka-series (β -rich) while the opposite was true for the samples from Ube-series (α -rich). Also the shape of distribution is narrower in Denka-series (β -rich) than Ube-series (α -rich). It can be explained by the fact that the nucleation of β particles in Ube-series (α -rich) takes place whereas only the growth of β grains happens in Denka-series (β -rich).

Method 1 has been carried out at Max-Planck-Institut and results will be compared in next report.

Status of Milestones

On schedule

Communications/Visit/Travel

None

Problems Encountered

None

Table 1. Results of grain size measurements by Method 1

Sample ID	Average Sizes(μm)		
	Length (L)	Width (W)	Aspect Ratio (AR)
MP1-0	4.63	0.71	6.71
MP1-1	5.20	0.84	6.29
MP1-3	6.79	1.09	6.24
MP1-6	8.29	1.39	5.96
MP2-0	2.57	0.63	4.11
MP2-1	4.09	0.87	4.66
MP2-3	6.99	1.14	5.94
MP2-6	6.62	1.24	5.82

Figure 1(a) and (b). Typical size distribution in length direction.

Microstructure Optimization of SRBSN

L.H. Qi, S.F. Kuang and T.Y. Tien

Objective/Scope

Sintered reaction bonded silicon nitride is one of the most cost effective method for producing silicon nitride ceramics in large quantities. This method involves the nitridation of the starting metallic silicon particle compacts and post nitridation sintering. The purpose of this project is to develop a process to produce SRBSN with minimum defects. This investigation is to obtain green compacts with uniform pore distribution. Nitridation process will also be optimized to produce uniform microstructure. Post nitridation sintering will also be studied to develop desirable morphology of the β -Si₃N₄ grains.

Technical Highlights:

In order to obtain the SRBSN with uniform microstructure and good properties, it is believed that green compacts of metallic silicon powders with narrow pore size distribution should be used. In previous work, we have reported the silicon powder with three groups of particle size distribution (A,B,C) were prepared. In this period, the effect of particle size distribution on the procedure of casting process and nitridation procedure were studied.

1. Optimization of pressure casting process

All slurries used in this study has 20vol%Si solid content using IPA plus 1[g(k-30)%gSi] as their organic solvents. The initial pressure used was 40 psi and followed by an increase in pressure of 5 psi minute. The maximum pressure used was 90 psi. Two processes to prepare slurry were studied to obtain slurry with better solid distribution (see Fig.1).

The filtration rate of slurry made with process (1) was higher than that of slurry made with process (2) under the same pressure casting condition. The green cake made with process (2) shows an obvious dividing line after drying. These results indicate that the solvent used could not stabilize the silicon powders. therefore it is believed that sedimentation experiment should be repeated to obtain finer powder separation.. These results also proved that changing the milling time in process(1) will affect the pressure casting time. Pressure casting time of 10 minutes gives the best pore size distribution in the green cake. If the pressure casting time is too short, such as 1 or 2 minutes, the density of cake will be low and pore size will be large (see Fig2).

2. Comparison of the pore size distribution of intruded compacts.

The green cake were placed in an open alundum crucible and nitrided in a graphite-element furnace under a flowing atmosphere of N₂. The following heating schedule was used:

10°C/min.	To	900°C	
0.5°C/min.	To	1200°C	hold 1hr.
0.5°C/min.	To	1350°C	hold 1hr.
0.5°C/min.	To	1450°C	hold 1hr.
10°C/min.	To	20°C	end.

The density of the green cake made from powder A, B and C was 92.7%, 97.6% and 91% respectively in the same nitriding condition. Lower the green density of the cake (powder B with narrow particle size distribution) can be intruded with the highest rate.

Their pore size distribution was measured and are shown in Fig 4. These results show that after nitration, the pore size of the nitride cake become small, but their pore size distribution become wider relative to the green cake.

Status of Milestones

On schedule

Communications/Visits/Travel

None

Problems Encountered

None

Publications

None

Fig.1 Slurries Preperation for pressure casting

(A)

(B)

Fig.2 The effect of Pressure Casting time on pore size distribution of green cakes

Fig.3 The effect of preparing process of slurry on filter rate during pressure casting

(A) Using silicon powder A

(B) Using silicon powder B

Fig. 4 The pore size distribution of the nitriding cake made from different silicon powders

(C) Using silicon powder C

Fig.4 The pore size distribution of the nitriding cake made from different silicon powders (cont)

Characterization of Grain Boundary Phases in Silicon Nitride Ceramics

I. M. Peterson and T. Y. Tien

Objective/Scope

The objective of this investigation is to develop silicon nitride ceramics with high flexural strength, high fracture toughness and superior creep resistance. The fiber-like structure of the β - Si_3N_4 grains can be obtained by sintering the silicon nitride ceramics at high temperature under high nitrogen pressure. The composition of the sintering additives will affect the microstructural development, grain boundary characteristics, and hence, the mechanical properties. The goal of this project is to synthesize and characterize the grain boundary phase and to understand the relationships between the nature of the grain boundary phase and the properties of silicon nitride ceramics. It is believed that with a thorough understanding of these relationships, ceramics with optimum mechanical properties can be obtained.

In previous reports, the boundary phases were synthesized separately and their properties were studied. The thermal expansion mismatch stresses between the grain boundary phase and the silicon nitride influenced the fracture toughness of the ceramic. However, the influence of thermal expansion mismatch stresses on the flexure strength of the ceramic was not known. In this report, the results of preliminary flexure strength tests are presented. The thermal expansion mismatch stress does not have a large effect on the flexure strength.

Technical Highlights

Two sets of silicon nitride powder batches were made. The first set contained silicon nitride with 4.2 wt % Al_2O_3 , 4.9 wt % SiO_2 and 1.65 wt % MgO . The second batch contained silicon nitride with 3.9 wt % Al_2O_3 , 4.6 wt % SiO_2 and 7.6 wt % BaCO_3 . The powder batches were attrition milled for three hours with silicon nitride media and isopropyl alcohol.

The powder was uniaxially cold pressed under 17 MPa into pellets which were 52 mm x 26 mm by 5.3 mm. The pellets were then isostatically cold pressed at 275 MPa. The pellets were sintered under 10 atmospheres of nitrogen for 3 hours at 1640°C, followed by three hours at 1840°C, followed by three hours at 1640°C. The specimens sintered to full density, but the shrinkage was non-uniform. The pellets were machined into 5 size A 4-pt bend specimens as described in MIL STD 1942A, without chamfered edges, and broken in 4-pt bending according to the standard. The fracture surfaces were examined using the SEM.

The shrinkage of the Mg-containing pellets was 26 % in the length direction, 24 % in the width direction and 12 % in the thickness direction. The shrinkage of the Ba-containing pellets was 26% in the length direction, 26 % in the width direction and 16% in the thickness direction. The fracture strengths of both the Mg-containing samples and the Ba-containing samples are shown in Figure 1. The wide distribution in fracture strengths is probably due to machining damage at the unchamfered edges of the sample. Both compositions showed an average fracture strength of about 840 MPa. SEM examination of the fracture surfaces revealed both intergranular and transgranular fracture.

These experiments demonstrate that the use of barium aluminosilicate sintering aids increased the fracture toughness of silicon nitride without decreasing the strength of the ceramic.

Status of Milestones

On schedule

Communications/Visits/Travel

None

Problems Encountered

None

Publications

L. M. Peterson and T. Y. Tien, Journal of the American Ceramic Society, 78 [7] 1977-79

L. M. Peterson and T. Y. Tien, Journal of the American Ceramic Society, 78 [9] 2345-52

Figure 1. The thermal expansion coefficient of the grain boundary phase does not exhibit a large effect on the flexure strength of silicon nitride

Microstructure Design of Si_3N_4

S. F. Kuang and T. Y. Tien

Objective/Scope

Liquid-phase sintering technique is most often used for the densification of Si_3N_4 materials. The presence of the remaining grain boundary phase after sintering will degrade the high temperature properties of these materials. α' - β' -SiAlON composites can be developed through transient liquid phase sintering which will not contain liquid phase after densification. In this process, the transient liquid is completely reacted and transformed into α' -SiAlON solid phase.

The objective of this task is to design a material, which could form sufficient liquid during densification and part of this liquid will be consumed after the densification. Part of the liquid will remain after densification which will help to develop of desirable β - Si_3N_4 morphology.

Technical Highlights:

Phases $2\text{Si}_3\text{N}_4 \cdot \text{La}_2\text{O}_3$ and $\text{Si}_3\text{N}_4 \cdot \text{Nd}_2\text{O}_3$ (s.s.) are compatible with $(\alpha' + \beta')$ -Sialon. Both of these compounds have good oxidation resistant at high temperature. Two systems were chosen for these studies: (1) the Si_3N_4 -AlN- Nd_2O_3 system, we changed the content of AlN while keeping the $\text{Si}_3\text{N}_4/\text{Nd}_2\text{O}_3$ ratio constant. (2) the Si_3N_4 -AlN- Nd_2O_3 - La_2O_3 system, we changed the content of grain boundary phase $\text{Si}_3\text{N}_4 \cdot \text{La}_2\text{O}_3$ while keeping the α'/β' ratio constant. Relationship between composition, densification process, microstructure and mechanical properties of samples will be studied. In this report, density, phase composition after sintering and microstructure development of sample in system (1) will be reported.

1. Density

Four compositions (see table 1 in June 1995's bimonthly report) were hot pressed at 1780C under 1 ATM nitrogen with holding time of 0.5, 1, 2 and 4 hours. Pressure was released after 1 hour and followed by holding without pressure. Densities of samples are shown in table 1. All of compositions, except composition A, reached full density within 30 minutes. Sample A is the only composition, which does not contain AlN. Composition A which does not contain liquid after sintering makes the densification difficult.

2. Phase composition

Fired samples were pulverized and analyzed with X-ray diffraction. Results are shown in Table 1. Sample A with holding time of 30 minutes contains unreacted α - Si_3N_4 . H-phase ($\text{Nd}_5(\text{SiO}_4)_3\text{N}$) was crystallized during cooling which is because of the exist of the oxidation layer on the surface of Si_3N_4 starting powder. The same reason caused the crystallization of K-phase (NdSiO_2N) from sample B. H-phase is oxygen-rich than K-phase.

It is interesting to point out that α' / β' ratio decreased with increasing of holding time at 1780C. It is known that α' -Sialon is stable at higher temperature and unstable at lower temperature. Our results showed that even at high temperature α' -Sialon is not stable after

long holding time. This character of α' -Sialon makes it possible for us to adjust microstructure of α' - β' -Sialon composites through changing the holding time.

3. Microstructure

SEM micrographs of samples sintered at 1780°C with holding time of 2 hours are shown in Fig. 1. Sample A contains only β - Si_3N_4 and has a homogenous microstructure. α' -Sialon grain size decreased with increasing of α'/β' -Sialon ratio, i.e. decreased from sample B to D. Aspect ratio of β' -Sialon seems increased at first with increasing of α'/β' ratio and then decreased. Sample B has the largest grain size. Excellent mechanical property is expected from sample C, whose microstructure contains high aspect ratio of β' -Sialon and fine grains of α' -Sialon.

Status of Milestones

none

Communications/Visits/Travel

None

Problems Encountered

None

Publications

None

Table 1. Density of sample and phase composition and α'/β' ration according to X-ray analyze

Sample	Holding time at 1780°C	Density (g/cm ³)	Phase composition	$\alpha'/(\alpha'+\beta')$ (theoretical)	$\alpha'/(\alpha'+\beta')$ (experimental)
A	0.5h	3.22	$\alpha+\beta$	0	0
	1h	3.28	β	0	0
	2h	3.27	$\beta + \text{H}$	0	0
	4h	3.27	$\beta + \text{H}$	0	0
B	0.5h	3.27	$\alpha'+\beta'$	0.14	0.19
	1h	3.27	$\alpha'+\beta'$	0.14	0.15
	2h	3.27	β'	0.14	0
	4h	3.27	$\beta' + \text{K}$	0.14	0
C	0.5h	3.26	$\alpha'+\beta'$	0.29	0.45
	1h	3.26	$\alpha'+\beta'$	0.29	0.38
	2h	3.26	$\alpha'+\beta'$	0.29	0.15
	4h	3.26	$\alpha'+\beta'$	0.29	0.03
D	0.5h	3.26	$\alpha'+\beta'$	0.40	0.47
	1h	3.26	$\alpha'+\beta'$	0.40	0.40
	2h	3.26	$\alpha'+\beta'$	0.40	0.28
	4h	3.26	$\alpha'+\beta'$	0.40	0.07

K-phase: NdSiO_2N H-phase: $\text{Nd}_5(\text{SiO}_4)_3\text{N}$ 6.0 μm

(Sample A, X 5000)

6.0 μm

(Sample B, X 5000)

6.0 μm

(Sample C, X 5000)

6.0 μm

(Sample D, X 5000)

Fig 1. SEM micrograph of α' -Sialon plus β' -Sialon two-phase material. Samples being hot-pressed at 1780C for 2hrs.

Development of Silicon Nitride Ceramic Materials With Elongated Grain Microstructures Exhibiting High Fracture Toughness, Phase II
H. Yeh, J. Wimmer, C-W Li, and J. Goldaker (AlliedSignal Inc.)

Objective/Scope

Under Phase I, an *in situ* reinforced (ISR) silicon nitride material (AS800) with elongated grain microstructure has been developed. It was accomplished through composition and processing optimization of a material which had initially been developed at AlliedSignal. The objective of this follow-on effort (Phase II) is to expand the AS800 material property database to meet the requirements for heat engine applications and to build on Phase I results to further improve material properties and processing. To accomplish this objective, a three-task effort shall be conducted over a two-year period. The technical effort was initiated in March 1994.

The AS800 material developed under Phase I (crystallized Composition 2) shall be the baseline for Phase II. Based on the property values measured under Phase I, AS800 is suitable for heat engine applications. However, in order for the material to be considered for these applications, a more comprehensive data base is required for life prediction and other design needs. A typical test matrix recommended by an engine company shall be conducted under Task 1--Expanded Characterization of AS800. The test matrix includes more comprehensive testing of mechanical and thermal properties from room temperature to 2500°F. In addition, an established cyclic oxidation durability test will also be conducted to determine the long-term durability of the material in a simulated gas turbine environment. Most of the tests shall be performed on the baseline material using fully machined test bars, which represent the bulk properties of the material.

For net-shape formed components, the as-processed surface properties are critical. Due to its rougher surface texture and the exposure to the sintering environment, the as-processed surface properties of a silicon nitride part are known to be inferior to the bulk properties. Under Task 2--As-Processed Material Surface Property Improvement, the baseline material surface property shall be characterized and then various techniques shall be investigated to improve the as-processed surface properties.

Although AS800 is densified by a relatively economical technique (gas pressure sintering), compared to glass encapsulation HIP or hot-pressing, there is a need to further reduce the cost of densification. The densification process developed under Phase I was primarily aimed at achieving the property goals, without addressing fabrication cost reduction issues. Under Task 3--Lower Cost Fabrication, the green processing procedures and the densification process shall be scaled up and further optimized to reduce the cost without degrading the properties.

TASK 1--EXPANDED CHARACTERIZATION OF AS800

The objective of this task is to conduct a comprehensive test matrix of mechanical properties for crystallized Composition 2 after demonstration of a reproducible process. The test matrix includes tensile, flexural strengths, tensile stress rupture, and toughness from RT through 2500°F, and cyclic oxidation durability test in a simulated engine environment. In addition, elastic and thermal properties from RT through 2500°F shall be measured.

All the required property results were reported in the last two bi-monthly reports except the tensile stress rupture, which were completed during this reporting period. Table 1 summarizes the tensile stress rupture results. Both tensile fast fracture strength and tensile stress rupture testings were conducted at University of Dayton Research Institute (UDRI) and a detailed discussion of the results can be found in their report in this issue of "Ceramic Technology Project Semiannual Progress Report".

Table 1 - Tensile Stress Rupture Test Results

Specimen I.D.	Temp (°F/°C)	Applied Stress (ksi/MPa)	Life (hour)	Fracture Origin
170-2-10	2200/1204	45.7/315	100	Surface
170-2-11	2200/1204	45.7/315	0.02	Volume
170-2-12	2200/1204	45.7/315	0.3	Surface
170-2-14	2200/1204	45.7/315	0.1	Volume
330-1-19	2200/1204	45.7/315	0.3	Surface
460-2-20	2200/1204	34.4/237	100	Volume @ 493 MPa
350-1-14	2200/1204	34.4/237	100	Volume @ 494 @ EG
353-1-7	2200/1204	34.4/237	27.4	?
460-2-18	2200/1204	45.7/315	19.7	Volume
460-2-19	2200/1204	45.7/315	14.7	Volume w/SCG
172-2-6	2300/1260	42.2/291	DL	Surface
172-2-7	2300/1260	42.2/291	DL	Surface
172-2-8	2300/1260	42.2/291	DL	Surface
172-2-9	2300/1260	42.2/291	DL	Surface
330-1-20	2300/1260	31.6/218	0.2	Surface
462-2-28	2300/1260	42.2/291	1	Volume
462-2-30	2300/1260	31.6/218	26.3	Volume
462-2-29	2300/1260	31.6/218	5.2	Volume w/SCG
462-2-26	2300/1260	42.2/291	37.5	? w/SCG
462-2-27	2300/1260	42.2/291	1.7	? w/SCG
519-1-15	2300/1260	21.2/146	100	Load raised to 219 Mpa, failed 0.7 h
519-3-23	2400/1316	20.2/139	12.5	-

Note: DL = Failed during loading; EG = Elongated grain; SCG = Slow crack growth

**Table 1 - Tensile Stress Rupture Test Results
(Continued)**

Specimen I.D.	Temp (°F/°C)	Applied Stress (ksi/MPa)	Life (hour)	Fracture Origin
519-3-26	2400/1316	20.2/139	11.75	-
519-3-24	2400/1316	20.2/139	5.1	? w/SCG
519-3-25	2400/1316	20.2/139	8.4	? w/SCG
519-1-0	2400/1316	20.2/139	4.4	-
514-2-7	2400/1316	20.2/139	100	-
520-2-35	2400/1316	20.2/139	6.6	-
520-1-30	2400/1316	20.2/139	2.6	-
168-1-24	2500/1371	30.5/210	DL	Volume
168-1-25	2500/1371	30.5/210	DL	?
168-1-26	2500/1371	30.5/210	DL	Volume
168-1-27	2500/1371	30.5/210	DL	-
353-1-48	2500/1371	30.5/210	0.1	Surface
460-2-16	2500/1371	31.6/218	1.2	Volume
460-2-17	2500/1371	31.6/218	0.1	Surface
520-3-39	2500/1371	20.3/140	0.8	-
519-1-16	2500/1371	20.3/140	1.4	-
520-2-32	2500/1371	20.3/140	5.5	-

Note: DL = Failed during loading; EG = Elongated grain; SCG = Slow crack growth

TASK 2 -- AS-PROCESSED SURFACE PROPERTY IMPROVEMENT

The objective of this task is to improve the as-processed surface properties of crystallized Composition 2, by various processing techniques to meet the mechanical property goals. Due to the large number of variables to be explored, this effort is conducted using the small laboratory scale equipment to fabricate the samples from green through sintering and crystallization.

Experimental samples achieving 99.5% theoretical density or higher were characterized. For a quick initial screening, room temperature flexural strength was measured. On selected samples, additional characterization were conducted which included elevated temperature flexural strength, stress rupture, and indentation toughness.

As discussed in the last three bi-monthly reports, one of the more promising techniques identified, in terms of as-processed surface properties and viability to mass production, was applying a coating on the green plate surfaces prior to sintering. The major parameter investigated was coating composition. During this reporting period, the focus was to determine an optimum composition based on the as processed surface

properties. Table 2 lists the strength results measured to date. Two coating compositions (A and B) were repeated to evaluate reproducibility.

Table 2: As-processed Surface Strength
(ksi)

Sample	Coating Composition	25°C	1200°C	1300°C	1370°C
SN572	A	104.4±5.1 (10)*	83.3±7.2 (3)	67.8±6.7 (3)	70.1±3.4 (3)
SN579	A	108.0±9.5 (15)	74.7±9.4 (3)	70.1± 2.7 (2)	70.7±5.8(3)
SN578	B	105.1±9.8 (10)	76.2±5.3 (3)	NA	NA
SN575	B	112.3±6.3 (20)	71.2 ± 11.8 (2)	71.4 ± 3.6 (2)	61.2± 4.6 (2)
SN577	C	101.7±4.5 (3)	80.1± 4.8 (2)	73.9±7.5 (3)	67.7±11.7 (3)
SN586	D	95.1±7.3 (10)	95.4 (1)	77.8±5.4 (2)	75.9±4.1 (2)

* (n), where n is number of test bars measured.

Note that the room temperature strengths coating compositions investigated are very close, suggesting that the room temperature strength is less sensitive to coating composition. However, the elevated temperature strength is more sensitive to coating composition, although only a small number of test bars were tested at each temperature for each sample. Also, the overall strengths of samples coated with composition A coating (samples SN572 and SN579) appear to be higher and more reproducible than the other two. Preliminary 4-point bend stress rupture testing of one of the Composition A sample (SN579) indicates that its as-processed surface could survive > 100 hours under 65 ksi at 1200°C and under 45 ksi at 1300°C, respectively, which are approaching to the goals of 70 ksi and 50 ksi, respectively. One test bar from SN586 (Composition D coating) has been stress-rupture tested at 1300°C under 55 ksi and survived 100 hours. Based on the results, an optimized composition has been selected and two plates have been fabricated. These two plates are now being machined into the required number of test bars for the test matrix to compare with the property goals. The results will be reported in the next report, and this will conclude this task.

TASK 3 - LOWER COST FABRICATION

The objective of this task is to lower the fabrication cost by scaling up the green forming process (primarily milling/slip preparation process) and the sintering/crystallization process from laboratory scale to production scale. Milling/slip preparation process will be scaled up by a factor of six (6) or more; sintering capacity will be increased by a factor of ten (10) or more from a small size furnace to a new production size furnace.

The results to date have successfully demonstrated that the slip preparation/milling procedure can be scaled up by a factor of six (6), and plates of various sizes can be consistently sintered in a production furnace, with ten (10) times capacity of the baseline furnace, to full density (> 99.5% theoretical) with similar strengths, reported in previous reports. To evaluate process reproducibility in the scaled up process, a processing matrix has been conducted. The variables included in the matrix are : powder lot (Lots I and II, both within the established powder specification), presintering run (Runs A and B), sintering run payload (Runs L, low, and H, high), and crucible (or part) location in sintering (Locations 1, 2, 3, 4 and 5, from bottom to top of the sintering furnace). The processing matrix has been completed through sintering, and all sintered plates have been crystallized in one run using the standard thermal cycle. The responses for the processing matrix include material density and properties. All crystallized plates achieved the required >99.5% theoretical density. Therefore the responses for the processing matrix will only be material properties. Strength properties will be used to evaluate the response. Flexural test bars are in the process of being machined for both room temperature and elevated temperature testing to be conducted in the next reporting period.

Powder Lot	I										II									
	5 Slip Batches										5 Slip Batches									
Pre-Sintering Run	A					B					A					B				
Sintering Run Payload	L		H			L		H			L		H			L		H		
Crucible Location	1	2	3	4		1	2	3	4		1	2	3	4		1	2	3	4	

Figure 1 - Processing Matrix

Communications/Visits/Travel

None

Problems Encountered

None

Publications

None

1.2.3 Oxide Matrix

W.B.S. ELEMENT 1.2.3.1

DISPERSION TOUGHENED CERAMIC COMPOSITE

T. N. Tiegs, F. C. Montgomery, P. A. Menchhofer, D. L. Barker and D. W. Coffey
Oak Ridge National Laboratory
Oak Ridge, TN 37831

Objective/Scope

Initially this work involved development and characterization of SiC whisker-reinforced ceramic composites for improved mechanical performance. To date, most of the efforts involving SiC whisker-reinforced alumina, mullite, silicon nitride, and sialon have been completed. In addition, studies of whisker-growth processes were initiated to improve the mechanical properties of SiC whiskers by reducing their flaw sizes and, thereby, improving the mechanical properties of the composites. Currently, in-situ acicular grain growth is being investigated to improve fracture toughness of silicon nitride materials.

Technical Highlights

In-Situ Toughening of Silicon Nitride by Microstructure Development

Characterization and Modification of As-Fabricated Surfaces Formed During Gas Pressure Sintering (GPS) - In the previous years, studies were done to reduce surface reactions layers during densification and to optimize the GPS process for silicon nitride. These processing techniques developed were used to fabricate silicon nitride materials to maximize the mechanical properties of the as-sintered surfaces. The studies included control of the sintering parameters to maximize bulk properties and minimizing the surface reaction layer. To further reduce the need for machining, investigations of the relationships between green machining, bisque machining and final machining on the mechanical properties were performed. In addition, the effects of post-sintering surface treatments, such as oxidation, inert gas heat-treatment and abrasive cleaning (blasting, vibratory agitation and rotary tumbling) were studied. For each of the conditions, two compositions of silicon nitride with different intergranular phases were tested. These compositions are Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 , and Si_3N_4 - $\text{Sr}_2\text{La}_4\text{Yb}_4(\text{SiO}_4)_6\text{O}_2$ (at 8 equivalent % oxygen).

Because a number variables were to be studied, a Taguchi experimental array was formulated to assess the impact of each of the surface processing variables on the final properties after gas-pressure sintering. The experimental array with the variables is shown in Table 1. The green body surface were tested under four conditions: as-cast (smooth), as-cast (rough), machined (coarse grit) and machined (fine grit). All of the samples were formed using gel-casting with a solids loading of ~43 vol. % and then isopressed to a green density of ~52 %. The as-cast (smooth) surfaces were cast against glass plates, while the as-cast (rough) surfaces were cast against 60 grit sand paper. The machined surfaces used gel-cast and isopressed specimens and then ground with either a 220 grit diamond wheel (smooth) or a 40 grit alumina wheel (rough). Approximately 1-2 mm were removed during the green machining process. The effect of machining after bisque firing was assessed by firing the samples to ~1400°C to slightly sinter the samples and give them some strength. Machining at this stage was done with a 220 grit diamond wheel. During sintering, the surfaces was either exposed to the nitrogen gas atmosphere inside of the sintering crucible or had a SiC setter plate adjacent to the test surface. Post-sintering surface treatments consisted of either a grit tumble operation, sandblasting or diamond wheel machining. Post-sintering thermal treatments using either oxidizing or inert gas atmospheres were examined. In addition, the effect of a thermal shock treatment was determined.

After the samples had been fabricated through the 'green' and bisque-fired stages, the as-fabricated surfaces were characterized for surface roughness using a laser profilometer. The results are summarized in Table 2. The values of R_a indicate the variance about the mean and the R_t values are a measure of the difference in the peak-to-valley of the surface roughness. As shown, the 'green' surface roughness is lowest for the as-fabricated materials where the casting was done against a glass plate and roughest for the as-fabricated where the casting was done against a roughened surface. Three dimensional plots of the different types of surfaces are shown in Figs. 1-4. The machining grooves are clearly visible along the length of the specimens.

The samples were fabricated by gas-pressure sintering. In previous years, studies have shown that surface reactions occur during sintering and that these reactions can cause weight changes as the material densifies. Table 3 shows the change in weight caused by the sintering process and the final density of the test samples prepared for this study. The samples sintered using $Y_2O_3-Al_2O_3$ as a sintering aid have a higher average density when SiC was used as the setter material than when BN was used. Additionally, when setting on BN during sintering, the weight loss and the final density both were dependent on the position of the sample within the crucible.

After sintering, the test surfaces were again characterized by measuring surface roughness parameters using a laser profilometer. Table 4 shows the effects that densification and post-sintering processing have on the surface roughness. Roughness measurements on the $Si_3N_4-SrLa_4Yb_4(SiO_4)_6O_2$ samples are not yet complete. The $Si_3N_4-6\%Y_2O_3-2\%Al_2O_3$ samples are being used to develop the procedures for the surface treatments. To simulate the scouring action obtained by tumbling, the appropriate samples were placed in individual bottles which were slightly larger than the width of the samples. The bottles were filled about half full with 2 - 2.4 mm B_4C grit and rolled on a standard laboratory mill roller. Grit blasting was accomplished using 240 grit SiC powder.

The sintering process increased the surface roughness of the samples except for the rough cast samples which were not machined before sintering. The roughness of samples setting on SiC plates increased from about 1 μm to about 2 μm ($R_{a,c} = 0.8$ mm). The roughness of samples setting on BN increased to about 1.5 μm , but, as explained below, the base roughness was obscured by the formation of a thick coating. Microscopic examination of the samples showed that the some porosity developed in the $Si_3N_4-6\%Y_2O_3-2\%Al_2O_3$ samples mainly in areas where the samples were not contacting the setter. For example, TRSN-52-21, and TRSN-52-22 were sintered with the test surface resting on the BN setter. The opposite surface, which was exposed to the furnace atmosphere, developed ~50 μm diameter holes (shown in Figure 5) which increased the maximum peak-to-valley distance (R_t in Table 4) of the surface to about 70 μm .

The $Si_3N_4-6\%Y_2O_3-2\%Al_2O_3$ surfaces which contacted BN plates during GPS generally were covered with a soft, white, adherent coating after sintering. This coating could easily be removed by grit blasting, but could not be removed by gentle brushing. When the coating was relatively thick, the surface roughness on the coating was substantially smoother than the underlying surface. This is evident from Table 4 when comparing the as-sintered roughness of sample TRSN-52-10 with the roughness of its grit-blasted surface. Figure 6 is a photograph of the grit blasted surface of TRSN-52-4 taken at 20x through a stereo microscope. Figure 6 shows the demarcation between an area which had been setting on BN during sintering, and an area that had not rested on the setter. The roughened surface caused by contact with the setter is clearly evident.

Initial results on the mechanical properties for the various surface treatments are shown in Table 5 for the samples of the Si_3N_4 -6% Y_2O_3 -2% Al_2O_3 composition. The post-sintering surface treatments are still under way.

Cooperative Research and Development Agreement (Materials and Electrochemical Research Corp.) -

The Cooperative Research and Development Agreement (CRADA) with Materials and Electrochemical Research Corp. (MER) is currently in progress. Materials were made with different starting α/β - Si_3N_4 ratios and with the addition of sintering aids as coatings instead of powders. Additional samples have been sintered by GPS using the optimum densification parameters developed for high toughness materials in the ORNL program. The densification results are shown in Table 6. These samples are currently being machined into test bars for mechanical property testing.

As shown, high densities were achieved for all of the samples fabricated at ORNL and containing up to 50% β - Si_3N_4 . The lowest densities were observed for samples containing the Shin-etsu β - Si_3N_4 and the material with the Y_2O_3 - SiO_2 plus the β - Si_3N_4 . The materials from MER containing the β - Si_3N_4 powder from Shin-etsu also showed low densities.

Status of Milestones

Milestone 123116, Development of high toughness silicon nitride with optimized as-sintered surface properties was not completed. Some additional data to complete the test matrix is required and will be done in the next reporting period

Communications/Visits/Travel

Travel by T. N. Tiegs and F. C. Montgomery on April 30-May 3, 1995 to the American Ceramic Society Annual Meeting in Cincinnati, OH.

Problems Encountered

Problems with the temperature control and pressure regulation valve on the gas pressure sintering furnace has caused some delay in fabrication of the samples for CRADA with MER Corp.

Publications

None.

Table 1. Experimental array to identify important surface property variables affecting the final properties of the sintered silicon nitride materials. The design is a L_{16} (4^5) with machine after bisque firing and surface sintering condition dummy-loaded to two variables.

Test No.	Surface Processing Variables				
	Green Surface Condition	Machine After Bisque Firing	Surface Sintering Condition	Post-Sinter Surface Treatment	Post-Sinter Thermal Treatment
1	As-Cast (Smooth)	No	Exposed to Atmosphere	None	None
2	As-Cast (Smooth)	No	Exposed to Atmosphere	Grit Tumble	Oxidize
3	As-Cast (Smooth)	Yes	Adjacent to SiC Setter	Sandblast	Thermal Shock
4	As-Cast (Smooth)	Yes	Adjacent to SiC Setter	Machine	Inert Gas Heat-treat
5	As-Cast (Rough)	No	Exposed to Atmosphere	Sandblast	Inert Gas Heat-treat
6	As-Cast (Rough)	No	Exposed to Atmosphere	Machine	Thermal Shock
7	As-Cast (Rough)	Yes	Adjacent to SiC Setter	None	Oxidize
8	As-Cast (Rough)	Yes	Adjacent to SiC Setter	Grit Tumble	None
9	Machined (Coarse Grit)	No	Adjacent to SiC Setter	Machine	Oxidize
10	Machined (Coarse Grit)	No	Adjacent to SiC Setter	Sandblast	None
11	Machined (Coarse Grit)	Yes	Exposed to Atmosphere	Grit Tumble	Inert Gas Heat-treat
12	Machined (Coarse Grit)	Yes	Exposed to Atmosphere	None	Thermal Shock
13	Machined (Fine Grit)	No	Adjacent to SiC Setter	Grit Tumble	Thermal Shock
14	Machined (Fine Grit)	No	Adjacent to SiC Setter	None	Inert Gas Heat-treat
15	Machined (Fine Grit)	Yes	Exposed to Atmosphere	Machine	None
16	Machined (Fine Grit)	Yes	Exposed to Atmosphere	Sandblast	Oxidize

Table 2. Summary of results on surface roughness of silicon nitride specimens prior to gas-pressure-sintering.

Sample ID	Sintering Aid Type	Green Surface Condition	Surface Roughness of Green Surface		Surface Roughness of Bisque Fired Surface		Surface Roughness After Machining of Bisque Fired Surface	
			Ra(μm)	Rt(μm)	Ra(μm)	Rt(μm)	Ra(μm)	Rt(μm)
TRSN-52-21	Y ₂ O ₃ -Al ₂ O ₃	as-cast smooth	0.86 $\pm$ 0.24	9.04 $\pm$ 4.20	0.78 $\pm$ 0.07	9.86 $\pm$ 2.85		
TRSN-52-22	Y ₂ O ₃ -Al ₂ O ₃	as-cast smooth	0.80 $\pm$ 0.14	7.86 $\pm$ 1.75	0.84 $\pm$ 0.19	8.19 $\pm$ 1.27		
TRSN-52-J	Y ₂ O ₃ -Al ₂ O ₃	as-cast smooth	--	--	--	--	1.12 $\pm$ 0.06	10.7 $\pm$ 0.5
TRSN-52-19	Y ₂ O ₃ -Al ₂ O ₃	as-cast rough	52.3 $\pm$ 6.3	364 $\pm$ 27	--	--	1.17 $\pm$ 0.06	11.1 $\pm$ 0.9
TRSN-52-14	Y ₂ O ₃ -Al ₂ O ₃	as-cast rough	51.7 $\pm$ 7.2	394 $\pm$ 47	51.6 $\pm$ 9.6	387 $\pm$ 58		
TRSN-52-9	Y ₂ O ₃ -Al ₂ O ₃	fine grit*	1.02 $\pm$ 0.06	10.5 $\pm$ 1.5	1.13 $\pm$ 0.45	13.2 $\pm$ 10.9		
TRSN-52-3	Y ₂ O ₃ -Al ₂ O ₃	fine grit*	1.16 $\pm$ 0.09	12.7 $\pm$ 4.9	1.08 $\pm$ 0.09	11.8 $\pm$ 2.3		
TRSN-52-10	Y ₂ O ₃ -Al ₂ O ₃	fine grit*	--	--	--	--	1.23 $\pm$ 0.07	11.2 $\pm$ 0.8
TRSN-52-I	Y ₂ O ₃ -Al ₂ O ₃	coarse grit*	2.29 $\pm$ 0.44	19.3 $\pm$ 1.8	2.31 $\pm$ 0.31	20.3 $\pm$ 2.4		
TRSN-52-G	Y ₂ O ₃ -Al ₂ O ₃	coarse grit*	1.71 $\pm$ 0.25	16.6 $\pm$ 2.7	1.64 $\pm$ 0.25	17.2 $\pm$ 4.2		
TRSN-52-F	Y ₂ O ₃ -Al ₂ O ₃	coarse grit*	--	--	--	--	1.23 $\pm$ 0.07	11.6 $\pm$ 1.3
TRSN-53-E	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	as-cast smooth	0.68 $\pm$ 0.07	7.58 $\pm$ 1.61	0.75 $\pm$ 0.04	7.70 $\pm$ 0.73		
TRSN-53-13	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	as-cast smooth	0.61 $\pm$ 0.11	7.20 $\pm$ 2.24	--	--		
TRSN-53-K	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	as-cast smooth	--	--	--	--	1.27 $\pm$ 0.10	12.4 $\pm$ 1.1
TRSN-53-17	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	as-cast rough	51.1 $\pm$ 3.3	396 $\pm$ 43	52.6 $\pm$ 2.9	447 $\pm$ 91	1.06 $\pm$ 0.05	9.98 $\pm$ 0.66
TRSN-53-20	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	as-cast rough	51.3 $\pm$ 3.1	363 $\pm$ 26	53.5 $\pm$ 2.9	388 $\pm$ 36		
TRSN-53-C	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	fine grit*	1.20 $\pm$ 0.12	13.0 $\pm$ 2.8	1.11 $\pm$ 0.11	12.8 $\pm$ 1.7		
TRSN-53-F	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	fine grit*	1.26 $\pm$ 0.21	13.1 $\pm$ 2.2	1.26 $\pm$ 0.19	12.3 $\pm$ 1.5		
TRSN-53-H	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	fine grit*	--	--	--	--	1.27 $\pm$ 0.09	13.2 $\pm$ 1.9
TRSN-53-J	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	coarse grit*	2.61 $\pm$ 0.26	22.2 $\pm$ 2.5	2.62 $\pm$ 0.28	22.3 $\pm$ 2.9		
TRSN-53-I	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	coarse grit*	2.53 $\pm$ 0.22	22.6 $\pm$ 1.5	--	--		
TRSN-53-B	Yb ₂ O ₃ -SrCO ₃ -La ₂ O ₃	coarse grit*	--	--	--	--	1.20 $\pm$ 0.09	10.8 $\pm$ 0.8

*Machined surface.

Table 3. Weight changes and density after sintering.

Sample ID	Setter Type	Position in Crucible(c)	Weight Loss (%)	Sintered Density			
				(g/cm ³)	(% T. D.)	Average	Std. Dev.
TRSN-52-3(a)	SiC	1	-3.3%	3.25	99.6%	99.5%	0.3%
TRSN-52-I	SiC	1	-3.8%	3.23	99.2%		
TRSN-52-9	SiC	2	-3.3%	3.25	99.7%		
TRSN-52-J	SiC	2	-4.1%	3.25	99.6%		
TRSN-52-G	SiC	3	-3.2%	3.25	99.6%		
TRSN-52-2	SiC	3	-4.8%	3.25	99.7%		
TRSN-52-19	SiC	4	-4.5%	3.23	99.1%		
TRSN-52-20	SiC	4	-4.5%	3.23	99.0%		
TRSN-52-10	BN	1	-2.5%	3.19	97.9%	98.5%	0.7%
TRSN-52-F	BN	1	-2.6%	3.19	97.9%		
TRSN-52-D	BN	2	-2.3%	3.19	97.9%		
TRSN-52-14	BN	2	-1.8%	3.19	97.9%		
TRSN-52-K	BN	2	-2.1%	3.20	98.1%		
TRSN-52-4	BN	3	-3.1%	3.23	99.1%		
TRSN-52-H	BN	3	-3.0%	3.22	98.8%		
TRSN-52-21	BN	4	-4.0%	3.24	99.4%		
TRSN-52-22	BN	4	-3.8%	3.24	99.4%		
TRSN-53-J(b)	SiC	1	-2.2%	3.54	100.0%	99.8%	0.2%
TRSN-53-K	SiC	1	-3.0%	3.53	100.0%		
TRSN-53-G	SiC	2	-2.3%	3.53	99.6%		
TRSN-53-G1	SiC	2	-3.0%				
TRSN-53-17	SiC	2	-4.1%	3.53	99.8%		
TRSN-53-I	SiC	3	-1.8%	3.51	99.6%		
TRSN-53-I1	SiC	3	-1.6%	3.52	99.9%		
TRSN-53-D	SiC	3	-3.0%	3.53	99.9%		
TRSN-53-D1	SiC	3	-2.8%	3.53	100.0%		
TRSN-53-F	SiC	4	-4.2%	3.54	99.6%		
TRSN-53-16	SiC	4	-4.8%	3.54	99.8%		
TRSN-53-20	BN	1	-1.0%	3.49	98.5%	99.2%	0.5%
TRSN-53-14	BN	1	-1.3%	3.53	99.4%		
TRSN-53-14B	BN	1	-1.7%	3.53	99.4%		
TRSN-53-C	BN	2	-3.5%	3.53	99.6%		
TRSN-53-E	BN	2	-1.8%	3.53	99.4%		
TRSN-53-B	BN	3	-1.8%	3.53	99.4%		
TRSN-53-13	BN	3	-1.5%	3.52	99.4%		
TRSN-53-H	BN	4	-3.4%	3.50	98.2%		
TRSN-53-A	BN	4	-2.1%	3.51	99.0%		
TRSN-53-18	BN	5	-3.9%	3.54	99.7%		
TRSN-53-15	BN	5	-2.5%	3.52	99.08%		

(a) TRSN-52 Samples: Sintering Aid $Y_2O_3-Al_2O_3$ (b) TRSN-53 Samples: Sintering Aid $Yb_2O_3-SrCO_3-La_2O_3$

(c) Position numbers identify the sample layer from the bottom of each crucible

Table 4. Summary of Surface Roughness Measurements after Processing and Post-Sintering Surface Treatments

Sample ID	Location of Measurement		Sintering Sinter Material	Surface Roughness After Machining of Bisque Fired Surface		Surface Roughness As-Sintered		Surface Roughness Tumbled 4 hr		Surface Roughness Tumbled 23.5 hr		Surface Roughness Grit Blasted	
		Green Surface		Ra(um)	Rt(um)	Ra(um)	Rt(um)	Ra(um)	Rt(um)	Ra(um)	Rt(um)	Ra(um)	Rt(um)
TRSN-52-21 ^(a)		smooth cast	BN	na ^(a)	na ^(a)	2.48±0.63	26.2±7.2						
TRSN-52-21	white coating	smooth cast	BN	na ^(a)	na ^(a)	2.26±1.76	19.9±14.0						
TRSN-52-21	backside	smooth cast	none	na ^(a)	na ^(a)	4.81±1.69	68.4±23.9						
TRSN-52-22		smooth cast	BN	na ^(a)	na ^(a)	2.48±0.24	28.4±4.9	1.82±0.28	18.6±4.0	1.78±0.15	20.1±3.4		
TRSN-52-22	backside	smooth cast	none	na ^(a)	na ^(a)	5.67±0.75	72.8±10.3			5.15±0.68	73.6±13.8		
TRSN-52-J		smooth cast	SiC	1.12±0.06	10.7±0.5	2.07±0.60	21.2±3.7					1.56±0.36	16.8±3.1
TRSN-52-2		smooth cast	SiC	nm ^(a)	nm ^(a)	—	—						
TRSN-52-14		rough cast	BN	na ^(a)	na ^(a)	49.2±10.5	360±75					52.4±7.5	368±26
TRSN-52-K		rough cast	BN	na ^(a)	na ^(a)	48.8±3.3	332±37						
TRSN-52-19		rough cast	SiC	1.17±0.06	11.1±0.9	2.15±0.29	22.4±3.1						
TRSN-52-20		rough cast	SiC	nm ^(a)	nm ^(a)	2.22±0.42	24.4±4.2	2.29±0.79	23.0±6.1	2.61±0.94	26.1±7.5		
TRSN-52-I		coarse grit ^(a)	SiC	na ^(a)	na ^(a)	3.06±0.25	30.8±3.4						
TRSN-52-G		coarse grit ^(a)	SiC	na ^(a)	na ^(a)	—	—						
TRSN-52-H		coarse grit ^(a)	BN	nm ^(a)	nm ^(a)	2.97±0.99	37.0±7.9						
TRSN-52-F		coarse grit ^(a)	BN	1.23±0.07	11.6±1.3	1.60±0.16	16.4±2.8	3.87±1.23	32.3±8.2	4.99±1.04	45.4±8.8		
TRSN-52-9		fine grit ^(a)	SiC	na ^(a)	na ^(a)	2.07±0.24	21.8±3.9	2.01±0.62	23.4±10.5	2.09±0.59	20.8±5.2		
TRSN-52-3		fine grit ^(a)	SiC	na ^(a)	na ^(a)	3.86±0.65	36.3±6.8						
TRSN-52-10		fine grit ^(a)	BN	1.23±0.07	11.2±0.8	—	—						
TRSN-52-10	white coating	fine grit ^(a)	BN			1.40±0.11	13.3±2.1					7.28±0.66	59.7±8.9
TRSN-52-4		fine grit ^(a)	BN	nm ^(a)	nm ^(a)	2.05±0.13	22.9±3.8					1.41±0.06	15.2±1.9
TRSN-52-4	white coating	fine grit ^(a)	BN			3.19±0.75	28.5±7.1					3.37±1.21	29.2±8.4
TRSN-53-B ^(b)		smooth cast	BN	none	none	2.44±0.86	34.1±10.6						
TRSN-53-13		smooth cast	BN										
TRSN-53-K		smooth cast	SiC	1.27±0.10	12.4±1.1	3.6±1.1	40.1±10.6						
TRSN-53-18		smooth cast	SiC	none	none								
TRSN-53-D,DI		smooth cast	SiC	yes	yes								
TRSN-53-20		rough cast	BN	none	none	38.5±2.9	321±52						
TRSN-53-14		rough cast	BN	none	none								
TRSN-53-15		rough cast	BN	none	none								
TRSN-53-16		rough cast	SiC	yes	yes	3.5±1.4	35.1±14.0						
TRSN-53-17		rough cast	SiC	1.06±0.05	9.98±0.66	3.3±1.3	28.7±5.4						
TRSN-53-III		coarse grit ^(a)	SiC	none	none								
TRSN-53-J		coarse grit ^(a)	SiC	none	none	2.40±0.16	24.7±1.9						
TRSN-53-B		coarse grit ^(a)	BN	1.20±0.09	10.8±0.8	1.48±0.10	15.9±0.7						
TRSN-53-A		coarse grit ^(a)	BN	yes	yes	1.46±0.08	14.6±1.5						
TRSN-53-F		fine grit ^(a)	SiC	none	none								

TRSN-53-C		fine grit ^(a)	BN	yes	yes	11.53±0.11	15.2±1.4			
TRSN-53-H		fine grit ^(d)	BN	12.27±0.09	13.2±1.9					
TRSN-53-G,G1		fine grit ^(d)		none	none					

^(a) TRSN-52 Samples: Sintering Aid $Y_2O_3-Al_2O_3$

^(b) TRSN-53 Samples: Sintering Aid $Yb_2O_3-SrCO_3-La_2O_3$

^(c) Machined Surface

^(d) nm - machined after bisque fire, but surface roughness was not measured

^(e) na - surface was not machined after bisque fire

Table 5. Initial results from Taguchi experimental array to identify important surface property variables affecting the final properties of the sintered silicon nitride materials.

Test No.	Surface Processing Variables					Surface Processing Properties		
	Green Surface Condition	Machine After Bisque Firing	Surface Sintering Condition	Post-Sinter Surface Treatment	Post-Sinter Thermal Treatment	Processed Surface Strength (MPa)	Indented Strength (MPa)	Fracture Toughness (MPa√m)
1	As-Cast (Smooth)	No	Exposed to Atmosphere	None	None	455±13	346±22	8.2±0.3
2	As-Cast (Smooth)	No	Exposed to Atmosphere	Grit Tumble	Oxidize			
3	As-Cast (Smooth)	Yes	Adjacent to SiC Setter	Sandblast	Thermal Shock	545±61	329±4	7.9±0.1
4	As-Cast (Smooth)	Yes	Adjacent to SiC Setter	Machine	Inert Gas Heattreat			
5	As-Cast (Rough)	No	Exposed to Atmosphere	Sandblast	Inert Gas Heattreat			
6	As-Cast (Rough)	No	Exposed to Atmosphere	Machine	Thermal Shock	681±29	333±45	8.0±0.7
7	As-Cast (Rough)	Yes	Adjacent to SiC Setter	None	Oxidize			
8	As-Cast (Rough)	Yes	Adjacent to SiC Setter	Grit Tumble	None	454±93	280±53	7.0±0.9
9	Machined (Coarse Grit)	No	Adjacent to SiC Setter	Machine	Oxidize			
10	Machined (Coarse Grit)	No	Adjacent to SiC Setter	Sandblast	None	472±56	348±17	8.3±0.2
11	Machined (Coarse Grit)	Yes	Exposed to Atmosphere	Grit Tumble	Inert Gas Heattreat			
12	Machined (Coarse Grit)	Yes	Exposed to Atmosphere	None	Thermal Shock	529±16	368±34	8.3±0.4
13	Machined (Fine Grit)	No	Adjacent to SiC Setter	Grit Tumble	Thermal Shock	404±67	185±4	5.1±0.1
14	Machined (Fine Grit)	No	Adjacent to SiC Setter	None	Inert Gas Heattreat			
15	Machined (Fine Grit)	Yes	Exposed to Atmosphere	Machine	None	620±21	351±5	8.3±0.1
16	Machined (Fine Grit)	Yes	Exposed to Atmosphere	Sandblast	Oxidize			

Table 6. Summary of results on densification of samples from CRADA with MER Corp. gas pressure sintered at 1900°C/1950°C.

Sample No.	Weight Loss (%)	Density (g/cm ³)	Density (% T. D.)
MR-1	5.4	3.50	99.5
MR-2	4.5	3.53	100.3
MR-3	4.1	3.54	100.5
MR-4	4.3	3.53	100.4
MR-5	3.7	3.54	100.5
MR-6	4.3	3.31	94.0
MR-7	2.7	3.52	99.9
MR-8	3.4	3.51	99.6
MR-9	1.3	3.22	96.1
MR-10	2.0	3.11	92.9
MR-11	4.8	3.52	100.0
MR-12	4.2	3.50	99.4
MC-1	3.4	3.22	98.1
MC-2	2.4	3.22	98.3
MC-3	4.2	2.81	85.7
MC-4	4.5	2.66	81.2
MC-5	1.1	3.18	97.0
MC-6	1.1	3.18	97.9
MC-7	1.6	3.15	97.0
MC-8	0.6	3.23	96.4
MC-9	2.5	3.05	91.0
MC-10	2.1	3.16	94.4

Fig. 1. Laser profilometer scan of as-cast smooth surface. The roughness scale is from $-6.5 \mu\text{m}$ to $+3.5 \mu\text{m}$.

Fig. 2. Laser profilometer scan of as-cast rough surface. The roughness scale is from $-300 \mu\text{m}$ to $+300 \mu\text{m}$.

Fig. 3. Laser profilometer scan of machined (fine grit) surface. The roughness scale is from $-5\text{ }\mu\text{m}$ to $+25\text{ }\mu\text{m}$. The peak in the corner represents an unground section.

Fig. 4. Laser profilometer scan of machined (coarse grit) surface. The roughness scale is from $-10\text{ }\mu\text{m}$ to $+20\text{ }\mu\text{m}$.

Fig. 5 . Photomicrograph showing roughness that resulted from sintering on BN setter (~20x).

Fig.6 . Surface of TRSN-52-22 showing porosity that developed on surface exposed to furnace atmosphere during sintering (~20x).

1.2.4 Low Expansion Materials

W. B. S. Element 1.2.4.3
CHARACTERIZATION AND TESTING OF
LOW EXPANSION CERAMIC MATERIALS

S. Shanmugham and D. P. Stinton

Objective/Scope

Insulated exhaust portliners are needed in advanced diesel engines to increase engine fuel efficiency by increasing the combustion temperatures and reducing the combustion heat that is lost through the head and into the water cooling system. Low expansion materials have potential for this application due to their very low thermal conductivity, extraordinary thermal shock resistance, and reduction of attachment stresses. Thermal shock resistance is critical because the shape of the portliners requires that they be cast into the metallic cylinder head. Functioning exhaust portliners are inaccessible after they are cast into cylinder heads and hence, must not require maintenance for the life of the head (~ 1 million miles). Contracts have been placed with Golden Technologies, Inc., formerly Coors Ceramic Co., and LoTEC, Inc., to develop cost effective processes for the fabrication of portliners. Coors is investigating Al_2TiO_5 and $\text{Ca}_{1-x}\text{Mg}_x\text{Zr}_4\text{P}_6\text{O}_{24}$, while LoTEC is investigating $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24}$ (BaZPS) and $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$. ORNL is assisting Golden Technologies and LoTEC with the characterization and evaluation of their compositions.

Technical Highlights

A systematic investigation of the mechanical and thermal properties of BaZPS ceramics as a function of composition (Si at%) and grain size has been initiated. Five compositions ($x=0, 0.175, 0.25, 0.375$, and 0.500) were synthesized from stoichiometric proportions of the reagent grade oxides using a solid-state reaction method and were sintered at 1600°C for 3000 minutes. To determine the influence of the grain size, three compositions ($x=0, 0.175$ and 0.500) were additionally sintered for 30 and 300 minutes to result in smaller grain sized samples. In this semi-annual report, the hardness results of the BaZPS compositions, the high temperature flexural strength of the BaZPS compositions ($x=0, 0.175$ and 0.5) as a function of grain size and the phase transition behavior of BaZPS with $x=0.25$ are presented.

The hardness testing was conducted on a Tukon Series 200 hardness tester (Wilson Instruments, Inc.) and the BaZPS samples used were 12 x 4 x 3 mm. The samples were mounted with the 12 x 4 mm side facing the die and epoxy was poured over it and allowed to set for 16 h. The specimens were then removed from the die and an identification mark was engraved. The samples were ground parallel using a 200 grit, resinoid bonded diamond grinding wheel on a surface grinder. The samples were rough polished using a 6 μ m diamond paste on a wire mesh cloth followed by rough polishing utilizing a 6 μ m diamond paste on a perforated cloth. Final polishing was carried out in two steps. First, the samples were polished using a 3 μ m diamond paste on a texmet cloth. Then, the sample was polished using a 0.5 μ m diamond paste on a nylon cloth to obtain an optical surface finish.

The hardness indentations were made using a Knoop indenter with loads of 50-300 gms at a constant loading time of 10 sec. The diagonal of the indentations were measured using a VIA-110 video hardness measurement system, which is attached to the hardness tester. The Knoop hardness was then calculated using the standard formula.

The high temperature flexural strength of the BaZPS compositions were determined using a specially designed flexure test system capable of separately testing up to three specimens concurrently in series. The testing was carried out using a four-point bend fixture with 40 mm and 20 mm as outer and inner spans, respectively. Three specimens of each of the compositions were tested at 200°C, 600°C, and 1000°C. The furnace was ramped to the desired test temperature and the sample soaked for 5 minutes, and tested using the series option.

BaZPS with $x=0.25$ (BS25) sintered for 3000 min was ground into a fine powder. Differential scanning calorimetry (DSC, Stanton Redcroft Instruments) runs were conducted in a platinum crucible for the BS25 powder with sapphire as the reference material. The DSC furnace was ramped at 50°C/min between 25°C and 1300°C in air and the data was collected and stored by an automated data collection system.

The hardness test results for the BaZPS compositions are summarized in Table 1. The hardness increased with increasing Si content to $x=0.375$ and then decreased sharply for $x=0.5$. Among the

BaZPS compositions, BaZPS with $x=0.375$ showed the highest hardness value (7.61 GPa). At lower loads, the indentation dimensions varied between 30 and 75 μm , and between 89 and 190 μm for higher loads. Also, the hardness values decreased with increase in indentation loads for all the BaZPS compositions.

Table 1 Hardness results for the BaZPS compositions

BaZPS composition Load (g)->	Hardness (GPa)			
	50	100	200	300
0	4.42 $\pm$ 0.10	4.12 $\pm$ 0.04	3.45 $\pm$ 0.08	3.29 $\pm$ 0.10
0.175	4.65 $\pm$ 0.16	4.30 $\pm$ 0.18	4.11 $\pm$ 0.10	3.66 $\pm$ 0.12
0.250	5.30 $\pm$ 0.09	4.65 $\pm$ 0.13	4.12 $\pm$ 0.06	3.73 $\pm$ 0.04
0.375	7.61 $\pm$ 0.26	5.55 $\pm$ 0.15	5.03 $\pm$ 0.10	5.19 $\pm$ 0.06
0.500	3.18 $\pm$ 0.19	2.72 $\pm$ 0.04	2.46 $\pm$ 0.04	2.41 $\pm$ 0.06

The grain sizes of the three BaZPS compositions were determined from optical micrographs of etched specimens and the results summarized in Table 2 are an average obtained from five micrographs with standard deviation less than 5%.

Table 2 Grain size measurements of the BaZPS compositions

BaZPS composition Sintering time (min)->	Grain size (μm)		
	30	300	3000
$x=0$ (BS0)	1.83	2.70	5.08
$X=0.175$ (BS17)	1.64	2.42	4.16
$X=0.5$ (BS50)	1.36	1.91	2.67

The high temperature flexural strengths of the BaZPS compositions are summarized in Table 3. The flexural strength of the BS0 compositions varied between 41 and 122 MPa. Among the BS0 compositions, the BS0 sintered for 3000 minutes had the lowest strength at all the temperatures. Flexural strength of the BS17 compositions with different grain sizes did not vary significantly with temperature. Similar trend was observed in the BS50 compositions. Among the three BaZPS compositions studied, BS50 had the lowest strength.

Table 3 High Temperature flexural strength results for the BaZPS compositions

Composition (grain size in μm)	Flexural Strength (MPa)			
	Test Temperature			
	25°C	200°C	600°C	1000°C
BS0 (1.83)	79.1 $\pm$ 5.3	81.4 $\pm$ 10.6	92.5 $\pm$ 9.10	95.2 $\pm$ 11.0
BS0 (2.70)	61.8 $\pm$ 1.1	74.3 $\pm$ 5.9	80.3 $\pm$ 4.7	122.7 $\pm$ 14.0
BS0 (5.08)	55.3 $\pm$ 4.9	66.0 $\pm$ 2.4	41.4 $\pm$ 14.4	83.0 $\pm$ 34.7
BS17 (1.64)	78.0 $\pm$ 2.3	76.6 $\pm$ 16.2	67.4 $\pm$ 25.2	93.7 $\pm$ 5.5
BS17 (2.42)	84.9 $\pm$ 11.2	94.0 $\pm$ 15.3	79.7 $\pm$ 16.7	96.6 $\pm$ 9.3
BS17 (4.16)	84.6 $\pm$ 12.2	84.2 $\pm$ 2.3	79.3 $\pm$ 9.6	95.2 $\pm$ 1.5
BS50 (1.36)	54.0 $\pm$ 4.0	48.4 $\pm$ 4.2	56.8 $\pm$ 6.3	55.8 $\pm$ 5.8
BS50 (1.91)	36.0 $\pm$ 5.4	43.3 $\pm$ 1.4	56.5 $\pm$ 1.3	56.5 $\pm$ 1.3
BS50 (2.67)	49.6 $\pm$ 7.6	45.1 $\pm$ 1.8	50.9 $\pm$ 3.5	50.9 $\pm$ 3.5

The DSC curve for BS25 showed a broad endothermic peak between 540 and 740°C (peaking at 620°C), thus suggesting that it exhibits a phase transition.

Reference

None

Milestones

On Schedule

Communications/Visits/Travel

D. P. Stinton attended a meeting at Chrysler Technical Center on High Temperature Catalyst Support in Detroit, Michigan and discussed low expansion ceramics at Cummins in Columbus, Ohio during February 22-24, 1995.

D. P. Stinton traveled to Salt Lake City, April 18th and 19th to discuss recent progress in the low-expansion ceramics contract with Santosh Limaye of LoTEC and Bob Schultz of DOE.

D. P. Stinton visited Jack Sibold and Bob Weaver of Golden Technologies Corporation on April 20th to discuss an extension of their low-expansion ceramics contract.

D. P. Stinton traveled to Virginia Polytechnic Institute, April 24th and 25th to discuss the development of low-cost processing of NZP powders with Jesse Brown and Gary Pickerell.

D. P. Stinton attended the Annual Meeting of the American Ceramic Society in Cincinnati, May 1st to 3rd. Participants in the low-expansion ceramics project met to discuss recent developments at Golden Technologies Corporation and LoTEC.

Problems Encountered

None

Development of NZP Ceramic Based "Cast-in-Place" Diesel Engine Port Liners

Rama Nageswaran, Jian Zheng, and Santosh Y. Limaye (LoTEC, Inc.).

Objective/Scope

The overall objective of this research is to develop sodium-zirconium-phosphate (NZP) ceramic based "cast-in-place" diesel engine port liners. Specific objectives are: (1) Development and optimization of the overall insulation system, (2) Refinement of the compliant layer formation process around the ceramic insulation system, (3) Development and adaptation of cost-effective powder and material fabrication processes, and (4) Creation of database of high temperature properties (stability in diesel exhaust environment, thermal cycling, thermal shock etc.).

Technical Progress

The list below summarizes work completed or started during the last six-month period, beginning March 1995 and ending October 1995, of this Phase II program. Detailed description of progress in each area succeeds the following list:

- (I) Characterized mechanical or thermo-mechanical properties such as elastic modulus, flexure strength, and compressive strength, and thermal shock resistance of the CS-50 ceramic;
- (II) Optimized the strain tolerance properties of the compliant layer for successful metal casting with the BS and CS tubes;
- (III) Performed finite element analysis (FEA) of cast-in-place BS-25 and CS-50 straight tube port liners with and without compliant layer and, in addition, optimized the thickness of the compliant layer;
- (IV) Conducted metal casting trials with straight tube BS-25 and CS-50 ceramics with and without compliant layer to (i) verify results of FEA and (ii) demonstrate successful casting of composite port liners based on such NZP ceramics;
- (V) Improved crystallinity of the BZP and CZP powders resulting from low cost Self-Propagating Chemical Decomposition (SCD) method.

Characterization of Mechanical Properties of CS-50: :

Elastic modulus as a function of temperature was evaluated using an ultrasonic measurement technique at Penn State University. In this procedure, a bar sample of the CS-

50 ceramic is suspended in a furnace by two sapphire threads acting as ultrasonic waveguides, connected to two transducers, one acting as a source and the other as receiver. The temperature is raised slowly to 1325°C and the resonance frequency noted at 100°C intervals. The Young's modulus is then calculated from:

$$E = \frac{0.94645 C m f^2}{W} \quad (1)$$

In Equation (1), C is a constant that depends upon the Poisson's ratio, ν , specimen thickness, t , and length, l ; and m is the mass; f is the flexural resonance frequency; and W is the width.

Figure 1 represents a plot of the elastic modulus of CS-50 as a function of temperature. It can be noted that the modulus is almost constant between room temperature and 1200°C during heat up, while there is a very small deviation from constancy during cool down. Clearly, this result is indicative of the high degree of isotropy of the CS-50 material. For this calculation CS-50's Poisson's was assumed to be 0.23.

Compressive Strength of CS-50 was measured in unconfined compression tests on 1"x 2" long cylinders at an outside facility. During the testing, axial and transverse strains were monitored using strain gauges. Poisson's ratio was calculated from the ratio of lateral to axial strains from the linear portion of the strain-strain curves. These values are tabulated in Table 1.

Thermal shock resistance tests were conducted on CS-50 bar samples by cyclically quenching from high temperature to a bath of ice water for between 1 and 50 cycles. The upper limit thermal shock temperature, T_h , for the test was estimated using the following equation for thermal shock parameter [1]:

$$\Delta T_f = \frac{\sigma_f (1 - \mu)}{E \alpha} \quad (2)$$

where, ΔT_f , represents the temperature difference of quench (that could initiate fracture at the surface); σ_f , E , μ , and α are the fracture stress, elastic modulus, Poisson's ratio, and the coefficient of thermal expansion, respectively, of the material. Using the fracture strength in flexure and values of other properties listed in Table 2 for CS-50, the thermal shock parameter was estimated to be ~ 311.5°C. From this calculation, T_h for the test was set at 400°C. To confirm if this estimate was reasonable, several bar samples were quenched into ice water from high temperatures ranging from 1200°C to 500°C. All quenched samples either cracked or showed significant degradation strength compared to the normal samples.

Samples thermal-shock cycled between 400°C and 0°C were tested for their (residual) flexure strengths in four-point bending. Ten samples each were cycled for 1, 10, and 50 cycles. Figure 3 is a bar chart of the residual strengths measured on the thermally-shocked samples. The residual strength after 1 thermal shock cycle is approximately 60% that of as-sintered samples. However, there is not much drop in strength upon further thermal shock cycling even up to 50 cycles. The lower thermal shock performance of CS-50 as compared to BS-25 is not surprising considering its higher thermal expansion coefficient.

Optimization of Strain Tolerance of Compliant Layer:

The role of the compliant layer in increasing the survivability of the cast-in-place NZP ceramic port liner has been adequately demonstrated during past work on this program. To improve manufacturability and reliability-in-service of the port liner, the compliant layer properties have to be adequately optimized. One of the approaches, proposed in Phase I, is to reduce the elastic modulus of the compliant layer without compromising its strength properties. Effectively, this results in a material with high strain-to-failure. Two different methods of reducing elastic modulus of the compliant layer viz. (i) reduction of the sintering temperature (sintering method) and (ii) introduction of artificial porosity (pore former method) were used. Both methods affect the elastic modulus via the nature, amount, and distribution of porosity in the material.

For actual measurements of elastic modulus and flexure strength due to each of these processing methods, 10 bar specimens (3 x 4 x 50 mm) of the compliant layer material were fabricated and tested. Results of these studies indicate that reduction of sintering temperature (sintering method) provides good strain tolerance characteristics - relatively high strength and low modulus - to the compliant layer. Strain tolerance was maximum at a particular sintering temperature. Also, failure strains resulting from the sintering approach were uniformly higher than those from the pore-former approach. These results have been summarized in the plot of Figure 2.

Finite Element based optimization of Cast-in-place Port liners :

Finite Element Analysis was conducted for the following straight tube cast-in-place NZP ceramic based Port liners. The intent of the analysis was to predict the outcome of metal casting trials involving BS-25 and CS-50 ceramics with and without a compliant layer. In addition, the analysis was used to study the effect of using BS-25 and CS-50 ceramics with lower elastic moduli (and higher strain-to-failure) on the shrinkage stresses.

(a) Regular modulus BS-25 ceramic : Previous analysis and experimentation has clearly shown the need for a crushable compliant layer to successfully fabricate cast-in-place regular BS-25 ceramic based port liners. It can be recalled that compressive stresses in the BS-25 ceramic were higher than the failure limits when BS-25 alone was used in the casting. This result is apparent from the plot in Figure 4.

For the FEA iterations, that were aimed at optimizing the compliant layer thickness for the BS-25 based port liners, the relevant properties of the compliant layer were estimated. These properties have been summarized in Table 1. Because of the very fragile and porous nature of the compliant layer, samples for property determination were deliberately made denser. Elastic modulus of the actual compliant layer was then extrapolated from these results. Coefficient of thermal expansion and Poisson's ratio were assumed to be same as that of the denser material.

Shrinkage stresses obtained from FEA for the different compliant layer thicknesses - 2mm and 3mm - suggest that compressive hoop stresses in the (regular) BS-25 ceramic are below its compressive failure limit only for a 3mm compliant layer. This can easily be inferred from the plots in Figures 5 and 6, and data in Table 1. This result corroborates observed cracking of the BS-25 ceramic tube in experimental trials when only ~ 2mm thickness of compliant layer was used for the casting.

(b) Low modulus BS-25 ceramic : The FEA based shrinkage stress plot of Figure 4 and data in Table 1 show that the low modulus BS-25 ceramic ($E \sim 35$ GPa) is also unlikely to survive the casting process because of the excessive compressive shrinkage stresses. With the low modulus BS-25 ceramic, however, FEA indicates the possibility of successfully casting the composite port liner in place with a smaller thickness of compliant layer (~ 2mm). This result - which is evident from Figure 5 and Table 1 - is based on the expected compressive strength of the lower modulus material rather than its true strength. Casting experiments with low modulus BS-25 ceramic are being done to verify FEA predictions.

(c) Regular modulus CS-50 ceramic : Properties of regular modulus CS-50 ceramic used for the FEA have been provided in Table 2. The first stage FEA involving regular modulus CS-50 ceramic predicts failure of the cast-in-place port liner because compressive shrinkage stresses are in excess of the compressive strength of CS-50. However, because of the higher coefficient of thermal expansion of the CS-50 ceramic as compared to BS-25 (and

lower CTE mismatch with gray-iron), compressive shrinkage stresses in CS-50 are lower after complete cooling of the composite. Figure 7 shows a plot of these FE analysis results.

For the second stage of FEA, a crushable compliant layer was introduced between the CS-50 ceramic and gray iron to induce reduction of the shrinkage stresses. The compliant layer material used in this model was almost the same as that used for BS-25; properties of which are included in Table 2. Results of the second stage FEA involving CS-50 with the compliant layer indicate that a 2 mm thick layer is clearly sufficient to keep shrinkage stresses in CS-50 within failure limits (max. compressive stress of 340 MPa vs compressive strength of 390 MPa). This result is evident from Figure 8.

(d) Low modulus CS-50 ceramic : As with BS-25, the chosen low modulus CS-50 ceramic has a higher strain-to-failure than regular CS-50. FEA for metal casting with this low modulus material suggested that: (i) compressive failure is imminent if this ceramic is used as is and (ii) failure can be avoided by using a compliant layer approx. 1mm thick in around the low modulus CS-50. These can be inferred from the shrinkage stress plots in Figures 7 and 9 and data in Table 2 corresponding to the low-modulus CS-50. As with BS-25, the compressive strength of the low modulus CS-50 material is not a measured value; rather it is an approximate value. A 1 mm thick compliant layer represents the best situation for cast-in-place port liners where rattling during operation of the diesel engine could pose a problem. (Rattling can lead to progressive degradation of such composite port liners because of lack of microstructural bonding between its different components.)

Metal Casting Trials with BS-25 and CS-50 Ceramics :

BS-25 Ceramic: Metal casting trials were performed using regular modulus BS-25 straight tubes having approximately 2 and 3 mm thick compliant layers to verify results of previous trials which suggested that a 2 mm thick compliant layer was inadequate for fail safe casting. Cracks could be seen in the BS-25 port liner tubes with just 2 mm thick compliant layer. As with the earlier trials, the strain-tolerant compliant layer material was deliberately made highly porous and crushable.

Result of the repeat metal casting experiments on BS-25 tubes with the 2 and 3 mm thick compliant layers again indicated that the latter was better for enhancing the survivability of the cast-in-place BS-25 port liners. These results are clear from the camera snap-shot of Figure 10. Arguably, the thicker the compliant layer the lesser will be the

compressive stresses in the ceramic. On the other hand, the compliant layer cannot be made very thick because of the likelihood of debonding the ceramic tube from the surrounding metal during rattling in actual service. For this reason, it is important to optimize the thickness of the compliant layer as much as possible using predictions from FEA.

CS-50 Ceramic: Casting trials were also performed using regular modulus CS-50 straight tubes with and without compliant layer to verify results of FEA. As predicted by the model, cast-in-place CS-50 tubes seemed to crack excessively in a manner of compressive failure. However, an interesting feature of the cast part was the presence of metal (gray-iron) in the interior of the CS-50 tube and away from the ends. Metal appeared to have penetrated across the wall (almost perpendicular to it) of the ceramic tube. This situation is possible only if the cracks had formed in the ceramic at the instant the molten metal was poured around the ceramic. Such can easily be the case considering the relatively low thermal shock resistance of CS-50 as compared to that of BS-25. These experimental results will be verified with a few more metal casting trials.

In addition, the finite difference heat transfer model used for metal casting with BS-25 will be employed for CS-50 also to predict the failure due to thermal gradient stresses arising from contact of hot metal with the exterior of the cold ceramic tube. Despite the possibility of thermal gradient stress type failure, it is very likely that CS-50 ceramic fails due to both thermal gradient and shrinkage stresses when molten gray iron is cast around it.

Metal casting experiments with CS-50 tubes having 1.5, 2, and 3 mm thick compliant layers resulted in successful cast port liners (see picture in Fig. 11). This result falls in line with the FEA predictions. It is inferred, at this point, that the role of the crushable compliant layer in the case of CS-50 might be two-fold: (i) reduction of thermal gradients across the CS-50 tube at the instant of casting and (ii) absorption of the shrinkage stresses during cooling of the gray iron around the ceramic. Again, these results will be further verified in future casting trials and also by heat-transfer modeling. (X-ray computer tomographs in further support of these observations and results will be presented in future reports.)

Low Cost Synthesis of NZP powders (SCD Method) :

During previous SCD experiments, reactant powders containing different amounts of urea and ammonium nitrate and stoichiometric amounts of other precursors were heated in wide necked pyrex beakers at a rate of 10°C/min to 500°C and held at 500°C for 5 minutes,

followed by cooling in air. The resulting crystallinity of the various BZP and CZP phases were qualified using X-ray analysis. In order to enhance crystallinity of BZP and CZP phases, the SCD based powders were heated to 800°C for 8 hrs to initiate further reaction. The as-heat treated powders were again X-rayed. Some amount of each powder was placed on glass plates and subjected to X-ray analysis to determine peak heights, and thereby, obtain a rough measure of crystallinity.

Results of these tests and analysis for CZP, BZP, CS50 and BS25 revealed that (i) a large amount of urea is necessary for the reaction to attain completion, especially for BZP and (ii) when lesser amounts of urea are present, the post-combustion heat treatment results in greater crystallinity of the powders. More detailed studies to improve crystallinity of the powders are being carried out.

Status of milestones : Program on schedule.

Communications/Visits/Travel : None.

Problems Encountered : None.

Publications : None.

References :

1. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, Second Edition (1976); John Wiley & Sons., New York.

Figure 1. Plot of variation of Elastic modulus of CS-50 as a function of Temperature.

Figure 2. Plot of Strain Tolerance of the Compliant layer as a function of Porosity and Processing Method.

Figure 3. Residual flexure strengths of cyclically thermal shocked CS-50 specimens.

TABLE 1: Relevant Material Properties for FEA of Cast-in-place BS-25 Port Liners with and without Compliant Layer.

PROPERTY	MATERIAL			
	BS-25 (REGULAR)	BS-25 (LOW MOD)	COMPLIANT LAYER	GRAY IRON
Density (gm/cc)	3.50	2.50	~1.0	7.0
Modulus (GPa)	70.0	35.0	~0.5	172.0
Poisson's Ratio	0.24	0.24	0.24	0.28
Thermal Expansion ($\times 10^{-6}$ per $^{\circ}\text{C}$)	1.0	1.0	1.0	12.1
Strength (MPa):				
Compressive	~400.0	~300	-	>1000.0
Flexural	75.0	50.0	2.0	~460.0

TABLE 2: Relevant Material Properties for FEA of Cast-in-place CS-50 Port Liners with and without Compliant Layer.

PROPERTY	MATERIAL			
	CS-50 (REGULAR)	CS-50 (LOW MOD)	COMPLIANT LAYER	GRAY IRON
Density (gm/cc)	3.30	2.55	~1.0	7.0
Modulus (GPa)	65.0	50.0	~0.5	172.0
Poisson's Ratio	0.19	0.19	0.24	0.28
Thermal Expansion ($\times 10^{-6}$ per $^{\circ}\text{C}$)	3.0	3.0	1.0	12.1
Strength (MPa):				
Compressive	~390.0*	~325.0		>1000.0
Flexural	75.0	50.0	2.0	~460.0

* Average of two tests.

Figure 4. Finite Element based Shrinkage Stresses in the BS-25+ Gray Iron cast-in-place Port liner after Complete Cooling.

Figure 5. Finite Element based Shrinkage Stresses in the BS-25+ 2mm Compliant Layer cast-in-place Port liner after Complete Cooling.

Figure 6. Finite Element based Shrinkage Stresses in the BS-25+ 3mm Compliant Layer cast-in-place Port liner after Complete Cooling.

Figure 7. Finite Element based shrinkage stresses in CS-50+Gray Iron cast-in-place Port liner after Complete Cooling.

Figure 8. Finite Element based shrinkage stresses in CS-50+2mm Compliant layer cast-in-place Port liner after Complete Cooling.

Figure 9. Finite Element based shrinkage stresses in low modulus CS-50+1mm Compliant layer Port liner after Complete Cooling.

Figure 10. Camera shot of cast-in-place BS-25 ceramic based port liners with and without compliant layer. (Even a 2 mm compliant layer is not sufficient to prevent cracking of regular BS-25 due to shrinkage stresses).

Figure 11. Camera shot of cast-in-place CS-50 ceramic based port liners with and without compliant layer. (Penetration of iron slivers across the wall of the CS-50 tube suggests thermal shock cracking right at the instant of molten iron pouring.)

1.3 THERMAL AND WEAR COATINGS

FABRICATION AND TESTING OF CORROSION-RESISTANT COATINGS

W.Y. Lee, D.P. Stinton, K.M. Cooley, and Y.W. Bae
Oak Ridge National Laboratory

Objective/Scope

Hot corrosion of SiC and Si₃N₄ components in gas turbine engines is potentially a serious problem. The outer surfaces of SiC and Si₃N₄ parts oxidize at high temperatures to form SiO₂ which inhibits further oxidation. However, sodium which is present in high-temperature combustion atmospheres reacts with the SiO₂ layer, such that it is no longer protective. The objective of this program is to develop a coating that will protect the underlying SiC or Si₃N₄ from sodium corrosion and provide simultaneous oxidation protection. To evaluate the behavior of potential materials such as stabilized ZrO₂ or HfO₂, TiO₂, Al₂O₃•TiO₂, 3Al₂O₃•2SiO₂ (mullite), and Ta₂O₅ in sodium-containing atmospheres, the corrosion resistance of hot-pressed samples of these materials have been evaluated. A chemical vapor deposition (CVD) process will be developed for the application of the most promising coatings. The effects of the combustion environment upon coating characteristics such as microstructure, strength, adherence, and other properties will also be evaluated.

Technical Progress

In this reporting period, the feasibility of using crystalline mullite prepared by chemical vapor deposition (CVD) as a corrosion-resistant coating has been addressed. Mullite is considered because it is one of a very few materials which exhibit relatively similar expansion characteristics relative to Si₃N₄ while also showing resistance to Na₂SO₄-induced corrosion. Note that mullite's coefficient of thermal expansion (CTE) is higher than that of Si₃N₄ ($\sim 5.7 \times 10^{-6}$ versus $\sim 3.0 \times 10^{-6}$ K⁻¹). Since CVD is an atomistic growth process, it can be used to produce high quality coating microstructures that are relatively free of structural defects such as porosity and splat boundaries typically found in plasma sprayed materials. For achieving long-term stability, a dense microstructure is usually preferred so as to inhibit salt penetration through the coating. Previously, Lee et al. [1,2] showed that mullite (3Al₂O₃•2SiO₂) coatings prepared by air plasma spray were relatively effective in protecting SiC/SiC composite substrates from hot corrosion. The mullite coatings, if crystalline as-deposited, were found to exhibit excellent adherence during cyclic oxidation. It was also observed that a small amount of Na penetrated through the plasma sprayed coatings during 40-h burner-rig tests [1].

In this study, hot isostatically pressed Si₃N₄ (GN10, AlliedSignal, Torrance, CA) was used as the substrate material. This material mainly consists of elongated 0.3 to 5 μ m β -Si₃N₄ grains along with grain boundary phases and impurities such as α -Si₃N₄, Y₅(SiO₄)₃N, Y₄Si₂O₇N₂, Ca, and Sr [3]. The Si₃N₄ specimens (2.0 cm x 0.4 cm x 0.3 cm) were uniformly coated at Boston University with CVD mullite using a hot-wall reactor at a deposition temperature of 950°C. The coating method, which utilizes AlCl₃, SiCl₄, CO₂, and H₂ as precursors, is described in detail elsewhere [4]. The specimens were typically loaded with about 5 mg/cm² of Na₂SO₄ using a procedure described

elsewhere [5]. The Na_2SO_4 -loaded specimens were placed on an Al_2O_3 holder and exposed to a flowing oxygen environment in a quartz tube heated to 1000°C by a resistance furnace. The flow rate of oxygen was $200\text{ cm}^3/\text{min}$ at STP, and was controlled using a mass flow meter. The use of an oxygen environment results in the formation of a basic molten salt (i.e., high Na_2O activity), thus facilitating the reaction of Na_2O with SiO_2 [6,7]. The temperature was measured and constantly monitored using an optical pyrometer and a thermocouple.

The corroded specimens were mounted in epoxy and polished using kerosene as a lubricant to examine corrosion products and resulting surface microstructures. A Hitachi S-800 field emission scanning electron microscope (SEM), a Scintag V X-ray diffractometer (XRD), a JEOL Superprobe 733 electron microprobe analyzer (EMPA), and a Hitachi HF-2000 transmission electron microscope (TEM) equipped with an energy dispersive spectrometer (EDS) were used for morphology characterization and phase identification. Cross-section TEM specimens were prepared by gluing coating surfaces together and cutting slices with a thickness of $\sim 300\text{ }\mu\text{m}$ perpendicular to the interface using a slow speed saw. Each slice was mechanically thinned to $\sim 75\text{ }\mu\text{m}$, dimpled across the center of the interface to $\sim 20\text{ }\mu\text{m}$, and ion milled to perforation at liquid nitrogen temperature.

Two Si_3N_4 specimens coated with CVD mullite were prepared. The coating, which was about $10\text{ }\mu\text{m}$ thick, was uniform in visual appearance and color. The as-deposited surface was highly faceted and well-coalesced as shown in Figure 1. The size of surface facets was in the range of about 1 to $10\text{ }\mu\text{m}$. The coating did not contain voids or porosity detectable to optical microscopy. The XRD pattern in Figure 2 suggested that the coating was crystalline mullite and somewhat textured. TEM and electron diffraction analyses on selected areas of one of the as-deposited specimens indicated that the coating mainly consisted of columnar mullite grains. These columns were mostly oriented perpendicular to the substrate. Interestingly, the presence of a microcrystalline layer was also observed between the columnar mullite and the Si_3N_4 substrate surface. This intermediate region contained Si, Al, and O, and was several microns thick. Although its electron diffraction pattern could not be indexed for exact phase determination, an EDS analysis suggested that the Si content in this region was substantially higher than that measured for the columnar mullite. Any strong reaction between the coating and Si_3N_4 substrate during processing might be precluded as a possible reason for the formation of the microcrystalline layer, since the initial microstructure and composition of the underlying Si_3N_4 substrate surface were found to be intact by TEM even after the coating was applied. More work is needed to discern whether the formation of the intermediate region is due to substrate or processing related effects.

The coated specimens were exposed to the $\text{Na}_2\text{SO}_4+\text{O}_2$ atmosphere for 100 h at 1000°C . The weight of the coated samples did not change substantially after corrosion and washing ($+0.2\text{ mg}/\text{cm}^2$ and $+0.1\text{ mg}/\text{cm}^2$, respectively, in reference to the weight of the coated specimens before corrosion). The XRD patterns shown in Figure 2 indicate that the crystal structure of the coating surface remained unchanged after corrosion. Also, the surface of the corroded samples was not visually affected by corrosion. However, at a microscopic level, it was observed that the sharp edges of the faceted surface features observed for the as-deposited coating were somewhat eroded by the

corrosion treatment. In addition, there was evidence that minor reactions occurred on some isolated areas of the coating surface. These localized regions which looked "glassy" by optical microscopy represented less than several percent of the total surface area of the coated specimens. The presence of microcracks was observed within or originating from the "glassy" areas. Further characterization with TEM and electron diffraction revealed that these "glassy" surface regions could be as thick as about 0.5 μm , and contained small amounts of Na and Al, as shown in Figure 3. These results suggested that the "glassy" regions were basically amorphous silica with Na and Al impurities.

Figure 4 shows a back-scattered electron image along with X-ray elemental maps of the cross-section of the coated specimens after corrosion. It was evident from this qualitative analysis that the coating was relatively stable at both Na_2SO_4 /mullite and Si_3N_4 /mullite interfaces except for the presence of a small amount of Na observed at the Na_2SO_4 interface. For comparison, an uncoated Si_3N_4 sample reacted significantly with Na_2SO_4 when it was exposed to the same corrosion conditions. The presence of Na is typically observed to a depth of $\sim 20\ \mu\text{m}$ below the initial substrate surface. Yttrium migrates to the substrate surface through grain boundaries, resulting in the formation of an yttrium depleted zone of $\sim 10\ \mu\text{m}$. This type of surface interaction of Si_3N_4 materials with corrosive environments has been previously described by other investigators [6,8]. Figure 4 clearly shows that there was no apparent migration of yttrium to the substrate-coating interface. In a more detailed EDS analysis, Na was not found within the mullite grains, but a trace amount of Na was detected on grain boundaries to a depth of about 1 μm below the coating surface. This observation indicated that the diffusion of Na preferentially took place along the grain boundaries during the 100-h test duration. It was also found from the TEM study that the remainder of the coating as well as the underlying Si_3N_4 substrate were not affected either microstructurally or compositionally by the corrosion exposure.

In summary, the coating was effective in preserving and therefore protecting the surface microstructure of the underlying Si_3N_4 substrates, although some minor changes were observed as a function of coating depth. Therefore, it seems that the use of the CVD mullite coating for protecting Si_3N_4 materials is feasible. For at least the 100 h duration tested in this study, the interaction between the coating and Na_2SO_4 was not substantial except for some localized reaction observed on the coating surface. More encouragingly, the coating was able to preserve the surface microstructure and composition of the Si_3N_4 substrate. However, a small degree of Na penetration through mullite grain boundaries was observed to a depth of about 1 μm , but its significance to long-term coating durability is not certain at this point. The determination of the corrosion kinetics will require data at several exposure times. In this way, the effectiveness of the coating over extended time periods can be properly assessed. From a processing point of view, controlling the composition and uniformity of the CVD mullite coating should be assessed. Burner-rig tests which are accompanied by post-corrosion strength measurements [9] are also needed.

Status of Milestones

On schedule.

Communications/Visits/Travel

W.Y. Lee presented a paper titled "In Search of A Coating System Which Protects Si-Based Materials from Hot Corrosion," at the ACerS 1995 Annual Meeting and Exposition, Cincinnati, Ohio, April 30 - May 4, 1995. The paper was co-authored with Y.W. Bae and D.P. Stinton of ORNL, R. Mulpuri and V.K. Sarin at Boston University, and T.E. Strangman at AlliedSignal Engines.

V.K. Sarin of Boston University visited ORNL on May 15, 1995 to discuss the preparation of corrosion test samples. Fourteen 0.5"x0.5"x0.25" NT154 substrates (supplied by AlliedSignal Engines) were sent to Boston University for CVD mullite coating.

Problems Encountered

None.

Publication

Y.W. Bae, W.Y. Lee, and D.P. Stinton, "Effects of Temperature and Reagent Concentration on the Morphology of Chemically Vapor Deposited β -Ta₂O₅," J. Am. Ceram. Soc., **78**, 1297 (1995).

W.Y. Lee, Y.W. Bae, and D.P. Stinton, "Na₂SO₄ Induced Corrosion of Si₃N₄ Coated with Chemically Vapor Deposited Ta₂O₅," J. Am. Ceram. Soc., **78**, 1927 (1995).

W.Y. Lee, D.P. Stinton, D.L. Joslin, "Interaction of Low-Expansion Ceramics with Na₂SO₄ at 1000°C," J. Am. Ceram. Soc., submitted, July 1995.

W.Y. Lee, K.L. More, D.P. Stinton, and Y.W. Bae, "Characterization of Si₃N₄ Coated with Chemically Vapor Deposited Mullite after Na₂SO₄ Induced Corrosion," J. Am. Ceram. Soc., prepared for submission, September 1995.

References

1. K.N. Lee, N.S. Jacobson, and R.A. Miller, "Refractory Oxide Coatings on SiC Ceramics," MRS Bulletin, **35**, (October 1994).
2. K.N. Lee, R.A. Miller, and N.S. Jacobson, "New Generation of Plasma-Sprayed Mullite Coatings on Silicon Carbide," J. Am. Ceram. Soc., **78**, 705 (1995).
3. B.J. Hockey and S.M. Wiederhorn, "Microstructural Analysis of Structural Ceramics," pp. 271-281 in Report No. ORNL/TM-12133, Oak Ridge National Laboratory, Oak Ridge, TN, 1992.

4. R. Mulpuri and V. Sarin, "Thermodynamic Analysis of CVD Mullite Coatings," *Ceram. Eng. Sci. Proc.*, **16**, 401 (July-August 1985).
5. W.Y. Lee, Y.W. Bae, and D.P. Stinton, " Na_2SO_4 Induced Corrosion of Si_3N_4 Coated with Chemically Vapor Deposited Ta_2O_5 ," *J. Am. Ceram. Soc.*, **78**, 1927 (1995).
6. N.S. Jacobson and D.S. Fox, "Molten-Salt Corrosion of Silicon Nitride: II, Sodium Sulfate," *J. Am. Ceram. Soc.*, **71**, 139 (1988).
7. N.S. Jacobson, "Corrosion of Silicon-Based Ceramics in Combustion Environments," *J. Am. Ceram. Soc.*, **76**, 3 (1993).
8. D.R. Clarke, "Thermodynamic Mechanism for Cation Diffusion through an Intergranular Phase: Application to Environmental Reactions with Nitrogen Ceramics," pp.421-426 in Progress in Nitrogen Ceramics, edited by F.L. Riley, Martinus Nijhoff Publishers, The Hague, The Netherlands, 1983.
9. T.E. Strangman and D.S. Fox, "Resistance of Silicon Nitride Turbine Components to Erosion and Hot Corrosion/Oxidation Attack," p. 36-1 in Proceedings of Advisory Group for Aerospace and Research & Development Symposium on Erosion, Corrosion, and Foreign Object Damage Effects in Gas Turbines, Printed by Canada Communication Group, Québec, Canada, November 1994.

Figure 1. Surface morphology of CVD mullite deposited on a Si₃N₄ substrate.

Figure 2. XRD patterns of CVD mullite coated on a Si₃N₄ substrate: (a) as-deposited and (b) after hot corrosion.

Figure 3. Some localized regions which looked "glassy" by optical microscopy were observed on the coating surface after hot corrosion. The "glassy" regions were found to be amorphous silicate with Al and Na impurities by TEM and EDS analyses.

Figure 4. Backscattered electron image and x-ray elemental maps of the cross-section of a mullite coated Si_3N_4 substrate after hot corrosion.

Development of Adherent Coatings to Reduce Contact Stress Damage of Ceramics

V.K.Sarin

Boston University, Department of Manufacturing Engineering
44 Cummington Street, Boston, MA 02215

Objective/Scope

The development of oxidation/corrosion resistant, high toughness, adherent coating configurations for silicon based ceramic substrates for use in advanced gas turbine engines.

Technical Progress

Additional thermodynamic analysis was performed on the $\text{AlCl}_3\text{-SiCl}_4\text{-CO}_2\text{-H}_2$ system for the chemical vapor deposition of mullite. The effect of changes in hydrogen concentration and the effects of using alternative halides was studied. A comprehensive thermodynamic analysis on the CVD formation of mullite was reported in an earlier bimonthly report.

Effect of Changing Hydrogen Concentration

Hydrogen concentration was increased from 500 moles (figure 1) to 1000 moles at the 1000 °C and 75 torr condition. The resultant phase diagram is as shown in Figure 2. No major changes were observed in the region near the high CO_2 concentration. However, the region where $\text{SiC+SiO}_2\text{+Si}$ composite phase forms is larger, and so is the SiC+SiO_2 region. The region over which $\text{SiO}_2\text{+C}$ forms is smaller, and the mullite+ $\text{SiO}_2\text{+C}$ region is slightly larger. When the hydrogen concentration was reduced to 250 moles, the opposite effects were observed. Figure 3 shows the CVD ternary phase diagram in this condition.

Mullite+Al₂O₃ region still remains more or less the same but the mullite+SiO₂ and the mullite+SiO₂+C region are now smaller. The SiO₂ and SiO₂+C regions are larger than they were in the H₂:500 moles condition. Also the SiC containing phases are now smaller as expected.

Effect of Using Alternative Halides

AlBr₃ and SiBr₄

In this calculation, AlCl₃ and SiCl₄ were replaced with AlBr₃ and SiBr₄ at the 1000 °C and 75 torr condition. The results of the analysis are presented in the CVD phase diagram in figure 4. The resulting phases are approximately the same as when AlCl₃ and SiCl₄ were used (figure 1) near the high CO₂ concentrations. The mullite+Al₂O₃ region is now smaller than before. The SiC+SiO₂+C region is approximately the same size as when AlCl₃ and SiCl₄ were used. SiC+SiO₂ region is now much larger, and SiO₂+C region starts to appear at lower CO₂ concentrations than before, however, the overall region is smaller than before.

AlF₃ and SiF₄

When AlCl₃ and SiCl₄ were replaced with AlF₃ and SiF₄, a completely different phase diagram emerges. The phase diagram is as shown in figure 5. A halide phase AlF₃ is observed at low CO₂ concentrations and high AlF₃ concentrations. This indicates that at low oxygen concentrations, AlF₃ does not react with the available hydrogen in order to form HF and Al as a deposit. A large region of pure Al₂O₃ is also observed in the diagram. Mullite is mostly observed along the SiCl₄-CO₂ line, and is again seen as a line compound, but formed over a much narrower range of reactant concentrations. There was also a region near the high CO₂ concentration where no solid phases were formed.

The deposition process is being studied in order to establish relationships between process parameters, coating microstructure, and performance of the mullite coatings. The process is being optimized using an iterative process utilizing the structure/property/performance relationships.

Status of Milestones

	<u>Schedule</u>	<u>Status</u>
<u>Task 1</u> : Optimize process parameters of codeposited mullite coatings to obtain desired structure/properties	6/95	On Schedule
<u>Task 2</u> : Coating Characterization	10/95	On Schedule
<u>Task 3</u> : Testing	11/95	On Schedule

Figure 1: CVD phase diagram of the $AlCl_3$ - $SiCl_4$ - CO_2 - H_2 system at 1000 °C and 75 torr condition.

Figure 2: CVD phase diagram of the $AlCl_3$ - $SiCl_4$ - CO_2 - H_2 system at 1000 °C and 75 torr condition with 1000 moles of hydrogen.

Figure 3: CVD phase diagram of the $AlCl_3$ - $SiCl_4$ - CO_2 - H_2 system at 1000 °C and 75 torr condition with 250 moles of hydrogen.

Problems Encountered

GN-10 grade Si_3N_4 billets were bought directly from Allied Signal. These billets were cut, ground and polished to 3x4 mm cross-sections as per Oak Ridge specifications for mullite deposition at BU and testing at ORNL. However, due to limitations in funding, this task could not be completed, and the costs involved had to be borne by us.

Credits

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Ceramic Technology Project of the Propulsion System Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

1.4.1 Ceramic-Metal Joints

WBS Element 1.4.1

JOINING OF CERAMICS FOR HEAT ENGINE APPLICATIONS

M. L. Santella

Objective/Scope

The objective of this task is to develop strong reliable joints containing ceramic components for applications in advanced heat engines. The overall emphasis of this task is on studying the brazing characteristics of advanced ceramics such as silicon nitride, silicon carbide and partially stabilized zirconia. The techniques of direct brazing with metallic and nonmetallic filler materials are being used. Vapor coatings are being used where appropriate to circumvent wetting problems associated with braze filler metals. The planned activities during FY 1995 will emphasize the use of structural analysis software to design joints for engine components such as valves and shaft attachments. The objective of this effort will be to identify material combinations and processing that would be feasible for these components, and to produce prototype parts whenever possible.

Technical Highlights

Ceramic-to-metal brazing: During this reporting period further analyses were completed on the brazed Ti alloy stem/ZrO₂ head engine valve, a brazed Ta stem/Si₃N₄ head valve, and designs for a ceramic-to-metal shaft attachment were evaluated. Three configurations of the Ti alloy stem/ZrO₂ head engine valve were analyzed: (1) a cylindrical ZrO₂ disk was used rather than a part shaped like a valve head; (2) the brazing temperature was increased to 975°C; and, (3) the situation where the joint area was completely filled with braze filler metal was considered. These additional cases were done to reflect the processing actually used to make the first Ti/ZrO₂ valve. The alteration in the shape of the ZrO₂ part did not result in any significant change in the residual stress distribution in the brazed joint. Increasing the brazing temperature to 975°C with the ZrO₂ disk did not alter the deformations compared with the original configuration, but it did result in lower predicted values of maximum principal stress (residual stress). Presumably, this was caused by the higher brazing temperature permitting plasticity in both the filler metal and the Ti alloy to accommodate more residual strain. This would have the effect of reducing residual stresses in the brazed valve. Lastly, altering the filler metal layer from selectively to completely filling the joint area resulted in a larger volume of the ZrO₂ being stressed, but the magnitude of the predicted stresses was very low. Based on this analysis, variation in joint filling would not be expected to result in unacceptably high residual stresses.

Materials needed to produce two additional Ti/ZrO₂ valves was committed for machining. The objective in making these valves is to begin optimizing the joint design and processing. Also, materials were prepared to make Ti/ZrO₂ coupons for testing of joint strength.

Also, an analysis was done on a valve configured with a Si₃N₄ head and a Ta shaft. Tantalum was selected for the shaft because of its relatively low coefficient of thermal expansion of $6.32 \times 10^{-6}/^{\circ}\text{C}$ at room temperature, and its relatively low yield strength and good ductility. These results indicated that for a brazing temperature of 870°C the entire Si₃N₄ part experienced positive residual stresses (maximum principal stresses) upon cooling to room temperature. A relatively large volume of the Si₃N₄ valve head was predicted to be under residual stresses in the range of 130 MPa, with smaller volumes experiencing stresses near 430 MPa. The extent and magnitude of residual stresses in this configuration are such that it would be impractical to produce prototypes. A least one additional analysis will be run for a valve configured with a Si₃N₄ head and a Mo stem when the property data file for Mo is available.

A design for a Si_3N_4 /metal shaft coupling was finalized and a finite element model was constructed for analysis. This finite element model required a full three-dimensional analysis because the shaft is configured such that the economies of an axisymmetric analysis cannot be used. For the initial analysis trials, the main metal shaft was a heat-resistant alloy, Incoloy 909. Initial trials indicated that there were no significant problems with the construction of the model, but completing the analyses required exceptionally long run times. Techniques for simplifying the model or our approach to the analysis are now being considered. Also, it is anticipated that a coupling between Si_3N_4 and the primary metal shaft alloy will ultimately require the use of a transition material to accommodate residual stresses. Consequently, property data files are being assembled for several refractory metals, including Mo, Nb, and Ta. These alloy were selected because of their desirable combinations of thermal expansion behavior and mechanical properties.

A experiment was completed to examine the effects of chemical reactions that occur during brazing on the properties of Si_3N_4 . The experiment was design to support work done previously at GTE Laboratories. It consisted of first vapor coating the tensile surface of 20 PY6 Si_3N_4 flexure bars (3 x 4 x 50 mm) with a 3- μm -layer of Ti, followed by vacuum brazing the bars to nickel coupons with a Au-5Pd-2Ni wt% filler metal. The bars where then detached from the Ni coupons by dissolving the filler metal in aqua regia. These 'brazed' bars were then four-point bend tested at room temperature along with a set of 20 control test bars. The data sets were analyzed with the CARES program and are plotted in Fig. 1. Compared to the control group, the brazed test bars had much lower average strength and Weibull modulus. The data suggest that chemical reactions that occur during brazing can dramatically reduce the strength of sintered Si_3N_4 independently of other factors such as residual stresses. Analysis of the data and specimens is continuing.

Status of Milestones

On schedule

Publications

None

Unpublished work

An invention disclosure entitled, "Engine poppet valve with a ceramic head bonded to a metal stem," was filed with the Department of Energy.

Fig. 1. Weibull plot of results from four-point bend testing of PY6 Si_3N_4 test bars.

1.5 CERAMIC MACHINING

W.B.S. Element 1.5.0.0

COST-EFFECTIVE CERAMIC MACHINING

P. J. Blau
Oak Ridge National Laboratory

Objective/Scope

The objective of this effort is to develop, in conjunction with U. S. industry, advanced technologies and the associated scientific and economic concepts necessary to reduce the costs associated with the machining of structural ceramics; especially, as related to the use of these materials in energy-efficient, low-emissions transportation systems. This effort consists of subcontracts to industry and in-house research at Oak Ridge National Laboratory, Argonne National Laboratory, and the National Institute of Standards and Technology. Progress reports for other than the ORNL in-house research portion of this work may be found elsewhere in this publication. The four subtasks in this effort are:

1. Technology Assessment and Future Needs
2. Advanced Machining Methods Development
3. Ceramic Machinability and Related Performance
4. Structure and Surface Quality of Machined Ceramics

ORNL in-house activities are aimed at two technical areas: (1) investigating the effects of machining practices on the durability of ceramics for valve and valve seat applications and (2) understanding and characterizing the detailed nature of machining-induced surface and sub-surface damage and their evolution in advanced ceramic materials using a range of analytical tools. The latter includes such methods as non-contact surface profiling, atomic force microscopy of ground surfaces, and scanning acoustic microscopy to detect subsurface flaws.

Technical Highlights

a. Annotated Bibliography of Grinding Wheel Characterization is Completed. An annotated bibliography of nearly 100 publications dealing with the characterization of the structure, properties, and performance of grinding wheels has been prepared by Robert W. McClung, Consultant to ORNL. The new report contains nine subsections on such topics as the non-destructive examination of wheels, wheel wear measuring methods, wheel property measuring methods, wheel surface texture, and in-process monitoring of wheel behavior. The report will be published by ORNL.

b. Study of Electrolytic In-Process Wheel Dressing Completed. Dr. B. P. Bandyopadhyay, University of N. Dakota, rejoined the laboratory of Prof. Ohmuri of the Institute of Physical and Chemical Research (RIKEN), Tokyo, Japan, to study the effects of grinding with and without ELID, the effects of ELID on the form and surface finish the part, and the effects of ELID on grinding ratio (i.e., ratio of the stock material removed to the amount of abrasive consumed). A draft report was delivered to ORNL and is currently under review for publication as an ORNL subcontract Report.

c. Development of a Next-Generation Grinding Wheel for Ceramics: Initiation of Phase II. As discussed in the previous semi-annual report, three groups of St. Gobain / Norton Company teamed up to develop a new grinding wheel optimized for cylindrical

grinding of silicon nitride parts such as poppet valves. The fifteen month effort began in September of 1993 and resulted in the delivery of a final report and six specimen grinding wheels for third-party evaluation. Some of the evaluations are being performed at ORNL on a new Ded-Tru™ grinding fixture which permits a surface grinder to be modified to conduct centerless-type operations. Distribution of the final report is expected within the next month. A follow-on, Phase II effort to scale up (to 14" (356 mm) diameter) and production-test the wheels has been initiated. Part of the effort involves evaluating the new wheel at higher speeds and modifying its construction, if necessary to meet those additional demands. Independent evaluations of the scaled-up wheel are also part of Phase II.

d. Three New Subcontracts Initiated. Three new Cost-Effective Ceramic Machining-related subcontracts have been initiated. They are:

Cost Modeling Analysis of Fabrication Approaches for Silicon Nitride Components
(AlliedSignal Ceramic Components and California Polytechnic University - Pomona)

The Effect of Machine Stiffness on the Grinding of Silicon Nitride
(University of Connecticut - Storrs)

Next Generation Spindle for High-Speed Centerless Grinding of Advanced Ceramics
(Eaton Corporation and Weldon Machine Tool Company)

Details of these new efforts will be incorporated as separate sections in future Ceramic Technology Project periodic reports.

e. Annual Project Review Held. A total of 51 people attended the Annual Cost-Effective Ceramic Machining (CECM) Project Review held on Wednesday, September 20, 1995. Figure 1 shows the titles, speakers, and schedule for the presentations. The last three presentations were included for the purpose of information and are not CECM-funded projects. Attendees were asked to critique and comment on the various projects. Overall, comments on the annual project review were positive and complimentary. Survey results related to individual projects will be provided as feedback to the presenters of those projects. Some of the attendees noted that it may have been advisable to allow more time for both presentations and discussions. The possibility of extending future reviews to one and one-half days is being considered as a result.

In addition to the formal presentations, C. Guo of Chand Kare Technical Ceramics displayed two prototype compact grindability testing machines which were developed under subcontract. One of the machines will be delivered to ORNL for use in the Machining and Inspection Research User Center. The other will be retained at CKTC. The machine uses small flexure bar-shaped specimens to obtain a relative grindability number which can be used to quickly screen new ceramics for their grinding behavior, as correlated to production grinding machines.

A report on the annual project review is being prepared for publication in the *Ceramic Technology Newsletter*.

Future Plans

An agreement has been reached to work jointly in the area of machining damage analysis with Dr. Kristin Breder, ORNL, who is coordinating U.S. efforts in the International Energy Agency (IEA) project on ceramic properties. Various subsurface damage assessment techniques will be applied at ORNL and ANL to GS-44 materials which have been ground under IEA conditions. Coupons of GS-44 are being prepared for study. Additional high-speed tests will

also be performed on the materials to assess the effects of rapid material removal rates on surface quality. This project is being coordinated with the help of Dr. David Richerson, Consultant, of Salt Lake City, UT.

Dr. Elmer Zanoria who is completing a post-doctoral appointment at Georgia Institute of Technology will join the CECM in-house effort in November 1995. His work will focus both on slip effects on repetitive impact testing and ground surface structural characterization.

Status of Milestones

On schedule.

Communications/Visitors/Travel

CECM Principal Investigators visited Oak Ridge to present summaries of their projects on September 20, 1995, at the Annual CECM Project Review.

Problems encountered

Late delivery of the centerless grinding fixture delayed in-house evaluation of the Norton advanced grinding wheels. This fixture is only now being installed on the instrumented Harig Grinder in the High Temperature Materials Laboratory at ORNL.

Publications/Presentations

- 1) L. Wei, H. H. K. Xu, and S. Jahanmir (1995) *Evaluation of Thermal Wave Imaging for Detection of Machining Damage in Ceramics*, NIST Report NISTIR 5645, National Institute of Standards and Technology, Gaithersburg, MD, 49 pp.
- 2) J. A. Kovach and S. Malkin (1995) *High-Speed, Low-Damage Grinding of Advanced Ceramics Phase I*, ORNL report ORNL/Sub/92-SL807/1, Oak Ridge National Laboratory, Oak Ridge, TN, 115 pp.
- 3) J. Kovach, M. Laurich and B. Zhu (1995) "High-Speed, Low-Damage Grinding of Silicon Nitride," *Abrasives Magazine*, August/September, pp.15-20.
- 4) B. P. Bandyopadhyay (1995) *Application of Electrolytic In-Process Dressing (ELID) for High Efficiency Grinding of Ceramic Parts*, ORNL Subcontract Report, to be published.
- 5) R. W. McClung (1995) *Characterization of Grinding Wheels: An Annotated Bibliography*, ORNL Report, to be published.

CECM Annual Project Review - Final Program

(September 20, 1995)

I. Introductions*Background of the CECM Effort*

P. J. Blau, ORNL

Ceramic Technology Project Update

D. R. Johnson, ORNL

II. Technology Assessment*ELID Grinding of Ceramics - Research in Japan*

B. P. Bandyopadhyay, University of North Dakota

Review of Ceramic Machining Methods and Markets in Europe

E. L. Long, ORNL

III. Advanced Machining Methods Development*Innovative Grinding Wheel Design for Machining Ceramics*

R. Licht, St. Gobain - Norton Company

Development of High-Speed Grinding Methods for Ceramic Parts - Phase II

J. Kovach, Eaton Corporation and S. Malkin, U. of Massachusetts

Development of a High-Speed Centerless Grinding Spindle

J. Kovach, Eaton Corporation and

J. Flinchbaugh, Weldon Machine Tool Company

Findings of the NIST Grinding Optimization Studies & Ceramic Machining Database

S. Jahanmir and L. K. Ives, NIST

Chemically-Assisted Ceramic Grinding

S. M. Hsu, NIST

Cost Analysis: Near-Net-Shape Processes vs. Ceramic Machining

R. Walecki, AlliedSignal Ceramic Components

Effects of Machine Stiffness on Ground Ceramic Part Quality

B. Zhang, University of Connecticut

(IV. Ceramic Machinability and Related Performance*Development of a Grindability Test for Ceramics*

R. Chand and C. Guo, Chand Kare Technical Ceramics

(continued)

V. Structure and Surface Quality of Machined Ceramics*Laser Light-Scattering and Dye Penetrant Studies*

S. Ahuja and W. Ellingson, Argonne National Laboratory

In-House Research on Surface Quality and Performance in Machined Ceramics

P. J. Blau, ORNL

VI. Update on Cost-Effective Machining of Ceramics-Related Programs*Update on International Energy Agency (IEA) Machining Studies*

K. Breder, ORNL

Update on Defense Programs Machining CRADAs

T. O. Morris, ORNL / Y-12

Update on the HTML User Program in Machining

S. McSpadden, ORNL

COST-EFFECTIVE METHOD FOR DETERMINING THE GRINDABILITY OF CERAMICS

Changsheng Guo, Ph.D.
Ronald H. Chand
Natesh Krishnan

Chand Kare Technical Ceramics, Inc.
2 Coppage Drive
Worcester, MA 01603-1252

Objective/Scope

The objective of this program is to develop a cost-effective method to determine the grindability of ceramics leading to cost-effective methods for machining such ceramics. In this first phase of activity, Chand Kare Technical Ceramics is engaged in directing its efforts towards review of literature related to ceramic grinding, development of a variable definition of grindability, design of grindability test experiments, and design of a ceramics grindability test system (CGTS). The grindability study underway also includes establishment of correlation between the grindability number and the conventional grinding practices.

Technical Highlights

The technical progress to date is summarized by activities in the attached Milestone Schedule. The remainder of this section describes activity from April 1 to September 30, 1995.

Development of the Final CGTS

The fabrication of the final prototype of the ceramic grindability test system has been completed. The finished machine was exhibited at the annual ceramic machining workshop on September 20, 1995. The earlier version of the test system was also exhibited at the workshop. Both test systems will be exhibited at the Annual Automobile Contractor's Coordination Meeting from October 23 to 27, 1995 in the Ritz Carlton Hotel, Dearborn, Michigan. Figures 1 and 2 are photographs of the final ceramic grindability test system, which has the following features:

- Fully computerized to eliminate operators influence.
- Grinding with diamond belt to eliminate influence of wheel dressing.
- Standard MOR bars as test specimen for cost-effectiveness.
- Computer controlled force and speed adjustment for various ceramics.
- In-process automatic gaging of material removal rate with analogue and digital read out.

After the exhibition, the CGTS will then be delivered to Oak Ridge National Laboratory.

Grindability Test

During the last period of time, additional grindability tests were conducted for six more silicon nitride ceramics and one more silicon carbide ceramics. The mechanical properties of those seven ceramics are listed in Table 1 (Materials 13-18) together with other ceramics tested before. For Materials 14 to 18, a batch of MOR bars were manufactured and their flexural strengths were measured by Oak Ridge National Laboratory. Some samples from the same batch used to measure the flexural strength were used to measure their grindability. The measured grindability is listed in the last column of Table 1. As discussed in the definition of grindability in the previous reports, the physical meaning the grindability is the material removal rate obtained under unit force and unit belt speed.

In Figure 3, grindabilities of various ceramics are plotted. It can be seen that the easiest material tested (Material 12, aluminum oxide) has a grindability more than 26 times of the most difficult material tested (Material 15, silicon nitride - I). If silicon nitride ceramics are compared, the easiest material tested (Material 18, silicon nitride - L) has a grindability about 5 times of the most difficult material tested (Material 15, silicon nitride - I). However, their mechanical properties are not so much different. The grindabilities of the silicon nitride ceramics tested are plotted in Figure 4.

Grindability and Mechanical Properties

A. Correlation between grindability and flexural strength

Extensive grindability tests have been conducted for various ceramics. Some of those tested ceramics have very similar mechanical properties, and others have very different ones (see Table 1). Therefore, it is interesting to know whether a correlation exists between grindability and mechanical properties such as hardness, flexural strength, and fracture toughness. Grindability is plotted versus flexural strength in Figure 5 for all the ceramics tested. These results seem to indicate that grindability generally decreases with flexural strength. However, more tests are needed to further prove this. In Figure 6, only silicon nitride ceramics are compared. From this graph, it is hard to accept the above preliminary conclusion.

B. Correlation between grindability and hardness

Any correlation between grindability and hardness is also of interest to both material manufacturers and ceramic machining factories. Grindabilities are plotted versus hardness (Vickers scale) in Figure 7 for all the ceramics tested. No simple correlation could be found between grindability and hardness. Silicon carbide ceramics tested are much harder than silicon nitride ceramics tested. But silicon carbide ceramics generally have higher grindabilities than silicon nitride ceramics. This may be due to their lower flexural strength and low fracture toughness. The results for silicon nitride are given in Figure 8.

C. Correlation between grindability and fracture toughness

Fracture toughness is another important mechanical properties of ceramics. Correlation between grindability and fracture toughness is also investigated. There seems no simple correlation between grindability and fracture toughness as indicated in Figures 9 and 10.

Based on the grindability test conducted for various ceramics, there seems no simple correlation between grindability and mechanical properties such as flexural strength, hardness, and fracture toughness. Grindability is a comprehensive parameter which cannot be replaced by any other mechanical properties commonly evaluated. It should be evaluated together with hardness, flexural strength, fracture toughness and other mechanical properties during the material development stage.

Grindability and Microstructure

In the previous section, correlation between grindability and mechanical properties (hardness, flexural strength and fracture toughness) were studied. No simple correlation was found between grindability and mechanical property for the 18 ceramics tested. More ceramic materials need to be tested in order to further support the preliminary conclusion. In order to find out factors determining the ceramic grindability, microstructure of some of the ceramics tested were studied. The as-ground surfaces were observed under a scanning electron microscope. Those surfaces were also observed after they were etched for one hour in a hydrofluoric solution (49% HF).

In Figure 11, the SEM photographs of the as ground surfaces of Materials 3, 4, 8 and 10 are given. It can be seen that the material is removed by both ductile flow (plastic deformation) and brittle fracture. However, the percentage of brittle fracture depends on the material. Material 10 (silicon carbide) shows much higher brittle fracture than Material 8 (silicon nitride). It should be noted that big holes (about 15 μm) were observed on the surface of Material 3. They do not look like holes caused by grinding rather inherent with the material itself. This is under further investigation.

Status of Milestones

Completed.

Communications/Visits/Travel

On June 14, 1995, Ronald Chand and Changsheng Guo visited Oak Ridge National Laboratory and discussed the project progress and the design of the test machine with Dr. Peter Blau and Mr. Earnest Long.

From August 20-23, 1995, Changsheng Guo attended the International Symposium on Advanced Ceramics for Structural and Tribological Applications in Vancouver, B.C. On August 22, 1995, he presented a paper titled "Characterization of Ceramics from the

Machining View Point." This paper was authored by Changsheng Guo and Ronald H. Chand.

From September 12-14, 1995, Changsheng Guo attended the 1st International Machining and Grinding Conference in Dearborn, Michigan. He presented a paper titled "Grindability of Ceramics" at the ceramic session. This paper was authored by Changsheng Guo and Ronald H. Chand.

On September 20, 1995, Ronald H. Chand, Changsheng Guo and Keith P. Costello attended the machining workshop at Oak Ridge National Laboratory. Ronald H. Chand and Changsheng Guo did a presentation about the project. The second prototype CGTS and the final CGTS were also exhibited at the workshop.

Problems Encountered

None.

Publications

Guo, C. and Chand, R.H., 1995, "Grindability of Ceramics," *Proceeding of the 1st International Machining and Grinding Conference*, SME, MR95-168, Dearborn, MI, pp.123-136.

Guo, C. and Chand, R.H., 1995, "Characterization of Ceramics from the Machining View Point," *Proceedings of the International Symposium on Advanced Ceramics for Structural and Tribological Applications*, Vancouver, British Columbia, Canada, pp.413-424.

Guo, C. and Chand, R.H., 1996, "Precision Machining of Technical Ceramics," *Ceramic Technology International*, pp.49-52.

Table 1 Summary of materials tested

Number	Material	Hardness HV	Strength (MPa)	Elastic modulus GPa	Poisson ratio	Fracture toughness	Grindability G_c (10^{-4} $\text{mm}^3/\text{m N}$)
1	Si_3N_4 - A	1860	590	276	0.28	5.70	24.3
2	Si_3N_4 - B	1500	620	172-241	0.22	6.60	18.5
3	Si_3N_4 - C	1500	620	172-241	0.22	6.60	17.1
4	ZrO_2 - A	1200	630	207-241	0.31	8-12	37.9
5	ZrO_2 - B	1200	630	207-241	0.31	8-12	37.0
6	Si_3N_4 - D	1500	620	172-241	0.22	6.60	22.9
7	Si_3N_4 - E	1500	620	172-241	0.22	6.60	22.2
8	Si_3N_4 - F	1460	1050	310	-	8.25	21.2
9	Si_3N_4 - G	1670	983	306	-	6.50	18.2
10	SiC - A	2500	595	466	0.21	2.70	70.2
11	SiC - B	2800	460	410	0.14	4.60	87.7
12	Al_2O_3	1360	310	-	-	-	181.3
13	SiC - C	1550	655	455	0.14	5.2	91.8
14	Si_3N_4 - H	1460	1027	310	-	8.25	19.6
15	Si_3N_4 - I	1610	891	310	0.27	6.4	6.9
16	Si_3N_4 - J	1420	849	300	0.28	6.7	15.5
17	Si_3N_4 - K	1540	756	319	0.28	6.9	23.7
18	Si_3N_4 - L	1550	566	320	0.28	6-7.5	34.3

Figure 1 Photograph of the ceramic grindability test system

Figure 2 Photograph of part of the CGTS

Figure 3 grindability of various ceramics

Figure 4 grindability of tested silicon nitride ceramics

Figure 5 grindability and flexural strength

Figure 6 grindability and strength (silicon nitride)

Figure 7 grindability and hardness

Figure 8 grindability and hardness (silicon nitride)

Figure 9 grindability and fracture toughness

Figure 10 Grindability and fracture toughness (silicon nitride)

(a) Material 3

(b) Material 4

Figure 11 SEM photograph of the as-ground surfaces

(c) Material 8

(d) Material 10

Figure 11 SEM photograph of the as ground surfaces (cont)

High-Speed, Low-Damage Grinding of Advanced Ceramics

Joseph A. Kovach
Eaton Manufacturing Technologies Center
Willoughby Hills, Ohio 44094

Stephen Malkin
University of Massachusetts
Amherst, Mass. 01003

Objective/Scope

The overall objective of the High Speed Low Damage (HSLD) grinding project is to develop a single step, roughing-finishing process suitable for producing high-quality advanced ceramic components at high material removal rates and at substantially lower cost than traditional, multi-stage grinding processes. Initial implications from Phase I have suggested that HSLD grinding of Si₃N₄ is technically feasible. Accordingly, to achieve the overall program objective, the Phase II effort is focused on:

- 1.0** Continued expansion of the existing HSLD science base,
- 2.0** Further development of the enabling HSLD technologies required for successful production implementation, and
- 3.0** Economic analysis of the HSLD production cost drivers.

Technical Progress

This semiannual report summarizes technical progress achieved during the period from April 1, 1995 through September 30, 1995. The report describes activities at the University of Massachusetts and the Eaton Manufacturing Technologies Center. A technical overview is presented in the following areas:

- 1. HSLD MOR Strength Evaluation and Fractography Analysis
- 2. Ceramic Grinding Mechanism Analysis
- 3. Infrared Detector System for Temperature Measurements
- 4. Hydrodynamic Forces in Grinding of Ceramics
- 5. Centerless Grinding - Simulation & High Speed Testing
- 6. High-Speed Grinding with Diamond Belts
- 7. Advanced Wheel Dressing Concepts

1.0 HSLD MOR Strength Evaluation and Fractography Analysis

Building upon the MOR test data presented in the previous semi-annual report, Eaton has completed a detailed MOR specimen fractography study of the MOR bars ground using a very coarse 120 grit wheel. This analysis was conducted to determine whether the measured fracture strength was a true indication of the material properties, or if low fracture strength was the result of edge crack effects, from specimen preparation, handling damage or unusual microstructural features (voids, inclusions, etc.). The fractography was carried out with optical and scanning electron microscopy (SEM).

Based on the fractographic analysis, a substantial number of specimens were removed from the MOR strength analysis, and a revised Weibull analysis was completed. Tables 1 & 2 list the test conditions, as well as the original and revised MOR strength data, along with the revised Weibull statistics based on the fractographic analysis. Also shown are the number of samples removed from the analysis for different failure modes. The high fall-out levels for the condition C samples indicated a problem in the chamfering operation after the grinding tests had been completed. Examination showed the chamfers on the tensile side of the MOR bars had large areas of fragmentation and pull out. The chamfer chipping is being investigated. Of the remaining samples, the optical and SEM examination clearly showed that the grinding grooves did initiate MOR fractures at the tensile surface.

Recognize that the new smaller sample size for each grinding condition (based on the samples eliminated by fractographic analysis) makes it more difficult to draw sweeping conclusions regarding the effects of grinding conditions on MOR strength. It does appear, however, that the average (63.2% failure) strengths for these extremely coarse (120 grit) grinding conditions did not change substantially after fractographic analysis. The samples ground under conditions A, B and D had very similar strength.

On the other hand, Condition C, which utilized the higher material removal rate and faster wheel speed, still displayed a lower average strength (see Table 2). The revised data also tends to indicate that when using a very coarse 120 grit wheel, lower material removal rates may provide a better Weibull modulus. Based on these examinations, it appears as if the 120 grit plated wheel was far too coarse to provide damage free components, even while operating at high wheel speeds.

In addition to the above fractography analyses, the characteristics of the ground surface that controlled the strength were also evaluated using several techniques. Atomic Force Microscopy (AFM) examinations were carried out with a Park Scientific unit at Case Western Reserve University. The original intent of this effort was to characterize the ground surface, using AFM as a very precise profilometer. AFM had the potential to provide the height and shape of the grinding grooves, show a profile of the grinding grooves and compare the surface fragmentation from different grinding conditions. However, the grinding groove depth and relative porosity levels were often beyond the travel limits of the AFM probe head, and ended up giving incomplete data.

While early evaluations using Scanning Acoustic Microscope (SAM) showed promise for detecting subsurface cracks, the surface roughness of the as-ground workpiece ultimately made most of the SAM analysis inconclusive. The relatively rough as-ground surface produced a great deal of surface waves that interfered with the subsurface return signal. More importantly, however, the rough surface produced reflections that would obscure any subsurface features. As a relatively new technique for grinding damage assessment, SAM requires an experienced operator to interpret rather confusing images of as-ground S/RBSN surfaces.

As follow-on efforts, additional HSLD tests are being setup at Eaton/MTC to fully characterize process removal rates and resulting affects on component quality. Unlike the previous test series (which utilized coarse plated wheels), the focus of this test series will be on industrializable processes using dressable wheels. To date, Beck Universal 170 and 320 grit high-temperature resin bonded wheels have been received. High speed Beck vit-bonded wheels are also due in shortly. In addition, a special high speed graphite fiber reinforced 170 grit vitrified bond wheel has been received from Noritake. A custom high speed hub has also been designed and is being built for the new Noritake wheel. All workpiece test material has been received (Allied Signal GS-44, Ceradyne Ceralloy 147-3, Kyocera SN-220, and Eaton S/RBSN).

2.0 Ceramic Grinding Mechanism Analysis

In a related effort, the University of Massachusetts (UMass) has been investigating the mechanisms of ceramic grinding to determine how the surface and sub-surface grinding damage, described above, is generated. In addition, the efforts are also aimed at identifying how the specific grinding energy is quantitatively balanced with respect to the energy consumed during material removal process. To date, UMass has conducted 54 additional experimental tests over a wide range of grinding conditions. Power and forces were measured and the results were analyzed using the "scratched surface parameter" described below. In addition, the ground surface and grinding debris were analyzed by scanning electron microscopy (SEM) for the following three cases:

	Depth of Cut (mm)	Work Speed (mm/s)	Wheel Speed (m/s)
Case I	0.038	200	10
Case II	0.0216	100	30
Case III	0.00508	5	40

Ground surfaces were initially generated and analyzed using a low wheel speed V_s of 10 m/s, workspeed V_w of 200 mm/sec, and depth of cut a of 0.025 mm. From those observations, it was suggested that the mechanism of material removal is mainly caused by fracturing associated with lateral cracking. In all cases, the surfaces generated by grinding appear to be covered with a smooth smeared layer, which can hide subsurface damage. Because the layer was chemically attacked by HF, it was assumed to be amorphous (glassy).

Hydrofluoric acid(49% HF) was used to etch the ground surface for 1 hour at 100 °C to remove the smeared (amorphous) layer. The grooves generated by abrasive grains were clearly observed after etching, which suggests that the deformation also extends beneath the smeared surface layer. This deformation, between the smeared layer and the original material beneath it, could account for much of the grinding energy input. What is important to note, however, is that little difference was observed between the etched surfaces for Cases I, II, and III at magnifications up to 2000X.

The smeared layer observed after grinding may be formed by reaction of Si_3N_4 with oxygen:

$$\text{Si}_3\text{N}_4 + 3\text{O}_2 = 3\text{SiO}_2 + 2\text{N}_2$$

This silicate oxidization layer would be glassy (amorphous), unlike the original crystalline ceramic structure. This oxidization process may be influenced by friction, water vapor, and temperature. The formation of the smeared layer will receive further study.

Scratched Surface Parameter

As of yet, no grinding model has been developed which can fully account for the forces and specific energy seen during the grinding of structural ceramics. From the observation of grinding debris and the ground surface, it appears that material is mainly removed by brittle fracture. The magnitude of the specific fracture energy can be roughly estimated from the fracture surface energy and size of particles. The magnitude of the specific fracture energy estimated in this way (10^6 J/mm^3) is three or four orders of magnitude less than the measured specific grinding energy ($10 \sim 100 \text{ J/mm}^3$). Therefore the fractured surface energy is negligible compared to the specific grinding energy.

From the observation of ground surfaces, it would appear that deformation associated with the smeared surface generated by successive contact with grains might play an important role in the energy consumption. With this in mind, a new parameter was developed which is the scratched surface area. For a single undeformed chip with a trapezoidal cross-section, the scratched surface area would comprise the bottom surface and two side surfaces.

For simplicity, it is assumed that the scratch width b_s is proportional to the undeformed chip thickness h :

$$b_s = rh \quad 1$$

where r is a geometrical constant, and that the angle θ of the trapezoidal cross section can be obtained from a scratch test. The maximum undeformed chip thickness h_m is obtained as

$$h_m = \left[\frac{4}{C(r - \tan\theta)} \left(\frac{v_w}{v_s} \right) \left(\frac{a}{d_s} \right)^{1/2} \right]^{1/2} \quad 2$$

where C is the number of cutting points per unit area on the wheel surface and d_s is the equivalent wheel diameter.

For this uncut chip geometry, the area of the bottom surface S_b is obtained as product of average width of the bottom surface b_a and the contact length l_c

$$S_b = b_a l_c = (r - 2 \tan \theta) h_a l_c = (r - 2 \tan \theta) \left(\frac{h_m}{2} \right) l_c \quad 3$$

or

$$S_b = \frac{(r - 2 \tan \theta)}{[C(r - \tan \theta)]^{1/2}} \left(\frac{v_w}{v_s} \right)^{1/2} (a)^{3/4} (d_s)^{1/4} \quad 4$$

The area of the two side surfaces S_s is similarly obtained as

$$S_s = \frac{2}{\cos \theta [C(r - \tan \theta)]^{1/2}} \left(\frac{v_w}{v_s} \right)^{1/2} (a)^{3/4} (d_s)^{1/4} \quad 5$$

Therefore the total scratched surface S_t produced by single grain after one complete pass is equal to the sum of S_s and S_b . Now the rate at which the scratched surface area is produced, S_w , can be obtained as :

$$S_w = C b S_t v_s \quad 6$$

where b is the grinding width. Assuming that the grinding power is proportional to S_w and combining Eqs.(4,5,& 6) leads to an expression for the power per unit width:

$$\frac{F_t v_s}{b} \propto [C]^{1/2} \frac{\left[r + \frac{2}{\cos \theta} (1 - \sin \theta) \right]}{[(r - \tan \theta)]^{1/2}} \left(v_w v_s \right)^{1/2} (a)^{3/4} (d_s)^{1/4} \quad 7$$

The specific grinding energy and tangential grinding force can also be obtained from Eq.(7). The specific energy is :

$$u = \frac{F_t v_s}{a v_w b} \propto \frac{[r + 2(1 - \sin \theta) / \cos \theta]}{[(r - \tan \theta) / C]^{1/2}} \left(\frac{v_s}{v_w} \right)^{1/2} \left(\frac{d_s}{a} \right)^{1/4} \quad 8$$

and the force per unit width is :

$$\frac{F_t}{b} \propto \frac{[r + 2(1 - \sin \theta) / \cos \theta]}{[(r - \tan \theta) / C]^{1/2}} \left(\frac{v_w}{v_s} \right)^{1/2} (a)^{3/4} (d_s)^{1/4} \quad 9$$

If the same wheel and workpiece is used (C , r , θ , and d_s constant), the only dependent variables should be a , v_w , and v_s . In case of different wheels, C and d_s can be considered as dependent variables with the assumption that the parameters r and θ are independent.

It can be seen that a proportional relationship between the power per unit width and the scratched surface parameter would imply a constant energy per unit contact area between the abrasive grains and the workpiece. Consequently, the measured power and forces were plotted against the scratched surface parameter. The present results in Figure 1 show two straight-line regions over the range covered by these test conditions. A proportional relationship with a smaller slope at very low values of the scratched surface parameter is followed by a straight line with a much steeper slope covering most of the grinding conditions of practical interest. Cases I, II and III for observation of ground surface and grinding debris are marked in this figure. The corresponding specific tangential and normal forces also displayed a similar trend. Additional experiments must be conducted to further define the grinding behavior. Models are being developed to quantitatively account for these experimental results.

3.0 Infrared Detector System for Temperature Measurements

In addition to analyzing the mechanically generated surfaces, the consequences of thermally induced surface effects are also being investigated. Recognize that high temperatures generated in high speed grinding of ceramics may significantly affect the grinding mechanisms and resulting surface quality. It has been suggested that elevated grinding zone temperatures could inhibit fracture and thereby promote a non-detrimental ductile mode of grinding. However, grinding with high wheel speeds may also adversely affect the process. Excess heating could substantially reduce the useful life of a grinding wheel. The objective of this work is to develop a thermal model to predict the grinding zone temperature based on the energy partition to the workpiece, which can be estimated by matching the measured temperature response to analytically computed values.

A two-color infrared detector with an optical fiber is used to measure the workpiece *subsurface* temperature in this investigation. Currently, the UMass infrared pyrometry system requires a hole drilled into the bottom of the workpiece for optical fiber insertion. In order to get good system response, the bottom of the blind hole must be in close proximity to the workpiece surface. It can be expected that the temperatures at the bottom of the hole are higher than the temperatures with no hole because the removal of the material from the workpiece reduces its ability to conduct heat. No analytical solutions are available for the temperature field of a solid containing a hole, subjected to a moving heat source. Therefore, a finite element analysis (FEA) was employed to gain insight into this temperature distribution. From the FEA analysis, it was concluded that the measurement error caused by a 1mm hole is significant, which could induce as high as 34% overestimation at a depth of 0.5 mm below the ground surface. A smaller hole should be recommended for future experiments, although it will be more difficult to instrument the workpiece.

Using the approach described above, it was found that the energy partition for wet grinding is 16 to 24%, and for dry grinding 59%. This difference in energy partition suggested that the grinding fluid plays an important role in cooling the grinding zone. It was also found that the grinding zone temperature for wet grinding with 400 grit size wheel can exceed the film boiling point of water (130 °C under one atmosphere pressure). Thus the cooling mechanism at the workpiece could be different from the one using conventional grinding wheels.

One possible cause for the difference in energy partition is that high fluid pressure in the workzone can suppress film boiling of the fluid, thus enhancing the cooling effectiveness of the fluid at the workpiece. In this case, the burn-out heat flux will depend on the fluid pressure which in turn depends on the wheel grit size, the wheelspeed, and the wheel surface condition. Another possibility to account for the high energy partition in the dry grinding case could be build up of the workpiece material on the wheel surface. By adding a thin layer of silicon nitride to the diamond grain, the finite element analysis showed a significant increase in the energy partition to the workpiece. Microscopic examination will be conducted to observe the wheel surface conditions after both wet and dry grinding tests.

4.0 Hydrodynamic Forces In Grinding of Ceramics

Grinding of structural ceramics at high removal rates with minimal surface damage may be achieved by using high wheel speeds. However, high wheel speeds coupled with relatively non-porous diamond wheels and copious fluid application, can result in significant hydrodynamic forces between the wheel and the workpiece. UMass has developed a hydrodynamic analysis to quantitatively account for these fluid related forces. In general, it was found that significant hydrodynamic forces are generated at the converging inlet to the grinding zone. These forces act in addition to those associated with actual grinding and the direct impingement of the applied fluid.

From an analytical perspective, the initial model was based on an assumption that both the grinding wheel and workpiece are perfectly smooth, thereby allowing for simple hydrodynamic modeling using the following relationships:

$$F_v = (F_{v_s} - F_{v_o})b = \mu(v_s - v_o)f(h_o) \quad (1)$$

where: F_v = hydrodynamic force per unit width of the specimen
 v_s = wheel speed, v_o = lowest velocity, b = workpiece width
 μ = dynamic viscosity, and

$$f(h_o) = b[12((Q - Q_o)/(v_s - v_o)) \int_0^1 \int_0^x \frac{dx}{h^3} dx - \int_0^1 \int_0^x \frac{dx}{h^2} dx] \quad (2)$$

where: Q = fluid flow passing under the wheel
 h = separation height between wheel & work ($h=0$ while grinding)

As expected, however, a significant difference between the analytical and experimental results was observed. To compensate for this difference an empirical correction factor h_c was used to account for the wheel roughness. In essence this approach suggests that the hydrodynamic thickness is increased by an amount h_c equal to the peak-to-valley wheel roughness. The influence of h_c can be discussed more conveniently by dividing equation (1) by $v_s - v_o$ which leads to:

$$(Fv_s - Fv_o) / (v_s - v_o) = \mu f(h_o) \quad (3)$$

For example to compute the theoretical force at an experimentally set gap thickness of 25 μm , a gap thickness of $h_o = 25 + 20\mu\text{m}$ was used. Repeating the analysis with $h(x)$ replaced by $h(x) + h_c$, or h_o replaced by $h_o + h_c$, and plotting according to equation 3 gives results as shown in Figure 2. Although there is some systematic deviation, the data fall reasonably close to the same straight line.

The slope of the straight line in Figure 2, obtained from least square fitting of the data, implies a dynamic viscosity of $\mu = 0.00485 \text{ N-s/m}^2$. The kinematic viscosity of the soluble oil used in the experiments was quoted by the supplier as 350 Saybolt Universal Seconds at 25 °C, which worked out to be approximately 80 centistokes. Using a simple law of mixtures, a 5% solution of this oil in water (kinematic viscosity, 1 centistoke) would imply a kinematic viscosity of 5 centistokes corresponding to a viscosity of 0.005 N-s/m^2 . This is remarkably close to the implied viscosity corresponding to the slope in Figure 2.

For the case of actual grinding, there is no set gap thickness for $h_o = 0$. The value of h_c depends on the characteristics of the grinding wheel. For $h_c = 20\mu\text{m}$ the calculated hydrodynamic forces agree very well with the measured values for the 400 grit wheel and for $h_c = 40\mu\text{m}$ for the 120 grit wheel. These values of h_c correspond to the measured peak-to-valley roughnesses for the respective wheels. This seems to indicate that equations (1) or (3) can be used to predict the hydrodynamic force for situations both with and without any set gap thickness h_o .

5.0 Centerless Grinding - Simulation & High Speed Testing

This part of the work is concerned with simulation of the centerless grinding process on a PC. The simulation program consists of two major parts. Part 1 performs a static analysis of the process under various setup conditions to predict whether or not the workpiece will spin. Part 2 performs a kinematic simulation of the process for both conventional above center grinding and below center grinding. The simulation has been useful in troubleshooting high material removal rate centerless grinding processes, particularly with respect to minimizing induced lobing.

High speed centerless grinding tests, using a Ded-Tru table mounted centerless grinding fixture, have been initiated at Eaton MTC. A 400 grit diamond resin bonded wheel is being used to grind 0.5" diameter S/RBSN cylinders at wheel speeds up to 15,000 SFM.

Grinding power, part roundness, straightness and surface finish are being measured to determine limiting material removal rates.

Initial tests, using vendor recommended setup conditions and wheelspeeds of 5,000 and 10,000 SFM, have resulted in unacceptable five lobed parts. While the Ded-Tru is grinding in a vertical plane, (i.e. the grinding wheel is above the regulating wheel) it is basically an "above center" centerless grinding process. Therefore, to identify an improved geometric setup, additional centerless grinding simulations were conducted. For the existing regulating wheel (4.25 inches in diameter), grinding wheel (12 inches in diameter), and work support angle (30 degrees), the center height was varied from 0.1 to 0.16 inches. As simulated and verified experimentally, 5-lobe parts are generated when a typical 2-lobed incoming part is used.

Additional simulations showed that if the grinding wheel diameter is reduced to 9.8 inches or less, a stable setup can be found. In many cases, however, this is not very practical. Moreover, the workpiece must be placed very far above center, which would increase the tendency for spinning - - particularly with ceramic components. Alternatively, the simulation program was then run using various values of workpiece center height, and workrest blade angles. It was found that the lobbing can be significantly reduced using a workrest blade angle of 45 degrees (see Fig. 3). This is a significant finding and will be verified experimentally. Workrest blade angle modifications are now underway.

6.0 High-Speed Grinding with Diamond Belts

In an effort to reduce ceramic finishing costs, alternative roughing processes utilizing diamond belts were investigated at Eaton/MTC. From a equipment capitalization perspective it is important to realize that typical precision centerless grinders cost approximately 10 times as much as throughfeed centerless abrasive belt machines. Additionally, current stock envelopes on as-fired cylindrical parts can average from 0.020 to 0.030 inches on the diameter. Traditionally, removing this amount of stock *can be* a time consuming process requiring multiple-stage processes using a bank of centerless grinders. Problems also arise when rough grinding silicon nitride blanks using high stiffness centerless grinding machines. The "hard" out-of-round blanks can jam in the workzone, damaging the part and possibly the wheel. Also, with minimal machine compliance, the rounding correction performance can be actually degenerate under certain geometric setup conditions.

As an alternative solution, a high compliance belt grinding approach was tried. S/RBSN cylinders were ground on a through-feed belt grinder to determine potential material removal rates as well as impact on part quality. The belt grinder was attractive due to its cost, throughput rates and inherent compliance. A 3M flexible diamond belt (220 grit, metal bond) was run at 5,000 SFM under wet conditions (using Cincinnati 1011 coolant) to "grind" S/RBSN workpieces, fed one at a time.

Parts were reduced on average from a rough OD of 0.532 inch to 0.491 inch in two passes across the four inch wide belt. At 3.5 seconds per pass, approximately .040 inch can be removed from the diameter in seven seconds. For comparison, a 15 HP ultra-stiff centerless grinder has been shown to have a maximum stock removal of 0.004 inch for every two second pass. To remove 0.040 inch of stock would take 20 seconds, nearly three times longer than the belt grinder.

During testing, the "grinding" load was determined by measuring motor amperage. The belt was held against the part with the motor drawing approximately one amp. Average results with the 220 grit diamond belt are:

Diameter (inch)	Taper (inch)	Surface Finish (R_a , minch)	Roundness (inch)	Straightness (inch)
0.491	0.003	54	0.0006	0.0024

From a material removal/quality perspective, the attractiveness of belt grinding is its compliance. For these tests, a 50 durometer polyurethane feed roll and a 50 durometer rubber contact wheel were used. With this level of compliance, irregularities in the part do not dramatically increase the grinding forces. Also, provided the setup geometry is correct, roundness correction can be accelerated. However, the part is much more susceptible to taper. Perhaps a stiffer contact wheel or running a gang of parts instead of one at a time would reduce the amount of taper.

As the above results indicate, the 220 grit belt appears to be quite effective for rough stock removal; but too coarse to achieve the desired finish surface quality. As such, a finishing operation on a rigid centerless grinder should be employed to achieve final size and tolerance. Subsequent polishing operations, using belt techniques, may again prove to be the most cost effective means of achieving a fine surface finish.

7.0 Advanced Wheel Dressing Concepts

Several methods were investigated to determine their relative effectiveness for truing and conditioning resin and metal bond diamond grinding wheels. In an effort to gain some practical insight into the ELID process under HSLD grinding conditions, the EATON corporation conducted a series of high speed O.D. cutoff grinding tests. Cylindrical S/RBSN samples (0.531" diameter) were cutoff at four different removal rates using a 100 grit metal bonded diamond wheel (Regal MD 100 N 100 M, 0.035" wide) operating at 25,000 ft/min.

In these preliminary tests, conventional stick dressing was compared to the ELID process in terms of resulting grinding forces, specific energy, dressing time, and workpiece surface finish. Note that unlike conventional stationary cutoff operations, the workpiece specimens in these tests were rotating (1100 RPM = 150 SFM peripheral velocity) to reduce the arc length of contact. By minimizing the arc length of contact the propensity for burnout is reduced, thus allowing for higher removal rates.

To initially dress the wheel conventional stick dressing was performed using a 220 grit aluminum oxide dressing stick. The wheel, rotating at 30,000 RPM (23,500 ft/min), was plunged into the stick at a rate of 0.000 007 in/rev. With this process, over half an hour was required to open the wheel. A similar amount of dressing time was also required between tests to fully open the metal bonded wheel.

For comparison, the ELID tests were also conducted using a wheel speed of 23,500 SFM (30,000 RPM). In these initial tests, stainless steel electrodes (SS41) were used in the ELID dressing head. A 60 volt DC potential was placed across the electrodes. The wheel was plunged into the electrode at 0.000 000 3 in/rev to a total depth of .000 15 in. and subsequently traversed across the electrode at this depth for 1.25 inches at a rate of 0.0003 in/rev. At the end of the stroke the wheel was then plunged again and traversed back to the starting point. One pass (plunge and traverse) required seven seconds. With this process a completely dull wheel could be fully conditioned in less than ten minutes. Note that between slicing tests only 30 passes, or three and a half minutes, was needed to fully recondition the wheel.

In all cases the ELID dressed wheel operated at a lower power than the conventionally dressed wheel. In addition, the specific grinding energy required for the ELID dressed wheel was about 60% (see Figure 4) of that needed for the stick dressed wheel, thereby indicating a much more open wheel had been produced. Interestingly, the normal forces were about the same with either dressing method. It is felt that the diamond penetration force would not be considerably affected by the soft surrounding bond. Conversely, from a tangential force standpoint (which is also proportional to power and specific energy) a more open wheel will reduce the amount of rubbing while providing increased chip clearance.

Also interesting was how the resulting surface finish remained relatively constant using ELID while the stick dressed wheel tended to produce a rougher finish as the removal rate was increased. This tends to indicate a more consistent dress was obtained using the ELID method. It was also noted that after grinding with the stick dressed wheel, the diamonds appeared quite dull with considerably more bond smearing than when dressing with ELID. The ELID process apparently opened up the wheel better than sticking, reducing the magnitude rubbing that occurred with the stick dressed wheel.

Status of Milestones

As of September 30, 1995 the hydrodynamic force model, centerless grinding stability simulation, and burnout prediction model for creep feed grinding have been completed. In addition, several Phase II milestones are nearing completion at this point; including energy partitioning at conventional wheel speeds and construction of a robust two-color precision pyrometry system.

Publications

1) "Measurement of Hydrodynamic Forces in Grinding" by M. Ganesan, Transactions of the North American Manufacturing Research Institution, Vol. XXIII, May, 24 - 26, 1995.

2) "Energy Partition to the Workpiece for Grinding of Ceramics," by B. Zhu, C. Guo, J.E. Sunderland, and S. Malkin, Annals of the CIRP, Vol, 45/1, 1995, pp 267-271, presented by S. Malkin at the CIRP Annual Convention, Enschede, Holland, August 21-26, 1995

3) "High-Speed, Low-Damage Grinding of Silicon Nitride", Kovach, J., et al., Abrasives Magazine, August/September Issue, 1995, pp. 15 - 20.

S/RBSN Grinding Conditions

Grinding condition	Grinding conditions				
	Material removal rate sq in / min	Wheel speed sfm	Feed rate in / min	Depth of cut inches	Number of passes
Unground	N/A				
A	0.125	5000	50	0.0025	4
B	1.0	5000	100	0.010	1
C	1.0	25000	100	0.010	1
D	0.125	25000	50	0.0025	4
Combined	N/A				

Table 1

S/RBSN Flexural Strength & Fractography

Grinding condition	Weibull statistics						Fractographic analysis			
	All data*		Data validated by fractography			Strength at 0.1% failure (psi Approx)	MOR bar failure modes for each grinding condition			
	Average Strength**	Weibull modulus***	Average Strength**	Valid data	Weibull modulus***		Grinding	Inclusion	Chamfer	Pore
Unground	65,329	13.34	N/A		N/A	38,000				
A	55,463	8.46	54,278	14	11.73	30,000	14	9	7	0
B	54,847	7.78	56,768	13	5.95	17,000	13	9	5	3
C	45,299	8.69	48,432	8	7.02	17,000	8	3	18	1
D	53,112	11.22	53,812	21	10.42	27,000	21	5	4	0
Combined	52,521	7.89	53,973	56	8.88	24,000	56	26	34	4

* 30 data points in grinding tests; 7 + historical data for baseline

** (psi) Determined at 63.2% probability of failure

*** (psi) slope of rank regression line

Table 2

Figure 1 A plot of specific power versus scratched surface parameter

Figure 2 Theoretical values of the forces obtained with a correction factor.

Figure 3 Workpiece profiles for blade angle of 45 degrees

Wheel

100 grit diamond metal bond (MD 100 N 100 M)

3 inch OD x 0.035 inch wide

$V_s = 25,000 \text{ ft/min}$

Material

S/RBSN cylinders

0.532 inch OD

$V_w = 150 \text{ ft/min}$

Figure 4

Grinding Optimization for Advanced Ceramics

Lewis K. Ives, Said Jahanmir, Venkata S. Nagarajan, and Mario Cellarosi
(National Institute of Standards and Technology)

Objective/Scope

The overall objective of this project is to develop guidelines and recommendations for grinding optimization of advanced structural ceramics to achieve minimum cost and maximum reliability. The following steps are being taken to achieve the objective: conduct grinding experiments jointly with industrial participants, determine effect of grinding parameters on machining damage and strength, elucidate mechanisms of material removal and damage formation, evaluate several damage detection techniques, and transfer data and information to industry in computerized database format.

Background

The goal of the ceramic machining program at NIST is to provide measurement methods, data, and mechanistic information needed by industry to develop innovative cost-effective methods for machining advanced structural ceramics. Research projects are carried out jointly with industry and academic institutions under the auspices of the Ceramic Machining Consortium. At the present, the Consortium has twenty-one members: Ceradyne, Inc.; Cercom, Inc.; Cincinnati Milacron, Inc.; Dow Chemical Company; Eaton Corporation; Ford Motor Company; General Electric Company; General Motors Corporation; Georgia Institute of Technology; Landis Company*; Lehigh University*; Norton Company; Stevens Institute of Technology; Torrington Company; Tower Oil and Technology Company; University of Connecticut; University of Delaware*; University of Maryland; University of Massachusetts*; University of Rochester; and West Advanced Ceramics, Inc. (The new members are marked by an asterisk.) Consortium members participate in the research projects by providing materials, testing services, advice, and other in-kind contributions. Funding for the projects, in addition to the DOE - Ceramic Technology Project, is provided by the Ceramics Division and the Standard Reference Data Program of NIST.

Technical progress

This report will focus on the results of a project that was undertaken in conjunction with the NIST Ceramics Machining Consortium to determine the grindability of three different commercially available silicon nitride ceramics. The project is one of several projects that are currently being conducted at NIST to investigate and characterize the grinding response of advanced ceramics.

Materials and test procedure

The main objectives of the project are to determine the influence of selected grinding conditions on flexure strength, surface roughness, and wear behavior of the three chosen ceramics. Of particular interest is the assessment of machining damage at relatively high removal rates. Information on the response at high removal rates is especially important with respect to optimizing the grinding process. A short list of properties of the three silicon nitrides is given in Table 1. Two of the silicon nitride materials, the sintered reaction bonded silicon nitride (SRBSN) and the sintered silicon nitride (SSN), are relatively high strength, structural ceramics, while the third material, a reaction bonded silicon nitride (RBSN), is a lower strength, low cost ceramic.

Table 1. Materials and properties.

MATERIAL	RBSN	SRBSN	SSN
SINTERING AIDS	---	AL ₂ O ₃ & Y ₂ O ₃	(N.A.)
DENSITY (g/cm ³)	2.36	3.22	*3.20
POROSITY	20%	<1%	---
ALPHA TO BETA RATIO	7.7 : 1	ALL BETA	ALL BETA
GRAIN SIZE LENGTH x WIDTH (μm)	1-2 x 0.5-1	6-8 x 1-3	**0.3 -1.3
ELASTIC MODULUS (GPa)	200	300	306
FRACTURE STRENGTH (MPa)	205	674	668
FRACTURE TOUGHNESS, K _{IC} (MPa√m)	2.5	6	***6.8
VICKERS HARDNESS (GPa)	6.8 ± 0.7	---	14.2±1

* >99% Theoretical density

**grains have 1:4 aspect ratio

***Chevron notch test

Eight industry affiliated consortium members participated in the experiment to determine the grinding response of the selected silicon nitrides. Grinding was done either in-house by the participant or by an independent contractor chosen by the participant. The only restriction was that the grinding be done by eight different and independent facilities.

A factorial design of experiments approach was employed for the project. This was done in order to maintain the required number of specimens and associated grinding and measurement effort within reasonable limits, and at the same time insure that a statistically sound outcome would result.

The grinding parameters were separated into three categories. These were 1) parameters selected for variation given in Table 2, each participant was assigned specific sets of varied parameters; 2) fixed parameters such as the wheel type, cross-feed and coolant type, all participants used the same fixed parameters; and 3) unspecified parameters, examples of such parameters are size and make of the grinding machine, machine stiffness, and the skill and experience of the operator.

Table 2. Varied grinding parameters

PARAMETER	1	2
TABLE SPEED	0.025 m/s	0.125 m/s
DOWN FEED	0.050 mm	0.125 mm
WHEEL GRIT SIZE	140/170	80/100
GRINDING DIRECTION	Longitudinal	Transverse

The specimens that were subjected to grinding were four-point bend flexure test specimens. These specimens not only allowed the determination of the effect of grinding conditions on flexure strength but the same specimens, or pieces thereof, could be used for roughness measurements, wear studies and other investigations, as desired, to assess grinding effects.

For each of the first three parameters—table speed, down feed, and grit size—two levels of severity were selected. A comparatively mild condition, column 1 in Table 2, and a condition of substantially greater severity, column 2 in Table 2. The actual choice of values for each condition was based on earlier screening studies. In terms of specific removal rate, the smallest value was 1.25 mm³/s per mm of wheel width and the largest value was 15.6 mm³/s per mm of wheel width.

All combinations of the parameters listed in Table 2 were evaluated. A factorial design of experiments approach was used resulting in the assignment of four different grinding conditions to each of the eight participants for each of the three materials. Each combination of conditions was duplicated by two different participants to allow an assessment of reproducibility. Thirty specimens were ground for each condition, a

sufficiently large number to provide a sound statistical evaluation. The thirty specimens were ground independently in groups of fifteen so that the results for each set of fifteen specimens could be used to assess experimental repeatability.

Flexure tests were carried out at NIST using the procedure described in ASTM Standard C1161-90. In order to establish the origin of the failures, fractographic examinations were conducted on all specimens by means of optical microscopy and on selected specimens by means of SEM. Weibull statistics using the maximum likelihood method was employed to determine the characteristic strength and Weibull modulus.

Surface roughness measurements were made with a stylus type profilometer instrument.

A Falex block-on-ring test machine was employed to conduct sliding wear tests. Small sections of the broken flexure bar specimens were used as the blocks. The rings were carburized 4620 steel bearing cups with a surface hardness of 58 - 63 HRC. A 10W-30 SH/CD motor oil was employed as the lubricant. All tests were conducted at a normal load of 670 N and sliding speed of 0.55 m/s.

Flexure test results

Flexure test results are summarized in Fig. 1a and b. Values for the grinding parameters such as table speed (T.S.), identified by the numbers 1 and 2, are given in Table 2. The grinding conditions are arranged on the x-axis according to increasing grit-

Fig. 1 Effect of grinding conditions on characteristic strength (a) longitudinal direction, (b) transverse direction. depth-of-cut.

Thus T.S. = 1, D.F. = 1 Grit = 1 corresponds to the smallest grit-depth-of-cut and T.S. = 2, D.F. = 2, Grit = 2, corresponds to the largest grit-depth-of-cut. The largest grit-depth-of-cut is approximately a factor of six greater than the smallest grit-depth-of-cut. The amount of damage or the severity of the process is expected to increase with increasing grit-depth-of-cut.

Figure 1a shows the influence of grinding conditions on characteristic strength for specimens ground in the longitudinal direction. For reference, characteristic strength values are also plotted for specimens ground according to the conditions specified in ASTM Standard C1161 (320 grit wheel and down feed of ≤ 0.003 mm for the final 0.060 mm of stock removal) which is designed to minimize the effect of grinding damage on flexure strength. Although the quantitative statistical analysis of the data which is currently under way has not yet been completed, visual examination of the results indicates that when grinding is in the longitudinal direction, i.e. parallel to the tensile axis of the flexure specimen, the grinding conditions used in this study have little or no effect on characteristic strength.

When grinding is done in the transverse direction, i.e. perpendicular to the tensile axis of the flexure specimen, the characteristic strength is apparently reduced by 25-30% for all conditions, Fig. 1b. However, in most cases the amount of reduction does not appear to change much from one condition to the next. Possible exceptions are that the larger grit size appears to result in a greater reduction in characteristic strength for the SSN and SRBSN materials, and the most severe grinding condition results in a noticeably lower characteristic strength for the RBSN material. It appears that within this range of grinding conditions, the characteristic strength, at least for the SSN and SRBSN materials, does not decrease significantly with increasing grit-depth-of-cut. For the SSN and SRBSN materials most of the reduction in characteristic strength apparently occurs at grit-depth-of-cut values less than that associated with the least severe condition employed in this study.

An important observation concerns the amount of scatter in the data and in particular the margin of difference between characteristic strength values obtained for two different participants using the same grinding conditions. In several instances that difference in reproducibility is as large as any effect that might be associated with the different grinding conditions. This suggests that factors other than the varied parameters can have a significant influence on damage. Factors that are likely to be important in this regard are the dressing of the grinding wheel, the trueness and balance of the wheel, and the machine stiffness. In future work a systematic study is planned to evaluate the influence of such factors.

Surface roughness results

A survey of surface roughness values obtained for all grinding conditions based on two or three measurements per condition indicated that the effect of grinding condition for a given material was not large.

A detailed evaluation of arithmetic roughness (R_a) values for the three silicon nitride materials was carried out for specimens ground under the least severe and most

severe conditions. The least severe condition comprises parameters (table speed, down feed, and grit size) listed in column 1 of Table 2 and will be designated (111). The most severe condition consists of parameters given in column 2 in Table 2 and will be designated (222). Grinding direction, the last parameter in Table 2, should have no influence on surface roughness. As noted previously, the least severe condition (111) corresponds to a grit depth of cut that is a factor of about six less than the most severe condition (222). A stylus profilometer was used for the roughness measurements; three traces were made on each specimen. A statistical analysis was then carried out to assess the repeatability and reproducibility of the results.

The results of the surface roughness measurements are shown in Fig. 2 for the three silicon nitride materials. For each grinding condition, sixty specimens were measured, thirty specimens from each of the two different participants that were assigned that condition. Grinding for each condition was performed in two groups of 15 specimens denoted by A and B in the figure. In each graph, the heights of the bars represent the mean value of 45 measurements, and the error bars indicate the standard deviation. The identifying numbers designate the participating consortium member and the test. Visual inspection of the bar graphs suggests that: (1) in most cases there is only a small difference between the R_a values for each A and B set and for each participant; (2) surface roughness increases as the severity of grinding is increased; and (3) the roughness of RBSN is generally higher than the other two silicon nitrides ground under identical conditions. It should be noted, however, for SRBSN ground under the mild condition, there is a large difference in the results obtained by the two participants and for one participant between the two fifteen specimen sets (5-7A and 5-7B). Also, for the RBSN ground under the severe condition, there is a noticeable difference between the average R_a values obtained for the two participants, but the large uncertainties associated with the results suggests that the difference is not statistically significant.

In order to compare these results, the coefficient of variation, i.e. the ratio of the standard deviation to the mean, was calculated for each data set. The coefficient of variation within each laboratory and in-between laboratories were taken as the measure of the repeatability and reproducibility, respectively. If a value less than 0.15 is taken as an indication of acceptable repeatability and/or reproducibility, the results show that both the repeatability and reproducibility were acceptable, with the exception of SRBSN ground under the mild condition. In that case, not only was the coefficient of variation for the results of the two participants large indicating poor reproducibility, but also on account of the large difference between the 5-7A and 5-7B sets the repeatability was poor. As was noted in the discussion of the flexure test results, it is clear that in the case of surface roughness there are also factors, perhaps associated with differences in the grinding machines or conditioning of the grinding wheel, that can have an effect that is nearly as large as that associated with the intentionally varied parameters.

In the future, similar detailed evaluations will be carried out on the three materials for other grinding conditions. Also to be included will be the evaluation of additional roughness characterization parameters.

Figure 2. Surface roughness results for (a) RBSN, (b) SRBSN and (c) SSN specimens ground under the least severe (111) and the most severe (222) conditions.

Wear results

Wear tests were conducted on SRBSN specimens ground under the two extreme conditions, (111) and (222). For comparison, tests were also performed on specimens that had been prepared by polishing. Sufficient material was removed during polishing to eliminate damage introduced during the grinding of the original surface. Wear tests on the ground surfaces were conducted both with sliding parallel to the grinding direction and perpendicular to the grinding direction as illustrated schematically in Fig. 3. Wear volume both for the SRBSN blocks and the steel rings was determined from the average cross-sectional area of the respective wear tracks. The average cross-sectional area was determined from profile traces taken across the wear tracks. Three wear tests were carried out for each condition.

Figure 3. Schematic illustration of the two orientations used for wear testing.

Surface roughness values for specimens measured prior to wear testing are given in Table 3. As expected, the roughness of the ground surfaces is significantly greater than that of the polished surface, and the roughness of the surface subjected to the most severe

Table 3. R_a roughness of SRBSN wear test specimens.

POLISHED	GROUND CONDITION (111)	GROUND CONDITION (222)
$<0.05 \mu\text{m}$	$0.15 \pm 0.01 \mu\text{m}$	$0.23 \pm 0.01 \mu\text{m}$

grinding condition is greater than that of the surface prepared by the least severe grinding condition.

The friction force was monitored during the wear test. The average steady state values of the friction coefficients for the different surface conditions and sliding directions are as shown in Fig. 4. It is seen that the steady state value of the friction coefficient is about 0.13, independent of the surface condition and the direction of sliding with respect to the grinding direction. This relatively high friction coefficient value is indicative of a condition of boundary lubrication.

Wear results for the SRBSN specimens prepared under different conditions are shown in Fig. 5. Clearly, the wear rate obtained for the polished surface is smaller than that for the ground surfaces. Although there is a fairly large standard deviation associated

Figure 4. Coefficient of friction for SRBSN sliding on steel for different surface conditions. Here, -PL indicates sliding parallel to the grinding direction and -PR perpendicular to the grinding direction.

with the data, it also appears that the wear rate is greater for the most severe grinding condition than for the least severe condition. Sliding direction does not seem to have a significant effect for the least severe grinding condition; but for the most severe grinding condition, the wear rate is higher when sliding is parallel to the grinding direction. It is thought that this difference may be related to the influence of surface topography on the efficiency of lubrication, although an effect associated with the anisotropy of the grinding induced surface damage can not be ruled out.

It should be noted that the maximum depth of the wear scars on the ground specimens was less than the observed depth of the grinding induced subsurface damage zone. For the SRBSN material and two grinding conditions used, that depth was about 10 μm . For continued sliding, resulting in a scar depth that exceeds the thickness of the damage zone, the wear rate would be expected to diminish, and the effect of different grinding conditions on wear rate would also be expected to decrease.

Figure 5. Wear rate of SRBSN against steel for different surface conditions.

The wear rates for the steel rings are shown in Fig. 6. The standard deviation for the measurements is relatively large; however, the results suggest that the wear rate of the rings increases as the severity of grinding of the blocks is increased (probably because the surface roughness of the blocks is increased). The wear test results also show that for a given test the wear rate of the steel ring is at least one order of magnitude higher than that of the mating SRBSN block.

Database

A suitable structure and format for the planned Ceramic Machinability Database has been developed. The aim is to provide a database that is appropriate for design

applications, tooling selection and machine tool setup, and that can be used to select appropriate grinding conditions both at the production and small shop application levels. In addition to the data generated at NIST in collaboration with the Consortium members, the data in recent publications were examined and collected for inclusion in the database. However, collection of data from the literature is not a simple matter. A very important issue is accuracy and applicability of the data. Also, a decision must be made as to the minimum amount of information required for the published data to be acceptable, because

Figure 6. Wear rate of steel used against SRBSN samples with different surface conditions.

sufficient information must be provided to describe the material, grinding conditions, and grinding response (e. g., surface roughness, strength, grinding forces). In addition, the units and terminology used in many papers are inconsistent, and much of the data is presented in a graphical form, which could introduce error in extraction into numerical form. At the present, these issues are still being considered.

Preliminary to entering the data in the database, data has been assembled in a spread-sheet. Approximately 60 key fields of information pertaining to the grinding of ceramics have been identified. The fields are divided into material identification, material

properties, process description, process parameters, process output, and references/comments. Approximately 300 publications were examined for completeness and applicability to the format of the database. From these publications, about 20 were selected and the data were added to the spreadsheet. This constitutes about 250 records (i.e., rows of data). This effort is still continuing, and it anticipated that the finished database will contain about 500 records including those from published literature, the data being generated in this project, other data from NIST research. Also, NIST is a one of the participating members of the DOE led IEA machining project. When available for release, the IEA project results will be a valuable source of well characterized grinding data for inclusion in the Database.

Conclusions

The results, although at this time lack the full support of a quantitative statistical evaluation, indicate for the materials under study that quite aggressive grinding conditions have little or no effect on characteristic strength when grinding is parallel to the tensile axis. It is likely that this result will also hold true for many other silicon nitrides having similar microstructures, but not necessarily all silicon nitrides.

Not unexpectedly, however, when grinding was perpendicular, or transverse, to the tensile stress axis, a reduction of 25-30% in characteristic strength was observed. An important finding was that, within the range of grinding conditions studied, this reduction in strength was not significantly influenced by fairly large changes in grinding condition. Under carefully controlled laboratory conditions, with grinding done by a single machine and the expected reduction in data scatter, it is likely that the effects of different grinding conditions could be observed. In other studies at NIST it has been shown by using appropriate grinding conditions and finer grit wheels that flexure strength values in transverse grinding approach those for longitudinal grinding.

Within the range of grinding conditions studied, the influence of grinding condition on surface roughness was small but could be distinguished when the least severe condition was compared with the most severe condition. In this case, the least severe condition resulted in a smaller roughness value than the most severe condition.

Utilizing a block and ring test under boundary lubrication conditions, the wear rate for SRBSN surfaces ground under the most severe condition was marginally higher than it was for surfaces ground under the least severe condition. For surfaces ground under the most severe condition it also appeared that the wear rate was greater when sliding was parallel to the grinding direction than when sliding was perpendicular to the grinding direction. In these experiments it was also shown that the wear rate for a polished surfaces was less than for ground surfaces.

With respect to practical applications, the results point out the importance of considering the relationship of the grinding direction to the directions of the principal stress axes that may be experienced by the part being manufactured. Orienting the grinding direction parallel to the axis of greatest tensile stress could offer a considerable benefit, since this could allow more aggressive grinding and higher removal rates than would normally be employed. Finally, the fact that grinding was carried out under

conditions that are typical of those found in existing industrial and commercial machining facility lends credibility to the use of the data in that kind of environment.

Status of Milestones

1. Evaluate the test results on fracture strength and surface roughness and develop guidelines for grinding optimization of selected materials (12/1/94 completed)
2. Issue a final report on evaluation of machining damage by thermal wave and ultrasonic techniques (2/1/95 completed)
3. Select three other types of ceramics for the next phase of the project and arrange for the billets from consortium members (4/1/95 completed)
4. Add recent data to the database and arrange for testing of the prototype by the consortium members (8/1/95 completed)

Publications

1. L. Wei, H. H. Xu, and S. Jahanmir, "Evaluation of Thermal Wave Imaging for the Detection of Machining Damage in Ceramics," NISTIR 5645, National Institute of Standards and Technology, March 1995.
2. T. Strakna, S. Jahanmir, R. Allor, and K. Kumar, "Effect of Grinding on Strength of Silicon Nitride," Technical Papers of the North American Manufacturing Research Institution, Society of Manufacturing Engineers, pp. 85-90, 1995. (Paper No. MR95-138).
3. T. Strakna, S. Jahanmir, R. Allor, and K. Kumar, "Influence of Grinding Direction on Fracture Strength of Silicon Nitride," *Machining of Advanced Materials*, S. Jain and D.C.H. Yang (Eds.) AMD-Vol. 208, pp. 53-64, American Society of Mechanical Engineers, 1995. Also accepted for publication in *J. Eng. Materials and Technology*.
4. H. H. Xu, L. Wei, and S. Jahanmir, "Effect of Grain Size on Grinding Damage in Alumina," accepted for publication in the Journal of the American Ceramic Society.

Chemically Assisted Machining of Ceramics

WBS Element 1.5.0.3 (SC-G)

S.M.Hsu, Y.Wang, R.S.Gates and T.N.Ying
(National Institute of Standards and Technology)

Objective/Scope

The machining of ceramics is very difficult and costly because ceramics are hard, wear-resistant, and chemically stable, even at high temperature. The ceramics industry has identified the lack of a rapid low cost ceramic machining technology as a major barrier for widespread use of ceramics. Current machining technology is slow and labor intensive. Residual surface damage is a primary concern. This project aims to increase the machining rate of ceramics by using chemical reactions at the interface. The chemical reactions at the interface produce a reaction layer that may function in several ways. It may behave as a lubricating layer, barrier film, passive protective film reducing the wear of the diamond, or it may reduce the contact stresses, therefore minimizing the surface damage. Si_3N_4 is the main material of focus.

The project involves several subtasks including:

1. Develop a bench test simulation to allow screening of chemistries under well-controlled conditions.
2. Identify new chemistries that can significantly improve the machining rate of ceramics, especially for silicon nitrides.
3. Provide understanding on the working mechanisms of the chemistries identified and develop correlations with the surface quality of the machined surface.
4. Establish limits of performance and applicability of the chemistry on different material compositions and processes. Establish optimum machining conditions for each chemistry/material combination.
5. Examine the environmental impact of the chemistry and work with industrial partners to optimize the chemistry and validate the concepts and methodology in industrial practice.

Technical Highlights

Previously, we have discussed the development a wheel-print method by which the wear of the diamond wheel can be measured and the G ratio (volume of silicon nitride material removed/volume of diamond wheel worn) can be calculated. This technique was used to evaluate the relative grinding performance of a commercial fluid and several experimental fluids using a surface grinder. We also reported that a vertical grinder loaned to us by Kennametal was set up and instrumented to evaluate developed coolants using a test procedure designed to measure the material removal rate and G ratio for this configuration. Testing has continued using the vertical

grinder to demonstrate the improvement in grinding rate and G ratio for our experimental grinding coolants. We have also examined the performance of an experimental fluid for grinding cemented tungsten carbide using a metal-bonded diamond wheel on the vertical grinder. An experimental coolant formulation has been optimized in preparation for a field trial by Kennametal. A 100 gallon sample of the experimental fluid was blended and sent to them for testing.

The vertical grinder lent by Kennametal, and instrumented to measure wear and friction during operation, is shown schematically in Figure 1. Sensors mounted on the sample holder allow continuous monitoring of applied normal force (f_n), tangential (friction) force (f_t), and sample displacement (wear) during a test. An example of the type of data obtained with this apparatus is shown in Figure 2 for a commercial coolant with silicon nitride. Initially, material removal rates are high. Grinding rates quickly diminish to low values. In contrast, an experimental coolant (Figure 3) maintains higher grinding rates throughout the test. The experimental coolant removes silicon nitride approximately four times faster than the commercial coolant under the conditions of this test.

The G ratio is defined as the ratio of volume of material removed by grinding / volume of diamond wheel worn. Wear of the diamond wheel is estimated by taking a print of the diamond grinding wheel before and after a test. By measuring the amount of wear using a surface profilometer, the G ratio is calculated. The experimental coolant has a G ratio of approximately 40, a factor of five increase over the commercial fluid (G ratio = 8).

Based on the positive results demonstrated by our experiments, Kennametal has offered to conduct field trials using our most promising coolant. Besides needing a large quantity of coolant (100 gallons), several other practical aspects must be considered for use and handling of a coolant. Viscosity, volatility, flammability, corrosion potential, and foaming tendencies are all important to the successful operation of a coolant in field use. In addition, health and safety aspects must be evaluated. The ability to support biological growth (bacteria and fungi) is an important practical consideration for long term storage and use of a coolant; therefore, biocides are often used to inhibit growth. The experimental fluids used for our tests originally did not have biocides or corrosion inhibitors and were not optimized for these practical considerations. The issue of corrosion inhibitors is especially important since these compounds are often surface active and could have antagonistic interactions with the surface active chemistries of our coolants. We set out to optimize the coolant formulation to have the desirable properties of a practical coolant, and still maintain the chemically enhanced machining rate for silicon nitride ceramics. We also evaluated the sensitivity of the experimental coolant to water contamination.

Effect of Water Contamination

The issue of grinding performance of the experimental fluid over a long time is important. A sample of the experimental grinding fluid was used, stored for one month, and reevaluated. The results of the tests are summarized in Table 1. The initial grinding experiment removed 277 mm³ silicon nitride during the test. The same fluid, after one month, removed 288 mm³ silicon nitride

from a similar sample. The results suggest that the grinding ability of the experimental fluid is stable over time.

Table 1.
Grinding Performance of Experimental Fluid with Time

Fluid	Volume of Silicon Nitride Removed, mm³
Experimental Fluid, new	277
Same Fluid, after one month	288

Another important practical aspect of a coolant is the sensitivity to water contaminants. Previous results suggested that water can have a detrimental effect on the wear of diamond and therefore reduce the grinding rates for silicon nitride. The fluid developed at NIST is thought to function, in part, by protecting the diamond surface from chemical attack by water. A grinding experiment was therefore conducted using the experimental coolant intentionally contaminated with 10% water-based coolant. This simulated a worst-case scenario that might occur during a changeover from a water-based commercial fluid to the experimental fluid without a coolant flushing procedure. The results, summarized in Table 2, indicate that the water contamination did not immediately affect the grinding performance of the experimental fluid. Another grinding test was conducted after one month. The amount of silicon nitride removed during this test had decreased to 230 mm, a change of approximately 17%.

Table 2.
Grinding Performance of Experimental Fluid Contaminated with Water-Based Coolant

Fluid	Volume of Silicon Nitride Removed, mm³
Experimental Fluid, new	277
Experimental Fluid, contaminated with approximately 10% water-based coolant	280
Same Fluid, used, after one month	230

While the performance of the experimental fluid is still much higher than the commercial fluid, the results indicate that avoiding contamination of the experimental grinding fluid with an aqueous-based coolant would be desirable. As a result, we will provide sufficient test fluid for Kennametal to flush the system before field evaluation.

Coolant Development

The coolants evaluated on our bench scale were formulated with pure paraffinic compound diluents. On a large industrial scale, the use of these compounds is not economical; therefore, other alternative base fluids were sought for the large scale blend of the experimental coolant. Additives such as corrosion inhibitors and biocides were also evaluated for their effect on the chemically assisted machining of silicon nitride ceramics. The corrosive nature of the coolant was also evaluated both with and without corrosion inhibitors.

Ten base fluids with appropriate characteristics (viscosity, volatility etc.) were studied as potential diluents for the field trial. These included paraffinic light oils, hydrotreated stocks, polyalphaolefins (PAO's), and naphthenic oils. Tests were conducted using the diamond wheel cutting apparatus used in our previous screenings and also the surface grinding apparatus. A suitable diluent was selected based on these results and sufficient quantity was obtained for a 100 gallon blend of experimental coolant.

If coolants are used over a long time, bacteria and fungus may grow and thrive. This poses not only a possible health hazard, but also could clog the coolant delivery system, resulting in considerable down time of the equipment. Coolants are therefore normally formulated with a biocide to prevent the development and growth of fungi and bacteria. Most biocides used in coolants contain significant amounts ($\approx 20\%$) of water. It has already been demonstrated that water can decrease the effectiveness of the experimental coolant over a long time; therefore, we did not want to add it to the formulation intentionally. A biocide was obtained that contained only 1% to 2% water. It was formulated into our experimental coolant at the high end of the treat rate recommended by the manufacturer to evaluate the effect of the biocide on grinding performance. A series of grinding tests conducted on the formulation containing the biocide reduced the grinding rate by approximately 15%. In order to reduce the effect of the biocide on grinding performance, it was treated with a molecular sieve to remove water, and reformulated at one third the previous concentration in the experimental fluid. This treat rate is still well within the manufacturers recommended treat rates for this biocide.

The issue of corrosion was addressed using cut pieces from an actual metal-bonded wheel supplied by Kennametal. A simple laboratory corrosion screening procedure was used to evaluate the corrosion tendencies of the coolant on the wheel. The screening procedure was based on industrial feedback. A sample of a metal-bonded diamond wheel was cut into coupons and polished. Samples of NIST coolant were formulated with a corrosion inhibitor at 0, 0.5, 1.0, and 2.0% concentration. The coupons were then dipped in the NIST coolant exposed to a

Commerical coolant

Developed coolant

Figure 3. Vertical grinding data for silicon nitride ceramics using the NIST experimental coolant.

Figure 4. SEM micrograph of a metal-bonded diamond grinding wheel cross section (cut and polished) after dipping in NIST coolant and exposure to laboratory atmosphere for 30 days. Marker in lower right corner is 100 μm .

Figure 5. Comparison of grinding performance as a function of time for two coolants.

Figure 6. The influence of contact area on material removal for two coolants.

Figure 7. The influence of contact area on "G ratio" for two coolants.

Laser Scatter Methods for Detecting Subsurface Machining Damage in Ceramics – Sanjay Ahuja, William A. Ellingson, George A. Forster (Argonne National Laboratory), Michael H. Haselkorn, and Charles J. Anderson (Caterpillar Inc.)

Objective/scope

The primary objective of this program is to develop a laser scattering procedure that would provide a direct (near-real-time) indication of changes in the subsurface (and surface) during machining. These changes include machining-induced damage (such as median crack formation) and surface roughness. A second objective is to evaluate dye penetrant technology as an off-line indicator of surface-breaking cracks. The laser program is being executed in three steps. The first is evaluating optimization of the laser scattering procedure to examine specimens machined by innovative techniques. The second step will involve correlation of the laser scattering results with mechanical properties in "real" machined ceramic specimens. The final step will be to develop a prototype instrument to be evaluated for on-line implementation in a production environment. The investigation into dye penetrants for surface-defect detection is being conducted in three steps: review of literature, off-site visits to appropriate current users (e.g., Norton) and vendors (e.g., Sherwin, Inc.), and laboratory experiments.

Technical progress

A1. Laser Scattering

The repaired motor for the translations stages of the laser scatter inspection system (for increased inspection speed) was received and installed. Software was modified to improve sensitivity to median crack damage, which is most critical in machining damage. So far, software had been written so that the specimen could be scanned and consequent row images could be acquired. After acquisition of pixels in one row from left to right, the next row was imaged again from left to right. This had the major drawback that there was a momentary lapse in data acquisition time when a "carriage return" was conducted and the laser positioned at the beginning of the next row. In this period and the upcoming reporting period, software modification is being continued to speed up the acquisition. Software was modified to continuously scan the specimen such that if the previous row was imaged from left to right, the next row was efficiently imaged from right to left and there was no lapse in acquisition time. This has improved the speed of acquisition considerably. Although the current system allows inspection speeds 90 times greater than the previous version of the system, continuing modification of the system software should improve these speeds even further. Effort is also being focused upon acquiring a high-speed low resolution row of the image and then scanning the same row multiply to convert it into a high resolution image format.

Two etched specimen scans were obtained from IIT using the elastic optical scattering, and are shown in Fig. 5. Fig. 1(a) shows the ratio image and Fig. 1(b) shows the sum image of the

side 940W of an etched specimen. The etchant used was HF and HNO₃ in the proportion of 97:3. The specimen was etched for 2 hours. The scans shown in Figs. 1(c) and (d) were 6.5x33mm at 50µm resolution. Figure 1(c) shows the ratio image and Fig. 1(d) shows the sum images of side 560 of the etched specimen. Lateral cracks are most visible in the "sum" images and median cracks are most visible in the "ratio" images.

Figure 1. Elastic Optical scattering on the etched (HF: HNO₃) specimen. (a) and (b) correspond to the "sum" images and (c) and (d) correspond to the "ratio" images.

Figure 2: Photograph of a typical specimen acquired from Caterpillar, Inc.

Table I: Experiment matrix for hot-pressed Si_3N_4 .

Sample	Run Order	MRR	Max Force (N)	Feed	Grit Size	Amplitude
HP38AAA1	13 Tool #7	108	168	1	1	1
HP38BAA1	3 Tool #5	108	236	1	-1	1
HP38BAB1	2 Tool #2	54	101	-1	-1	1
HP38BBB1	5 Tool #5	54	132	-1	-1	-1

*MRR = Material Removal Rate ($\times 10^{-3} \text{ mm}^3/\text{s}$)

Laser scattering was conducted on four specimen obtained from Caterpillar, Inc., each similar to that shown in Fig. 2. The specimen were 5 cm x 3 cm with a thickness of 3 mm. The laser scans were conducted on select sections corresponding to the regions for the Talysurf plots provided by Caterpillar, Inc. Figures 3 through 6 show the sum and ratio images of the Caterpillar specimen with details about median cracks (ratio images) and the lateral cracks (sum images). The rectangular regions are machined portions, on which several details are visible. The resolution of all the images was 15 μm and the specimen image size was consistently 3 mm x 3 mm. Defects, inclusions and discontinuities are inherent in all the images. The sum image indicates the lateral cracks and the ratio images show the median cracks in the specimen. The images have been correlated according to the machining conditions of the specimen given in Table I.

Machining conditions are easily differentiated with respect to the MRR of the specimen. Samples HP38AAA1 and HP38BAA1 had MRR's of 108 and samples HP38BAB1 and HP38BBB1 had MRR's of 54. This difference is directly visible in the images. A higher MRR enhanced the intensity of the inclusions whereas a lower MRR decreased the intensity. The lower the intensity of the inclusions/defects, the more easily visible they are in the acquired images. The maximum force applied during machining is also prominent in the acquired images. For the same MRR, increasing the maximum force decreased the intensity of the inclusions thereby making them more distinct and identifiable. Additional samples will be provided by Caterpillar, Inc. and optical scatter data will be correlated to machining conditions and mechanical properties.

RATIO

SUM

Figure 3: HP38AAA1 specimen. Sum and Ratio Images. 3 mm x 3 mm scans at 15 μ m resolution.

RATIO **SUM**

Figure 4: HP38BAA1 specimen. Sum and Ratio Images. 3 mm x 3 mm scans at 15 μ m resolution.

RATIO **SUM**

Figure 5: HP38BAB1 specimen. Sum and Ratio Images. 3 mm x 3 mm scans at 15 μm resolution.

RATIO **SUM**

Figure 6: HP38BBB2 specimen. Sum and Ratio Images. 3 mm x 3 mm scans at 15 μ m resolution.

A2. Automation for on-line inspection

Future efforts are being focused on altering system magnification to improve sensitivity to lower penetration materials. In addition, alternative detection schemes are being examined to focus on specifically oriented median cracks to verify improved sensitivity. Development continues in trying to improve system speed with the current detection hardware. A third detector is being installed which will capture all specular reflections and help in separating the two components, surface and subsurface detection more precisely while giving an in situ depth of the defects.

A3. System Modification

The current laser scatter technique has proven capable of detecting subsurface (and surface) machining damage. A system modification has been implemented to improve sensitivity to subsurface median cracks without sacrificing lateral crack detection. In addition, future efforts will improve acquisition speed (by using point detectors rather than the CCD array of the current setup). Hardware for the modified system, which uses an imaging system rather than the Fourier arrangement, has been installed. For improved detection speed, the system's translation stages are being upgraded for greater velocity capabilities. The translational stages were modified to include an additional degree of freedom for increased capability in analyzing spherical specimen. Further, a motorized stage has been developed for on-line detection of subsurface defects. This stage consists of a computer-controlled highly sensitive motor driven shaft held by a bearing on the other side for minimal frictional forces and located on one of the X-Y-Z translational stages. When the laser beam is incident on a section of the shaft rotating at a high speed, acquisition is being made instantaneous and will depend upon rotation speed rather than the translational movement of the specimen under study.

B. Dye Penetrant

B1. Facility Upgrade

The new Newport-Klinger Motion Control stage received for the dye penetrant laboratory allows automated data acquisition and automated pattern recognition work has been initiated.

B2. Report

The final report for Phase I has been submitted.

B3. Technology Transfer

The development of the initial aspects of the dye penetrant work were successfully transferred in the last period. Solar Turbines, Inc., as part of the Ceramics in Stationary Gas

Turbine Project (CSGT), requested the information which was provided after discussion with the ORNL program manager of this project

FY 1996

Technical progress for this year will include two major concentrations. First, results of flat plate laser scatter analysis (which will continue into FY 1995) will be correlated with mechanical properties, as measured by Caterpillar. Because of the large number of possible parameters which the laser scattering technique can measure, the inspection process will be refined to determine those parameters with the greatest correlation. Second, upon determining which parameters will be of interest, the laser scatter inspection system will be modified to measure only those parameters, thereby accelerating component inspection. Future effort will focus on altering system magnification to improve sensitivity to lower penetration materials. In addition, alternative detection schemes will be examined to focus on specifically oriented median cracks to see whether this can also improve sensitivity.

In our continued work in dye penetrants, we intend to compare ASTM Level 4 high-sensitivity fluorescent penetrants for their ability to detect microcracks on various microstructure materials containing various surface machining conditions. Once we have established the exact protocol to use, i.e., time in ultrasonic cleaner, time in oven, setting time of penetrant, and best optical magnification, we will then begin to determine if automated digital imaging methods can be used to inspect components.

FY 1997

Technical progress for this year will be an extension of the technology to further modify the laser scattering system. This will involve using a tunable dye laser to increase the capability of the system. The dye laser will allow varied wavelengths of the laser beam leading to varied intensities and characterization of different microstructures in the realm of the laser scattering process. The applications of the laser scattering process will be in analyzing carbides, nitrides, and other hard materials.

FY 1998

Technical progress for this year will be concentrated on ceramic matrix composites. The main issue in the fabrication of particulate ceramic matrix composites by melt processing techniques is that of uniform distribution of particles in the solid matrix. A uniform distribution can only be achieved by controlling the particle behavior at the solid/liquid interface during solidification. In this work, an attempt will be made to extend the current understanding of particle/interface interaction. There is extensive ambiguity in quality consistency in incorporating ceramic particles in the ceramic matrix. Laser scattering of ceramic matrix composites will allow greater confidence in the quality of the composite with respect to less or no agglomeration, porosity, oxide gas entrapment, and therefore no defects. The tunable dye laser will be applied to study sub-surface defects to the order of millimeters and the technology will be implemented in to industry.

Status of Milestones

Milestone 150701 complete. Milestone 150702 (Correlate Argonne National Laboratory (ANL) laser scatter results with Caterpillar (CAT) mechanical properties) has begun by receipt of specimen from Caterpillar, Inc. Communication continues with CAT on the delivery of additional specimens. All other ANL milestones are on or ahead of schedule.

Communications/Visits/Travel

Mark Vanroode and Bill Brentnall of Solar Turbines, Inc. visited Argonne National Laboratory.

W. A. Ellingson was invited to present the dye penetrant work to the ARPA Ceramic Program Review, Annapolis, MD, Aug. 29, 1995.

S. Ahuja presented a paper entitled "Development of Novel Laser Scattering Methods for In Situ Flaw and Damage Detection" to the Cost-Effective Machining of Ceramic Workshop 1995, Oak Ridge National Laboratory, Oak Ridge, TN, September 1995.

W. A. Ellingson and S. Ahuja attended the Automotive Technology Development Contractor's Coordination Meeting, Dearborn, MI, October 24-27, 1995.

Problems Encountered

The computer motion controller and a motor of the translational stages underwent repair and have been reinstalled in the system.

Publications

W. A. Ellingson, J. P. Singh, E. A. Sivers, J. B. Stuckey, D. Christopher, S. L. Dieckman, S. Ahuja, and D. Singh, "Development of NonDestructive Evaluation Methods and Prediction of Effects of Flaws on the Fracture Behavior of Structural Ceramics", Invited Paper, Proceedings of the Ninth Annual Conference on Fossil Energy Materials, Oak Ridge National Laboratory, Oak Ridge TN, May 16-18, 1995.

Milestone Schedule

Determine optical properties of SiAlON and GS-44 for optimum optical detection parameters (polarization, wavelength, angle of incidence, etc.). Completed	Feb. 28, 1994
Conduct exploratory studies of dye penetrant on machined surfaces. Completed	May 31, 1994
Submit report on dye penetrants. Completed	Dec. 1, 1994
Correlate laser scatter analysis (ANL) of contoured specimens with mechanical properties, residual stress measurements, and mechanical surface roughness measurements (CAT).	Feb. 29, 1996
Develop a protocol to use the dye penetrant technology	April 30, 1996
Correlate laser scatter results (ANL) with mechanical properties (CAT)	May. 28, 1996
Install and demonstrate prototype laser scatter device.	Aug. 31, 1996
Submit topical report on dye penetrants.	Sept. 15, 1996
Modify the laser system with a tunable dye laser to increase applications	March 30, 1997
Complete study of carbides, nitrides and other advanced ceramic materials	Sept. 30, 1997
Complete study of ceramic matrix composites and transfer technology in to industry.	Sept. 30, 1998

1.5.2 Advanced Ceramic Manufacturing Technology

W.B.S. 1.5.2.0

Advanced Manufacturing Technology for Ceramic Heavy Duty Diesel Turborotors

E. Kraft, Kyocera Industrial Ceramics Corp.

S. Roby, Schwitzer U.S., Inc.

J. McCormack, Caterpillar, Inc.

Objective / Scope

The objective of this program is to develop the cost effective manufacturing technology required for ceramic turbine rotors for use in turbochargers for heavy duty diesel truck and bus applications. A team, led by Kyocera (KICC, the ceramic component manufacturer) and including Schwitzer U.S., Inc. (the turbocharger manufacturer) and Caterpillar, Inc. (the diesel engine manufacturer) will develop and demonstrate production readiness for reliable, cost affordable turbochargers with ceramic turborotors. Program goals include a nominal order of magnitude reduction in cost over the present cost for small quantities, and process capability for critical component attributes which is adequate for the performance and reliability specifications of the application. Silicon nitride, SN 235, is the material of choice for this application. Program goals are to be achieved utilizing Kyocera's production proven Hybrid Molding, gas pressure sintering and cylindrical grinding processes. Yield, quality and cycle time improvements will be achieved through process modeling, statistical process control and intelligent processing.

Technical Highlights

Task 1 Component Design and Specification

Discussion has continued at Schwitzer and Caterpillar on final selection of the application and turbocharger model and design for production. Caterpillar has selected a new version of the 3176 engine, to be released in 1996, for application of the ceramic turborotor. This new version incorporates the most advanced engine control technology as well as other improved design features. Discussions are also being held between Schwitzer and Kyocera regarding design details for reduced manufacturing cost. Effort is now beginning on design of a rotor for this application, and will be followed by design of the mold for the second process demonstration. Design discussions regarding fixturing for shaft attachment trials by friction welding has also begun.

Task 2 Component Manufacturing Technology Development

Task 2.1 Cost Model

Following the processing of three rotor lots in the first process demonstration, the cost model was again revised to reflect this learning in the baseline prototype case. A base case, three cases reflecting cost reduction scenarios, and a case combining all three cost reductions were constructed. Three observations can be made from these case studies:

1. For producing prototype rotors, the material cost is relatively small.
2. The cost is very sensitive to the number of lots produced, and how they may be combined in some unit operations.
3. As process yield improves, inspection cost becomes the dominant cost.

Model configuration for full production has also been completed. Data and estimates for production of up to 1500 rotors per month has been collected, entered and analyzed. Comparison of prototype and production cost are shown in Figure 1 for all operations excluding rotor/shaft attachment. In each scenario, a base case and an improved case are shown. For production, the improvements identified to date represent a 40% reduction in cost from the production base case, and a 93.8% reduction from the prototype base case. As a result of analysis of the production base case, four

Figure 1. Comparison of Prototype and Production Cost Analyses

production cost improvement strategies were evaluated. These strategies were:

1. Combined Lots - By combining forming lots to completely fill each densification run, the unit cost is reduced. This savings is somewhat offset by the need to provide material characterization and traceability for each forming and densification lot.
2. Use of Large Sintering Furnace - The base cases assumed use of the smaller of two production furnaces. Use of the larger furnace would reduce unit cost and reduce the impact on material characterization cost.
3. Improved Sinterability - Effort is now underway to improve the sinterability of the SN235 material in order to reduce the complexity and therefore cost of the densification cycle. The cost impact of success in this effort is forecast.
4. Improved Yield - Since yield has a dramatic impact on cost, and is also one of the major results of experience, one yield improvement case was tested. Unit operation yields were selected which represent a reasonable early production yield level. The total yield for all processes up to joining totaled 77%.

Figure 2 shows the cumulative results of improvements 1 through 4. As mentioned above, the total cost reduction is 40%. If all four improvements are realized, the major cost categories would contribute the portions shown in Figure 3. It must be noted, that this analysis does not show the cost reduction which

Figure 2. Cumulative Production Cost Improvements

would result from the reduced inspections permitted by the forming improvements being investigated. The large portion of cost contributed by inspection was forecast early in this program, and is the reason for the heavy emphasis on forming process understanding and control. The second largest contributor in this figure is grinding. This estimate includes the assumption of a new machine tool for flexible manufacturing of rotor components. While the specifications for this machine have not been established, the costs are based on experience with other production situations. The relatively high cost of raw materials shown in this analysis has led to a new effort in evaluation of alternative sources.

Figure 3. Major Cost Contributions in Ceramic Rotor Production

Since ceramic rotor cost and joining cost are relatively independent, these are being analyzed separately. Production cost for the joining operations is estimated at 10 to 15% of the "Best Case to Date" shown above. While this represents a reduction of cost of 85% of the prototype cost, it would still represent a substantial portion of the target cost.

As a result of these analyses, major cost objectives confirmed or established at this point in the program are as follows:

- I. Raw material cost reduction - Evaluate alternate, lower cost sources.
- II. Improved yield in forming - Process modeling and control; in-process sensors.
- III. Reduced dewax and sinter cost
 - A. Implement reduced dewax cycle time
 - B. Improve sinterability through improved raw material mixing
 - C. Reduce sintering cycle time through process control
- IV. Reduce grinding cost - Develop new machine specification; reduce grinding steps; reduce grinding stock.
- V. Reduce Inspection Cost - Reduced x-ray inspection due to low ppm voids; rationalize inspections and tests to eliminate duplicate assurances of quality.

Task 2.2 Environmental Safety and Health

All air emissions questions from the air pollution control agency have been addressed; no emissions issues related to this program remain. Solid waste disposal testing on sintered rotors has been conducted. Leachate, solvent scan and fish toxicity testing was conducted with satisfactory results. This concludes all testing required and planned for this program. Continuing activities will include periodic voluntary visits by State safety and industrial hygiene consultants, and assessments of plant emission control capacities as activity expands.

Task 2.3 Process Control

Task 2.3.1 Statistical Process Control:

An SPC deployment plan has been established for the entire plant. Software (WinSPC) has been installed on the facility LAN. A pilot program on short run SPC was carried out in grinding and the subject process capability determined. Further deployment in grinding and forming departments has begun. Decision and process capability models have been created for "out of control" and Corrective Action situations. Gage R&R and measurement system evaluation methods have been established. Key characteristics for select parts have been identified for the purpose of preparing a Master Key List for use with generic keys to new and existing processes. SPC Control Plans such as shown in Figure 4 are being developed for several pilot processes.

SPC Control Plan

Kyocera Industrial Ceramics Corp.
 Statistical Process Control Group
 Vancouver, Washington

Control Plan Number	Part Number	Supermarket	Control Date
Process Name		Out-Line	Page ___ of ___

KEY Characteristic	SPC Characteristic Variation						Gage Variation		Process Variation	
	Target Tolerance	Process Step Where Monitoring Taken	Statistical (SPC) Method	Sample Size	Initial Cpk	Cpk	Measurement Method/Gage Type	Gage R&R	Process Parameter Setting	Control Method

(1)

Prepared By	SPC Manager
-------------	-------------

Advanced Quality System

Figure 4. SPC Control Plan to be applied to each production unit operation.

Task 2.3.2 Raw Material Preparation:

Further analysis of green part sintering aid distribution has been performed utilizing SEM backscatter image analysis. No significant segregation could be observed. Previously reported liquid mobility experiments had demonstrated the ability of the species to move sufficiently by diffusion and capillary action to affect densification over a distance up to one mm. The present method has therefore been tentatively judged adequate. These techniques are also being developed for observation of binder distribution. A plan has been formulated to test elimination of several process steps using a new process for combining raw material and slip preparation. The cost savings as well as technical benefits of this change are being evaluated. Alternate sources of sintering aids have been identified and tested. No adverse effects have been noted to date. Initial samples of a potentially lower cost Si_3N_4 powder have been received and analyzed. Impurity levels on the coarse powder were close to, but not within the specification for this program. An attrition milling trial has been completed, and the material is being reanalyzed. Further trials are planned to assess the impact of the deviation from specification. Tests of cost optimized processing of the powder are also planned.

Task 2.3.3 Slip Preparation:

Domestic sources of binder system constituents are being investigated in order to reduce cost and improve delivery. One lot of test plates using these binders was hybrid molded using forming parameters with the standard procedure. Visual and x-ray examination of the green plates showed a high yield, comparable with that using binders from the standard vendors. Initial tests were inconclusive due to an insufficient database on the conventional materials to permit accurate statistical analysis. An additional lot of material will be made using the domestic binders, and one using the conventional binders. MOR testing on these lots will provide the additional data required. Using the slip constituent analyses, and slip property analyses previously performed, modified slips were prepared for further process demonstration lots. The objective of these modifications was reduced viscosity and improved green strength. Modification of the solids content and binder system composition provided three levels of viscosity and an improved green strength. Results are reported below under Task 4.

Task 2.3.4 Forming:

Work on creating an analytical model of the hybrid molding process has progressed in the following subtasks, with Technalysis, Inc. as subcontractor for the FEM model development.

Subtask 3. 3-D Filling Analysis - The forming conditions used in the previously reported experimental forming trials were used in an additional model analysis. Initially, this analysis did not show the lack of blade fill observed experimentally. Since a method of obtaining useful measurement of the mold-slip heat transfer coefficient has not been found, sequentially higher coefficients were used until correlation with experiment was obtained. The resulting analysis showed incomplete blade fill similar to that observed experimentally.

Subtask 4. Solidification Analysis - The solidification fronts for the case corresponding to incomplete blade fill were then studied. In addition to confirming solidification prior to blade fill, the model also indicates the possibility of a solidification defect in the center of the hub. This defect was subsequently observed by x-ray NDE in a small percentage of the rotors formed. The conditions under which this defect occurs are being investigated.

Subtask 5. Model Iteration - All tasks for development of the process model have been completed. The model is being used to forecast results of forming trials using operating parameters from the process demonstration. Mold filling has been simulated for two values of forming pressure, with two variations in molding hardware configuration. These hardware configuration changes were made in an attempt to correct the lack of blade tip filling. According to this simulation, one change reduced mold fill time by a factor of five, but did not produce filling of the blade tips. The simulations did, however, show combinations of configuration and operating parameters which eliminated or minimized other forming defects.

The model was next used to perform a non-isothermal filling analysis using data on forming conditions utilized in the process demonstration. The analysis gave results consistent with experimental results on conditions required to avoid the backface voids caused by a filling "fountain effect" seen in previous simulations. In addition, this simulation showed the sequence of filling and solidification leading to incomplete blade fill. Figure 5 shows the progression at three time steps. Solidification at the hub between blades is evident. In addition, the sequence illustrates initial solidification in the thin exducer portion of the blade while filling is still occurring, leading to "choking" of the material flow.

The model was next improved with the inclusion of data on temperature dependence of slip viscosity and thermal conductivity which was received during this period. The non-isothermal filling analysis was repeated to verify the mold-cavity interface heat transfer coefficient. Fill time was affected by this refinement due to the higher viscosity on cooling. The amount of non-filling remained approximately the same, validating the heat transfer coefficient.

Figure 5 Time steps in non-isothermal filling.

Task 2.3.5 Drying: Effort on this operation has been postponed due to it's low contribution to cost.

Task 2.3.6 Binder Removal Investigation:

Seven lots of parts have been processed as reported in Task 4, using the baseline profile. No yield loss was observed, confirming capability of the baseline process. Using data from earlier in-situ analysis, a reduced cycle time profile has been devised. Parts from the same lots have been set aside and an evaluation run scheduled.

Task 2.3.7 Sintering Investigation:

Effort in sintering during this period was focused on processing parts according to the standard procedure for the initial process demonstration. No significant problems due to sintering were encountered requiring investigation. Efforts to simulate the production process in a laboratory furnace were unsuccessful due to scaling factors. Indications of improved properties during some slip preparation and forming trials suggests that improved sinterability may result from modifications to the raw material mixing and slip preparation processes. Future experiments are planned to explore the effect of such modifications on sinterability and resultant mechanical properties.

Task 2.3.8 Grinding:

Data from grinding trials on rotors from the initial lots of the process demonstration showed that no significant barriers exist to achieving dimensional or surface finish requirements. Cost reduction is planned through use of formed wheels, grinding parameter changes and reduced rework through experience. Cost reduction opportunities identified to date are expected to reduce grinding time by over 74%. Effort on confirmation of the cost reductions identified will be conducted during the second process demonstration. Discussions have continued on additional cost reduction through identification and specification of alternate machine tools, and elimination of grinding operations.

Milestone 3 was "Implementation of in-process dressing and dimensional inspection". It has been found that electrolytic in-process dressing (ELID), while very effective for flat grinding wheels, is not practical and therefore cost effective for formed grinding wheels. Since it has been determined that significant cost reduction is available through use of formed wheels, application of ELID has been canceled. The use of in-process dimensional inspection is still a viable cost reduction strategy. However, selection of the best measurement tools and methods has been postponed until the alternate machine tools are specified, and operations to be eliminated finalized. These operations will be determined during the design phase of the second process iteration.

Task 2.4 Intelligent Processing

Since it has been confirmed that bubble detection in slip preparation is unnecessary, work on ultrasonic bubble detection is concentrated on its application in the hybrid molding machine at a location just before

the slip enters the mold. Sonoscan has acquired a Waveform Digitizer in order to automatically acquire data and perform spectrum analysis on the captured waveform. The board offers high resolution waveform capture at high speeds, with a signal bandwidth from dc to 30 Mhz. Research on frequency dependent scattering loss has been conducted. The 1/4 wavelength cutoff frequency of strong frequency-dependent scattering loss has been confirmed using 50 and 100 μm glass beads in water and oil. The transducers used were 5 Mhz for 100 μm beads and 10 Mhz for 50 μm beads.

As previously reported, the absorption attenuation of ultrasound propagating in hybrid molding slip is a 1.55 power of the frequency. The absorption attenuation has been calculated for the case of a 100 μm void, using a 5 Mhz transducer, and a propagation distance appropriate for application to the injection portion of the hybrid molding machine. The required input filter and acoustic pump, and receiver gain were determined which would bring the signal to a manageable level.

The center frequency of the acoustic transducer was selected to be 3.5 Mhz with a 10-dB bandwidth of about 5 Mhz in order to be able to detect 100 μm bubbles. With the high attenuation measured in this material, the propagation distance of ultrasound is limited to 1/2 inch maximum. To maintain flow and pressure in the molding system, a rectangular cross section pipe of appropriate width and depth was designed to incorporate a 5 element cascade transducer. The elements will be adhered to a MACOR delay line with a cooling device to protect the transducers from overheating. The electronic boards have been modified to match the designed transducer, with a center frequency of 3.5 Mhz. The gated RF card was modified to provide gate position and width adjustment. A software program was developed to evaluate the Waveform Digitizer. Difficulty in translating source code is being resolved.

A Signatec DA 60 waveform digitizer was tested for frequency resolution using a fluid suspension of 50 μm glass beads. Resolution of 0.977 Mhz per pixel was judged as too coarse for the requirements of this application. A custom board was then modified and similarly tested, using a Hewlett Packard 8591E portable spectrum analyzer for comparison. The custom card achieved 0.244 Mhz/pixel, which was judged adequate pending further evaluation. In addition, the data processing time was superior to the HP unit. The stability and reliability of the custom board was then tested by repeated analysis of a similar suspension. The five analyses gave essentially identical results, and the noise level was below 0.03 dB. This board was therefor judged as meeting specification.

In order to detect and measure bubbles in the hybrid molding slip, it is necessary to have a transducer with a wide band width. However, the severe attenuation in this slip at high frequencies limits the useful range of band widths. Available transducers have narrow band widths so that a new transducer needed to be designed. Separate transducers in the 1 to 10 Mhz range were used to acquire and analyze spectrum information on a simulated slip using 100 μm glass beads. The data, Figure 6, shows a noticeable increase in scattering loss at a quarter wavelength around 110 μm , which confirms the underlying principle. A lithium niobate transducer was then designed with a fundamental frequency around 3.5 Mhz, a third harmonic at 10.5 Mhz, and a fifth at 17.5 Mhz. Testing of this transducer, with a MACOR delay line confirmed the expected increase in scattering loss at quarter wavelength.

Figure 6. Combined signals of a transducer array confirms the principle of increased scattering loss at a quarter wavelength equal to the bubble size.

Task 3 Inspection and Test

The rotor inspection plan has been completed and established as a controlled process. The procedures for ultrasonic inspection of the electron beam weld have been qualified at both internal and vendor facilities. Likewise, the technique for ultrasonic inspection of the braze joint has been established. Techniques for rotor inspection using fluorescent penetrant, x-ray radiography, ultrasonics and coordinate measurement machine techniques have been established. Inspection of rotors produced in the process control and process demonstration tasks is now routine. Metallographic examination of the weld heat affected zone has shown no microstructural degradation, so that continuing inspection is not required. Push and cantilever bend test fixtures and techniques have been established for testing of braze joint strength, and testing of braze joint strength has confirmed the reliability of the ultrasonic inspection.

Task 4 Process Demonstration

Three lots of rotors were processed to completion, including binder removal, sintering and grinding of a limited number of rotors. All rotors in these three preliminary lots contained one or more defects, including incomplete blade fill, inclusions, voids, knit lines and two types of cracks. The predominant crack is associated with the backface knit line previously discussed as being caused by a "fountain effect" in molding at high fill rates as predicted by the Technalysis model. A corrective action plan was developed to address all defects, and additional forming trials conducted. Control methods were established for all defects except incomplete blade fill. Two additional approaches to blade fill were devised, and four additional lots of rotors were processed to test these approaches. Two lots with reduced viscosity were formed, and the forming parameters for complete blade fill identified. The fourth lot utilized a slp formulated for increased green strength to allow a more robust process. 90% blade fill was achieved with this slp, and a wider range of operating parameters demonstrated with no other forming defects. One concern identified during this investigation was the fired strength of parts formed with these modified slips. Test bars were therefor cut from three of these lots and tested at room temperature and 950°C. Results from this limited testing indicate that strengths are at least as high as baseline material. A final lot was formed which incorporated all advances in slp composition and forming parameters. Forming conditions were identified which produced approximately 95% blade fill. Use of conditions which produced complete blade fill unfortunately produced one or more of the other defects previously encountered. The information produced in this process demonstration will be used to design the rotor and mold for the second process demonstration. It is expected that this rotor will have blades of sufficient thickness to avoid the fill problem.

While the braze and electron beam weld processes used in production rotor fabrication have proven reliability, concern for cost has prompted a further evaluation of alternatives to the present weld. Candidate processes are lower cost electron beam welding techniques, laser welding and friction welding. Discussion with experts and potential vendors for these processes has begun.

Status of Milestones

Milestone 1, Design Package, was completed and submitted on time. The design package was approved. Milestone 2, Process Improvement Goals, has been submitted based on the initial process demonstration effort. Milestone 3, Implementation of Grinding Process Control, has been deferred as discussed in Task 2.3.8; a redefinition and completion date for this milestone is pending.

**W.B.S. Element 1.5.2.1
DEVELOPMENT OF
ADVANCED CERAMIC MANUFACTURING TECHNOLOGY**

E. Bright, C. Burk, J. Eckalbar, T.P. Leo B.J. McEntire - Norton Advanced Ceramics
R. Begin, Y. Kalish - Detroit Diesel Corporation
M. Hauptman, L.E. Mains - Deco Technologies, Inc.
M. Tricard, J. Picone, R. Ramanath - Norton World Grinding Technology Center
C. Miller - Centorr/Vacuum Industries
V.K. Pujari, W.T. Collins, R.L. Yeckley - Saint-Gobain/Norton Industrial Ceramics Corp.
T. Zahrah, S.D. Hollo - MATSYS
J. Busch, A.E. Mascarin - Ibis Associates
D. Wittmer - Wittmer Consultants

Report Prepared by
Eric Bright
Saint-Gobain/Norton Industrial Ceramics Corporation
Norton Advanced Ceramics
10 Airport Park Road
East Granby, CT 06026

Objective/Scope

The objectives of this program are to design, develop, and demonstrate advanced manufacturing technology for the production of ceramic exhaust valves for a diesel engine. The ceramic material for this program is Norton Advanced Ceramic's NT451 SiAlON, and the component to be developed and tested is the exhaust valve for DDC's Series 149 engine. Specific objectives are to: (1) Reduce manufacturing cost by at least an order of magnitude over current levels; (2) Develop and demonstrate process capability values (C_{pk}) of 1.4 or greater for all critical component attributes; and (3) Validate the performance, durability, and reliability of this ceramic valve in rig and engine testing.

Technical Highlights

Task 1 - Component Design and Specification.

Task 1a - Preliminary Design.

During the previous reporting period, NAC utilized its standard axial-pull proof test apparatus to purposely fail a total of 11 finished NT451 SiAlON Series 149 valves. The purpose of this activity was to determine the actual failure load and geometric location, and to compare these results to the specified proof test load and FEA modeling results. A summary of the valve axial pull testing data is provided in Table I. Over 50 % (6 of 11) of these valves broke at the base of the lock at loads ranging from 3,530 lbs to 4,275 lbs. The nature of the fracture surfaces for these valves indicated failure from a bending load.

As correlated by the degree of uniformity of copper witness marks on the ceramic valves, it is believed that the DDC-supplied two-piece copper-coated locks did not always load the stems in a uniform manner.

NAC designed and fabricated an alternate lock design in an attempt to eliminate the bending failure mode and increase the break load. This lock design incorporated a more contact area on the stem and tighter dimensional control. A total of 11 additional finished valves were axial-pull tested to failure. A summary of these results is provided in Table II. The modified lock design reduced the frequency of breakage at the base of the lock by a factor of two, and increased the average break load from $4,000 \pm 424$ lbs to 5220 ± 879 lbs. This lock design is being reviewed by DDC, and will be considered for use in the final valve design. A detailed assessment of the benefit of this lock design versus the additional cost will be made.

Task 1b- Final Design Analysis.

No Activity to Report.

Task 2 - Component Manufacturing Technology Development.

Task 2a - Environmental Safety and Health.

No Activity to Report.

Task 2b.- Process Cost Modeling.

NAC is developing a Technical Cost Model for SiAlON Series 149 exhaust valves in conjunction with IBIS Associates. During the reporting period, IBIS completed work under their Task 1 which included development and documentation of the base cost model. This effort involved expanding the cost model to incorporate valve grinding sub-operations. Data for three valve grinding process options was built into the model, including: (1) The current prototype machining process; (2) A centerless grinding based approach; and (3) Peel or Junker Quickpoint grinding. A preliminary cost sensitivity analysis was performed using the expanded model. Results of the preliminary cost analyses were presented at NAC's ACMT Semi-Annual review meeting in July. Three separate sensitivity analyses were presented including: (1) A comparison of the two production ceramic valve grinding scenarios; (2) A learning curve analysis to estimate the impact of a combination of process improvements when valves are fabricated on a production scale; and (3) A comparison of various process options with different amounts of grinding stock and process yields.

IBIS continued work under their Task 2 (Cost and Sensitivity Analysis) and Task 3 (Ongoing Analysis and Support). The focus of Task 2 is on: (1) Incorporation of continuous sintering into the model; (2) Refinement of the learning curve analysis to estimate the effect of production quantities; (3) Revision of the preliminary cost estimates for centerless grinding of valves based on inputs from Deco Technologies; and (4) Refinement of the stock removal versus process yield cost sensitivity analysis. All of the inputs for these analyses was collected and verified during the reporting period.

Task 2c - Process Control

Raw Material Selection - Based on sintering trials performed in the previous reporting

period and updated pricing information, NAC has selected and placed an order for a low cost silicon nitride raw material for use in the balance of the ACMT effort.

Milling and Spray Drying Process Control - Efforts are in progress to optimize the spray-drying process step using a low cost silicon nitride raw material selected in the previous reporting period. Work is focused on assessing various binder additions to the aqueous suspension. Five powder mixes each containing a different commercially available binder were prepared. These binders were selected from two types of binders systems - soluble versus emulsion. A fixed amount of each of the five binders was added to a milled silicon nitride slurry along with a dispersant and plasticizer. The dispersant and plasticizer type and quantity were held constant for all five slurries. Spray drying parameters (air inlet temperature, slurry feed rate, and atomizer rpm) were specified for each binder system based on prior experimentation. Characteristics of binderized spray dried powder from each treatment are summarized in Table III. Binder B exhibited acceptable flowability and high green strength. However, fracture surfaces of disks CIP'ed at 24 Ksi with this mix revealed inter-granular fracture of the spray dried agglomerates. This characteristic is undesirable as it is an indication that the spray dried agglomerates are too hard and remain as defects in the sintered part. The results of this experiment led to screening and selection of a lower T_g formulation of binder B. This binder, when used in conjunction with the optimized milling process, produced high green strength as well as trans-granular fracture in CIP'ed parts (ie, no relics of spray dried agglomerates).

Continuous Sintering - Development of continuous sintering continued during the reporting period in conjunction with Centorr/Vacuum Industries (CVI) and Wittmer Consultants. The CVI/Wittmer team is performing work under their Sub-task 1.2 (Dimensional Control); Sub-task 1.3 (Continuous Sintering Optimization); and Task 2 (Continuous Furnace Design Study for SiAlON Exhaust Valves). Under the continuous sintering optimization sub-task, the CVI/Wittmer team is developing a continuous sintering cycle for NAC's low cost silicon nitride, designated NT551. This material, developed under an internally-funded R&D program, utilizes a low cost silicon nitride raw material and a lower overall amount of sintering aid. During the reporting period, test billets of NT551 silicon nitride were processed through eight continuous sintering treatments. The highest density achieved in this sintering matrix was approximately 97% of theoretical. Weight loss during sintering was excessive for all of the treatments, indicating the possibility that one or more of the sintering aid constituents went through a decomposition reaction. A subsequent batch of NT551 silicon nitride test billets was fabricated, presintered, and processed through the same matrix of continuous sintering treatments. In this case, several time-temperature combinations were identified which resulted in densities greater than 99% of theoretical.

Machining - Work is ongoing in the development of a cost effective machining process for valves. This activity is being performed in conjunction with Norton's World Grinding Technology Center (WGTC) and Deco Technologies.

Work at the WGTC has focused on (1) Development of a centerless plunge grinding approach for ceramic valves; and (2) Assessment of various alternative valve grinding technologies. The centerless grinding approach was evaluated on a DedTru centerless simulation device mounted on the table of an Elb Super Brilliant surface grinder in consignment in the World Grinding Technology Center. A schematic of this test setup is shown in Figure 1. Half-inch long parts (cut from the stem sections of valve blanks received from NAC) were successfully centerless-ground with this DedTru device. Based on these initial results, a total of 15 8" x 1/2" x 3" wheels were ordered and received from

Norton Superabraisives - 11 for rough grinding and 4 four finish grinding. A test procedure was defined for the rough grinding operations with three different plunge feeds: $V_w = 10$, 20 and 30 mm/minute corresponding to material removal rates of 2.5, 5 and 8 mm³/second per mm of wheel width. Power, normal and tangential forces, surface finish and wheel wear were monitored for these screening tests. Results of these centerless grinding simulation tests were summarized in previous reports. Two wheel types from the rough grinding screening experiment and two wheel types from the finish grinding screening experiment were selected for evaluation in larger-scale centerless grinding trials. These four wheels were fabricated during the reporting period.

A Super-Tec centerless grinder was acquired by the WGTC for use in larger-scale centerless grinding trials. The purpose of this larger-scale centerless grinding study is to: (1) Identify the optimum wheel specifications for centerless grinding of valves; (2) Determine the machine tool stiffness and power required to operate at high MRR for full-length valves; and (3) Develop the appropriate truing and dressing procedures. The Super-Tec centerless grinder was dismantled during the reporting period and found to be an unsuitable machine tool. A Norton No. 3 centerless grinder was identified as an alternate.

Efforts at Deco Technologies are focused on applying the centerless grinding technology being developed at the WGTC to full-size components. During the reporting period, Deco purchased a used Lidkoping centerless grinder for performing ceramic valve grinding trials. A process routing for centerless grinding Series 149 exhaust valves was finalized, including detailed wheel specifications for each grinding operation. A total of three centerless grinding wheels for rough and finish stem, underhead, and head grinding were ordered from Norton Superabraisives Division with assistance from WGTC personnel.

In parallel to the centerless grinding development activity, several alternative grinding technologies are being assessed by the WGTC and Deco. WGTC and Deco have completed a review of ceramic valve grinding processes offered by Studer, Junker, Micron, and other machine tool builders. A Studer S40 high speed CNC grinder has been received on consignment at the World Grinding Technology Center. High speed CNC profile grinding of NT451 SiAlON valves has been successfully demonstrated on this Studer S40 machine. A diamond MSL grinding wheel rotating at 150 m/s was used for rough profile grinding in these preliminary valve grinding trials. Conventional speed grinding was utilized for the finish profile unit operation using a 320 grit vitrified bond wheel. The cycle time of the initial demonstration of Studer high-speed grinding was less than 3X NAC's current prototype grinding process. An additional reduction in process cycle time is expected once the Studer high-speed grinding process is optimized. Upon completion of optimizing this valve grinding process, a demonstration run of 30 valves will be performed on the Studer machine.

NAC and Junker finalized plans to carry out a ceramic valve grinding demonstration for the Series 149 design at Junker's facility in Nordrach, Germany. During the reporting period, a batch of 35 Series 149 NT451 SiAlON valve blanks were fabricated and sent to Junker for grinding trials to be completed in October.

Task 2d - Intelligent Processing

NAC is working in conjunction with its research and development group located at SGNICC's Northboro, MA Research and Development Center (NRDC) and MATSYS (formerly part of BDM Federal Inc.) to develop intelligent processing methodologies for

ceramic valve manufacturing. The objectives of this effort are to: (1) Develop, implement, and demonstrate an intelligent control system for milling and spray drying of silicon nitride powder; and (2) Adapt existing consolidation models to the valve dry-bag iso-pressing. The objectives of the ICS effort for spray drying are to establish intelligent, closed-loop control of the spray drying process in order to produce dried spherical silicon nitride agglomerates with: 1) a controllable mean size, 2) narrow size distribution, 3) high CIP density (i.e., minimize agglomerate hardness and the occurrence of dimpled or doughnut-shaped agglomerates and internal voids), 4) high flowability, and 5) high yield.

Milling - The milling ICS was designed to monitor slurry characteristics in real-time and make appropriate adjustments to keep the process in control. This ICS was designed to monitor and adjust process variables such as pH, temperature, viscosity and percent solids on-line, with automated feedback. Surface area and particle size distribution are monitored manually, with adjustments made in real time. During the reporting period, all of the individual IPC modules were assembled and demonstrated. The specific on-line sensors (pH meter, viscosity meter, and level controller) were tested for range and accuracy. This activity was performed in preparation for a demonstration of the complete ICS system for milling and spray drying as part of NAC's ACMT Semi-Annual review meeting in July.

Slurry-ICP equipment was setup for automated sampling and analysis of slip composition and impurity levels. Operation of this instrument required the determination of the following factors: (1) Appropriate concentration level of slurry which will not clog the nebulizer; (2) Incident plasma power; (3) Plasma observation height; (4) Nebulization flow rate; and (5) Sample up-take rate. A designed experiment was performed which varied these variables at 5 levels and resulted in settings which optimized the signal intensity, S/N ratio, R (= slurry/solution intensity) and the objective factor (OF). Follow on work was performed to establish a calibration curve using artificial standards to determine slurry concentration levels. Based on the constraints of complex sample preparation requirements, it was decided not to pursue development of on-line slurry-ICP as part of the milling ICS.

Spray Drying Process Model - In order to identify the relationships between spray drying input and output variables, MATSYS developed mathematical models for droplet generation and droplet drying. The microscopic drying model described in previous reports was adapted to spray drying of spherical droplets. The drying process is modeled using conservation of mass and energy. The current model takes into account the migration of liquid to the droplet surface by capillary action, vapor phase diffusion of the evaporated solvent through the tortuous pores of the agglomerate, and convection of the vapor phase products from the droplet surface by the surrounding hot air. The microscopic drying model is being linked to the macroscopic process variables of the spray drying process, such as the slurry flowrate, the inlet and outlet temperature, and the ambient and outlet humidity. The linked model will be validated using the results of experimental trials being conducted at the NRDC. The validated model will be used to develop the fuzzy logic rules for controlling moisture content, agglomerate hardness, and possibly agglomerate shape.

Spray Drying Intelligent Control System (ICS) - In fulfillment of NAC's ACMT Milestone No. 3, MATSYS and NRDC personnel completed the selection and specification of the control hardware for the spray drying ICS. This control hardware included: (1) A digital temperature controller for the spray dryer inlet air temperature; (2) A digital peristaltic pump, (3) A motor drive for the atomizer with a closed-loop motor speed controller; and (4) A non-contact infrared moisture sensor; and (5) Several input/output boards and other

equipment. The control hardware was set-up and debugged by MATSYS using an off-line simulator prior to installation on the NRDC spray dryer.

MATSYS completed design of the graphical user interface and data acquisition system for the spray drying ICS. This control software has been acquired by NRDC as well. After reviewing several PC-based industrial control and automation software packages, MATSYS selected FIX DMACS Version 5.0 by Intellution, Inc. as the software platform for implementation of the spray drying intelligent control system. During the reporting period, MATSYS integrated the IPC hardware with the FIX DMACS graphical data acquisition interface. Communication between the IPC software and the inlet temperature controller, atomizer speed controller, and humidity sensor was demonstrated. An illustration of the customized graphical user interface for NAC's spray drying ICS is shown in Figure 2.

An experimental matrix was performed to establish cause/effect relationships between spray dryer settings and spray dried powder characteristics. During this series of experiments, the revised ICS hardware and software was utilized and determined to be capable of controlling the spray drying process. Air inlet temperature, slurry feed rate, and atomizer rpm were varied to assess their effect on spray dried powder flowability and pressability. A summary of the spray drying conditions and powder characteristics is provided in Table IV. An IR sensor was used to measure the moisture content of spray dried powder as it collected in the chamber bucket. To calibrate the on-line IR moisture sensor, powder moisture content was measured off-line using a weight loss technique. The data in Table IV indicates that a lower inlet temperature and slower atomizer speed produce spray dried powder with improved flowability and pressability. Dimpled agglomerates were found in samples of spray dried powder from all of the treatments.

Process Model for Dry-Bag Iso-Pressing - Current process valve blanks formed by dry-bag iso-pressing (CIP) exhibit distortions such as narrowing of the stem near the valve underhead radius, "elephant's feet" at the end of the stem, and chipping around the valve head. In addition, density and stress gradients exist within the CIP'ed part which contribute to warpage during the presinter and sintering operations. The dimensional distortions and density and stress gradients make it necessary to fabricate the pressed blank significantly larger than required. At present, the formed blank to finished part weight ratio is 2.75. Presintering and single-point green machining are required to remove stock from the oversized pressed blank. NAC envisions CIP'ing followed immediately by automated single pass green machining or green grinding as a more cost effective for producing near net shape valve blanks. This approach can be employed only if the CIP'ed blanks are produced with less stock. NAC has established the following process performance goals for valve blanks: (1) A finished part weight ratio of ≤ 1.8 ; and (2) A reduction in fired blank stem total indicated runout (TIR) by least a factor of two over the current process.

To achieve these goals, MATSYS utilized their PDT™ and PROSIM™ process simulation tools to guide design of the dry-bag tooling and pressing schedule. MATSYS performed a PROSIM™ simulation of the dry-bag isopressing operation for the current blank geometry and process conditions. PROSIM™ was used to predict the shape of the valve blank after pressing. As summarized in previous reports, the modeled versus actual valve blank geometry was found to be in close agreement. Starting with the current dry-bag geometry, MATSYS in conjunction with NAC performed several iterative simulations of the dry-bag geometry to arrive at an improved tool design. A new dry-bag design was finalized using this process to reduce excess material in the valve head and shoulder area. In

addition, the PROSIM™ simulation for this new dry-bag geometry predicts reduced density and stress gradients in the pressed blank. NAC incorporated minor geometry modifications to the modeled design, and ordered this revised design dry-bag tool. This revised design tool was fabricated and delivered to NAC through a subcontracted effort with Elastomers Inc. Valve blank pressing trials were conducted with this new tool. This revised design tool eliminated chipping on the head OD and reduced the pressed part weight by greater than 20% (formed blank to finished part ratio = 2.18). However, necking down of the of the stem diameter near the head was not reduced. A subsequent dry-bag tool design iteration is planned using actual versus predicted geometry obtained from this new design. The goal for this next iteration is to eliminate the necking down of the stem so that additional stock can be removed from the pressed blank.

Task 3 - Inspection and Testing

A total of 160 (80 30° seat angle, 80 45° seat angle) finished NT451 SiAlON Series 149 valves were received at DDC. Vacuum checking of the 30° seat angle ceramic valves was performed in accordance with DDC specification 67T-2 "Intake and Exhaust Valve Sealing Test Procedure". All 80 of these valves passed this specification. NAC's dimensional inspection data for all of the valves was received by DDC and reviewed as part of receiving inspection.

A complete package of raw data generated from NAC's testing in accordance with DDC specification 15T-4/S149 "Engineering Product Approval Requirements for Experimental SiAlON Exhaust Valve" was received by DDC. Except for fracture toughness, a review of mechanical and physical properties, grain size, aspect ratio, porosity, phase assemblage, and proof test data for each batch of valves indicated compliance with the DDC material specification.

A total of 27 of the 30° seat angle valves delivered to DDC were forwarded to ORNL for fatigue testing.

A 6V-149 overhead fixture was assembled with fourteen 30° seat angle ceramic valves, eight 45° seat angle ceramic valves, and two production metal valves. The seat inserts were checked for runout and repaired as necessary to remain within a specification of 0.002". Valve guide ID's were measured and recorded for this test. Initial testing at 1,900 rpm for 100 hours was completed with no valve failures. Additional overspeed tests at 2,100 rpm, 2,500 rpm and 3,000 rpm were performed. The overspeed tests at 2,100 rpm and 2,500 rpm were suspended after 200 hours with no failures. The 3,000 rpm test ended at 23 hours with breakage in a total of five of the 16 valves tested. The following observations were made upon inspection of the failed valves:

- (1) Two failure modes were present - Two of the five failures were in the stem just above the underhead radius, and three of the five failures were in the lock groove.
- (2) A higher percentage of 45° seat angle valves failed (3/8) compared to the 30° seat angle design (2/14). None of the 30° seat angle valves failed in the stem.
- (3) Visual examination of the three valves that failed in the lock groove revealed severe chipping at the lock groove-stem OD intersection (tip side only). These were the only valves that exhibited this chipping. Visual examination of the copper coated locks for these components showed contact with the ceramic valve only in two narrow regions 180° apart, which coincided with the seams in the two piece lock. This observation provides evidence that the locks distorted to the point where contact stresses

became high enough to induce chipping and eventual breakage of the valve through the lock groove.

Despite these failures, DDC's minimum overspeed testing requirement of 20 hours at 3,000 rpm was met. Completion of the overspeed fixture testing was performed in fulfillment of NAC's ACMT Milestone No. 4. Engine durability testing of these preliminary design valves, an activity beyond the scope of the Milestone No. 4 requirements, is planned to start in January 1996.

Task 4 - Process Demonstration.

Task 4a - During the previous reporting period, a total of 200 preliminary design valves were fabricated - 100 with a 30° seat angle; and 100 with a 45° seat angle. All of these valves were inspected and delivered in fulfillment of NAC's ACMT Milestone No. 2 as follows:

- 160 to DDC (80 with a 30° seat angle; and 80 with a 45° seat angle).
- 40 to ORNL (22 with a 30° seat angle; and 18 with a 45° seat angle).

All of these valve were processed through axial pull proof testing using a proof test load of 3,000 lbs.

NAC has completed an analysis of the manufacturing data for these valves to determine: (1) The current actual process capability for each critical component attribute; (2) The actual process yields by process step; and (3) Actual variable costs by process step. These data are being used to: (1) Establish absolute goals for the Task 4b production process demonstration; (2) Validate the Process Cost Model being developed by IBIS; and (3) Guide production process development efforts.

Task 4b.

No Activity to Report.

Status of Milestones

Milestone No.'s 2, 3, 4 were completed during the reporting period.

Communications/Visits/Travel

5/2/95- DEWittmer (Wittmer Consultants), EBright (NAC), RYeckley (SGNICC), VPujari (SGNICC), MAbouaf (SGNICC), and GBGranger (SGNICC) met at the American Ceramic Society meeting to discuss continuous sintering results and program plans.

5/7/95- Steve Hollo of MATSYS visited NRDC for performing experiments on the spray-dryer.

5/30/95 - EObert (Machinotech), FZiermann (Machinotech), visited EBright, JEckalbar, and CBurk at NAC to present and review Junker's machine tool proposal.

5/31/95 - BBenoit (Deco), RBurrell (Deco), EBright (NAC), JEckalbar (NAC), MTricard (WGTC) met at the WGTC to review centerless grinding simulation tests and program plans.

7/13/95- CMiller (Centorr/Vacuum Industries), DEWittmer (Wittmer Consultants), EBright (NAC), and RYeckley (SGNICC) met at Centorr/Vacuum Industries to discuss continuous sintering results and to update program plans.

7/18/95 - All participants attended NAC's ACMT Semi-Annual Review Meeting, Northboro Research and Development Center, Northboro, MA.

7/19/95 - BBenoit (Deco), LMains (Deco), VKPujari (SGNICC), EBright (NAC), JEckalbar (NAC), MTricard (WGTC) met at the WGTC to review plans for valve grinding trials.

1

7/19/95 - 7/20/95 - VKPujari (SGNICC) visited SHollo (MATSYS) at BDM, Arlington, VA to plan the logistics of integrating the spray drying IPC system at the NRDC.

8/2/95 - JPicone (WGTC) and MHauptman (Deco) met at Altman in Chicago to examine the Lidkoping centerless grinder as a candidate machine tool for ceramic valve grinding trials.

9/12/95 - JPicone (WGTC) visited and LMains (Deco) and MHauptman (Deco) at Deco Technologies in Detroit to discuss centerless grinding wheel specifications.

9/25/95 - EBright (NAC) met with MTricard (WGTC) at the WGTC to review plans for ceramic valve grinding development.

9/5-9/15/95 - SHollo (MATSYS) visited VKPujari (SGNICC) and WTCollins (SGNICC) at the NRDC to install process control hardware and conducts tests of the spray drying ICS.

Problems Encountered

A main bearing failure on the Series 149 overhead fixture caused a two week delay in testing.

Publications

NAC participated in preparing an article for the ORNL newsletter regarding the ACMT program. EBright submitted a technical paper entitled "Advanced Ceramic Manufacturing of SIAION Exhaust Valves" for presentation and publication at the 1996 SAE Exposition, Detroit, MI, February 26-29, 1996. MTricard from the WGTC made a presentation at the NIST Ceramic Machining Consortium in Gaithersburg, MD on September 27, 1995 regarding ceramic valve grinding development under the ACMT.

Table I
Axial-Pull Testing To Failure Summary Using the Standard Lock Design

Test No.	Part ID	Failure Load (Lbs)	Location of Break	Uniform Witness Mark?
1	295	4,087	Bottom of Lock	No
2	235	3,618	Stem	No
3	282	4,898	Lock Groove	Yes - Very Distinct, Uneven at Bottom.
4	288	3,449	Bottom of Lock	No
5	230	4,275	Bottom of Lock	No - Non-uniform, 2 Places at Gaps in Lock Halves.
6	179	4,240	Lock Groove	Yes
7	281	3,898	Bottom of Lock	No - Non-uniform, 2 Places at Gaps in Lock Halves.
8	217	4,297	Lock Groove	Yes
9	248	3,710	Bottom of Lock	No - Non-uniform Mark One Side of Stem Dia.
10	431	3,530	Bottom of Lock	No
11	450	≥ 4,000	Lock Groove	Yes

Table II
Axial-Pull Testing To Failure Summary Using NAC's Alternate Lock Design

Test No.	Part ID	Failure Load (Lbs)	Location of Break	Uniform Witness Mark?
1	460	5,730	Lock Groove	Yes
2	417	4,637	Stem	Yes
3	413	6,008	Lock Groove	Yes
4	532	4,875	Stem	Yes
5	471	6,009	Lock Groove	Yes
6	357	5,191	Lock Groove	Yes
7	469	3,013	Bottom of Lock	Yes
8	319	4,930	Bottom of Lock	Yes
9	526	5,494	Bottom of Lock	Yes
10	374	5,521	Stem	Yes
11	486	6,011	Stem	Yes

Figure 1
Schematic of Centerless Grinding Simulation Test Setup at the WGTC.

Figure 2
Customized Graphical User Interface for the Spray Drying ICS System.

Table III
Characteristics of Spray Dried Powder from Binder Screening Experiment

Binder Type	Loose Packing Density (g/cc)	Powder Flowability by Hall Flow Meter (sec/25 cc)	Moisture Content (Weight %)	CIP Density (g/cc)	Diametrical Compression Strength (psi)	Characteristics of Fracture Surface
A	.91	38	1.8	2.110	216	Smooth Trans-granular
B	.95	43	1.6	2.147	250	Rough Inter-granular
C	.95	44	1.0	2.129	176	Rough Inter-granular
D	.94	43	1.0	2.115	176	Rough Inter-granular
E	.98	53	1.4	2.170	121	Smooth Trans-granular

Table IV
Results of Spray Drying ICS Cause/Effect Screening Experiment

Run No.	Inlet Temp.	Slurry Feed Rate	Atomizer rpm	Powder Flowability by Hall Flow Meter (sec/25 cc)	Loose Packing Density (g/cc)	Moisture Content (Weight %)	CIP Density (g/cc)	Qualitative Assessment of Agglomerate Shape Dimpled Particles Present?
1	T ₁	Q ₁	W ₁	44.5	.95	.16	2.025	Yes
2	T ₁	Q ₂	W ₁	41.8	.95	.21	2.038	Yes
3	T ₂	Q ₁	W ₁	42.9	.95	N/A	2.030	Yes
4	T ₂	Q ₂	W ₁	42.0	.97	.28	2.035	Yes
5	T ₃	Q ₂	W ₁	42.2	.98	N/A	2.040	Yes
6	T ₃	Q ₂	W ₂	37.4	.98	.36	2.045	Yes
7	T ₄	Q ₂	W ₂	37.6	.99	.89	2.042	Yes

2.0 MATERIALS DESIGN METHODOLOGY

INTRODUCTION

This portion of the program is identified as program element 2 within the work breakdown structure (WBS). It contains three subelements: (1) Modeling, (2) Contact Interfaces, and (3) New Concepts. The sub-elements include macromodeling and micromodeling of ceramic micro-structures, properties of static and dynamic interfaces between ceramics and between ceramics and alloys, and advanced statistical and design approaches for describing mechanical behavior and for employing ceramics in structural design.

The major objectives of research in Materials Design Methodology elements include determining analytical techniques for predicting structural ceramic mechanical behavior from mechanical properties and microstructure, tribological behavior at high temperatures, and improved methods for describing the fracture statistics of structural ceramics. Success in meeting these objectives will provide U.S. companies with methods for optimizing mechanical properties through microstructural control, for predicting and controlling interfacial bonding and minimizing interfacial friction, and for developing a properly descriptive statistical data base for their structural ceramics.

2.2 CONTACT INTERFACES

2.2.2 Dynamic Interfaces

Development of Standard Test Methods for Evaluating the Wear Performance of Ceramics

P. J. Blau
Oak Ridge National Laboratory

Objective/Scope

The goal of this effort is to improve consistency in reporting ceramic wear data by helping to develop a standard test method for quantitatively determining the wear resistance of structural ceramics, in reciprocating sliding, a type of motion which is experienced by several types of automotive and truck engine wear parts. ORNL is working with ASTM Committee G-2 on "Wear and Erosion." In 1990, P. J. Blau was appointed chairman of a newly-established Task Group G02.40.07 "Reciprocating Sliding Wear Testing," within the G-2 committee. This report describes the continuing activities of the Task Group as work proceeds toward standardization.

Technical Highlights

A number of changes, both editorial and technical, resulted from the late spring 1995 ballot, including a change in the title of the standard to "Standard Test Method for Linearly-Reciprocating Ball-on-Flat Sliding Wear." A revised ballot (version 1.7) was completed and submitted for rebalancing at the subcommittee and main committee level (concurrent ballot). There were three negative votes on the ballot due to the accidental omission of a paragraph in printing. This omission was corrected administratively in a separate mailing to the voters and the negatives were subsequently withdrawn. Thus, the reciprocating wear test for ceramics is expected to become available as a published ASTM standard test method within the next year.

Future Plans

We plan to participate in the November 9-10, 1995, ASTM G-2 committee meeting in Norfolk, Virginia. The final tally of ballots will be presented and the editorial changes to the final draft will be noted. A research report, which is required by ASTM for interlaboratory projects performed during the development of a new standard test method, is being prepared for submission.

Status of Milestones

- 222211 Address comments on the joint subcommittee/main committee ballot. December 1994 (Completed).
- 222212 Resubmit revised ballot and address final comments. June 1995 (Completed)
- 222213 Revise and resubmit draft for main and subcommittee ballot. November 1995. (Completed)
- 222214 Write and submit an ASTM Research Report. March 1996.

Communications/Visits/Travel

None.

Publications/Presentations

None.

3.0 DATA BASE AND LIFE PREDICTION

INTRODUCTION

This portion of the program is identified as program element 3 within the work breakdown structure (WBS). It contains five subelements, including (1) Structural Qualification, (2) Time-Dependent Behavior, (3) Environmental Effects, (4) Fracture Mechanics, and (5) Nondestructive Evaluation (NDE) Development. Work in the Structural Qualification sub-element includes proof testing, correlations with NDE results and microstructure, and application to components. Work in the Time-Dependent Behavior subelement includes studies of fatigue and creep in structural ceramics at high temperatures. Research in the Environmental Effects subelement includes study of the long-term effects of oxidation, corrosion, and erosion on the mechanical properties and microstructures of structural ceramics. Work in the Fracture Mechanics subelement includes development of techniques for measuring the tensile strength and creep resistance of ceramic materials at high temperatures, and testing ceramic materials at high temperatures under uniaxial tension. Work in the NDE Development subelement is directed at identifying approaches for quantitative determination of conditions in ceramics that affect their structural performance.

Major objectives of research in the Data Base and Life Prediction program element are understanding and application of predictive models for structural ceramic mechanical reliability, measurement techniques for long-term mechanical property behavior in structural ceramics, and physical understanding of time-dependent mechanical failure. Success in meeting these objectives will provide U.S. companies with the tools needed for accurately predicting the mechanical reliability of ceramic heat engine components, including the effects of applied stress, time, temperature, and atmosphere on the critical ceramic properties.

3.1 STRUCTURAL QUALIFICATION

Microstructural Analysis of Structural Ceramics

B. J. Hockey and S. M. Wiederhorn

(National Institute of Standards and Technology)

Objective/Scope

The objective of this part of the program is to identify mechanisms of failure in structural ceramics subjected to mechanical loads at elevated test temperatures. Of particular interest is the damage that accumulates in structural ceramics as a consequence of high temperature exposure to stresses normally present in heat engines.

Design criteria for the use of ceramics at low temperature differ from those at high temperature. At low temperature ceramics are elastic and brittle; failure is controlled by a distribution of flaws arising from processing or machining operations, and the largest flaw determines the strength or lifetime of a component. By contrast, at high temperature where ceramics are viscoelastic, failure occurs as a consequence of accumulated, or distributed damage in the form of small cavities or cracks that are generated by the creep process. This damage effectively reduces the cross-section of the component and increases the stress that must be supported. Such increases in stress are autocatalytic, since they increase the rate of damage and eventually lead to failure as a consequence of loss in cross section. When this happens, the individual flaw loses its importance as a determinant of component lifetime. Lifetime now depends on the total amount of damage that has occurred as a consequence of the creep process. The total damage is now the important factor controlling lifetime.

Recent studies of high temperature failure of the non-oxide ceramics intended for use for heat engines indicates that for long term usage, damage accumulation will be the primary cause of specimen failure. Mechanical defects, if present in these materials, are healed or removed by high temperature exposure so that they have little influence on long term lifetime at elevated temperature. In this situation, lifetime can be determined by characterizing the damage and the rate of damage accumulation in the material at elevated temperatures. In ceramic materials such as silicon nitride and SiAlON, such characterization required high resolution analyses because of the fine grain size of these materials: hence the need for transmission electron microscopy as an adjunct to the mechanical testing of ceramics for high temperature applications is apparent.

In this project, the creep and creep-rupture behavior of several ceramic materials will be correlated with microstructural damage that occurs as a function of creep strain and rupture time. Materials to be studied include: SiAlON; hot-pressed silicon nitride; sintered silicon carbide. This project will be coordinated with WBS 3.4.1.3, Tensile Creep Testing, with the ultimate goal of developing a test methodology for assuring the reliability of structural ceramics for high temperature applications.

Technical Highlights

Microstructural analysis studies related to the tensile creep behavior of SN-88 silicon nitride were continued and additional results on the characterization of microstructure and creep damage were obtained. TEM examination has revealed that SN-88 contains a wide range of silicon nitride grain sizes of both blocky and whisker-like morphology. While most grain sizes are from 0.1 to 3 microns, SN-88 also contains a significant fraction of whisker-shaped grains of 10 microns or more in length. SN-88 also contains a relatively high volume fraction of an intergranular second phase, whose composition is consistent with yttria and ytterbia being the primary sintering aid additives. The second phase is distributed within multi-grain junctions of varying shape and sizes (roughly, 10 nm to over 2 microns), where it is largely crystalline, and also within interfaces separating adjacent grains. In general, the interphase at two-grain interfaces varied in width, both from interface to interface and also along the same interface from about 1 nm and glassy to tens of nanometers and largely crystalline. SEM and optical examination of samples crept in tension at 1200 C. to over 1% strain, 1300 C. to over 2% strain, and at 1400 C. to over 4 and 5% strain revealed the presence of surface cracks, whose distribution, density, and lengths appeared to increase with increased strain. At all temperatures, the morphology of these cracks suggested plastic blunting restricted their growth; consistent with this, the cracks (other than those responsible for failure) rarely extended more than 300 microns into the test sample interior. TEM examination of the same set of samples revealed that, for this material, creep cavities form almost exclusively within the second phase situated at multi-grain junctions. At 1300 C. and above, the sizes of these interstitial cavities scales with the multi-grain junction size and ranges from roughly 0.1 to over 2 microns. At 1200 C., cavities rarely exceeded about 300 nm in size and were often contained within crystalline second phase remaining within the multi-grain junction, suggesting that the transport of second phase required for cavity growth is limited at this temperature. Unlike all other grades of silicon nitride investigated in this project, SN-88 exhibited limited evidence for cavitation at narrow, two-grain interfaces. Even at 1400 C. cavity growth along narrow interfaces appears to occur only along small interface segments connecting neighboring multi-grain junctions. Nevertheless, such limited interfacial growth can lead to the linking-up of interstitial cavities to form larger cavities of crack-like morphology.

Experimental Technique

The results of this study were obtained primarily by analytical transmission electron microscopy (ATEM). During this period, ATEM was used to examine thin sections obtained from the near-surface and interior of SN-88 silicon nitride after tensile creep tests at 1200 C. to 1.1% strain, 1300 C. to 2.1% strain, and 1400 C. to 4.2% strain. Additional results were also obtained on another sample tested at 1400 C. to over 5% strain. Initially, optical and scanning electron microscopy was used to examine the external surfaces after removal of the oxide "scale". All samples were tested to failure under the tensile

test task of this project (WBS 3.4.1.3). Standard ceramographic techniques were used to prepare TEM specimen from the gauge sections of tensile test samples.

Results and Discussion

During the past six months, studies relating to the tensile creep of SN-88 silicon nitride were continued and additional results on the microstructure and on creep damage were obtained. Based on tensile creep data (Task 2), the creep behavior of this material differs from that of other grades of silicon nitride studied under this project. In particular, SN-88 exhibits large strains to failure, typically ranging from 1 to 5% depending on stress and temperature, whereas the other grades tend to fail at strains of 1% or less. Interest in this material, thus, relates to its inherent "plasticity" or, alternatively, its high temperature toughness. Evidence for such implied toughness is obtained from examination the external surfaces of crept samples after polishing to remove the oxide scale. These observations have shown that creep results in distributions of surface cracks, whose size and density tend to increase with increasing strain. Although most of these tensile cracks originate at the corners of the square cross-sectioned test samples, their formation is not restricted to these sites. As illustrated in Figure 1, all exhibit relatively large crack opening displacements, indicative of blunting by plastic deformation. Consistent with this implied behavior, these cracks are not found to extend further than approximately 200 to 300 microns into the interior of the samples. The underlying mechanisms for such crack blunting/toughening cannot as yet be explained.

More detailed examination of crept samples by TEM has, however, provided results that allow a general description of the microstructure and of creep damage in SN-88. As indicated above, results to date have been obtained from both near-surface and interior sections from two samples crept at 1400 C to strains of 4 and over 5%, one sample crept at 1300 C. to over 2% strain, and one sample crept at 1200 C. to about 1% strain. Based on these samples, SN-88 is found to consist of beta-silicon nitride grains of both blocky and acicular shapes having a wide range of sizes. While most of the blocky grains range in dimensions from about 100 nm to 3 or 4 microns, SN-88 also contains acicular shaped grains of 10 or more microns in length. Relative to other grades of silicon nitride (notably, NT-154), SN-88 contains a relatively high volume fraction of an intergranular second phase. While not thoroughly analyzed, the composition of this intergranular phase is consistent with the addition of Yb_2O_3 and Y_2O_3 as sintering aids. Much of this second phase is contained within multi-grain junctions, interstitial to the silicon nitride grains, which vary in size from about 10 nm to over two microns. In crept samples, the second phase contained in these interstitial pockets is largely crystalline. As in all other grades of silicon nitride, there is evidence of an apparently glassy interphase (presumably of Yb-Y-Si-O-N composition) at all crystalline two-grain interfaces. Although still under investigation, the widths of two-grain interfaces separating adjacent silicon nitride grains can be described as variable. Based on initial high resolution studies, many of these interfaces appear to contain a glassy interphase

having a thickness of about 1 nm or less. However, as illustrated in Figure 2, many others are either uniformly wider (up to about 100 nm wide) or exhibit an abrupt change from the minimum width to widths of tens of nanometers. In all cases, these wider interfaces contain the crystalline second phase. Apparently, the development of uniformly narrow two-grain interfaces has been attained, possibly due to the large volume fraction of second phase present in this material. Finally, microstructural examination has also revealed the presence of widely distributed grains of SiC and (apparently) MoSi, of 1 to 2 microns in size. Other than exhibiting oxidation, these impurity grains do not appear to contribute to creep damage.

As in past efforts, an emphasis was placed on characterizing cavitation damage that accumulates during creep and leads to failure. For SN-88, creep cavities were found to be almost exclusively within the second phase situated interstitial to the silicon nitride grains, i.e., within the multi-grain junctions of varying sizes and shapes. While the density of these cavities appeared to increase with strain, this result could not be established quantitatively. For creep temperatures of 1300 and 1400 C., the sizes of these interstitial cavities tended to scale with the sizes of the multi-grain junctions and thus ranged in dimensions from 10 nm to upwards of 2 microns. As illustrated in Figure 3, the complete cavitation of material not only from individual sites but neighboring sites suggests rapid cavity growth by transport of the second phase at these temperatures. In contrast, creep at 1200 C. resulted in smaller cavities which, as seen in Figure 4, were often contained within the crystalline second phase at multi-grain junctions. As cavity density rather than size is normally found to be more strongly related to strain, the presence of contained cavities at 1200 C. more likely relate to restricted cavity growth by transport.

Unlike all other grades of silicon nitride examined during the course of this project, tensile creep has not been found to result in what can be clearly defined as interfacial cavitation in SN-88. For these other materials, tensile creep at these temperatures typically results in either crack-like cavities or discrete, lenticular shaped cavities within the narrow interfaces separating adjacent silicon nitride grains. At best initial high resolution studies have suggested interfacial widening, from about 1 to 2 nm, occurs at selected, tensile-oriented interfaces. Moreover, creep of SN-88 is found to result in crack-like cavities, such as seen in Figure 5. In these cases, however, closer inspection invariably reveals that the crack-like cavity morphology is due to the linking-up of neighboring multi-grain cavities. As such, interfacial cavity growth in SN-88 appears limited to the final stage of interstitial cavity consolidation. At present, no definitive explanation can be given for the lack of interfacial cavitation within narrow two-grain interfaces of grain size dimensions in this material.

Figure 1. Surface cracks produced in SN-88 silicon nitride during tensile creep. Sample was tested at 1300 C to a failure strain of 2.1%.

Figure 2. Two-grain interfaces in SN-88. Note variation in thickness of second phase (dark contrast) contained within the two vertical interfaces.

Figure 3. Interstitial cavities produced in SN-88 during tensile creep at 1300 C. At 1300 C. and above, cavity growth results in the complete transport of the second phase normally contained within such multi-grain junctions.

Figure 4. Interstitial cavities produced in SN-88 after tensile creep at 1200 C. At 1200 C., diffusive growth of cavities is limited and results in incomplete cavitation of the second phase contained within multi-grain junctions.

Figure 5. Crack-like cavity morphology in SN-88 due to the linking of neighboring multi-grain cavities.

Status of Milestones

On schedule

Publications

None

Mechanical Properties and Microstructural Characterization of Si_3N_4 Ceramics**K. L. More and L. F. Allard (Oak Ridge National Laboratory)****OBJECTIVE/SCOPE**

The objective of the research is to use analytical and high resolution electron microscopy to characterize the microstructures of several silicon nitride materials. This report will focus on the analysis of a self-reinforced silicon nitride ceramic, GS-44, manufactured by AlliedSignal, Garrett Ceramic Components.

TECHNICAL HIGHLIGHTS**Silicon Nitride Ceramics:**

Several GS-44 tensile rods, exposed to pre-test heat treatments and creep tested under similar conditions, have been received from Ken Liu, Oak Ridge National Laboratory, for microstructural evaluation to determine differences in observed creep behavior between the samples. The GS-44 was exposed to either of two treatments prior to the tensile creep experiments and compared to the as-sintered material; microwave annealed at 1200°C, 1300°C, 1400°C, 1500°C, or 1600°C for 10 h (some combinations of temperatures were also used) or furnace annealed at 1200°C for 100 h. Each specimen was subsequently creep tested in tension at 1200°C and 100 MPa. In general, the higher temperature microwave anneals (temperature range 1400°C-1600°C) resulted in poor creep behavior as compared to the lower temperature microwave annealed GS-44 (1100°C and 1200°C, or a combination of these temperatures). Also, the lower temperature microwave annealed GS-44 showed improved creep resistance over the as-sintered and furnace annealed material. Thus, to determine the reason for these observed differences in creep behavior, a complete microstructural evaluation using several techniques (including X-ray diffraction, scanning electron microscopy, and transmission electron microscopy) of the samples is underway.

A New Catalyst Research Initiative

As a part of the Ceramic Technology Program we have begun to study emission catalysts for use in heavy duty transport and automobiles. The optimization of currently available catalysts and the development of new ones requires a detailed understanding of the effects of both microstructure and composition on function. With the development of new analytical tools (high resolution electron microscopy, electron holography, Z-contrast microscopy, advanced surface analysis, etc.) that permit direct characterization of materials at the atomic level, a materials science approach to catalysis research has emerged. Correlations derived between the catalytic activity and selectivity, and the catalyst electronic character, lattice structure and surface morphology, for example, have advanced catalysis from an art to a "near" science. In the latter part of FY-1995 we began to re-direct a portion of the funding in the Ceramic Technology Project to apply to both commercial and experimental catalysts modern techniques of catalyst characterization by direct imaging methods, particularly using field emission electron microscopes. Our efforts have concentrated on the direct characterization of catalytic materials at the atomic and near atomic level, utilizing our strengths in electron microscopy and related imaging techniques, to conduct research that will advance the reputation of this laboratory in the field of catalytic science.

The initial efforts in FY 1995 were aimed at determining the major issues in catalyst characterization as viewed by catalyst manufacturers and end users. Alliances were established with numerous industry and university researchers; these have resulted in a number of research initiatives with companies like AlliedSignal, Ford Research, W.R. Grace etc., in several areas of catalyst research, concentrating in the area of automotive catalysts. We also have begun collaborations with several internationally recognized professors in this field (University of Delaware, University of New Mexico etc.), who are providing input to our fledgling effort. Early research in association with several of our contacts resulted in 5 papers and 4 posters presented at the North American Catalysis Society meeting in June.

As a result of several industry requests, we have undertaken the construction of a reaction system that will permit catalyst specimens for TEM observation to be treated under high temperature and atmospheric pressure of chosen gas compositions, then

transferred into the TEM without exposure to the atmosphere. This requires a special design of specimen holder that permits the TEM grid supporting the catalyst specimen to be encapsulated and surrounded by an inert atmosphere during the few seconds required for the transfer from the reaction chamber to the microscope. Unlike some commercially available systems, the unique design of this specimen holder ensures that the resolution of the electron microscope will not be compromised.

STATUS OF MILESTONES

Program on schedule.

COMMUNICATIONS/VISITS/TRAVEL

1. K.L. More, A.A. Wereszczak, M.K. Ferber, and R. Yeckley, "A Kinetic Study of the Formation of Voids in a Silicon Nitride Ceramic During High Temperature Creep Deformation," presented at the 96th Meeting of The American Ceramic Society, Indianapolis, IN, April 24-28, 1994.
2. T.A. Nolan, K.L. More, L.F. Allard, M.K. Ferber, and D.W. Coffey, "Microstructural Characterization of Silicon Nitride Intended for Use in Reciprocating Engines," presented at The 96th Meeting of The American Ceramic Society, Indianapolis, IN, April 24-28, 1994.

PROBLEMS ENCOUNTERED

None

PUBLICATIONS

1. K.L. More, D.A. Koester, and R.F. Davis, "Microstructural Characterization of a Creep-Deformed SiC Whisker-Reinforced Si₃N₄ Composite," *Ultramicroscopy*, 37 (1991) 263.
2. K.L. More, D.A. Koester, and R.F. Davis, "The Role of Interfaces in the Creep-Deformation of a SiC Whisker-Reinforced Si₃N₄ Composite," in *Electron Microscopy 1990*, 4, L.D. Peachey and D.B. Williams, eds., San Francisco Press, San Francisco, CA.

Project Database

B. L. Keyes (Oak Ridge National Laboratory)

Objective/scope

The objective of this task is to develop a comprehensive computer database containing the experimental data on properties of ceramic materials generated in the total effort. This computer system should provide a convenient and efficient mechanism for the compilation and distribution of the large amounts of data involved. The database will be available in electronic form to all project participants. In addition, periodic hard copy summaries of the data, including graphical representation and tabulation of raw data, will be issued to provide convenient information sources for project participants.

Technical highlights

The CTP database presently contains 14110 records on 27 types of tests on 927 materials, including 781 ceramics, 13 lubricants, 102 coatings and 31 other materials. About 3500 records cover associated information (test backgrounds, test and material notes, etc.) A detailed description can be found in Table 1.

Efforts to integrate existing graphic images into FoxPro™ files on the Macintosh system began during this period. Images of test specimens, set-up diagrams, and processing flow charts were integrated into the DRAWINGS file so that the picture captions and other details would be readily available to the user. Prior to this effort, the images were stored in Kodak's Shoebox, making linking to the FoxPro files more difficult. Adding the images greatly increased the size of the file, to over nine megabytes from a pre-image-inclusion size of well under one megabyte. To facilitate data transfer, a separate copy of DRAWINGS was created without the images, so that the information would still fit on a floppy disk. DRAWINGS with images will be added to the data set that will be available on the World Wide Web soon. Other images, such as micrographs, creep curves, and other data plots, will be added in the future.

Database personnel met with local World Wide Web information providers in June to discuss possible ways to make the CTP database accessible through the web. The chosen method will place the database on ORNL's new NT-based FoxPro server. Data updates, gateway interfaces (CGI's), text-based help and tutorial files, and file maintenance will be provided by CTP database personnel. John Munro from Instrumentation and Controls Division, Gloria Caton from Health Research Sciences Division, and Amy Shippy from Computing and Telecommunications Division, all ORNL, have provided excellent help in this effort.

Only approved sets of data, usually everything stored on a specific material, will be available on the WWW-accessible database initially, with more information to be added at least semiannually. NT-154 and GTE PY6 have been chosen as the first materials to be available. The initial version will be very stripped-down to get the information online, with more capabilities to be made afterwards. Enhanced graphics will be a major priority in future releases. Some provisions for on-screen summations, basic math functions, and maximum-likelihood Weibull calculations are also on the list of capabilities under consideration.

Computer hardware problems that surfaced in later summer have caused a delay in making the

database accessible through the World Wide Web. The local NT-based Web server for FoxPro databases was not ready until early August. Windows 95™, needed to develop and test the interface between the database and the Web, required more space and memory (RAM) than the present PC system has available. The Bernoulli™ 150 megabyte drives have not been working properly. A larger hard disk will be needed to hold the space-hungry software upgrades Windows uses. These problems were not discovered until Windows 95 was released in late summer, after which funding was insufficient to cover the cost. When funding is approved for the next fiscal year, these problems will be fixed.

The Macintosh used to process graphics for the database was upgraded from a Ilox to a PowerPc 9500/120 during this period. Since the processor for this new machine is so new, some of the existing software has caused problems. Many upgrades have been ordered, and some received, but a few snags still exist. Fortunately, the speed of the 9500 permits a quick reboot, a process performed often recently. The one gigabyte hard disk and speedy image processing has been a tremendous help, regardless of the other problems yet to conquer.

Database personnel are gleaning as much information from a variety of sources on writing interfaces to the Web from FoxPro databases. A local seminar on the PERL language offered the most encouragement. Much has been gained, via Web surfing and document viewing, from seeing how others have handled similar situations. Actual interface construction will begin once the PC system upgrade is complete and the Bernoulli drives are once again working properly and reliably, since those drives are required to back up the system.

Other plans call for data input to resume while awaiting the system upgrade, since the present system works with the DOS version of FoxPro 2.6. Creation of new files on grinding tests, updates to test background descriptions, and revision of locally-created batch-codes to include date information are all on the list of tasks to do. More data plots, creep curve information, micrographs, test and specimen details and other graphics will be added to external files (non-FoxPro, for now, due to space considerations). Database personnel are also looking for a user-friendly way to quickly access the graphics pertaining to a specific test; the problem is in the quantity of graphics that may be involved and the type of computer being used.

Part of this reporting period was spent completing the CTP database summary report. Original plans to produce a summary covering all of the major materials stored in the database were scrapped when the stack of data tables alone grew to an enormous height. The revised content will cover major silicon nitrides only, including some recently released AS800 data. As in previous data summary reports, comparative graphs will accompany the usual test data plots and Weibull analyses. That report should be in review soon.

Database personnel are again requesting that any participant in the Ceramic Technology Project who has test data (especially from recent tests) to please send a copy to the database administrator at Oak Ridge National Laboratory. Graphic images as photographs or data files are also requested, along with some background information about each one (such as material, microscope type and power/magnification, responsible facility and person, etc.). Data are acceptable on disk or hard copy. Please identify the format (Lotus, Wordperfect, etc.) and platform (PC or Macintosh) in which the data are recorded if on a disk. Data in reasonable quantities may be sent via e-mail to "blp@ornl.gov". All sources will be noted and preserved in the database.

Work on standards for ASTM Committee E-49 have been suspended until the catch-up work on the database is completed.

Communications/Visits/Travel

The CTP Database was sent to four requestors during this period.

BLP Keyes met with local WWW information providers to discuss access methods and attended training sessions on creating World Wide Web pages and writing interfaces for the Web.

Database personnel provided Robert Schulz with a copy of CTPVIEW, including a special boot program to facilitate loading on his machine.

Problems Encountered

Software required to work on the Web-FoxPro interface demand more resources than the present system can provide, so the Web-accessible database has been temporarily delayed. Problems with other computer hardware have also been a nuisance.

Status of Milestones

Efforts to get a subset of the database on the World Wide Web have been hampered by space-consuming software upgrades required to create the interface for the database, and by hardware poltergeists .

Publications

None.

TABLE 1. CTP DATABASE SUMMARY AS OF SEPTEMBER 30, 1995

Material Class	Braze Specimens					Creep	Cyclic Fatigue	Density	Dynamic Fatigue	Elasticity
	MOR 4	Shear Str.	Toughness	Torsion	Tor. Fatigue					
Alumina							15	5	9	28
Alumina + reinforcing fibers							10	7		
Alumina + Zirconia										
Mullite										2
Mullite + reinforcing fibers										11
SiAlON										
Silicon Carbide		12					17	10	23	15
Silicon Nitride	77	48		15	7	448	51	64	309	135
Silicon Nitride + reinforcing fibers								38	14	74
Zirconia	241	58	43				51	158		119
Zirconia + reinforcing fibers										
Other				6				4		
Totals	318	118	43	21	7	448	144	286	355	384

Material Class	Fracture Toughness	Hardness	Interrupted Fatigue	MOR 3 Pt Bend	MOR 4 Pt Bend	Notched Creep	Oxidation Rate	Poisson's Ratio	Shear Modulus	Stress Rupture
Alumina	39	4			418					13
Alumina + reinforcing fibers	39				145					
Alumina + Zirconia					7					
Mullite	1			1	4					
Mullite + reinforcing fibers	12			9	20					
SiAlON					52				1	
Silicon Carbide	38	27			414					13
Silicon Nitride	158	116		10	2414	38	63	31	31	251
Silicon Nitride + reinforcing fibers	56				164		3	62	61	
Zirconia	377	24	239		1615					17
Zirconia + reinforcing fibers					2					
Other	2	39			61					3
Totals	722	210	239	20	5316	38	66	93	93	297

(CONTINUED)

TABLE 1. CIP DATABASE SUMMARY AS OF SEPTEMBER 30, 1995

Material Class	Specific Heat	Tensile	Thermal Conductivity	Thermal Contraction	Thermal Diffusivity	Thermal Expansion	Thermal Shock	Torsion	Material Char.	Chemistry
Alumina		15	16			1	2		25	14
Alumina + reinforcing fibers		11	39		20	4	6		95	
Alumina + Zirconia				23		21			2	
Mullite									2	
Mullite + reinforcing fibers			8						33	
SiAlON			6						3	
Silicon Carbide		86				23			77	68
Silicon Nitride	22	589	24		23	58		3	391	8
Silicon Nitride + reinforcing fibers	9		9		17	14			66	
Zirconia		16							49	44
Zirconia + reinforcing fibers									5	
Other					6	40		4	39	17
Totals	31	717	102	23	66	161	8	7	787	151

Material Class	Wear Resistance	Coatings	Lubricants	X-Ray Diffraction	Micro-graphs
Alumina-based	9	3			4
Alumina + reinforcing fibers	1				5
SiAlON					4
Silicon Carbide	3				68
Silicon Nitride	22			17	261
Silicon Nitride + reinforcing fibers				49	38
Chromia-based	98	20			
Zirconia-based	13	16		72	23
Enamels	5	10			
Other	126	53	13		8

Totals	277	102	13	138	411	
Grand Total(characterization data not including text records)						1602
Grand Total (test data only)						10610

3.2 TIME-DEPENDENT BEHAVIOR

**W.B.S. ELEMENT 3.2.1.3
FRACTURE BEHAVIOR OF TOUGHENED CERAMICS
H. T. Lin and P. F. Becher**Objective /Scope

Ceramics with reinforcing microstructures and ceramic composites offer important advantages for heat engine applications. Chief among these is the improved fracture toughness that can be achieved by appropriate design of microstructural and material parameters. Previous studies show that these materials often exhibit substantial improvement in damage, thermal shock, and slow crack growth resistances. However, design of such systems must also consider those factors influencing their performance at elevated temperatures.

In response to these needs, studies are conducted to determine the mechanical properties, (e.g., creep, delayed failure, strength, and toughness) at elevated temperatures for these toughened ceramics. Particular emphasis is placed on understanding how microstructure and composition influence the mechanical performance at elevated temperatures and the stability of these properties for extended periods at these temperatures. The knowledge gained from these studies provides input on how to modify materials to optimize their mechanical properties for the temperature ranges of interest.

Technical Highlights

The long-term mechanical reliability of silicon nitride ceramics at elevated temperatures is mainly governed by the time-dependent deformation processes such as slow crack growth (SCG) and/or creep. The dominant degradation processes depend upon the applied stress levels and test temperature and may also be closely related to the test environment. Previous fatigue studies^{1,2} have indicated that oxidizing environments can promote either SCG or creep process in silicon nitride ceramics at elevated temperatures as compared to the inert environments (i.e., argon and nitrogen). In addition, tensile creep results reported by Kossowsky et al.³ showed that the Norton HS-130A specimens (with 0.4 wt% MgO additive) tested in helium atmosphere exhibited lower creep rates but with shorter lifetimes than those tested in air. Furthermore, tensile creep studies conducted by Wereszczak et al.⁴ (in WBS Element 3.2.1.6 Life Prediction Verification) on a Norton NCX-5102 silicon nitride (4 wt% Y_2O_3) showed that the specimens tested in argon exhibited higher creep rates and shorter lifetimes than those tested in air. These results suggest that the fatigue and creep responses of silicon nitride ceramics are greatly influenced by the testing environments and sintering aid systems.

Tensile creep studies were, therefore, conducted in nitrogen (N_2) and in air on (1) gas-pressure sintered (GPS) silicon nitride and (2) hot isostatically pressed (HIP) silicon nitride to elucidate environmental effects on the creep rate and controlling mechanism. The GPS silicon nitride ceramics contained additive mixtures of 5 vol% Yb_2O_3 -0.5 vol% Al_2O_3 (designated SN5YbAl) and 10 vol% Yb_2O_3 -0.5 vol% Al_2O_3 (designated SN10YbAl). A post annealing at 1250°C for 12 h was carried out to

convert the intergranular amorphous phase in these two GPS silicon nitride ceramics to crystalline phase(s). On the other hand, the silicon nitride (designated as NT164, Saint-Gobain/Norton Industrial Ceramics) was hot isostatically pressed (HIPed) with 4 wt% Y_2O_3 additive and then post-annealed to crystallize the secondary phase(s). Small dog-bone type tensile creep specimens were employed in the present study and the creep displacements were continuously monitored using an optical-based laser extensometer.

1. Gas-pressure sintered silicon nitride ceramics

Figure 1 shows the creep rate versus applied stress curves for both GPS SN5YbAl and SN10YbAl materials tested at 1300°C in air or in N_2 atmosphere. The data show that the creep rates obtained in N_2 for the both SN5YbAl and SN10YbAl materials are at least four times lower than those tested in air at 1300°C under the stress levels employed. This illustrates that the creep rates of both the SN10YbAl and SN5YbAl materials are accelerated when conducting the tests in an air environment. In addition, the SN10YbAl material exhibits lower creep rates (about ten times) as compared with the SN5YbAl material tested in air or in N_2 environments. Furthermore, the slopes of the creep rate versus applied stress curves in air and in N_2 show that the SN10YbAl material exhibits a stress exponent of ~ 6 , which is lower than the exponents obtained for the SN5YbAl material (9.8 and 12). The high stress exponent obtained in tension with Si_3N_4 materials is generally attributed to the accumulated creep damage, i.e., cavitation. The lifetime versus applied stress curves for both the SN10YbAl and SN5YbAl in air or N_2 are shown in Fig. 2. For both GPS silicon nitride materials the specimens tested in N_2 generally exhibit lifetimes that are four to ten times longer than those tested in air. In addition, the SN10YbAl material reveals a 10-fold longer life than the SN5YbAl material under the same test environment. The higher creep rates and shorter lifetimes for both the SN5YbAl and SN10YbAl materials tested in air at 1300°C could be a consequence of oxidation reactions and formation of additional amorphous intergranular phase(s). The difference in creep response at 1300°C between SN5YbAl and SN10YbAl may be due to variation in the glassy phase content and the difference in oxidation reaction. Detailed electron microscopy studies are in progress to understand the changes in microstructural characteristics and compositions associated with the creep in these two test environments.

2. Hot isostatically pressed silicon nitride

Figure 3 shows the creep strain versus time curves for Norton NT164 tested at 1430°C and at an applied stress of 100 MPa in air or N_2 atmosphere. The creep curve in N_2 exhibited primary and secondary creep stages, whereas the one in air revealed primary, secondary, and tertiary creep stages. In addition, the specimen tested in N_2 exhibited lower creep rate and longer life as compared with the one tested in air (as shown in Fig. 3), consistent with the results obtained for GPS silicon nitride materials as mentioned in the above (Figs. 1 and 2). It is apparent that the air environment (oxidation reaction) promoted the creep deformation process, thus shortening the creep life of silicon nitride ceramics. Additional creep tests under different applied stress levels and temperatures are in progress to understand the creep controlling mechanisms as a function of test environment.

Status of Milestones

Milestone No. 321317: "Evaluation of static fatigue and creep behavior of gas-pressure-sintering Si_3N_4 ceramics" was completed.

Milestone No. 32119: "Complete characterization of the effects of material parameters and oxidation process on the transition from slow crack growth to creep failure process in Si_3N_4 ceramics" was completed.

Milestone No. 321320: "Complete evaluation of the effect of an oxidizing, moist environment on the lifetime of candidate engine valve materials" will be delayed to March 1996 due to the difficulty to obtain the candidate SiAlON valve materials.

Publications

1. H. T. Lin, J. O. Kiggans, and T. N. Tiegs, "High Temperature Deformation and Fracture Processes in Sintered Reaction-Bonded Silicon Nitride," submitted to *J. Mater. Sci.*

References

1. A. A. Wereszczak, *et al.*, "Role of Oxidation in the Time-Dependent Failure Behavior of Hot Isostatically Pressed Silicon Nitride at 1370°C," *J. Am. Ceram. Soc.* 76 [11] 2919-22 (1993).
2. Y. Shigegaki, *et al.*, "High Temperature Fatigue Properties of Silicon Nitride in Nitrogen Atmosphere," pp. 461-466 in *Mat. Res. Soc. Symp. Proc. Vol. 287, Silicon Nitride Ceramics-Scientific and Technology Advances* (1993).
3. R. Kossowsky, D. G. Miller, and E. S. Diaz, "Tensile and Creep Strength of Hot-Pressed Si_3N_4 ," *J. Mater. Sci.* 10 (1975) 983-997.
4. A. A. Wereszczak, T. P. Kirkland, H. Cai, and M. K. Ferber, "Life Prediction Verification," pp. 55-61 in *Ceramic Technology Project Bimonthly Technical Progress Report, August-September 1994, ORNL/CF-94/218, October 31, 1994.*

Figure 1. Creep rate versus stress curves for gas-pressure-sintered silicon nitride ceramics tested at 1300°C in air or nitrogen atmosphere.

Figure 2. Stress versus lifetime curves for gas-pressure-sintered silicon nitride ceramics tested at 1300°C in air or nitrogen atmosphere.

Figure 3. Creep strain versus time curves for Norton NT164 tested at 1430°C in air or nitrogen atmosphere.

Cyclic Fatigue of Toughened Ceramics

K. C. Liu, C. O. Stevens, and C. R. Brinkman (Oak Ridge National Laboratory)

Objective/Scope

The objective of this task is multifold:

1. To develop, design, fabricate, and demonstrate the capability of performing cyclic fatigue in tension-tension/compression and static fatigue testing in uniaxial tension/compression on candidate structural ceramics at elevated temperatures. Significant progress has been made in several areas on the experimental front (such as specimen/grip alignment, specimen heating, and high-temperature extensometry), including recent introduction of new testing capabilities in fully reversed tension-compression cyclic fatigue and compressive creep in the uniaxial mode.
2. To develop baseline information on cyclic fatigue behavior of candidate ceramics and, in turn, to establish a design database.
3. To develop creep and creep-rupture databases for advanced heat-engines design applications in the 1150 to 1370°C range.
4. To evaluate and refine existing constitutive models based on the information generated above.
5. To develop new constitutive models to facilitate design analyses of high-temperature structural components and improve their reliability.

Technical HighlightsCyclic fatigue of GS-44 Si_3N_4 at 1200°C

The objective of the tests described in this section is to determine cyclic fatigue behavior and the influence of cyclic waveform on the fatigue of Si_3N_4 ceramics. The waveforms shown in Fig. 1 were used to control cyclic fatigue testing in: (a) fully reversed tension-compression (T/C) mode with R-ratio (= min./max. stress amplitude) = -1, (b) tension-tension (T/T) mode with R = 0.1, and (c) compression-compression (C/C) mode with R = 0. A small R-ratio was used to prevent the load-train backlash during T/T fatigue loading. Hourglass-shaped (HG) specimens (Fig. 2a) were used in all three modes of fatigue testing and buttonhead (BH) specimens (Fig. 2b) in T/T mode testing only.

Results obtained from a series of previous tests on GN-10 Si_3N_4 at 1200°C indicated that T/T mode loading was more deleterious compared to T/C mode loading. Since T/T fatigue tests were performed on both HG and BH specimens using two different test machines, the influence of machine bias was rather remote. However, results obtained from fatigue tests of GS-44 Si_3N_4 , shown in Fig. 3,

do not support the same finding conclusively because the T/T fatigue data generated from HG specimens (filled circles) do not agree well with those of BH specimens (filled squares). Material variation was suspected to be the cause of the discrepancy, since HG specimens were fabricated from a tile and BH specimens from another. To reconcile the differences, three HG specimens and two BH specimens are currently being fabricated from a single tile for further testing.

An exploratory fatigue test was performed on a specimen (HG-10) in C/C mode using the triangular waveform with $R = 0$ (Fig. 1c). Because it was a pilot test, a cyclic stress amplitude of -300 MPa was used as a starting point. The stress amplitude was increased intermittently in steps of -20 MPa each time the specimen completed -50,000 to -200,000 cycles without specimen failure. During the testing, acoustic emission (AE) was monitored continuously. Finally, the test was discontinued after the specimen completed -150,000 cycles at -600 MPa with a total of -3,690,000 cycles accumulated. The test was discontinued to prevent the specimen from buckling although no imminent failure was noticed. It is of interesting to note that no AE signals with amplitude in excess of a preset value of 45 db were detected through the entire period of testing on this specimen, suggesting that little or no fatigue damage may have been done to the specimen under C/C loading. Test results for specimen HG-10 (unfilled diamonds) are plotted in Fig. 3, in which the numbers refer to specimen numbers; filled symbols indicate rupture at the test condition indicated and unfilled symbols indicate no specimen failure when the test condition was changed. The unfilled symbols with an arrow indicate the last test condition when the tests were discontinued. Two fatigue curve were drawn visually using the upper one to approximate the fatigue behavior of the material under T/C loading and the lower one as a lower bound to bracket the three square data.

A second fatigue test (specimen HG-12) was performed from the beginning with a stress amplitude of -600 MPa in C/C mode. The test was discontinued after completing 50,000 cycles because no AE signals were detected as was the case observed in the pilot test discussed previously. A lack of AE signals being detected during the course of testing led to an optimistic assumption that no fatigue damage had been done to the test specimen. With the assumption that the specimen remained in the unadulterated condition, the specimen was cycled in T/C mode with a stress amplitude of 300 MPa. The specimen failed at 11,654 cycles. For comparison with T/T and C/C data, the number of cycles has been doubled, as explained in a previous report¹, and was plotted accordingly as shown in Fig. 3. Acoustic emission data were recorded during T/C loading. Audible signals were detected near the end of life only, indicating that lower-energy AE signals may have escaped from detection. The current value of the threshold set point may need to be lowered in order to capture more information, but it must be determined experimentally. The specimen ruptured at the mid-length which coincides with the

location that the AE data predicted to occur before actual failure. AE data are currently being analyzed to determine the optimum signal threshold value for GS-44 Si_3N_4 .

Creep testing of NT-154 Si_3N_4

Creep curves of two long-term creep tests on NT-154 specimens have been updated. The status of both tests is as follows.

Specimen 20-56 (Fig. 4): This specimen has completed 37,000 h (4.22 years) of testing. The test has been interrupted twice during this reporting period due to weather-caused power failures. Although pronounced transient creep was discerned following each time the specimen was reloaded, showing a sharp rise in creep rate due to consecutive reloading within a short period of time, the creep rate has decelerated to about the same as that prior to the occurrence of test disruptions.

Specimen 20-32 (Fig. 5): This specimen always showed transient creep of various intensities following each restarting of the test due to power outage. Examination indicates that fast transient creep was usually followed by a strain recovery, whereas moderate transient creep crossed over directly into steady-state creep with no visible strain recovery. The specimen has completed ~30,000 h (3.42 years) of testing, and shows no unusual creep behavior since the system was down at $t = -26,000$ h. The current plan is to discontinue both tests for microstructural examinations of the tested samples.

Creep testing of GN-10 Si_3N_4

Two creep tests on GN-10 Si_3N_4 being tested at the low-stress end of the creep-rupture range (long-term tests) are still in progress. The status of both tests is as follows.

Specimen 89367-1-2 (Fig. 6): Shortly before the end of the last report period, the specimen showed steady-state negative creep. The problem was found to have resulted from steady drift of the electronic zero at a rate of 0.3 mV/h in the electronic conditioner for the mechanical extensometer. The creep curve reported in the last report¹ has been revised accordingly and updated with new data.

Specimen 89367-1-3 (Fig. 7): The specimen had been undergoing steady-state creep at a rate of $\sim 1.7 \times 10^{-10} \text{ s}^{-1}$ for about 3500 h before the test was disrupted recently. Following the latest restarting, the specimen is currently showing strain recovery as occurred in previous situations.

Creep testing of furnace-annealed GS-44 Si_3N_4

To examine whether conventional furnace annealing can also effectively enhance the creep resistance of GS-44 Si_3N_4 as microwave annealing did or not, a virgin tile in the as-fabricated condition was annealed in a resistance-heating furnace at 1200°C for 100 h in air. Five specimens were machined from the tile and designated with a prefix of "FA". The specimens were tested in the as-machined condition with no post-machining surface finishing.

Specimen FA-3: This specimen was tested at 1200°C with an applied stress of 120 MPa. Test results are shown in Fig. 8 and compared with data reported previously for specimens tested in the as-sintered (specimen AS-8) and microwave-annealed (specimen MA12-2) conditions. The prefix of "MA12" indicates microwave annealing at 1200°C for 10 h with preannealing at 1100°C for 10 h. Although a direct comparison with the data for MA12-2 specimen is not valid due to the intermittent changes in applied stress, the trend portrayed by the first segment of the creep curve obtained at 120 MPa indicates that microwave annealing was clearly beneficial to the creep resistance of the material. Furnace annealing was also shown to be beneficial compared to the unannealed condition by an order of magnitude in creep rupture life.

Specimen FA-4: This specimen was tested at 1200°C with an applied stress of 140 MPa. Test results are shown in Fig. 9 and compared with previously reported creep data for specimens MA12-3 and -4 tested under the same condition. The creep curve of MA12-4 and that of FA-4 are shown to be about the same; however, specimen MA12-3 showed that the creep rate will remain relatively low and the creep rupture life will be long. No creep data for as-sintered specimens tested at 140 MPa are available, but its creep rupture life will be less than 30 h, inferring from the rupture life of specimen AS-8 indicated in Fig. 8. It is evident that furnace annealing is also beneficial to the enhancement of creep resistance but not as effective as annealing by microwave heating, which apparently needs further improvement to attain the desired consistency in creep behavior.

Creep testing of microwave-annealed GS-44 Si_3N_4

Low-temperature microwave annealing (M/A) at 1200°C was found to be much more effective than high-temperature annealing above 1400°C in enhancing the creep resistance of GS-44 Si_3N_4 . However, it is important that the material behavior must be consistently reproducible. To this end, two additional tiles were microwave annealed in the same furnace using the low-temperature heating schedule designated as "MA12". To facilitate discussions, locations of specimens are marked in each common tile shown in Fig. 10.

Specimen MA12-6 was tested with an applied stress of 140 MPa. Test results are plotted in Fig. 9 and compared with previously reported creep data¹ generated from specimens, which were machined

from another tile marked as tile A in Fig. 10. Specimen MA12-6 was clearly the weakest in terms of creep life among the three MA12 specimens. The differences in creep behavior exhibited by the three specimens were not totally unexpected because specimens, such as MA12-3 and -4 although made from the same tile, still behaved quite differently. However, it was disturbing to find that specimen MA12-6 underperformed severely compared to a furnace annealed specimen FA-4, which was tested on the same machine, identical heating environment, and the same test condition.

Creep tests were performed on specimens MA12-7, -9, -10 at 1200°C with an applied stress of 100 MPa. To ensure that material, heat treatment, and test method are consistent, each of the specimens, all made from tile B, were tested in the same machine using the same equipment and test method. Test results shown in Fig. 11 confirm that data are reproducible under the controlled test environment. To facilitate comparison, the same data were replotted in Fig. 12. The severity of difference in creep behavior was again exhibited even though specimens were tested in the same creep testing machine. Creep resistance of specimen FA-1 was found to be better, although marginally, in comparison to that exhibited by the M/A specimens made from tile B.

In summary, the information gleaned from data shown in Figs. 9 and 12 suggests that inconsistent creep behavior exhibited by tiles A and B is due to either inconsistency in current techniques of microwave annealing or the difference in the base material or combination of both.

Compressive creep testing of ceramic materials at elevated temperatures

An exploratory compressive creep test was initiated on GN-10 Si_3N_4 at 1300°C with an applied stress of -125 MPa, using a dumb-bell shaped specimen shown in Fig. 2c. Compressive creep virtually ceased after 100 h of testing, as shown in Fig. 13. Therefore, the applied stress was increased to -150 MPa after the specimen completed 210 h of testing at -125 MPa with a total creep strain of -0.084%. In contrast, a specimen tested in tension with the same magnitude of stress exhibited creep at a very high creep rate; hence, the specimen had a short rupture life. Subsequently, the applied stress was increased intermittently in steps of -25 MPa when the specimen showed no significant progress in creep deformation. Results obtained to date are summarized in Fig. 14. The specimen has just completed a period of -1500 h of testing at -250 MPa with a creep rate of $-1.07 \times 10^{-1} \text{ s}^{-1}$. A review of overall data indicates that the creep rate increases approximately proportional to applied stress, suggesting that creep of Si_3N_4 under compression may be promoted by a shearing mechanism. No indication of imminent failure has been observed to date and the load-train remains stable.

The second compressive creep machine is now in operation. The final checkout tests indicate the machine is capable of uniform compressive loading with a minimal bending below 2%. The optical extensometer was calibrated at elevated temperatures in the range from 900°C to 1400°C. Interferences by convective air in the furnace tended to have reduced the resolution of signal output due to the temperature induced noise; however, its overall performance will still meet the minimum accuracy needed in creep strain measurement.

A GS-44 Si_3N_4 specimen was initially tested at 1200°C with an applied stress of -100 MPa, as shown in Fig. 14. Due to the failure of load control, the test was interrupted at $t = 233$ h. Subsequently, the specimen was reheated and reloaded to the original test condition. However, a change in creep behavior was clearly discernible showing transient creep immediately following the reloading. Although the creep curve is somewhat wavy, a reasonably steady-state creep rate can be inferred from the creep data obtained during the last 300 h of testing. Creep rate in tension for GS-44 at the same temperature and stress is also orders of magnitude higher than that in compression as is the case for GN-10. This asymmetric creep behavior in tension versus that in compression suggests that there is a serious flaw in current practice of analyzing and reporting bending creep data that are based on the elastic beam theory. Therefore, a revision is needed for current format of reporting such data so that bend data can be rationally correlated with uniaxial creep data.

The above work resulted in a draft paper entitled "A Multiaxial Viscoplastic Model for Advanced Si_3N_4 Ceramics." The paper has been submitted and accepted for oral presentation at the 20th Annual Cocoa Beach Conference, Cocoa Beach FL, January 7-11, 1996. The following is the abstract.

A MULTIAXIAL VISCOPLASTIC MODEL FOR ADVANCED Si_3N_4 CERAMICS,
J. L. Ding, Washington State University, Pullman, WA 99164;
K. C. Liu and C. R. Brinkman, Oak Ridge National Laboratory,
Oak Ridge, TN 37831

This is a refinement of a creep/creep rupture model developed previously based on results obtained from uniaxial tensile creep tests of an advanced Si_3N_4 ceramic. The exploratory model in scalar form is limited for general applications due to the lack of generality. Severity of asymmetric creep behavior in tension compared to that in compression observed in recent experimental results necessitates this revision. The tensorial formulation follows the plasticity theories developed for soils. Material sensitivity to pressure, dilatancy and compaction, asymmetry between tension and compression, changes of material structure due to hardening of grain boundary phase, and deformation induced hardening and softening have all been considered. Provisions of such features in the proposed multiaxial model are shown to have elevated modeling flexibility, which permits that

a particular model form can be tailored to reflect some desired features of material behavior.

The following abstract has been submitted to the 41st ASME Gas Turbine and Aeroengine Conference, Birmingham, UK, June 10-13, 1996.

A TECHNIQUE TO ACHIEVE UNIFORM STRESS DISTRIBUTION IN COMPRESSIVE CREEP TESTING OF ADVANCED CERAMICS AT HIGH TEMPERATURES

K. C. Liu, N. E. Holshauser (North Carolina A&T State University, Greensboro, NC), C. O. Stevens, and C. R. Brinkman

Previously, uniaxial testing of brittle materials in tension was considered to be more difficult than that in compression due to the lack of appropriate equipment to achieve good load column alignment and, hence, low bending stress. To circumvent the experimental difficulty, a short cylindrical specimen was often tested in compression as an indirect method of generating desired information. However, result of neither test can substitute for the others due to the peculiar nature of ceramic materials. With the use of the self-aligning coupler in the load-column, robust tensile testing of brittle materials can now be accomplished routinely. Contrastingly, little or no innovative techniques have been presented for compressive testing in recent years.

A cursory conclusion might lead an investigator to believe that compressive testing of brittle materials is simple to perform. However, careful examination can easily show otherwise because bending stress due to initial eccentric loading is increasingly accentuated under compression loading if no self-aligning feature is built in the load-column system. The paper describes an innovative load-column assembly with such special features. Key elements and techniques to achieve uniform stress distribution in compressive loading are discussed. Strain-gaged specimens have been used to verify that low bending stress below 2% is routinely achievable with the use of the self-aligning coupler. Results of a compression creep test are presented for a dumb-bell shaped silicon nitride specimens tested at 1300°C over a period in excess of 1000 h.

A simulation study on creep of Si₃N₄ under four-point bending based on the ORNL viscoplastic model - J. L. Ding (Washington State University) and K. C. Liu

Correlation of creep data obtained by uniaxial tensile creep testing and those by four-point bending has been difficult because the intrinsic stress distribution of the ceramic beam specimen under constant load creep is time dependent and can not be measured directly. The major difficulty stems from: (1) the use of the elastic beam theory which assumes the initial elastic stress distribution in the bend specimen remains unchanged during the

course of creep under constant load and (2) the assumption that creep rate under tension is the same as that under compression. As the test data illustrated in preceding sections, the latter assumption is not valid and this, in turn, invalidates the former.

Several studies on the topics have been reported using various postulates in order to simplify their analyses. In our simulation study, no simplifications are used in the fundamental equations. While reviewing previous papers for comparative studies, we found that a paper frequently referenced in the studies of four-point bending creep was seriously flawed. The authors of the paper were informed of the error. Preliminary results of our study show that the asymmetry in stress distribution along the depth of the bend bar is severe based on the new information generated in earlier discussions. A draft paper describing the above work is being prepared for publication.

Tensile stress-rupture testing of NT-154 Si_3N_4 in support of the Ceramic Turbine Engine Demonstration Project (CTEDP)

The objective of this Project is to understand the effect of proof testing on the reliability of turbine engine components such as blades and stators. ORNL has agreed to conduct thirty tests on NT-154 tensile specimens in support of the program. Fifteen specimens are to be tested at 1204°C with a stress of 310 MPa and remaining at 1315°C and 276 MPa.

A total of six specimens, two specimens at 1204°C and four at 1315°C, were tested. Results are summarized in the following table.

Table 1 - Summary of results for tensile stress-rupture tests on NT-154 Si_3N_4 specimens.

Specimen No.	Temperature °C	Stress MPa	Creep Strain at Rupture, %	Life h
35293	1204	310	0.298	428.7
35308	"	"	0.388	363.1
35277	1315	276	0.214	3.85
35298	"	"	0.004	0.1
35300	"	"	0.136	1.9
35355	"	256 ^a		

Note: a = Failed on loading at the stress indicated.

The above information and test data have been transmitted to AlliedSignal for review and analysis.

Important Findings and Observations

Results of cyclic fatigue tests on GS-44 Si_3N_4 indicate that C/C cyclic fatigue loading is the least damaging mode compared to other loading modes used in T/T and T/C tests. A total lack of AE signals detected during C/C fatigue testing appears to reinforce the above finding.

Status of Milestones

Completed technical report covering results of the fully reversed tension/compression cyclic fatigue tests on Si_3N_4 ceramics - Milestone 321422, due on April 30, 1995

Publications

1. The abstract entitled "A Multiaxial Viscoplastic Model for Advanced Si_3N_4 Ceramics" by J. L. Ding, K. C. Liu, and C. R. Brinkman, has been accepted for the 20th Annual Cocoa Beach Conference, Cocoa Beach FL, January 7-11, 1996.
2. The abstract entitled "The Influence of Heat Treatment on Creep Behavior of a Sintered Si_3N_4 Ceramic" by K. C. Liu, C. O. Stevens, C. R. Brinkman, K. L. More, J. O. Kiggans, and T. N. Tiegs has been accepted for the Cocoa Beach Conference.
3. The abstract entitled "A Technique to Achieve Uniform Stress Distribution in Compressive Creep Testing of Advanced Ceramics at High Temperatures" by K. C. Liu, N. E. Holshauser, C. O. Stevens, and C. R. Brinkman has been accepted by the 41st ASME Gas Turbine and Aeroengine Conference, Birmingham, UK, June 10-13, 1996
4. K. C. Liu, C. O. Stevens, C. R. Brinkman, K. L. More, J. D. Kiggans, Jr., and T. N. Tiegs, "Enhancement of creep resistance of a sintered Si_3N_4 by microwave annealing," pp. 27-31 in the proceedings of the Science and Technology Alliance Materials Conference '93, North Carolina A & T State University, Greensboro, N.C., October 27-29, 1993, Technomic Publishing Co., 1995

References

1. K. C. Liu, C. O. Stevens, and C. R. Brinkman, "Cyclic Fatigue of Toughened Ceramics," pp. 286-306, in Ceramic Technology Project Semiannual Progress Report for April 1994 through September 1994, ORNL/TM-12924, Lockheed Martin Energy Systems, Inc., Oak Ridge National Laboratory, June 1995.

LIST OF FIGURES

Fig. 1 - Triangular waveforms used in fatigue tests: (a) for fully reversed tension-compression (T/C), (b) tension-tension (T/T), and (c) compression-compression (C/C) fatigue testing.

Fig. 2 - (a) An hourglass shaped specimen, (b) a buttonhead tensile specimen, and (c) a dumb-bell shaped specimen for compressive testing.

Fig. 3. Cyclic fatigue behavior of GS-44 Si_3N_4 tested at 1200°C. Test results hint that cyclic fatigue damage under C/C mode may require a much greater stress amplitude than 600 MPa.

Fig. 4. Creep curve of NT-154 Si_3N_4 (specimen 20-56) tested at 1250°C and 175 MPa. The specimen has accumulated a total of 37,000 h (or 4.22 years) of testing. Despite the recent test disruptions by power outages, the creep behavior did not appear to have been altered.

Fig. 5. Creep curve of NT-154 Si_3N_4 (specimen 20-32) tested at 1250°C and 150 MPa. The current creep rate shows to be about the same as that observed prior to the most recent test disruption by a power outage. The specimen has accumulated a total of 30,000 h (or 3.42 years) of testing.

Fig. 6. Creep curve of GN-10 Si_3N_4 (specimen 89367-1-2) tested at 1200°C and 125 MPa. The creep curve has been revised according to the signal drift rate of 0.3 mV/h measured in the recent extensometer calibration.

Fig. 7. Creep curve of GN-10 Si_3N_4 (specimen 89367-1-3) being tested at 1150°C and 200 MPa. The test has been interrupted recently due to a power outage, and the specimen is currently undergoing the strain recovery phase.

Fig. 8. Comparison of creep curves of GS-44 Si_3N_4 specimens tested at 1200°C with applied stresses as indicated. Specimen numbers with a prefix of "AS" indicated the specimen was tested in as-sintered condition, "FA" indicates furnace annealing at 1200°C for 100 h in air, and "MA12" microwave annealing at 1200°C for 10 h with preannealing at 1100°C for 10 h.

Fig. 9. Comparison of creep curve of GS-44 Si_3N_4 specimens tested at 1200°C with an applied stress of 140 MPa.

Fig. 10. Layout diagrams showing the locations of specimens in two tiles which were microwave annealed at 1200°C for 10 h with preannealing at 1100°C for 10 h.

Fig. 11. Creep curves of three GS-44 Si_3N_4 specimens which were fabricated from the same tile and tested under the same condition. Test results illustrate that data are reproducible under the

controlled test environment.

Fig. 12. Comparison of creep curve of GS-44 Si_3N_4 specimens tested at 1200°C with an applied stress of 100 MPa.

Fig. 13. Creep curve of GN-10 Si_3N_4 currently being tested at 1300°C in compression.

Fig. 14. Creep curve of GS-44 Si_3N_4 currently being tested at 1200°C with an applied stress of 100 MPa in compression.

Stressing Rate = 21,000 MPa/min.
 R = Minimum/Maximum Stress

Fig. 1. Triangular wave forms used in fatigue tests: (a) for fully reversed tension-compression (T/C), (b) tension-tension (T/T), and (c) compression-compression (C/C) fatigue testing.

Fig. 2 - (a) An hourglass shaped specimen, (b) a buttonhead tensile specimen, and (c) a dumb-bell shaped specimen for compressive testing.

Fig. 3. Cyclic fatigue behavior of GS-44 Si₃N₄ tested at 1200°C. Test results hint that cyclic fatigue damage under C/C mode may require a much greater stress amplitude than 600 MPa.

Fig. 4. Creep curve of NT-154 Si_3N_4 (specimen 20-56) tested at 1250°C and 175 MPa. The specimen has accumulated a total of 37,000 h (or 4.22 years) of testing. Despite the recent test disruptions by power outages, the creep behavior did not appear to have been altered.

Fig. 5. Creep curve of NT-154 Si_3N_4 (specimen 20-32) tested at 1250°C and 150 MPa. The current creep rate shows to be about the same as that observed prior to the most recent test disruption by a power outage. The specimen has accumulated a total of 30,000 h (or 3.42 years) of testing.

Fig. 6. Creep curve of GN-10 Si_3N_4 (specimen 89367-1-2) tested at 1200°C and 125 MPa. The creep curve has been revised according to the signal drift rate of 0.3 mV/h measured in the recent extensometer calibration.

Fig. 7. Creep curve of GN-10 Si_3N_4 (specimen 89367-1-3) being tested at 1150°C and 200 MPa. The test has been interrupted recently due to a power outage, and the specimen is currently undergoing the strain recovery phase.

Fig. 8. Comparison of creep curves of GS-44 Si_3N_4 specimens tested at 1200°C with applied stresses as indicated. Specimen numbers with a prefix of "AS" indicated the specimen was tested in as-sintered condition, "FA" indicates furnace annealing at 1200°C for 100 h in air, and "MA12" microwave annealing at 1200°C for 10 h with preannealing at 1100°C for 10 h.

Fig. 9. Comparison of creep curve of GS-44 Si_3N_4 specimens tested at 1200°C with an applied stress of 140 MPa.

Specimen MA12-1
MA12-2
MA12-3
MA12-4
MA12-5

Tile A

Specimen MA12-6
MA12-7
MA12-8 (reserved)
MA12-9
MA12-10

Tile B

Fig. 10. Layout diagrams showing the locations of specimens in two tiles which were microwave annealed at 1200°C for 10 h with preannealing at 1100°C for 10 h.

Fig. 11. Creep curves of three GS-44 Si_3N_4 specimens which were fabricated from the same tile and tested under the same condition. Test results illustrate that data are reproducible under the controlled test environment.

Fig. 12. Comparison of creep curve of GS-44 Si_3N_4 specimens tested at 1200°C with an applied stress of 100 MPa.

ORNL-DWG 94-14047

Fig. 13. Creep curve of GN-10 Si₃N₄ currently being tested at 1300°C in compression.

Fig. 14. Creep curve of GS-44 Si₃N₄ currently being tested at 1200°C with an applied stress of 100 MPa in compression.

3.2.1. Life Prediction Verification

A. A. Wereszczak, H. Cai, M. K. Ferber, and T. P. Kirkland (ORNL)

Objective/Scope

There are three central goals of the proposed research program: the generation of engineering data from high temperature mechanical testing; microstructural characterization of failure phenomena; and the implementation and verification of life prediction methods involving structural ceramics. Ultimately the prediction of the high temperature mechanical performance and service life, is information that is critical for the progress towards implementation of structural ceramics as components in internal combustion and automotive gas turbine engines.

The systematic study of the high temperature mechanical performance of silicon nitride and SiAlON is undertaken as a function of temperature and time. A different temperature regime will serve as an independent parameter for each material. Studies on both SiAlON and silicon nitride will be conducted at temperatures $\approx <1000^{\circ}\text{C}$, while studies with only silicon nitride will be at temperatures $\approx >1000^{\circ}\text{C}$; these are desired operating temperature ranges for internal combustion and automotive gas turbine engines, respectively. For the lower temperature regime, properties such as strength and fatigue life will be measured in the SiAlON and silicon nitride material as a function of temperature. For the higher temperature regime, tensile stress-rupture data will be generated on silicon nitride by measuring fatigue life at a constant or cyclic stress. The time-dependent deformation will also be monitored so that high-temperature creep and its effects may be studied.

The second goal of the program is to characterize the evolution and role of damage mechanisms associated with high temperature deformation. The damage will be examined using established ceramographic, SEM, TEM, and non-destructive acoustic techniques. Several microstructural aspects of high-temperature failure will be examined:

- (1) the extent of slow crack growth;
- (2) the evolution of cavitation-induced damage and fracture;
- (3) the transition between brittle crack extension and cavitation-induced growth;
- (4) crack blunting; and
- (5) the evolution and role of oxidation assisted damage.

Lastly, available analytical and numerical models will be utilized to predict the life of complex-shaped components and prototype engine parts (e.g., valves). The applicability of analytical models such as the Monkman-Grant (represents a relationship of creep rate to time-to-failure) and the Sherby-Dorn models (represents a temperature compensated

relationship of time-to-failure and applied stress) to structural ceramics will be examined and modifications will be made where necessary to refine the models and improve their predictive capabilities. Numerical models (i.e., life prediction codes) will also be used in conjunction with generated strength data from standard test specimens to predict the failure probability and reliability of complex-shaped components, such as a SiAlON or silicon nitride diesel engine valve. As a consequence of these efforts, the data generated in this program will not only provide a critically needed base for component utilization in internal combustion and automotive gas turbine engines, but also facilitate the development of a design methodology for high-temperature structural ceramics.

Technical Progress

The discussion of the past six-month's technical progress is separated into two sections. The first describes the program's ongoing efforts with the life prediction and reliability analysis of SiAlON diesel engine valves (applications temperatures < 1000°C). The second section describes the program's ongoing efforts with high temperature mechanical tests and microstructural analysis of a silicon nitride (application temperatures > 1000°C), which is an effort approaching completion.

1. Life Prediction of SiAlON Valves

An example of the methodology that will be used to predict failure probability in a valve is described first and this is followed by analysis that was performed to predict what force will be required to experimentally fracture a prototype SiAlON valve.

1.A. Example of Failure Probability Prediction

The prediction of the probability of failure, and its associated reliability, for a SiAlON engine valve (that is subjected to a known mechanical loading state) is one of the most important efforts in this program. The prediction of the probability of failure is the culmination and blending of a series of theoretical and experimental analyses. Finite element (FE) analysis (ANSYS software) is first conducted to compute the stress distribution in a mechanically loaded engine valve. The strength and Weibull statistics of the valve material are determined (in parallel with the FE analysis) from experiment using standard test specimens (e.g., bend bars, tensile rods, etc.). The results of the FE analysis and the material's associated Weibull statistics are then used in conjunction to predict the

component reliability as a function of the severity of the applied mechanical loading. For this program's effort, life prediction codes ERICA and CERAMIC (developed at AlliedSignal under the sponsorship of the Ceramic Technology Project) will lastly be applied for the reliability analyses. An example of this method follows.

Two different ceramic materials are considered in this example, one with a relatively high Weibull Modulus ($m = 20$, designated as material "M20") and one with a relatively low Weibull Modulus ($m = 10$, designated as material "M10"). Both materials have a characteristic flexure strength of 800 MPa, as determined from four-point flexure tests using MIL-B size bend bars. The corresponding Weibull analyses are represented in Fig. 1. All failures were a consequence of crack growth from surface flaws.

The sample test data were analyzed to extract material design data which were characteristically independent of the test specimen size and geometry. The design data analyzed for an effective unit surface area (1 mm^2) with corresponding 95% confidence bounds are shown in Fig. 2.

The valve was analyzed with axisymmetric boundary conditions and a valve-face combustion pressure of 16 MPa (2.3 ksi). The valve was in frictional contact with the seat; other sources of stresses (e.g., thermal) were neglected in this analysis. The FE mesh and the representative maximum principal stress distribution are shown in Figure 3. The greatest tensile stress was identified to be 147 MPa and existed along the contour between the valve head and valve stem. Risk integration was then performed using a combination of the flexure strength test results and the surface definition from the FE analysis (ERICA). Lastly, the component reliability was then computed from the risk factor and material design data (CERAMIC). The results of the predicted reliability as a function of the combustion pressure are shown in Figure 4.

Under a combustion pressure of 16 MPa, the valve reliability for material M10 was approximately 99.999% at the 95% confidence lower bound, signifying that there is a slight chance of component failure. However, the probability of failure could significantly increase with over-pressurization. In addition, the reliability would decrease with increasing service time as a result of time-dependent crack growth. As a consequence of this reliability analysis, material M10 may not be an acceptable candidate material for a component for this application.

In comparison, the component made from material M20 has a higher reliability (>99.999%) than material M10 at equivalent combustion pressures. There is a greater margin of safety for over-pressurization and for time-dependent crack growth too. Therefore, material M20 would be preferred as a candidate material for a component in

this example. Further analysis is ongoing to predict the reliability as a function of service time, which will acknowledge the effects of slow crack growth.

1.B. Predicting the Force Required to Break a Prototype SiAlON Valve

Several SiAlON valves will eventually be loaded to failure using a loading arrangement such as what is schematically shown in Fig. 5; however, it is not known what the typical force will be required to produce fracture of this complex-shaped component. A copper loading ram will be used to load the SiAlON valve head while a steel valve seat provides support. Finite element analysis was utilized to determine what force would be required to break such a SiAlON valve using this loading configuration. The following material properties were used for the various components in the loading arrangement shown in Fig. 5 (axisymmetry assumed): $E = 300$ GPa and $\nu = 0.24$ for the SiAlON, $E = 210$ GPa and $\nu = 0.28$ for the steel, and $E = 120$ GPa and $\nu = 0.37$ for the copper.

The FE analysis predicted that the maximum tangential tensile stresses existed along the valve head - valve stem contour with the tangential tensile stress being a function of the applied load to the copper ram. To verify that the loading configuration shown in Fig. 5 mimicked the service loading, analysis was also performed by applying a uniform pressure across the valve head; the maximum tangential tensile stresses were found to be at the same four nodes. The four nodes showing the greatest tangential tensile stresses are identified in Fig. 5 as numbers 236 to 239; their tangential tensile stress as a function of the applied load to the copper ram is shown in Fig. 6. This information will be useful for the future valve tests because it provides insight into what forces will be expected to produce fracture. As an example, it will take about 13 kN of compressive loading using the arrangement shown in Fig. 5 to cause fracture of a valve that has a strength of approximately 600 MPa. Several valves will be strain gaged along their valve head - valve stem contour and mechanically loaded to verify the FE analysis.

1.C. Mechanical Testing of NT451 SiAlON Standard Specimen Coupons & Valves

The delay in mechanical testing (flexure and tensile testing of standard test coupons) to date has been a consequence of the SiAlON supplier (Norton Advanced Ceramics) changing their composition to their newer NT551 grade from the older NT451 grade. Norton Advanced Ceramics has already supplied S149 NT451 valves for this effort (through their own "Development of Advanced Ceramic Manufacturing Technology" effort). To exercise the Life Prediction Verification methodology *in the present*, NT451 will serve

as the vehicle material because it is already available. Norton Advanced Ceramics has provided supply of data that was generated on flexure bars at their facility, and also a supply of NT451 stock material; this will enable mechanical tests to be conducted here as well. Even though the supply of data and stock material of NT451 will not be enough to satisfy the entire test matrix for this Life Prediction Verification effort, which was described in an earlier bimonthly report,¹ it will provide a foundation of engineering data that can be used in the life prediction of the S149 NT451 valves using the codes ERICA and CERAMIC. NT551 SiAlON test coupons and valves should be available in late FY95 or early FY96. Once a material supply of NT551 is available to the Life Prediction Verification effort, the entire test matrix described in Ref. [1] will be examined and a more thorough life prediction of NT551 valves will be made using data that results from the completed test matrix.

As mentioned, valve blank material of NT451 SiAlON was sent by Eric Bright of Norton Advanced Ceramics, East Granby, CT, and received during the present reporting period. The NT451 SiAlON composition is no longer fabricated, so this material was acquired with the intent of: (1) fabricating standard test coupons (flexure bars, biaxial flexure disks, tensile rods, and rotary bend fatigue specimens [see Figs. 7 and 8]) out of it, (2) generating engineering data from them, and (3) using the engineering creep with finite element analysis to predict the mechanical performance of the NT451 SiAlON S149 valves. To ultimately verify the capabilities of the life prediction codes, the predicted performance of the valves will be compared to data generated when the actual valves are mechanically characterized.

Useful information was generated from a strain-gaged, rotary bend fatigue specimen that was loaded to failure using the rotary bend fatigue tester belonging to our Mechanical Characterization and Analysis Group. After the strain-gaged specimen was mounted in the tester, the applied bending moment was linearly increased until fracture occurred. The outer fiber tensile stress (S) was calculated using the expression,

$$S = \frac{M}{0.0982} \cdot \frac{1}{D^3}$$

where M is the applied moment (in in-lbs) and D is the specimen's minimum diameter (in inches); the equation is derived from elastic beam bending theory. The stress-strain response that was measured is shown in Fig. 9. The calculated Young's Modulus was consistent with what the manufacturer has reported for NT451 SiAlON.² Due to the small volume of material that was subjected to this high tensile stress, and the statistical nature

of strength in ceramics, it is believed that higher strengths will be typical of these rotary bend fatigue specimens as compared to bend bars and tensile rods of the same material.

Pre-mechanical testing efforts have been initiated on the S149 NT451 valves. These assessment efforts will generate (and serve as) an integral database that will be referred to after the S149 NT451 valves are mechanically loaded to failure; It is hoped that any anomalous or unexpected results obtained during the mechanical tests will be explained by information generated from the pre-testing dimensional and material-integrity characterization. The description of the test plan effort for these valves is divided into two sections: "Dimension and Material Integrity" which describes the pre-testing characterization of the S149 NT451 valves, and "Mechanical Analysis" which describes the proof-testing tests that the S149 NT451 valves will be subjected to, along with the load to failure tests. The description of each of these sections is further subdivided into more detailed task descriptions.

1.C.I. Dimensional and Material Integrity

Four efforts will be at the core of the characterization efforts to assess the dimensional and material-integrity of the as-received S149 NT451 valves.

1.C.I.a. Non-Destructive Evaluation (NDE)

Computed Tomography (CT) scans are being acquired on all the supplied S149 valves through a collaboration with W.B.S. Element 3.5 "Nondestructive Evaluation Development." The areas of the valves that will be subjected to the highest stress concentrations will be examined and the presence of defects or flaws will be sought; the whole volume of the valve is not being inspected because the testing time per valve would be extremely excessive. The two regions of the valves that are subjected to the highest stress concentrations during service are the valve head/stem contour and the valve-spring keeper groove; these volumes in each valve under investigation are shown in Fig. 10. All the valves will be documented by the CT scans and later referenced after they are mechanically tested.

1.C.I.b. Dimensional Verification

Dimensional verification of the supplied NT451 valves will be conducted with staff of the Ceramic Machining Users Center (CMUC) in the High Temperature Materials

Laboratory. A new Starrett Criterion coordinate measurement machine (CMM) will be used to measure the longitudinal-axis profiles of all the S149 NT451 valves at four 90° orientations about the valve's axis of symmetry. The measured profiles will be compared with the valves original schematic drawing using the system's software.

An examination of the as-received dimensions of the S149 valves has yielded some interesting results to date. The CCM showed that the faces of the as-received valves indeed may not be planar. Figure 11 shows that a slightly concave contour of one valve existed. Analysis such as this is being documented and will later be accessed after mechanical testing to examine if the measured dimensional state of the valve may explain how it mechanically performed.

1.C.I.c. Optical Inspection

Low-powered (~ 10 - 30x) optical microscopy is being conducted on all the S149 NT451 valves. All surface imperfections (spots, regions of discoloration, other apparent flaws) are being marked on the specimen with permanent pen and appropriately identified in a logbook. The positions of the imperfections on the valve are also being logged using a cylindrical-based coordinate system. All the valves will be documented by optical inspection and the results will later be referenced after they are mechanically tested.

1.C.I.d. Machining Inspection

The surface machining of all the valves will be examined by staff in the CMUC who will be using a Rodenstock Laser Surface Profilometer. Like the areas of high stress concentration that will be examined by CT scans, the surface finish of these same regions, and additional surfaces if necessary, will be measured to ensure that the machine shop responsible for the machining of these S149 NT451 valves satisfied the machining specifications. All the valves will be documented by laser profilometry and the results will later be referenced after they are mechanically tested.

1.C.II. Mechanical Analysis

Prior to their shipment to the HTML, the S149 NT451 valves were subjected to a testing procedure performed by Norton Advanced Ceramics. To some extent, these tests will likely be repeated as part of this effort for verification purposes, and perhaps others too will be conducted. Lastly, the S149 NT451 valves will be mechanically loaded to failure. Any

anomalous mechanical behavior will be examined in reference to the dimensional and material-integrity analysis that was performed. Most importantly though, the results from the strength tests will be compared to the life predicted values from S149 NT451 test data.

1.C.II.a. Valve Proof Tests

Stem-bend and axial-pull proof tests were performed on the S149 NT451 valves at Norton Advanced Ceramics prior to their shipment to the HTML. With the servohydraulic and rotary bend testers purchased on the CT Project, these tests can either be readily repeated or mimicked in some form. The proof tests would verify the as-received mechanical integrity of the material prior to its mechanical loading to failure, which is described next.

1.C.II.b. Valve Strength Tests

Fixturing has been designed to facilitate the mechanical loading to failure of the S149 NT451 valves; the FE analysis of its usage was described in Section 1.B. The fixturing will be mounted on the servohydraulic testing machine purchased on the CT Project, and the testing will be performed on the same machine. To ensure that the fixturing was appropriately designed, a 30° and a 45° seat-angled S149 NT451 valve are being commercially strain-gaged along their valve head - valve stem contours. A schematic drawing of the arrangement of the strain-gages on the S149 NT451 valves is shown in Fig. 12. This strain gaging will serve two purposes: (1) it will experimentally measure the surface strains that result from mechanical loading which can be compared to what was predicted from finite element analysis, and (2) it will yield information regarding the alignment of the valve in the fixture as it is being mechanically loaded.

2. High Temperature Mechanical Testing of Silicon Nitride

A manuscript detailing the recently completed reverse cyclic loading performance of NCX-5102 silicon nitride at 1370°C was submitted to *The Journal of Materials Science*. There were three primary conclusions that stemmed from this study, and they were:

- NCX-5102 silicon nitride will not fail under reverse cyclic fatigue at 1370°C if the stress amplitude is < 280 MPa and if a sinusoidal waveform is applied at 1 Hz. This threshold stress amplitude is ~ 60% of the manufacturer's reported average tensile strength for this material at 1370°C. Slow crack growth will eventually

occur at stress amplitudes ≥ 280 MPa and the event of fracture will occur during the tensile stroke of the waveform.

- Multi-grain junction cavities resulted as a consequence of the reverse cyclic loading at 1370°C. Even though the failed, cyclic fatigued specimens endured half their life under tensile stress and the other half of their life under compressive stress, there was a net gain of cavitation due to tensile creep strain. The presence of cavitation due to tensile creep strain supports the fact that the stress exponent of tensile creep strain is greater than the stress exponent of compressive creep strain in HIPed silicon nitrides.
- The static creep resistance of NCX-5102 at 1370°C will improve if it is first subjected to reverse cyclic loading at 1370°C for at least 10^6 cycles at 1 Hz (even though some cavitation was present prior to static creep testing). This improvement in creep resistance was likely due to grain coarsening and the activity of extensive grain-grain interlocking; which was ultimately due to the completion of the α to β silicon nitride solution/reprecipitation process that occurred during the history of reverse cyclic loading. It is not discernible from this study whether the reverse cyclic loading history, or the time at temperature, or a combination of both were responsible for the completion of the α to β phase transformation. Even though the NCX-5102 specimens had been subjected to reverse cyclic loading at 1370°C for $\sim 10^6$ cycles, creep damage was still the dominant failure mechanism (and not slow crack growth) during static creep rupture tests.

Studies are ongoing and nearing completion on the effect of testing environment on the tensile static creep and dynamic fatigue performance of NCX-5102 at 1370°C. To date, the test matrix has been completed for ambient air and argon tests and only those tests in nitrogen require completion. Preliminary data for the minimum creep rate as a function applied tensile stress for tests in the three environments are shown in Fig. 13. Microstructural studies are ongoing in an effort to explain the observed discrepancies. Tests in argon at 1370°C subject the silicon nitride specimen to both low partial pressures of oxygen and nitrogen, while those tests in nitrogen only subject the silicon nitride to low partial pressures of oxygen. Tests in ambient air are the only tests where oxygen from the ambient environment can play a role in the development of damage in this silicon nitride material at 1370°C. These various combinations are serving as useful independent parameters during the microstructural analysis of the tested material. It is hoped that these environmental studies will provide insight into how damage evolves in these materials at elevated temperatures.

Status of Milestones

A problem with waveform fidelity was found to exist in the servohydraulic testing system that was purchased from MTS, Eden Prairie, MN [Milestone 3.2.1.6]. The problem was identified by a MTS representative and the system will be replaced during Nov. 1995.

An article entitled "Reverse Cyclic Fatigue of a HIPed Silicon Nitride at 1370°C, by A. A. Wereszczak, T. P. Kirkland, and M. K. Ferber, was submitted to *The Journal of Materials Science* [Milestone 3.2.1.8].

An letter report entitled "Preliminary Mechanical Performance of SiAlON Valve Material" was issued to the Ceramic Technology Program Manager [Milestone 3.2.1.6.11].

Communications / Visitors / Travel

Eric Bright of Norton Advanced Ceramics furnished a supply of NT451 stock material. This supplied NT451 material will be machined into flexure bars and tensile rods for strength and fatigue characterization. In addition, Eric Bright and Yuri Kalish of the Detroit Diesel Corporation, Detroit, MI, supplied an extensive flexure database that was generated on NT451 SiAlON through their collaboration. X-ray diffraction data, fractography information, and batch identification information was also included. The data will serve as a supplement to the data that will be generated in-house on NT451, and will be used in the life prediction verification effort on NT451 S149 diesel engine valves.

Problems Encountered

None.

Publications

An article entitled "Effect of Cyclic Loading on the Creep Performance of Silicon Nitride," by A. A. Wereszczak, M K. Ferber, T. P. Kirkland, and C. -K. J. Lin, was

accepted for publication in the ASME Turbo Expo 95 Proceedings, Houston, TX, June 1995.

An article entitled "Reverse Cyclic Fatigue of a HIPed Silicon Nitride at 1370°C, by A. A. Wereszczak, T. P. Kirkland, and M. K. Ferber, was submitted to *The Journal of Materials Science*.

An abstract entitled "Mechanical Performance and Life Prediction of SiAlON Diesel Engine Valves," by A. A. Wereszczak, H. Cai, M. K. Ferber, and T. P. Kirkland, was submitted for inclusion in the 20th Annual Cocoa Beach Conference and Exposition on Composites, Advanced Ceramics, Materials and Structures, to be held Jan. 7-11, 1996, Cocoa Beach, FL.

A presentation entitled "Verification of Life Prediction Methodology as Applied to a Ceramic Valve," by A. A. Wereszczak, H. Cai, and M. K. Ferber, was submitted and will be given at the Annual Automotive Technology Development Contractors' Coordination Meeting, Dearborn, MI, Oct 23-27, 1995.

References

- [1]. A. A. Wereszczak, H. Cai, M. K. Ferber, and T. P. Kirkland, "Life Prediction Verification," pp 61-69 in the *Ceramic Technology Project Bimonthly Technical Progress Report to DOE Office of Transportation Technologies, December - January 1995*.
- [2]. Personal communication with Eric Bright, Norton Advanced Ceramics, East Granby, CT.

Fig. 1. Failure probability as a function of applied flexure stress for two arbitrary ceramic materials. Four-point flexure MIL-B test specimens were used for the data generation.

Fig. 2. Material designed data for an effective unit surface area of 1 mm^2 . Confidence bounds are shown.

Fig. 3. Finite element mesh of the valve component and the principal stress distribution. Shown units of stress: MPa. The maximum principle tensile stress (147 MPa) occurs along the contour between the valve head and valve stem.

Fig. 4. Reliability of the valve component as a function of the applied combustion pressure. The normal combustion pressure of 16 MPa yields a maximum principle tensile stress of 147 MPa (see Fig. 3). Two structural ceramics are compared in this example, each with a different Weibull Modulus.

Fig. 5. Schematic of the loading arrangement that will be used to examine the strength of SiAlON valves. Using the shown mesh, finite element analysis showed that the greatest tangential tensile stresses exist at the four nodes shown.

Fig. 6. The tangential tensile stress as a function of applied load for the four nodes shown in Fig. 5. Nodes 237 and 238 possess equivalent stresses for any given applied load to the copper ram, while nodes 236 and 238 are subjected to slightly less tensile stresses. Due to the statistical nature of strength in ceramics, failure may occur at *any* location where a tensile stress exists in the valve; such a valve *will not necessarily* fail along the regions bounded by nodes 236 through 239, but the likelihood is greater for failure in their bounded region because the tensile stresses have the largest magnitudes here.

<p>4.00 mm 3.00 mm Length = 50.0 mm</p>	3-PT Bending & 4-PT Bending
<p>$D/2$ 1.000 2.000 3.000 Dimensions shown are in inches $D = 0.375 +0.001/-0.000$</p>	Rotary Bending
<p>$\varnothing 1.00 - 1.25"$ 0.10"</p>	Biaxial Flexure

Fig. 7. Three NT451 specimen geometries will be mechanically tested in uniaxial or biaxial flexure. All three geometries are conveniently machined from as-received valve blanks; bend bars and rotary bend specimens are readily machined from the valve stem, while biaxial flexure disks are readily machined from the valve head.

Fig. 8. A buttonhead specimen was designed that could be readily machined from the stems of the as-received NT451 valve blanks. Its size is smaller than the standard ORNL buttonhead specimen, which has a characteristic gage diameter of 6.35 mm and an overall length that is typically in excess of 150 mm.

Fig. 9. Stress-strain curve generated from a strain-gaged, rotary bend fatigue NT451 specimen.

Fig. 10. Prior to mechanical testing, the material integrity within two regions of every S149 NT451 valve will be examined using computed tomography. The mechanical performance of the valve will later be correlated to this.

Fig. 11. The face of this particular S149 NT451 valve was found to be slightly concave in nature (as represented by cross-sectional profile shown), as identified by a coordinate measuring machine.

Fig. 12. Two S149 NT451 valves are being strain-gaged with orientations shown. Information yielded by the strain-gages during mechanical loading will be used to verify finite element analysis and to maximize fixturing alignment.

Fig. 13. Minimum creep rate as a function applied static tensile stress for NCX-5102 silicon nitride at 1370°C in air, argon, and nitrogen environments.

TOUGHENED CERAMICS LIFE PREDICTION

Sung R. Choe, Jonathan A. Salem and John P. Gyekenyesi
(NASA Lewis Research Center)

Objective/Scope

The purpose of this research is to understand the room temperature and high temperature [$\leq 1370^{\circ}\text{C}$ (2500°F)] behavior of toughened ceramics as the basis for developing a life prediction methodology. A major objective is to understand the relationship between microstructure and mechanical behavior within the bounds of a limited number of materials. A second major objective is to determine the behavior as a function of time and temperature. Specifically, the room temperature and elevated strength and reliability, the fracture toughness, slow crack growth and the creep behavior will be determined for the as-manufactured material. The same properties will also be evaluated after long-time exposure to various high temperature isothermal and cyclic environments. These results will provide input for parallel materials development and design methodology programs. Resultant design codes will be verified.

Technical Highlights

Dynamic fatigue testing has been used for several decades to characterize slow crack growth behavior of glass and ceramics materials at both ambient and elevated temperatures.^{1,7} The advantage of dynamic fatigue testing over other methods lies in its simplicity: Strengths are measured in a routine manner at three to four stressing rates by applying a constant crosshead speed or constant loading rate. The slow crack growth (fatigue) parameters required for design are simply calculated from a relationship between fatigue strength and stressing rate.² These merits have prompted an effort to establish an ASTM testing standard for dynamic fatigue.⁶

With a proper use of preloading in dynamic fatigue testing (see Fig. 1), a dramatic saving of testing time can be achieved with no change in fatigue strength. In the previous papers,^{9,10} the present authors developed the analytical solution of dynamic fatigue strength as a function of preloading for the Griffith (natural) flaw system. The solution was verified by dynamic fatigue experiments conducted with soda-lime glass and alumina at room temperature⁹ and with alumina and silicon nitride at elevated temperatures.¹⁰

In this paper the preloading technique was extended to an indentation-induced flaw system. A numerical solution of dynamic fatigue strength as a function of preloading was developed. To verify the solution, dynamic fatigue testing as well as preloading experiments were carried out in room temperature distilled water using soda-lime glass and alumina specimens with as-indented flaws.

ANALYSIS

In many cases slow crack growth of glass and ceramics under Mode I loading condition above fatigue limit is described by the following empirical power-law relation¹¹

$$v = \frac{da}{dt} = A \left(\frac{K_I}{K_{IC}} \right)^n \quad (1)$$

where v , a and t are crack velocity, crack size, and time, respectively. A and n are the material/environment-dependent fatigue parameters. K_I is the Mode I stress intensity factor and K_{IC} is the critical stress intensity factor or fracture toughness of material under Mode I loading. Under dynamic fatigue loading (see Fig. 1) with a constant displacement or loading rate, the corresponding fatigue strength (σ_f) can be derived with some manipulations as a function of stressing rate ($\dot{\sigma}$) as²

$$\sigma_f = [B(n+1) S_f^{n+2}]^{\frac{1}{n+1}} \dot{\sigma}^{\frac{1}{n+1}} \quad (2)$$

where $B = 2K_{IC}^2/AY^2(n-2)$ with Y being a crack geometry factor, and S_f is the inert strength. Equation 2 is called a dynamic fatigue equation. The fatigue parameter n can be obtained from the slope of a dynamic fatigue curve by using a linear regression analysis when $\log \sigma_f$ is plotted as a function of $\log \dot{\sigma}$. The parameter A is determined from the intercept of the curve together with appropriate constants.

(1) Griffith Flaws (Natural Flaws)

In this section, the previously derived analytical solution⁹ of dynamic fatigue strength as a function of preloading is briefly presented. For the Griffith (natural) flaw system, the 'reduced' dynamic fatigue strength as a function of preloading can be expressed as⁹

$$\bar{\sigma}_f = (1 + \alpha_p^{n+1})^{\frac{1}{n+1}} \quad (3)$$

where $\bar{\sigma}_f$ is the 'reduced' fatigue strength, in which the fatigue strength with preloading is normalized with respect to the fatigue strength with zero preloading (σ_m), and α_p is the preloading factor ($0 \leq \alpha_p \leq 1$), where the preloading stress (σ_0) is normalized with respect to the fatigue strength with zero preloading (σ_m). The resulting plot of Eq. (3) for various values of n is shown in Fig. 2. When $\alpha_p = 0$, in which no preloading is applied, Eq. (3) reduces to unity, which is the case for Eq. (2).

(2) Indentation-Induced Flaws

The dynamic fatigue analysis of as-indented cracks produced by a Vickers microhardness indenter was developed previously using indentation fracture mechanics.¹² Because of an additional term appeared in the net stress intensity factor, due to residual contact stress produced by elastic/plastic indentation deformation, analytical solution is not feasible for the as-indented crack system. Solution has to be made via numerical methods. To minimize having to specify several parameters, it is convenient to utilize a normalized scheme, as used previously in the fatigue analysis of postthreshold indentation flaws¹² and subthreshold flaws.¹³ With reference to the previous studies,^{12,13} the normalized variables are introduced as follows:

$$K^* = \frac{K_I}{K_{IC}}; J = \frac{A}{a_s}; \sigma^* = \frac{\sigma_a}{S_f}; C^* = \frac{a}{a_s}; \dot{\sigma}^* = \frac{\sigma^*}{J} \quad (4)$$

where K^* , J , σ^* , C^* and $\dot{\sigma}^*$ are, respectively, normalized stress intensity factor, normalized time, normalized applied stress, normalized crack size, and normalized stressing rate. a_s and σ_a are the critical crack size in inert condition and the remote applied stress, respectively. Using these

variables, the power-law crack velocity of Eq. (1) yields as

$$\begin{aligned}\frac{dC^*}{dJ} &= [K']^n \\ K' &= \frac{3}{4}\sigma^* C^{*\frac{1}{2}} + \frac{1}{4}C^{*\frac{-3}{2}} \\ \sigma^* &= \dot{\sigma}^* J + \sigma_0^*\end{aligned}\quad (5)$$

where σ_0^* is the normalized preloading stress, which has the following relation

$$\alpha_p = \frac{\sigma_0^*}{\sigma_h^*} = \frac{\sigma_0}{\sigma_h} \quad (6)$$

with σ_h^* being a normalized fatigue strength with zero preloading. Note that the normalized net stress intensity factor (K') consists of two terms: the first by remote applied stress and the second by residual contact stress.¹² The solution of the differential equation of Eq. (5) in term of the normalized variables such as failure time, fatigue strength and critical crack size was obtained by using a fourth-order Runge-Kutta method. The initial condition¹² was $C^* = 0.3967$ at $J = 0$ and the instability conditions were $K' = 1$ and $dK'/dC^* > 0$.

The solution procedure was first initiated to determine the normalized fatigue strength with zero preloading (σ_h^*) as a function of normalized stressing rate ($\dot{\sigma}^*$) for the selected values of $n = 5 - 160$. A range of $\dot{\sigma}^* = 1.0 \times 10^{-2}$ to 1.0×10^{-7} was used. The normalized fatigue strength with preloading (σ_p^*) was then determined for a given n as a function of normalized preloading stress (σ_0^*), ranging from $\alpha_p = 0.3$ to 0.9 . This procedure was continued to complete for $n = 5 - 160$. The input variable σ_0^* was calculated using Eq. (6) with the known α_p and σ_h^* .

A summary of the 'reduced' fatigue strength $\bar{\sigma}_f$ as a function of preloading for as-indentured cracks is shown in Fig. 3. The figure shows that the effect of preloading on the reduced fatigue strength (or fatigue strength) becomes dominant with decreasing fatigue parameter n . For example, at a preloading of 90 % ($\alpha_p = 0.9$), $\bar{\sigma}_f = 1.1091$ and 1.0457 , respectively, for $n = 5$ and 10 ; whereas, $\bar{\sigma}_f = 1.0124$, 1.0014 , 1.0000 and 1.0000 , respectively, for $n = 20$, 40 , 80 and 160 . Hence, it is very important to note that for most of glass and ceramic materials that exhibit usually $n \geq 20$, the use of preloading up to 90 % gives rise to a maximum inaccuracy of 1.2 % in dynamic fatigue strength. Of course, the less preloading the higher accuracy. The result shown in Fig. 3 is very similar to that of the Griffith flaw system (Fig. 2). However, the effect of preloading on dynamic fatigue strength is more predominant for as-indentured cracks than for Griffith flaws, as can be seen by comparing Figs. 2 and 3. The existence of residual contact stress around indent is believed to result in more enhanced slow crack growth for the as-indentured crack system. The simple analytical solution of Eq. (2) (or Fig. 2) for Griffith flaws and the numerical solution of Fig. 3 for as-indentured cracks can thus provide an excellent tool of dynamic fatigue test methodologies with which a considerable amount of testing time can be saved through an appropriate choice of preloading.

EXPERIMENTAL PROCEDURE

Dynamic fatigue experiments were conducted to verify the above numerical solution using soda-lime glass and alumina in room-temperature distilled water. Microslides of soda-lime glass (Product # 2954-F, Erie Scientific Co., Portsmouth, NH) measuring 75 mm (length) x 25 mm (width) x 1.2 mm (thickness) were annealed at 520°C in air for 20 h to remove any spurious residual stress.

Figure 1. Mode of loading applied in dynamic fatigue testing: (a) without preloading (regular, conventional testing); (b) with preloading.

Figure 2. Analytical solution (Eq. 3) of 'reduced' fatigue strength ($\bar{\sigma}_f$) as a function of preloading for different n 's for Griffith flaws.⁹

Figure 3. Numerical solution of 'reduced' fatigue strength ($\bar{\sigma}_f$) as a function of preloading for different n 's for as-indented cracks.

After annealing, the center of each specimen was indented in air with a Vickers microhardness indenter (Model 3212, Zwick, Germany) for about 15 s with one of indentation diagonals being aligned along the direction of the prospective tensile stress of the specimen. One indentation load of 19.6 N was used. Dynamic fatigue testing for the indented specimens was conducted using a four-point flexure fixture with 20 mm- inner and 40 mm- outer spans. Six different actuator speeds from 5 mm/min to 0.00005 mm/min were applied using an electromechanical testing machine (Model 8562, Instron, Canton). A total of six specimens was used at each actuator speed. The dynamic fatigue testing is required to determine fatigue parameter (n) as well as fatigue strength without preloading. After this dynamic fatigue testing with zero preloading, additional dynamic fatigue testing were also conducted to determine the effect of preloading on fatigue strength. Four different actuator speeds of 0.5, 0.005, 0.0005, 0.00005 mm/min were used. Typically, four preloadings from 50 to 90 % were employed at each actuator speed. Six specimens were used at each preloading. The required preloading was achieved within a few seconds by using the specially designed load-controlled mode of the testing machine.

96 wt % alumina flexure beam specimens (ALSIMAG 614, G.E. Ceramics, Laurens, SC) measuring 3 mm by 4 mm by 30 mm, respectively, in height, width and length, were indented using an indentation load of $P = 49$ N. Dynamic fatigue testing of the indented alumina specimens was carried out using a servohydraulic testing machine (Model 8501, Instron, Canton) with a four-point flexure fixture with 6.35/19.05 mm spans. Four different actuator speeds from 0.005 mm/min to 5 mm/min were utilized. A total of five specimens was used at each actuator speed. Dynamic fatigue testing with preloading were conducted at an actuator speed of 0.005 mm/min using five different preloadings from 50 to 90 %. Five specimens at each preloading were utilized. Since the coefficient of variation in strengths was usually less than 5 % for both materials with well-defined crack configurations, the number of test specimens ranging from five to six that were used per actuator speed or preloading in this series of testing was considered to be sufficient for reliable statistical data.

RESULTS AND DISCUSSION

(1) Experimental Results

Glass Specimens The dynamic fatigue results for the as-indented soda-lime glass specimens are presented in Fig. 4, where fatigue strength ($\log \sigma_f$) was plotted as a function of applied actuator speed ($\log \dot{\epsilon}$) based on Eq. (2). (Note that $\dot{\sigma}$ is a linear function of $\dot{\epsilon}$ so that fatigue parameter n remains unchanged, using either $\dot{\sigma}$ or $\dot{\epsilon}$.) A decrease in fatigue strength with decreasing stressing rate, which represents fatigue susceptibility, was evident in a range of actuator speeds from 5 to 0.00005 mm/min. For indentation cracks, the fatigue parameter n obtained from data in Fig. 4 in conjunction with Eq. (2) is not the one that is truly representative of n , attributed to the additional driving force by residual contact stress.^{11,12} The true fatigue parameter n is calculated from the following formulation that takes into account the additional driving force¹¹

$$n = \frac{4}{3}n' - \frac{2}{3} \quad (7)$$

where n' is the 'apparent' fatigue parameter that is simply evaluated from the slope of Fig. 4 together with Eq. (2). The apparent parameter n' was thus found to be $n' = 17.4 \pm 0.4$. Therefore, using Eq. (7) a value of $n = 22.5$ was obtained. Note that the coefficient of correlation of curve fit was ≥ 0.999 , showing an excellent data fit to the dynamic fatigue relation. The effect of preloading on dynamic fatigue strength is shown in Fig. 5, where fatigue strength was plotted as a function of preloading from 0 to 90 % for four different actuator speeds utilized. The solid line represents the

Figure 4. Dynamic fatigue results of as-indented soda-lime glass specimens in room-temperature distilled water with zero preloading (indentation load = 19.6 N). The solid line indicates the best-fit line based on Eq. (2). Error bar represents one standard deviation.

Figure 5. Dynamic fatigue strength of as-indented soda-lime glass specimens as a function of preloading for different actuator speeds in room-temperature distilled water (indentation load = 19.6 N). Error bar indicates one standard deviation. The solid line represents the fatigue strength with zero preloading at each actuator speed.

fatigue strength with zero preloading determined at each actuator speed. No appreciable change in fatigue strength with preloading is observed.

Alumina Specimens The results of dynamic fatigue for the as-indentured alumina specimens are shown in Fig. 6. The apparent fatigue parameter of $n = 40.2 \pm 4.9$ was obtained, which gives a true fatigue parameter of $n = 52.9 \pm 5.9$ from Eq. (7). Dynamic fatigue strength as a function of preloading is shown in Fig. 7, where the solid line represents the fatigue strength with zero preloading. The effect of preloading on fatigue strength is negligible.

(2) Comparison between Solution and Experimental Data

A comparison between the solution and the experimental data was made for the two materials investigated. The dynamic fatigue strength with preloading was normalized with respect to the dynamic fatigue strength with zero preloading at each actuator speed, thereby to obtain σ_r in accordance with the schema shown in Fig. 3. This was done for all of the actuator speeds used. The result is shown in Fig. 8. Included in each figure was the theoretical prediction of σ_r obtained numerically for each material. For the as-indentured soda-lime glass, the prediction with $n = 22.5$ gives $\bar{\sigma}_r = 1.000, 1.000, 1.000, 1.002$ and 1.010 , respectively, for $\alpha_p = 30, 50, 70, 80$ and 90% , indicating that a preloading of 90% gives rise to the highest fatigue strength only 1.0% higher than the fatigue strength with zero preloading. The average 'reduced' fatigue strength for glass (Fig. 8 (a)) was $\bar{\sigma}_r = 0.9913 \pm 0.001$. Because of low fatigue susceptibility for alumina ($n = 52.9$), the theoretical prediction, $\bar{\sigma}_r = 1.000$, remains unchanged up to a preloading of 90% , indicative of independence of dynamic fatigue strength on preloading. The average experimental value of $\bar{\sigma}_r$ (Fig. 8 (b)) was found to be $\bar{\sigma}_r = 0.9882 \pm 0.011$. All of these results indicate that the theory agrees very well with the experimental data obtained from the two material systems.

(3) Crack Growth Behavior

Figure 9 shows the normalized crack size (C^*) as a function of normalized time (J) for the as-indentured crack system subjected to dynamic fatigue with zero preloading. The figure is for $\hat{\sigma}^* = 1.0 \times 10^{-5}$ with $n = 5$ to 80 . Due to increased fatigue susceptibility, crack growth is dominant with decreasing n , resulting in shorter failure time and consequently lower fatigue strength. The crack growth for as-indentured cracks was found to be much greater than that of Griffith flaws because of the additional driving force due to residual tensile contact stress. This additional driving force results in not only stable crack growth but slow crack growth during loading.¹² However, as seen in the figure, most of crack growth still occurs close to and/or at failure time at which a dynamic fatigue strength is defined. The nature of this long 'incubation' time of an initial crack is a key aspect that makes preloading technique feasible in dynamic fatigue testing.

IMPLICATIONS

The most direct, powerful effect of preloading technique is the saving of testing time. For example, if it takes about 9 h at a certain low stressing rate (say, 0.005 mm/min) to test one optical glass fiber with a strength of ≈ 5 GPa and with $n \approx 20$, and if a minimum of twenty specimens is required to obtain reliable statistical data, then total testing time at that stressing rate would be 180 h. But if a preloading of 90% is applied, the total testing time would be reduced to only 18 h so that 90% of the total testing time can be saved. And 80% saving for a preloading of 80% , and so on. Since most of testing time is consumed at the lowest stressing rate to be used, the contribution of preloading can be maximized when preloading is applied at the lowest stressing rate.⁹

With a proper use of preloading in conjunction with Eq. (3) (or Fig. 2) for Griffith flaws and with Fig. 3 for as-indentured cracks, a considerable saving of testing time can be achieved, which gives

Figure 6. Dynamic fatigue results of as-indented 96 wt % alumina flexure specimens in room-temperature distilled water with zero preloading (indentation load = 49 N). The solid line indicates the best-fit line based on Eq. (2). Error bar represents one standard deviation.

Figure 7. Dynamic fatigue strength of as-indented 96 wt % alumina flexure specimens as a function of preloading in room-temperature distilled water (indentation load = 49 N). Error bar indicates one standard deviation. The solid line represents the fatigue strength with zero preloading.

(a)

(b)

Figure 8. 'Reduced' fatigue strength ($\bar{\sigma}_f$) as a function of preloading: (a) as-indented soda-lime glass specimens; (b) as-indented 96 wt % alumina specimens. Each solid line in the figures represents the theoretical solution.

Figure 9. Numerical solution of normalized crack size (C^*) as a function of normalized time (J) for different n 's ($\delta^* = 1.0 \times 10^{-5}$).

a great impact on testing economy. However, it should be noted that an appropriate selection of preloading is also dependent upon the scatter of strength data or Weibull modulus. Therefore, a care should be taken particularly for material with low Weibull modulus ($m \leq 10$) when one intends to use higher preloading $\geq 85\%$. The preloading technique has been successfully applied to high-temperature dynamic fatigue testing of alumina and silicon nitride.¹⁰ Several failure mechanisms such as slow crack growth, creep, plastic flow¹⁴ and oxidation can sometimes occur simultaneously at higher temperatures ($\geq 1200^\circ\text{C}$) and at lower stressing rates ($\leq 2\text{ MPa/min}$), which makes it difficult to distinguish the controlling failure mechanism. In this case, the application of preloading has been proven as an effective tool to pinpoint the prevailing mechanism associated with failure.¹⁰

CONCLUSIONS

The numerical solution of dynamic fatigue strength as a function of preloading was obtained for indentation-induced cracks. The dynamic fatigue strength depends on both fatigue parameter (n) and preloading. The effect of preloading on fatigue strength decreases with increasing fatigue parameter: For $n \geq 20$ the effect was negligible up to a preloading of 90 % with a maximum increase in fatigue strength by 1.2 %. The solution was verified by dynamic fatigue experiments in room temperature distilled water using soda-lime glass and alumina specimens with indentation cracks produced by a Vickers microhardness indenter. The results indicate that one can apply a preloading up to 90 % in dynamic fatigue testing for most brittle materials with almost no change in fatigue strength, since most of these materials exhibit fatigue parameter $n \geq 20$ at room temperature in a moisture environment. The preloading technique thus contributes a dramatic saving of testing time in dynamic fatigue of brittle materials.

Acknowledgement

The authors are grateful to R. Pawlik for the experimental work.

References

1. A. G. Evans, "Slow Crack Growth in Brittle Materials Under Dynamic Loading Conditions," *Int. J. Fract.*, **10**[2] 252-59 (1974).
2. J. E. Ritter, "Engineering Design and Fatigue Failure of Brittle Materials," pp. 661-686 in *Fracture Mechanics of Ceramics*, Vol 4, R. C. Bradt, D. P. H. Hasselman, and F. F. Lange, Eds., Plenum Publishing Co., NY (1978).
3. G. G. Trantina, "Strength and Life Prediction for Hot-Pressed Silicon Nitride," *J. Am. Ceram. Soc.*, **62**[7-8] 377-80 (1979).
4. D. Kallish and B. K. Turiyal, "Static and Dynamic Fatigue of a Polymer-Coated Fused Silica Optical Fiber," *Ibid.*, **61**[11-12] 518-23 (1978).
5. R. K. Govila, *Ceramic Life Prediction Parameters*, AMMRC TR 80-18, Army Material and Mechanics Research Center, Watertown, MA (1980) (U. S. Department of Energy).
6. P. K. Khandelwal, J. Chang, and P. W. Heitman, "Slow Crack Growth in Sintered Silicon Nitride," pp. 351-362 in *Fracture Mechanics of Ceramics*, Vol 8, R. C. Bradt, A. G. Evans, D. P. H. Hasselman, and F. F. Lange, Eds., Plenum Press, NY (1986).
7. J. P. Singh, A. V. Virkar, D. K. Shetty, and R. S. Gordon, "Microstructural Effects on the Subcritical Crack Growth in Polycrystalline $8''$ -Alumina," pp. 273-84, *Ibid* (1986).
8. S. R. Choi and J. A. Salem, "Standard Test Method for Determination of Slow Crack Growth Parameters of Advanced Ceramics Using Dynamic Fatigue Testing at Ambient Temperature" (draft), presented at the ASTM C28 Subcommittee Meeting, January 9, 1994, Cocoa Beach, FL, ASTM (on-

going).

9. S. R. Choi, J. A. Salem and J. P. Gyekenyesi, "Fatigue Strength as a Function of Preloading In Dynamic Fatigue Testing of Glass and Ceramics," submitted for the 41st ASME Gas Turbine and Aeroengine Congress, Exposition, and Users Symposium, June 10-13, 1996, Birmingham, UK.

10. S. R. Choi and J. A. Salem, "Effect of Preloading on Fatigue Strength In Dynamic Fatigue Testing of Ceramic Materials at Elevated Temperatures," *Ceram. Sci. Eng. Proc.*, **16**[4] 87-94 (1995).

11. E. R. Fuller, B. R. Lawn, and R. F. Cook, "Theory of Fatigue for Brittle Flaws Originating from Residual Stress Concentrations," *J. Am. Ceram. Soc.*, **66**[5] 314-21 (1983).

12. B. R. Lawn, D. B. Marshall, G. R. Anstis, and T. P. Dabbs, "Fatigue Analysis of Brittle Materials Using Indentation Flaws, Part 1. General Theory," *J. Mater. Sci.*, **16**[10] 2846-2854 (1981).

13. S. R. Choi, J. E. Ritter, and K. Jakus, "Failure of Glass with Subthreshold Flaws," *J. Am. Ceram. Soc.*, **73**[2] 268-74 (1990).

14. R. W. Davidge and G. Tappin, "The Effects of Temperature and Environment on the Strength of Two Polycrystalline Aluminas," *Proc. Br. Ceram. Soc.*, **1970** [15] 47-60.

Status of Milestones

Milestones are on time

Communication/Visits/Travel

None

Problems Encountered

None

Publications

1. S. R. Choi and J. A. Salem, "Dynamic, Static and Cyclic Fatigue of Alumina with Indentation-Induced Flaws," *J. Mater. Sci. Lett.*, **14** 1286-1288 (1995).

2. S. R. Choi and J. A. Salem, "Effect of Preloading on Fatigue Strength In Dynamic Fatigue Testing of Ceramic Materials at Elevated Temperatures," *Ceram. Sci. Eng. Proc.*, **16**[4] 87-94 (1995).

3. S. R. Choi, N. N. Nemeth, J. A. Salem, L. M. Powers, and J. P. Gyekenyesi, "High-Temperature Slow Crack Growth of Si_3N_4 Specimens Subjected to Uniaxial and Biaxial Dynamic Fatigue Loading Conditions," *ibid.*, **16**[4] 509-517 (1995).

W.B.S. Element 3.2.2.3**LIFE PREDICTION METHODOLOGY FOR CERAMIC COMPONENTS
OF ADVANCED HEAT ENGINES -- PHASE II****FOURTH SEMIANNUAL PROGRESS REPORT
APRIL - SEPTEMBER 1995****PRINCIPAL INVESTIGATORS:**

**D. Wu, A. Peralta, N. Menon, A. Kinney, P. Brehm,
R. Morey, J. Cuccio, and J. Wade**

**AlliedSignal Engines
111 S. 34th Street
MS 57-72/1303-203
P.O. Box 52181
Phoenix, Arizona 85072-52181**

Objectives/Scope

AlliedSignal Engines (AE) has defined a program that builds on the progress made in Phase I of the Life Prediction Methodology for Ceramic Components of Advanced Vehicular Heat Engines program. This Phase II program will develop the methodology required to adequately predict the useful life of ceramic components used in advanced heat engines. Phase II will concentrate on predictive methodology for time- and cycle-dependent failure modes, as well as proof testing and nondestructive evaluation (NDE) methodology to enhance component reliability through screening out of low-strength components.

The life prediction methodologies developed will be generic and hence will be applicable to ceramic components that operate under known temperature and stress conditions.

The technical effort has been organized into six tasks, as follows:

- 1) Material Baseline
- 2) Compressive Creep Methodology
- 3) Flaw Growth Methodology
- 4) Cyclic Fatigue Methodology
- 5) Proof Test Methodology
- 6) NDE Reliability Methodology.

Integration of the methodologies will be undertaken through continued development of the statistical and risk integration computer codes previously developed during the Phase I program. Progress made under these objectives during the April through September 1995 semiannual reporting period is described in the following sections.

Technical Highlights

1.0 Material Baseline

1.1 Phase I Closure

In order to resolve the discrepancy between the surface strength predictions and the actual test results from the spin disk fast fracture tests performed during Phase I of this program, 108 MIL-A test bars were excised as shown in Figure 1 from six available NT154 silicon nitride spin disks, numbered A through F. The objective was to capture in the MIL-A test bar specimens as much of the region as possible from the spin disks in which a majority of the surface failures occurred in the Phase I spin disk testing. The test bars were inspected with profilometry to determine the surface roughness, and then tested at room temperature.

Figure 1. MIL-A Test Bar Specimens Were Excised From Indicated Locations On Six NT154 Spin Disks.

1.1.1 Profilometry Results And MOR Values

The mechanical profilometer (Giddings & Lewis, Universal Linear Profile System) used for measuring the surface roughness of the MIL-A test bars had a stylus radius of 0.0004 inch. Table 1 shows the MOR values (characteristic strength from Weibull plots) calculated from the profilometry results and the various roughness (R) values. Definitions of terms are given at the bottom of the Table. Figures 2 and 3 show plots of the strength with various R values. When all the data is taken into account, there seems to be no major correlation between the strength values and the roughness.

TABLE 1. PROFILOMETRY MEASUREMENTS AND MOR VALUES.

Spin Disk No.	Total No. of Specimens	MOR	Weibull Modulus, m	Rt	Rz	Rv	Rtm	Rzm	Rvm
A	19	126.3	16.6	95	61	51	74	64	40
B	20	81.6	8.1	66	45	33	51	44	27
C	19	75.0	7.3	89	54	45	63	52	33
D	10	62.4	10.2	150	62	76	103	61	56
E	20	80.5	4.6	144	74	74	101	73	53
F	20	85.0	10.8	134	61	69	90	62	45

Rt = Maximum peak-to-valley height over one assessment length

Rtm = Arithmetic average of the maximum peak-to-valley heights in each of five consecutive sampling lengths

Rv = Minimum valley height (most negative value) over one assessment length

Rvm = Arithmetic average of the minimum valley heights of each of five consecutive sampling lengths

Rz = Arithmetic average of the five greatest peak-to-valley heights within one sampling length

Rzm = Arithmetic average of the five greatest peak-to-valley heights in each of five consecutive sampling lengths

Sampling Length = 0.03 inch

Assessment Length = 0.15 inch

Figure 2. Flexure Strength Of MIL-A Test Specimens From Spin Disks Vs. Profilometry R Values. (Rt, Rz, And Rv Values).

Figure 3. Flexure Strength Of MIL-A Test Specimens From Spin Disks Vs. Profilometry R Values. (Rtm, Rzm, And Rvm Values).

1.1.2 Weibull Data Analysis

Following four-point bend testing to failure of the excised MIL-A type specimens, fractographic evaluation was conducted, and a Weibull analysis of the data was performed. The data is shown in Figure 4, and the Weibull parameters of the individual data sets are summarized in Table 2. As shown in the Figure and Table, the specimen strengths are not consistent at all. Given that these specimens were excised from seemingly identical components, it is somewhat puzzling to see this poor agreement in the strength values. In an attempt to understand what this means, several analyses were performed to predict the strength of the spin disks from the excised specimens using various techniques. First, the spin disk failure data from Phase I was analyzed and plotted, as shown in Figure 5. This analysis assumed that the disk effective area was that delineated by the locations from which the MIL-A type specimens were excised, as shown schematically in Figure 1. Second, the spin disk strength was predicted from an analysis of all the MIL-A specimen data pooled into one database. The results of this prediction procedure were so poor that the spin disk failure data did not appear within the scale of the plot. Hence, we then proceeded to make a third set of spin disk predictions using one specimen data set at a time. The predicted strength values for specimens from Spin Disk F matched the measured strength data very well; for specimens from Disk A the procedure over-predicted the strength of the Phase I spin disks; and for the remaining spin disk specimens the procedure under-predicted the strength, compared to the actual Phase I spin disk strength values. The predicted strength values for Disk F specimens are shown in Figures 6 and 7. The over-prediction results for specimens from Disk A are shown in Figures 8 and 9.

The fact that the predicted values from the third procedure matched the measured values well for the spin disk specimens that have strength values intermediate between the highest and lowest range of values is at least a comforting event. One may therefore assume that the spin disk specimens tested to failure captured the average strength of the total population.

Figure 4. Weibull Plot Showing The Strength Values For All The Excised MIL-A Specimens.

TABLE 2. WEIBULL PARAMETER SUMMARY FOR THE EXCISED MIL-A TYPE SPECIMENS.

Data Origin	Specimen Quantity	Weibull Modulus, m	Second Weibull Parameter, σ_0
Disk A	19	16.6	96.0
Disk B	20	8.1	46.6
Disk C	19	7.32	40.5
Disk D	10	10.2	40.1
Disk E	20	4.61	30.6
Disk F	20	10.8	55.8
Combined (All)	108	3.82	28.5
Combined B, C, E, and F	79	6.47	40.5
Phase I Spin Disk Tests	13	7.93	62.5

Figure 5. Weibull Analysis Results From The Spin Disks.

Figure 6. Predicted Strength Values For Specimens Excised From Disk F.

Figure 7. Comparison Of Phase I Spin Disk Test And Disk F Specimens Strength Values.

Figure 8. Predicted Strength Values For Specimens Excised From Disk A.

Figure 9. Comparison Of Phase I Spin Disk Test And Disk A Specimens Strength Values.

1.2 Tensile And Flexure Testing of CLP NT154

During April through June 1995, material qualification testing of the closed-loop processed (CLP) NT154 silicon nitride specimens continued, in anticipation of the use of this material in the planned Phase II testing. The qualification testing involved tensile creep rupture and flexure fast fracture specimens.

A summary of the creep tests completed at the Oak Ridge National Laboratories High Temperature Materials Laboratory (ORNL-HTML) is given in Table 3 (courtesy of Dr. A.A. Wereszczak, ORNL-HTML). The test results indicated that the CLP NT154 material had superior rupture life properties, compared to the earlier Phase I NT154 material. Under the same test conditions, 16 Phase I specimens had life values ranging from 57 to 443 hours.

TABLE 3. CLP NT154 STRESS RUPTURE SPECIMEN TEST RESULTS SUMMARY.

Batch No.	Specimen ID	Life, Hours	Comments
1	XX18	811	Terminated At Failure
1	XX25	288	Terminated At Failure
1	XX19	1270	Failure Due To Power Outage
1	XX27	1775	Terminated At Failure
2	YY15	709	Terminated At Failure
2	YY08	398	Failure Due To Power Outage
2	YY10	33	Failure Due To Broken Thermocouple
3	ZZ14	351	Terminated At Failure
3	ZZ15	1125	Terminated At Failure
3	ZZ33	1028	Terminated At Failure

A summary of the flexure fast fracture test results for the CLP NT154 specimens is listed in Table 4. The CLP NT154 specimens in Batch Nos. 1 and 2 showed excellent strength and Weibull modulus values for both the longitudinally-machined and transverse-machined orientations. However, the specimens in Batch No. 3 showed lower values overall, primarily because of the presence of amorphous defects on the surfaces of the flexure test bars. This was suspected to be due to insufficient removal of the encapsulating material used during the hot isostatic pressing (HIPping) process.

From the point of view of the agreed-upon qualification criteria, all three batches of CLP NT154 specimens would have passed the acceptance criteria. Additionally, scanning electron micrographic (SEM) analysis of the flexure test bars showed that the closed-loop process was able to eliminate all failures due to iron inclusions. The only volumetric failures noted in these CLP NT154 flexure test bars occurred from small carbon inclusions.

The ceramic material supplier, Norton Advanced Ceramics (NAC), Worcester, MA had agreed to take steps to reduce the incidence of discrepancies found in the Batch No. 3 specimens. In view of their assurance and considering the above-mentioned qualification test results, AlliedSignal Engines was prepared to place orders for CLP NT154 specimens for the planned Phase II testing.

TABLE 4. CLP NT154 TEST SPECIMENS FLEXURE FAST FRACTURE TEST RESULTS.

Test Temperature, F	Specimen Description	Specimen Quantity	σ_0 Characteristic Strength, ksi	Weibull Modulus, m	Volume Flaws, Inclusions
BATCH NO. 1					
RT	Longitudinal Machined	20	168.7	18.8	3, Carbon
2100	Longitudinal Machined	19	110.7	20.9	1, No Detection
2500	Longitudinal Machined	10	98.5	12.0	3, No Detection
RT	Transverse Machined	10	131.8	28.6	1, Carbon
RT	As-Processed	10	82.9	16.8	None
BATCH NO. 2					
RT	Longitudinal Machined	20	176.5	16.5	2, No Inclusions
2100	Longitudinal Machined	20	114.8	16.5	None
2500	Longitudinal Machined	10	101.6	29.6	3, No Detection
RT	Transverse Machined	10	134.7	12.7	None
RT	As-Processed	10	83.7	6.7	None
BATCH NO. 3					
RT	Longitudinal Machined	20	153.1	9.7	7, Carbon
2100	Longitudinal Machined	19	113.6	15.46	0
2500	Longitudinal Machined	10	99.4	27.49	1, No Detection
RT	Transverse Machined	10	112.2	24.1	0
RT	As-Processed	10	70.0	6.98	0
RT = Room Temperature.					

However, in late June, 1995 NAC advised AlliedSignal Engines that they will no longer pursue business in the ceramic gas turbine components market, resulting in the discontinuation of production of ceramic components manufactured from NT154 and NT164 silicon nitride. NAC indicated their willingness to continue to support the present program, but given that the original selected material, NT154, will no longer be available for the manufacture of gas turbine components, alternatives for the present program were examined by AlliedSignal Engines.

Alternate silicon nitride materials from the two remaining domestic U.S. suppliers were considered for use in this program. These included SN-252 and SN-253 from Kyocera Industrial Ceramics Corp. (KICC), Vancouver, WA, and AS-800 produced by AlliedSignal Ceramic Components (ACC), Torrance, CA. KICC indicated that,

following the announcement by NAC and in view of the resulting increased business, they did not have the resources to support additional programs at this time, especially a "specimen-oriented" program. AlliedSignal Ceramic Components indicated their willingness to supply AS-800 specimens for the program. However, they cautioned that the maturity of the AS-800 material is less than that of NT154. The pros and cons of using AS-800 versus CLP NT154, were discussed at length by AlliedSignal Engines. With the concurrence of ORNL, AS-800 was selected as the go-forward material for this program, primarily based upon its future potential.

1.3 Change of Material For Part of Phase II

Specimens of AS-800 silicon nitride, produced by ACC, will be used in the planned Cyclic Fatigue Testing and Proof Testing Methodology Development tasks in the present program. In addition, AS-800 will also be used in the generation of a significant amount of Material Baseline data. However, NT154 silicon nitride specimens from Phase I are being used for the planned Compressive Creep and Flaw Growth Methodology Development tasks. NAC has also supplied the required ceramic stators and square plate specimens made from slip-cast NT154 silicon nitride for the planned Nondestructive Evaluation Probability Of Detection (NDE-POD) study

All creep testing in anticipation of the use of closed-loop processed (CLP) NT154 which was underway at the Oak Ridge National Laboratory High Temperature Materials Laboratory (ORNL-HTML) has been terminated, since NT154 will not be used for any future mechanical property testing directed towards methods development.

1.4 AS-800 Test Matrix

As a result of the change in material to AS-800 silicon nitride, a new test matrix was developed, incorporating all of the basic testing planned for NT154. A temperature limit of 2200F (1204C) has been placed on the test matrices, since the high-temperature properties of the current AS-800 material are not completely understood. An additional important change was the decision to test most of the specimens with the machined surfaces in a transverse direction to the loading, since during service most components will be subjected to stresses oriented transverse to the machining direction.

Table 5 lists the AS-800 test matrix. All the required specimens have been ordered, and delivery is expected by February, 1996.

Table 6 lists the test efforts continuing on NT154 specimens, which were initiated in 1994.

2.0 Compressive Creep Methodology

Compressive creep testing of NT154 specimens was initiated at ORNL-HTML by Dr. A.A. Wereszczak in 1994. The test specimens were machined from remnants of the Phase I NT154 material, in the form of right circular cylinders, 5 mm in diameter and 10 mm long. Tests have been completed at stresses of 100, 300, and 500 MPa at 1371C (2500F). The test results (Figure 10) show that the minimum creep rates measured in compression are at least two orders of magnitude lower than the values predicted for creep rates in tension at the same stress levels from the Phase I test data.[Ref. 1, Cuccio, et. al. 1994] In addition, the dependence of the compressive creep rate on the stress level is considerably lower than that measured in tension. The next series of tests will be conducted at 1315C (2400F). Planned testing will be continued at other stress levels as well as at other temperatures.

TABLE 5. PHASE II AS-800 SPECIMEN TEST MATRIX.

Test Objective	Specimen Type	Test Description	Machining Orientation	Test Temperature, F		
				75	1300	2200
				No. of Specimens		
Baseline	MIL-B Flexure	FF	TM	30	30	30
	MIL-B Flexure	FF	LM	30	30	---
	MIL-B Flexure	FF	AP	30	---	30
	Tensile	FF	TM	20	20	20
	Tensile	SR	TM	---	---	20
	MIL-E Notched Flexure	FF	TM	20	20	---
Cyclic Fatigue	Tensile/Compression	R = -1.0	TM	---	15	15
	Tension	R = 0.05	TM	---	15	15
	MIL-B Flexure	R = 0.05	LM	---	25	---
	MIL-B Flexure	R = 0.05	TM	---	25	25
	MIL-B Flexure	R = 0.05	AP	---	25	25
	MIL-E Notched Flexure	R = 0.05	TM	---	20	---
Proof Testing	MIL-B Flexure	Machining Anisotropy	Machined at 60, 65, 70 Degrees	90	---	---
	MIL-B	Residual Strength 3Pt/4Pt	TM	30	---	---
	MIL-B	Residual Strength, RT/HT	TM	---	---	30
	MIL-B, Proof Tested (Rate No. 1)	Dynamic Fatigue	TM	---	15	15
	MIL-B, Proof Tested (Rate No. 2)		TM	---	15	15
	MIL-B, Non Proof Tested (Rate No. 1)		TM	---	15	15
	MIL-B, Non Proof Tested (Rate No. 2)		TM	---	15	15
	Round Plate	Non-Proportional Loading	Machined	60	---	---
	Round Plate		AP	30	---	---

3Pt/4Pt = 3-Point Proof Test, Followed By 4-Point Loading

AP = As-Processed

FF = Fast Fracture

LM = Longitudinally Machined

RT/HT = Room Temperature Proof Test/ High Temperature Loading

SR = Stress Rupture

TM = Transverse Machined

TABLE 6. PHASE II NT154 TEST MATRIX (ONGOING TESTS).

Test Objective	Specimen Type	Test Temperature, F	Total No. of Specimens
Compressive Creep	Cylinders, 5 mm Diameter by 10 mm Length	2300 to 2500	15
Spin Disks	MIL-A Flexure From Spin Disks	---	110
Flaw Growth	Static And Cyclic Flexure, MIL-B	1300 to 2400	42
NDE-POD	Machined Square Plate	---	4
	Machined GTCP85 APU Stators	---	55
	As-Processed Square Plates	---	4
	As-Processed GTCP85 APU Stators	---	55

GS99-20

Figure 10. Compressive Creep Test Results For NT154 Specimens At 1371C (2500F).

3.0 Flaw Growth Methodology

Experimental flaw growth methodology efforts have continued under subcontract at Stanford University, Palo Alto, CA under the direction of Professor R. Dauskardt and Dr. F. Haubensak. These efforts included defining methods for introducing small, controlled cracks into specimens on the order of inherent material flaws. The techniques which were studied are listed in Table 7. Methods to monitor these flaws under loading were defined, as listed in Table 8.

Preliminary data was generated from indentation-induced cracks under static and cyclic loading, as shown in Figures 11 and 12. The minimum crack dimensions achieved so far for indentation cracks are in the neighborhood of 50 micrometers (μm).

Of the three major techniques of introducing artificial flaws, the indentation technique was found to be the most successful and repeatable. For crack monitoring, in-situ optical examination and the replication techniques were most successful.

TABLE 7. FLAW INITIATION TECHNIQUES STUDIED.

No.	Method	Minimum Size, μm	Residual Stresses	Status
1	Indentation	50	$K_I = \chi^2/c^{3/2}$	Demonstrated
2	Micromachining With Laser Drilling	10	Minimal	Good Results
3	Micromachining With Chemical Etching	10	Minimal	Acceptable Results
4	Indentation And Removal By Grinding Surface Layer	<10	Minimal	Acceptable Results
5	Repetitive Indentation	<10	$0 < K_I = \chi^2/c^{3/2}$	Undetermined
6	Indentation And Applied Loading	<10	$0 < K_I = \chi^2/c^{3/2}$	Experimental

TABLE 8. CRACK LENGTH MEASUREMENT TECHNIQUES STUDIED.

No.	Method	Temperature Range	Crack Size Regime	Status
1	Surface Replication	Low	Short	Demonstrated
2	Crack Gage	Low	Long	Demonstrated
3	Miniature Crack Gage	Low	Short	High Likelihood of Success
4	Direct Optical Observations	Low	Long, Short	High Likelihood of Success
5	Elevated Temperature Crack Gage	Elevated	Long, Short	Experimental
6	Elevated Temperature Direct Optical	Elevated	Long, Short	Experimental
7	Compliance	Low, Elevated	Long	Demonstrated
8	Compliance	Low, Elevated	Short	Low Resolution

Figure 11. Preliminary Subcritical Crack Growth Rate From Indentation-Induced Cracks; Small Crack 1204C Static Fatigue Data.

Figure 12. Preliminary Subcritical Crack Growth Rate Data From Indentation-Induced Cracks; Small Crack Room Temperature Cyclic Fatigue Data [Ref. 2, Salmon 1992].

4.0 Cyclic Fatigue Testing

The efforts reported above under flaw growth methodology are to be closely coordinated with planned cyclic fatigue testing of unflawed flexure and tensile specimens. Specimen testing will begin after delivery of the test specimens, scheduled in February, 1996. Consultation has taken place between AlliedSignal Engines and Dr. A.A. Wereszczak of the ORNL High Temperature Materials Laboratory (ORNL-HTML) on the planned experimental efforts. The test plans include testing a portion of the specimens at ORNL-HTML and a portion in-house.

5.0 Proof Testing Methodology

Efforts during this period have concentrated on the development of statistical methods for incorporation of proof test data into evaluation of the Weibull parameters, and methods for improving the efficiency of Weibull parameter calculations for multitemperature data.

5.1 Censored and Proof Tested Data Analysis Weibull Parameter Estimation

As part of the proof testing methodology development, specimen testing will be performed for correlation of the developed methodology. The resulting data will first be obtained for proof tests at stress levels selected to fail approximately one third of the specimens; then test data will be obtained for specimen failure under different loading conditions. Data analysis will be performed after the proof testing to calculate the Weibull parameters by performing a censored data analysis using the data from the unfailed specimens as the censored data at the proof

stress level. But, since the analysis capabilities are required to incorporate the specimens that have been proof tested and subsequently tested to failure, the analysis capabilities should be capable of analyzing the data from these specimens by themselves and also pooled with other non-proof tested data. The derivation of the analysis equations is presented in the following sections. The derivation is carried out for specimens that are proof tested and have failed at the same temperature. The derivation for proof testing and failure at different temperatures is more complicated and will be derived later.

One may start by defining the likelihood function:

$$L(m, \sigma_o) = \prod_{i=1}^r f(\sigma_i, m, \sigma_o) \cdot \prod_{j=r+1}^n P_S(\sigma_j, m, \sigma_o) \quad [1]$$

Where the probability and cumulative density functions are defined, respectively, as:

$$f(\sigma_i, m, \sigma_o) = -\frac{dS(\sigma)}{d\sigma} \quad [2]$$

$$S(\sigma) = \exp \left[-I_f V \left(\frac{\sigma}{\sigma_o} \right)^m - I_p V \left(\frac{\sigma_p}{\sigma_o} \right)^m \right] \quad \text{for: } I_f V \left(\frac{\sigma}{\sigma_o} \right)^m - I_p V \left(\frac{\sigma_p}{\sigma_o} \right)^m > 0 \quad [3]$$

Where:

I and I_p are the multiaxial factors for failure and proof, respectively;

σ and σ_p are the maximum effective stress for failure and proof, respectively;

m and σ_o are the first and second Weibull parameters,

V is the physical size of the failure mode in question,

i is the index for failed specimens,

j is the index for specimens that survived,

k is the index for all specimens,

n is the total number of specimens, and

r is the total number of failures.

Notice that Equation [3] becomes the regular Weibull distribution for ceramic materials if σ_p is set to zero.

The log likelihood function can be constructed from the above equations:

$$l = \sum_{i=1}^r \ln(I_i) + \sum_{i=1}^r \ln(V_i) + r \ln(m) + \sum_{i=1}^r (m-1) \ln(\sigma_i) - rm \cdot \ln(\sigma_o) - \sum_{i=1}^r I_i V_i \left(\frac{\sigma_i}{\sigma_o} \right)^m - \sum_{j=r+1}^n I_j V_j \left(\frac{\sigma_j}{\sigma_o} \right)^m + \sum_{k=1}^n I_k V_k \left(\frac{\sigma_k}{\sigma_o} \right)^m \quad [4]$$

Such function is then used to calculate the Weibull parameters. The Weibull parameters are given by the values of m and σ_o that maximize the log likelihood function. The log likelihood function is maximized when its derivatives with respect to m and σ_o equal zero, as defined by the following equations:

$$\frac{\partial l}{\partial m} = 0 \quad \frac{\partial l}{\partial \sigma_o} = 0 \quad [5]$$

Performing these operations one obtains the following results:

$$\sigma_o = \left\{ \frac{1}{r} \left[\sum_{k=1}^n [I_k V_k \sigma_k^m - I_{rk} V_k \sigma_{rk}^m] \right] \right\}^{\frac{1}{m}} \text{ for: } I_k V_k \left(\frac{\sigma_k}{\sigma_{ok}} \right)^m - I_{rk} V_k \left(\frac{\sigma_{rk}}{\sigma_{ok}} \right)^m > 0 \quad [6]$$

And:

$$\frac{1}{m} = \frac{\sum_{k=1}^n V_k \sigma_k^m [I'_k + I_k \ln(\sigma_k)]}{\sum_{k=1}^n (I_k V_k \sigma_k^m - I_{rk} V_k \sigma_{rk}^m)} - \frac{1}{r} \sum_{i=1}^r \left[\frac{I'_i}{I_i} + \ln(\sigma_i) \right] - \frac{\sum_{k=1}^n V_k \sigma_{rk}^m [I'_{rk} + I_{rk} \ln(\sigma_{rk})]}{\sum_{k=1}^n (I_k V_k \sigma_k^m - I_{rk} V_k \sigma_{rk}^m)} \quad [7]$$

With the same restriction imposed on Equation [6], where r is the total number of failures and the indices summation is over all specimens for k and over all the failures for i .

These equations were derived to analyze data from specimens which have been proof tested and the surviving specimens subsequently tested to failure under a second loading condition. To show the effectiveness of the analysis, a test case was analyzed in which 500 tensile specimens were proof tested to a stress of 60 ksi. It was assumed that the failure modes present are as listed in Table 9, with the given Weibull parameters. The specimens were assumed to be of the ORNL tensile specimen configuration. First, a simulation was performed and 500 failure points were generated. Then these simulated data points were analyzed to predict their respective Weibull parameters. The results are listed in Table 9 and shown in Figures 13 through 15. Then the data was reanalyzed with specimens below 60 ksi as failures and the specimens above 60 ksi as suspended tests. Hence, the information provided by the left tail of the distribution is used to predict the Weibull parameters. The results of this second analysis are summarized in Table 9 and in Figures 16 through 18. The last analysis performed was the case for which the specimens below 60 ksi are removed; i.e., no information is given on the failure stresses below this stress, and only the information from the specimens that failed above 60 ksi is present. The results of this analysis are shown in Table 9 and in Figures 19 through 21.

TABLE 9. WEIBULL PARAMETERS CALCULATED FROM PROOF TESTED SPECIMENS.

Data Case	Failure Mode	Number Of Remaining Specimens	Failures Due To Test	Weibull Modulus, m	Second Weibull Parameter, σ_o
Seed Parameters	Volume	---	---	10.00	50.0
	Surface	---	---	6.00	90.0
Data Simulation	Volume	399	-	9.79	49.2
	Surface	101	-	6.37	89.1
After Proof Test	Volume	381	18	12.68	48.9
	Surface	90	11	6.33	90.9
After Test to Failure	Volume	0	381	10.13	50.0
	Surface	0	90	5.97	89.4

Figure 13. Simulated Data Used In The Proof Test Study. Combined Failure Mode Plot.

Figure 14. Simulated Data, Plot Of The VOLUME Failure Mode.

Figure 15. Simulated Data Plot Of The SURFACE Failure Mode.

Figure 16. Censored Data Analysis Of The Simulated Data Set, Combined Failure Mode, Censoring At 60 ksi.

Figure 17. Censored Data Analysis Of The Simulated Data Set, VOLUME Failure Mode, Censoring At 60 ksi.

Figure 18. Censored Data Analysis Of The Simulated Data Set, SURFACE Failure Mode, Censoring At 60 ksi.

Figure 19. Proof Tested Data Analysis Of The Simulated Data Set, Combined Failure Mode. Only Data Above 60 ksi Is Present.

Figure 20. Proof Tested Data Analysis Of The Simulated Data Set, VOLUME Failure Mode. Only Data Above 60 ksi Is Present.

**Figure 21. Proof Tested Data Analysis Of The Simulated Data Set, SURFACE Failure Mode.
Only Data Above 60 ksi Is Present.**

It is important to note that a new data ranking technique developed under this program has been employed to plot the proof tested data. This new ranking approach makes use of Weibull parameter calculated by the maximum likelihood approach. The method consists of adjusting the specimen count used in the ranking, in the following way:

- 1) Calculate the probability of failure and success for the specimen type for the given proof test stress level. Use the calculated Weibull parameters obtained from the likelihood analysis.
- 2) Calculate a pseudo number of total specimens tested; this number may not be an integer number:

$$N_i = \frac{N}{1 - P_f(\sigma_p)} \quad N_i = \frac{N}{P_s(\sigma_p)} \quad [8]$$

$$P_f(\sigma_p) = \exp - \left[IV \left(\frac{\sigma_p}{\sigma_0} \right)^m \right] \quad [9]$$

- 3) Calculate the number of specimens that were removed by the proof test:

$$n_r = P_f(\sigma_p) \cdot N_i \quad [10]$$

- 4) Calculate the new ranks by replacing i by $n_r + i$, i.e.:

$$\text{Rank} = \frac{n_r + i - 0.5}{N_i} \quad [11]$$

- 5) For censored data, adjust the increment in the following way:

$$\text{Inc} = \frac{N_i + 1 - \text{PMON}}{1 + \text{NIBPSS}} \quad [12]$$

For the very first failure after a suspended item, use n_r for PMON; from there on, use the standard definition for PMON, as described in the Phase I Final Report, p. 5-80 [Ref. 1, Cuccio, et. al. 1994].

5.2 Multitemperature Data Weibull Parameter Calculation

During Phase I of this program, AlliedSignal Engines [Ref. 1, Cuccio, et. al. 1994] developed a data analysis approach which assumed that the first Weibull parameter is invariant with temperature, and that the second Weibull parameter was a function of temperature. This approach allows the pooling of multitemperature data into one single analysis for calculation of the Weibull parameters, yielding more accurate estimates of these parameters because of the increased number of specimens used in the calculations. The effort presented here outlines an approach which will increase the numerical efficiency of the calculation for censored data.

We start by defining a likelihood function. In this case it is defined as the product of the likelihood at each temperature:

$$L(m, \sigma_{ol}) = \prod_l \left\{ \prod_{i=1}^{r_l} f_i(\sigma_i, m, \sigma_{ol}) \cdot \prod_{j=r_l+1}^{n_l} P_j(\sigma_j, m, \sigma_{ol}) \right\} \quad [13]$$

and the log likelihood function:

$$l(m, \sigma_{ol}) = \sum_l \left\{ \sum_{i=1}^{r_l} \ln(m) + \sum_{i=1}^{r_l} \ln(I_{il}) + \sum_{i=1}^{r_l} \ln(V_{il}) + \sum_{i=1}^{r_l} (m-1) \ln(\sigma_{il}) + \sum_{i=1}^{r_l} -m \ln(\sigma_{ol}) \right. \\ \left. + \sum_{i=1}^{r_l} \left[I_{il} V_{il} \left(\frac{\sigma_{il}}{\sigma_{ol}} \right)^m \right] + \sum_{j=r_l+1}^{n_l} \left[I_{jl} V_{jl} \left(\frac{\sigma_{jl}}{\sigma_{ol}} \right)^m \right] \right\} \quad [14]$$

Where the different parameters are defined as in 5.1 above and the index l ranges over all the temperatures. This analysis assumes that the σ_{ol} 's are independent from each other. Maximization of the likelihood function yields uncoupled equations for the σ_{ol} 's as outlined below:

$$\frac{\partial l}{\partial m} = 0 \quad \frac{\partial l}{\partial \sigma_{ol}} = 0 \quad [15]$$

Performing these operations yields:

$$\frac{\partial l(m, \sigma_{ol})}{\partial \sigma_{ol}} = -\frac{r_l m}{\sigma_{ol}} + \frac{m}{\sigma_{ol}^m} \sum_{k=1}^{n_l} [I_{kl} V_{kl} \sigma_{kl}^m] \quad [16]$$

Which reduces to:

$$\sigma_{ol} = \left[\frac{1}{r_l} \sum_{k=1}^{n_l} [I_{kl} V_{kl} \sigma_{kl}^m] \right]^{1/m} \quad [17]$$

And:

$$\frac{\partial l(m, \sigma_{ol})}{\partial m} = \sum_l \left\{ \frac{r_l}{m} + \sum_{i=1}^{r_l} \frac{I'_{il}}{I_{il}} + \sum_{i=1}^{r_l} \ln(\sigma_{il}) - r_l \ln(\sigma_{ol}) \right. \\ \left. - \sum_{k=1}^{n_l} \left[I'_{kl} V_{kl} \left(\frac{\sigma_{kl}}{\sigma_{ol}} \right)^m \right] - \sum_{k=1}^{n_l} \left[I_{kl} V_{kl} \left(\frac{\sigma_{kl}}{\sigma_{ol}} \right)^m \ln \left(\frac{\sigma_{kl}}{\sigma_{ol}} \right) \right] \right\} \quad [18]$$

Substituting Equation [17] into Equation [18] and simplifying gives:

$$\frac{1}{m} = \frac{1}{\sum_l r_l} \sum_{l=1}^s \left\{ \sum_{k=1}^{n_l} \frac{r_l}{\sum_{k=1}^{n_l} [I_{kl} V_{kl} \sigma_{kl}^m]} [I'_{kl} V_{kl} \sigma_{kl}^m + I_{kl} V_{kl} \sigma_{kl}^m \ln(\sigma_{kl})] - \sum_{i=1}^{r_l} \left[\frac{I'_{il}}{I_{il}} + \ln(\sigma_{il}) \right] \right\} \quad [19]$$

These equations can then be solved by normal optimization methods.

Note that the σ_{ol} 's are dependent only on the Weibull modulus and the existing data at each temperature and that the Weibull modulus is a function of all of the available data at all of the temperatures.

Efforts have continued in development of statistical methods for analysis of pooled multitemperature data. Approaches for confidence bounds predictions for the Weibull parameters of multitemperature data have been outlined, as described in 5.3. A description of the Bootstrap approach for calculation of the confidence bounds is presented in 5.4, below; the Likelihood Ratio approach is still under development.

5.3 Derivation Of Weibull Parameters For Multitemperature Data Assuming A Functional Relationship For The Second Weibull Parameter

The analysis of multitemperature data is important, because ceramic components used in turbine engine applications experience operating conditions at a variety of temperatures and significant temperature gradients, that impose severe thermal stresses on the components. In order to determine the strength of a component at elevated temperatures, specimen testing is usually performed at a variety of temperatures. But it is usually cost-prohibitive to test enough specimens to completely span the envelope of operating temperatures, hence the need to develop methodologies to extract the most information possible out of a few data points at each temperature condition. The question remains, what must be done to determine the material strength for temperatures other than those for which test data exist? Hence, interpolation and extrapolation schemes must be defined for such purposes.

The approach selected for this program assumes that there is a continuous variation of the fast fracture strength of ceramic materials with temperature, and that such variation can be represented by a function of the form given in Equation [20]. The challenge, then, is to determine the coefficients for this equation. Previously adopted classical approaches have assumed that a curve can be fitted through the data by assuming a normal distribution of the error about a best-fit line. The approach we have taken goes further, in that we assume that the data follows a Weibull distribution: not the errors about the best fit, but the actual data. This approach enables the use of a consistent methodology, with the second Weibull parameter as a function of temperature, represented by the best-fit line. This methodology will eventually enable the prediction of reliability confidence bounds for components with temperature gradients.

$$\sigma_o = A_o + A_1 \tan^{-1} \left(\frac{T - K_1}{K_2} \right) + A_2 \tan^{-1} \left(\frac{T - K_3}{K_4} \right) \quad [20]$$

This form of Equation [20] is chosen because it has been observed that the inverse tangent relationship fits very well the sharp drop observed in material strength at elevated temperatures. The approach consists of substituting Equation [20] into the likelihood function for the second Weibull parameter. Calculation of these constants and of the first Weibull parameter is performed as usual, then differentiating the likelihood function with respect to the unknowns and setting to zero.

Substitution of Equation [20] into the likelihood function results in Equation [21]:

$$l(m, \sigma_o) = r \ln(m) + \sum_{i=1}^r \ln(I_i) + \sum_{i=1}^r \ln(V_i) + \sum_{i=1}^r (m-1) \ln(\sigma_o) \\ - \sum_{i=1}^r m \ln(\sigma_o(A_0, A_1, A_2, K_1, K_2, K_3, K_4)) - \sum_{k=1}^n I_k V_k \left(\frac{\sigma_k}{\sigma_o(A_0, A_1, A_2, K_1, K_2, K_3, K_4)} \right)^m \quad [21]$$

Differentiating with respect to the unknowns, one obtains Equations [22] through [24]. The differentiation of the likelihood function with respect to the constants is more easily accomplished using the chain rule of differentiation; hence:

$$\frac{\partial l}{\partial A_1} = \frac{\partial l}{\partial \sigma} \frac{\partial \sigma}{\partial A_1} \quad [22]$$

$$\frac{\partial l(m, \sigma_o)}{\partial \sigma_o} = - \sum_{i=1}^r \frac{m}{\sigma_o} + \frac{m}{\sigma_o^m} \sum_{k=1}^n [I_k V_k \sigma_k^m] \quad [23]$$

$$\frac{\partial l}{\partial A_1} = \frac{\partial l(m, \sigma_o)}{\partial \sigma_o} \frac{\partial \sigma_o}{\partial A_1} = - \sum_{i=1}^r \frac{m}{\sigma_o} \frac{\partial \sigma_o}{\partial A_1} + \sum_{k=1}^n [I_k V_k \sigma_k^m] \frac{m}{\sigma_o^m} \frac{\partial \sigma_o}{\partial A_1} \quad [24]$$

Differentiating the second Weibull parameter function with respect of each one of the constants:

$$\frac{\partial \sigma_o}{\partial A_1} = \frac{\partial}{\partial A_1} \left[A_0 + A_1 \tan^{-1} \left(\frac{T - K_1}{K_2} \right) + A_2 \tan^{-1} \left(\frac{T - K_3}{K_4} \right) \right] \quad [25]$$

$$\frac{\partial \sigma_o}{\partial A_0} = 1 \quad [26]$$

$$\frac{\partial \sigma_o}{\partial A_1} = \tan^{-1} \left(\frac{T - K_1}{K_2} \right) \quad [27]$$

$$\frac{\partial \sigma_o}{\partial A_2} = \tan^{-1} \left(\frac{T - K_3}{K_4} \right) \quad [28]$$

$$\frac{\partial \sigma_o}{\partial K_1} = \frac{\partial}{\partial K_1} \left[A_1 \tan^{-1} \left(\frac{T - K_1}{K_2} \right) \right] \Rightarrow \frac{\partial \sigma_o}{\partial K_1} = A_1 \frac{1}{1 + \left(\frac{T - K_1}{K_2} \right)^2} \frac{1}{K_2} \quad [29]$$

$$\frac{\partial \sigma_o}{\partial K_2} = \frac{\partial}{\partial K_2} \left[A_1 \tan^{-1} \left(\frac{T - K_1}{K_2} \right) \right] \Rightarrow \frac{\partial \sigma_o}{\partial K_2} = A_1 \frac{1}{1 + \left(\frac{T - K_1}{K_2} \right)^2} \frac{T - K_1 - 1}{K_2^2} \quad [30]$$

$$\frac{\partial \sigma_o}{\partial K_3} = \frac{\partial}{\partial K_3} \left[A_2 \tan^{-1} \left(\frac{T - K_3}{K_4} \right) \right] \Rightarrow \frac{\partial \sigma_o}{\partial K_3} = A_2 \frac{1}{1 + \left(\frac{T - K_3}{K_4} \right)^2} \frac{-1}{K_4} \quad [31]$$

$$\frac{\partial \sigma_a}{\partial K_4} = \frac{\partial}{\partial K_4} \left[A_2 \tan^{-1} \left(\frac{T - K_3}{K_4} \right) \right] \Rightarrow \frac{\partial \sigma_a}{\partial K_4} = A_2 \frac{1}{1 + \left(\frac{T - K_3}{K_4} \right)^2} \frac{T - K_3}{K_4} \frac{-1}{K_4} \quad [32]$$

These equations can now be substituted into Equation [24] to form seven equations for the seven unknowns in the interpolation function. But one still needs the equation for the first Weibull parameter, or the Weibull slope. Hence, one must differentiate the likelihood function with respect to the first Weibull parameter and obtain:

$$\begin{aligned} \frac{\partial l(m, \sigma_a)}{\partial m} &= \frac{r}{m} + \sum_{i=1}^r \frac{I_i}{I_i} + \sum_{i=1}^r \ln(\sigma_i) - \sum_{i=1}^r \ln(\sigma_a(\bar{A}, \bar{K})) \\ &\quad - \sum_{k=1}^n I_k V_k \left(\frac{\sigma_k}{\sigma_a(\bar{A}, \bar{K})} \right)^m - \sum_{k=1}^n I_k V_k \left(\frac{\sigma_k}{\sigma_a(\bar{A}, \bar{K})} \right)^m \ln \left(\frac{\sigma_k}{\sigma_a(\bar{A}, \bar{K})} \right) \end{aligned} \quad [33]$$

Equation [33] along with the seven equations from the seven unknowns in the interpolation function are used to calculate the value of the unknowns. As can be seen in the above equations, a closed-form solution for the unknowns is not possible. This is a nonlinear system of equations which must be solved using appropriate nonlinear solution methods.

In an effort to test the effectiveness of this approach, the data presented in Figures 22 and 23 has been reanalyzed. The results are shown in Figures 24 and 25, respectively. Asterisks represent the second Weibull parameters calculated using Equations [17] and [19], and the solid lines represent the result using the interpolation function approach given in Equation [20]. As can be seen, for a well-behaved set of data, the approach is successful, allowing for calculation of the second Weibull parameters at any temperature in the interpolation range and over a carefully considered extrapolation range. The fit used for the data in the above figures consisted of only the constants A_0, A_1, K_1, K_2 , assuming the others to be zero.

Figure 22. ORNL Tensile Specimen Multitemperature Data, Volume Failure Mode.

Figure 23. Combined ORNL Tensile Specimen and MIL-B Specimen Multitemperature Data, Machined Surface Failure Mode.

Figure 24. Analysis of ORNL Tensile Specimen Multitemperature Data, Surface Failures (From Figure 22).

Figure 25. Analysis of Combined ORNL Tensile Specimen and MIL-B Specimen Multitemperature Data, Machined Surfaces Failures (From Figure 23).

5.4 Bootstrap Approach For Calculation Of Confidence Bounds For Weibull Parameters Of Multitemperature Data

Given that the Bootstrap method relies heavily on evaluation of the process to calculate the confidence intervals, the approach is better described on a step-by-step basis. The confidence limits of the Weibull parameters can be calculated simultaneously; both calculations are presented in this section.

a) The first step consists of estimating the Weibull parameters using the Maximum Likelihood method. The estimates are computed from Equations [34] and [35]:

$$\sigma_m = \left[\frac{1}{r_1} \sum_{k=1}^{n_1} [I_{k1} V_{k1} \sigma_{k1}^m] \right]^{1/m} \quad [34]$$

$$\frac{1}{m} = \frac{1}{\sum_{i=1}^j r_i} \sum_{i=1}^j \left\{ \sum_{k=1}^{n_i} \frac{r_i}{\sum_{k=1}^{n_i} [I_{ki} V_{ki} \sigma_{ki}^m]} [I_{ki} V_{ki} \sigma_{ki}^m + I_{ki} V_{ki} \sigma_{ki}^m \ln(\sigma_{ki})] - \sum_{i=1}^{n_i} \left[\frac{I'_{ki}}{I_{ki}} + \ln(\sigma_{ki}) \right] \right\} \quad [35]$$

b) Second, a random number between zero and one is chosen; this number is the selected reliability value, R . Do the same for each different temperature. The calculations for the different temperatures may be done at the same time, or for one temperature at a time. This is basically the only difference in the procedures between the multitemperature data and the regular pooled data approach developed during Phase I.

c) Next, select a specimen type from the original data set, with its corresponding V_i and I_i . Using the above $\hat{m}$ and $\hat{\sigma}_m$, compute the fracture strength of this pseudo specimen using Equation [36], given that it has the reliability equivalent to the value of the random number chosen in step (b):

$$\sigma_i = \hat{\sigma}_m \left(-\frac{\ln(R_{ii})}{\hat{I}_i V_i} \right)^{1/\hat{m}} \quad [36]$$

d) Repeat steps(b) and (c) for each specimen type and size a number of times equal to the number of specimens in the individual data set.

e) Calculate the Weibull parameters for this newly-generated data set using Equations [37] and [38] and save these values:

$$\tilde{\sigma}_m = \left[\frac{1}{\tilde{n}} \sum \tilde{I}_i V_i \sigma_i^{\tilde{m}} \right]^{1/\tilde{m}} \quad [37]$$

$$\frac{1}{\bar{m}} = \frac{1}{\sum_{i=1}^j r_i} \left\{ \sum_{k=1}^{n_i} \frac{r_i}{\sum_{k=1}^{n_i} [I_{ki} V_{ki} \sigma_{ki}^m]} [I'_{ki} V_{ki} \sigma_{ki}^m + I_{ki} V_{ki} \sigma_{ki}^m \ln(\sigma_{ki})] - \sum_{i=1}^j \left[\frac{I'_n}{I_n} + \ln(\sigma_n) \right] \right\} \quad [38]$$

f) Repeat steps (b) through (e) 1000 times.

g) Sort the $\tilde{m}$ and $\tilde{\sigma}_a$ pair(s) in ascending order for $\tilde{m}$ without losing the pair(s), and also for $\tilde{\sigma}_a$ without losing the pair(s).

h) To calculate the x th confidence interval, pick the $(100-x)(1000/2)(1/100)$ points from the upper and lower ends of the sorted values in step (g); these define the limits. For example: if the 95-percent confidence interval is required, substitute the number 95 for x to obtain 5, then multiply by the adjoining factor to get 25. Hence, the 95-percent confidence interval is given by the 25th point from the lowest and the 25th point from the highest of the sorted values $\tilde{m}$ and $\tilde{\sigma}_a$ in step (g).

5.5 Confidence Limits For The Design Stress Level

a) The design stress level can be obtained from the Weibull parameters calculated in Equations [37] and [38] by using Equation [39], where "p" is the desired probability of failure, V is the component volume and $\tilde{I}$ is the component multiaxial and stress gradient factor:

$$\sigma_p = \tilde{\sigma}_a \left[\frac{1}{\tilde{I}V} \ln \left(\frac{1}{1-p} \right) \right]^{1/m} \quad [39]$$

b) Given that we have a set of $\tilde{m}$ and $\tilde{\sigma}_a$ from the steps in Section 5.4, compute σ_p from Equation [39] for each one of these values and save them.

c) Sort the σ_p values and obtain the x th confidence interval by picking the $(100-x)(10/2)$ points from the upper and lower ends, using the same approach as in step 5.4(h).

5.6 Confidence Limits for the Reliability Prediction

a) Similarly to σ_p , the reliability, R, has a functional relationship to σ_a , given by Equation [40], where Z is the maximum stress level of the component, and $\tilde{I}$ and V are the component multiaxial and stress gradient factor and volume, respectively:

$$R(Z) = \exp \left[- \tilde{I}V \left(\frac{Z}{\tilde{\sigma}_a} \right)^{\tilde{m}} \right] \quad [40]$$

- b) Given the $\bar{m}$ and $\bar{\sigma}_m$ values from the steps in 5.1, substitute these values into Equation [7] to find a list of R's.
- c) Sort the R's and obtain the xth confidence interval by picking the (100-x)(10/2) points from the upper and lower ends, using the same approach as in step 5.4(h).

6.0 NDE Reliability

Samples of artificial defects, recommended to supplement the naturally-occurring discontinuity population, that were produced earlier under the Phase I program by Resonetics, Inc. (Nashua, NH) were evaluated by the AlliedSignal Engines Materials Laboratory. These simulated pits produced by excimer laser ablation were found to be satisfactory. The simulated pits measured a maximum material depth of 0.0787 inch and a minimum surface dimension of 0.0063 inch. However, the simulated cracks or linear indications were found to be too shallow in depth and too wide at the surface. For example, a nominal 0.020 inch long artificial flaw measured only 0.0041 inch deep and 0.0018 inch wide.

Destructive evaluation was conducted by AlliedSignal Engines on five additional specimens with laser-produced notches that were supplied by Resonetics, Inc. as a follow-on to the Task I destructive testing planned as part of the nondestructive evaluation probability of detection (NDE-POD) study. Resonetics was able to produce narrower notches than in the previous specimens, to serve as supplementary linear discontinuities in the POD specimens. The minimum surface width achieved appeared to be approximately 10 μm (0.0004 inch). The intent of the destructive evaluation of these additional laser-notched specimens was to verify the minimum specified notch width of 10 μm . Due to the narrowness of the notches, the depths were estimated by Resonetics by counting the laser pulses used to create the notches, with an expected width of 0.08 to 0.10 μm per pulse. The destructive evaluation results obtained are listed in Table 10.

TABLE 10. DESTRUCTIVE EVALUATION RESULTS OF LASER-NOTCHED SPECIMENS.

Specimen No.	Notch Length, μm	Notch Width, μm	Estimated Depth, μm	Actual Depth, μm
1	483	10	240 to 300	*
2	274	12.7	120 to 150	15
3	140	11.4	60 to 75	14
4	64	10	24 to 30	53
5	51	10	24 to 30	15

* = Polished through profile.

Note that the actual depths are much less than the estimated depths, with the exception of Specimen No. 4, which was greater than estimated. In discussions with Dr. A. Berens of the University of Dayton Research Institute (UDRI), only surface dimensions will be used for the NDE-POD study. Therefore, a defect is usable for the study so long as it contains penetrant for bleed-back during the inspection development process, i.e., not emulsified and washed out. From penetrant testing results on the Task I defects, the minimum depth should be 51 μm (0.002 inch). In Task II then, the goal will be to consistently produce indications of this minimum depth while maintaining a 10 or 25 μm width.

The estimated depths did not correspond to measurements from the destructive evaluations (sections). The narrow notch size is desirable for the POD study, due to the greater difficulty in detection visually, and also for reduced FPI penetrant volume. Work is continuing with Resonetics to produce narrow notches of reliable depth.

As a potential worst-case situation, it may be necessary to destructively evaluate the notch dimensions at the conclusion of the POD study.

The set of 55 machined surface Probability of Detection (POD) specimens have undergone fluorescent penetrant inspection (FPI) with Level 4 sensitivity, post-emulsified penetrant. The indications were documented as to location, maximum surface dimensions, and flaw type per ASTM Specification F109. Documentation has been completed of the FPI indications on all the specimens planned for the NDE-POD test objective. Dr. Berens of UDRI has entered this data into a computer spreadsheet to facilitate making recommendations for supplementing the naturally-occurring discontinuity population in the specimens. In general, the data shows that there is a shortage of linear discontinuities in the specimens.

Publications

1. D.C. Wu, A.D. Peralta, M.N. Menon, and J.C. Cuccio, "Subcritical Crack Growth Life Prediction for Ceramic Components of Advanced Heat Engines," ASME paper 95-GT-236, American Society of Mechanical Engineers, 1995.
2. A.D. Peralta, D.C. Wu, P.J. Brehm, J.C. Cuccio, and M.N. Menon, "Strength Prediction of Ceramic Components Under Complex Stress States," ASME paper 95-GT-394, American Society of Mechanical Engineers, 1995.

Acknowledgments

We would like to extend our appreciation to Dr. A.A. Wereszczak of the Oak Ridge National Laboratories High Temperature Materials Laboratory (ORNL-HTML) Mechanical Property User Center for the help he has extended to AlliedSignal Engines in the tensile testing of CLP NT154 specimens, and commend his success in establishing an excellent compressive creep testing facility at HTML, where the specimen tests for the compressive creep tasks of this program are being performed.

References

- (1) J.C. Cuccio, et. al., "Life Prediction Methodology For Ceramic Components Of Advanced Heat Engines Phase I Final Report, Contract No. 86X-SC674C," DOE/ORNL Report No. ORNL/Sub/89-SC674/1/V1&V2, 1995; (AlliedSignal Report No. 31-11591 (Two Volumes), AlliedSignal Engines, Phoenix, AZ March 1, 1994).
- (2) D.C. Salmon, Ph.D. Thesis, Dept. of Mechanical Engineering, U. of Utah, Salt Lake City, UT 1992.

3.3 ENVIRONMENTAL EFFECTS

3.3 ENVIRONMENTAL EFFECTS

Environmental Effects in Toughened Ceramics*

N. L. Hecht (University of Dayton)

Objective/scope

Since December 1984, the University of Dayton has been involved in a project to investigate the effects of environment on the mechanical behavior of ceramics being considered for heat engine applications. In the first phase of this project, the effects of environment on the mechanical behavior of transformation-toughened ZrO_2 ceramics were investigated. In subsequent phases, Si_3N_4 and SiC ceramic were evaluated. Tensile, flexural, and fatigue strength of the SiC and Si_3N_4 ceramics were evaluated at temperatures ranging from 20 to 1400°C. Microstructure, chemistry, and physical properties were also investigated. In the current phase, newly developed or enhanced SiC and Si_3N_4 ceramics are being investigated. In addition, the effects of different machining processes on the mechanical behavior of selected $\text{SiC}/\text{Si}_3\text{N}_4$ ceramics are being studied.

Technical progress

During the past six months of the project, the mechanical behavior of Carborundum's Hexoloy SA, Allied Signal's AS-800, and Ceradyne's Ceralloy 147-3 were investigated. Flexural, tensile, and fatigue properties from 20 to 1350°C were measured. The flexural strength was measured using B-type test bars following ASTM C-1161 in an Instron Model 5500R123. All of the tensile property measurements were made using buttonhead specimens in an Instron 8561 with supergrips and a high-temperature short furnace. Elastic modulus was measured using a Grindo-sonic (Model MR35T) Transient Impulse Elastic Modulus Apparatus. In addition, the effects of machining methods on the mechanical behavior of Hexoloy SA and Kyocera SN-252 were investigated. The status of the workscope tasks are outlined below:

1. Investigation of the 1994/95 vintage AS-800 has been completed.
2. Investigation of the new generation Hexoloy SA will be completed with the measurement of fracture toughness at 20°C, 1150°C, and 1350°C.
3. Investigation of Ceralloy 147-3 is in progress and will be continued.
4. Investigation of Golden Technologies' RBSN tubes and MgO PSZ rods will be initiated shortly.

5. Investigation of the effects of machining on the flexural strength of Hexoloy SA and SN-252 will be continued. Ultrasonic machined specimens will be investigated, and the effects of oxidation treatment on the SN-252 flexural specimens will be studied. Raman microprobe and SEM evaluations of the machined specimens will also be continued.
6. As part of a project renewal, the thermal mechanical behavior of new vintage (1996) AS-800 Si_3N_4 and Norton NT-551 SiAlON will be initiated this winter (1996).

AS-800

The results of the flexural and tensile strength measurements are summarized in Figure 1, and the tensile stress rupture behavior is summarized in Figure 2. The step stress and step temperature ITSR are summarized in Table 1.

Hexoloy SA (new vintage)

The results of the flexural and tensile strength measurements are summarized in Figure 3. The Interrupted tensile stress rupture results are compiled in Table 2 and the tension-tension cyclic fatigue behavior are compiled in Table 3. The Young's modulus measured versus temperature is plotted in Figure 4.

Figure 1. Comparison of Flexural and Tensile Strength for AS-800.

Figure 2. Tensile Stress Rupture for AS-800 .

Table 1. Step Stress and Step Temperature ITSR of AS-800

Specimen Number	Temperature (°F)	Stress Level (MPa)	Time (hours)	Residual Tensile Strength (MPa)	Fracture Origin
S94-0520-3 #3	2000	146	100	530	?
	2000	219	24		
	2000	291	24		
S94-0514-2 #5	2300	146	100	458	Volume
	2300	219	24		
S94-0514-1 #4	2300	100	72		?
	2300	146	24		
	2400	146	40.5		
S940-354-1 #17	2300	100	72		?
	2300	146	24		
	2400	146	9.2		
S94-0519-1 #15	2300	146	100		?
	2300	219	0.7

Figure 3. Comparison of Flexural and Tensile Strength for Hexoloy SA.

Table 2. Summary of the Tensile Fatigue Results for Hexoloy SA

Specimen Number	Lifetime	Failure Origin
72	25 min	near surface
25	22 min	near surface (large grain)
35	99 hrs (test duration)*	surface

*After surviving 99 hours the specimen was loaded to failure @ 100 MPa/s and failed at 467 MPa.

**Table 3. Tension-Tension Cyclic Fatigue Test Results
Carborundum Hexoloy SA**

3(A): Test Conditions
 Temperature: 1000°C
 Atmosphere: Air
 Stress Level: ± 106 MPa
 Mean Level: 130 MPa
 R: 0.1
 Frequency: 1.25 Hz

Specimen Number	Cycles Completed	Diameter (in)	Load (lbs)	Residual Tensile Strength		Fracture Origin
				(ksi)	(MPa)	
15	450,000	0.2503	3,499	71.1	490	?
40	450,000	0.2505	3,089	62.3	429	Volume
44	450,000	0.2531	2,646	52.6	363	Volume
53	450,000	0.2501	3,222	65.6	452	Volume
30	450,000	0.2529	3,139	62.5	431	Volume
			Avg.	62.8	434	

Note: No fracture origin could be identified for specimen #15

3(B): Test Conditions
 Temperature: 1350°C
 Atmosphere: Air
 Stress Level: ± 96 MPa
 Mean Level: 118 MPa
 R: 0.1
 Frequency: 1.25 Hz

Specimen Number	Cycles Completed	Diameter (in)	Load (lbs)	Residual Tensile Strength		Fracture Origin
				(ksi)	(MPa)	
32	450,000	0.2502	3,367	68.5	472	?
49	450,000	0.2504	2,810	57.1	393	Surface
45	429	0.2780	---	---	---	---
62	450,000	0.2505	3,807	77.4	534	?
102	450,000	0.2499	2,912	59.4	409	Surface
			Avg.	65.6	467	

Notes: Fracture origins for specimens 32 and 62 could not be determined. Specimen 45 failed prematurely.

Figure 4. Young's Modulus vs Temperature for Hexoloy SA.

Ceralloy 147-3

The flexural and tensile strength measurements of Ceralloy 147-3 have been initiated. Room temperature flexural strength measurements at 500 and 0.1 MPa/s have been made and tensile strength measurements at 20°C, 1150°C, and 1250°C have also been made. The results of these strength measurements are summarized in Figures 5 and 6, respectively.

A comparison of the flexural and tensile strengths obtained for the different ceramics evaluated in this phase of our project are presented in Figures 7 and 8.

Figure 5. Flexural Strength for Ceradyne Ceralloy 147-3.

Figure 6. Tensile Strength of Ceradyne Ceralloy 147-3.

Figure 7. Comparison of Flexural Strength.

Figure 8. Comparison of Tensile Strength.

Machining Studies

An investigation of machining effects on the mechanical behavior of Hexoloy SA SiC, and SN-252 Si₃N₄ was initiated. The effect of transverse grinding, grinding the tensile surface at a 15° bias, 24 hour surface heat treatment, creep feed grinding at 88.8 and 25.4 mm/min feed rates, and exposure of the machined specimens to 500 hours oxidation at 1400°C on the flexural strength of Hexoloy SA was investigated. The baseline flexural specimens were final ground in the longitudinal (parallel) direction using a 320 grit abrasive wheel following ASTM C1161. The average flexural strengths measured for the different machining treatments are presented in Table 4. From the results shown in Table 4, it would appear that neither the 15° bias grinding nor the creep feed grinding had much effect on the flexural strength compared to the baseline treatment. Specimens ground in the transverse direction had a strength reduction of ~30%. The heat treated and oxidized specimens showed ~10% strength improvement.

Table 4. Flexural Strength of Hexoloy SA as a Function of Different Machining Methods

Machining Methods/ Treatments	Loading Rate (MPa/s)	Specimens Tested	Average Flexural Strength (MPa)	Std. Deviation (MPa)	Weibull Modulus
Baseline grind (320 grit)*	100	13	377	±50	10
Baseline grind (320 grit)*	0.1	10	372	±36	13
Perpendicular grind (320 grit)	100	16	261	±25	14
Bias Grind 15°	100	11	387	±18	27
Bias Grind 15°	0.1	10	372	±39	15
Heat Treated Baseline Grind†	100	20	418	±25	17
Heat Treated Baseline Grind†	0.1	9	410	±31	14
Oxidized Baseline Grind‡	100	8	405	±28	20
Oxidized Bias Grind 15°§	100	8	410	±57	9
Creep feed grind 88.9 mm/min	100	13	369	±42	12
Creep feed grind 88.9 mm/min	0.1	10	367	±45	16
Perpendicular creep grind 88.9 mm/min	100	16	289	±59	6
Oxidized creep feed grind 88.9 mm/min¶	100	8	403	±24	18
Creep feed grind 25.4 mm/min	100	12	371	±41	11
Creep feed grind 25.4 mm/min	0.1	10	392	±24	19
Perpendicular creep feed grind 25.4 mm/min	100	15	268	±66	5
Oxidized creep feed grind 25.4 mm/min¶	100	8	392	±21	21

*Almost all specimens failed from surface-initiated flaws.

†Baseline grinding followed ASTM C1161.

‡Heat treatment @ 1250°C for 24 hours.

§Oxidation exposure 500 hrs @ 1400°C.

¶Oxidation exposure 500 hrs @ 1400°C.

Two specimens baseline ground, two ground at a 15° bias, two creep feed ground at 88.8 mm/min, and two ground at 25.4 mm/min were studied with the Raman microprobe. The Raman microprobe procedures used to measure primary peak shifts and peak broadening have been described previously. Peak broadening is attributed to an increase in microsurface strain. Peak shifting is a measure of the macro-surface strain in the tensile or compressive mode. The Raman microprobe results for the machined Hexoloy SA flexural specimens are presented in Table 5.

These interim results indicate greater compressive residual surface strain in the baseline machined specimens than for the 15° bias grind or the two creep feed ground specimens. In subsequent efforts, the Raman microprobe will be used to investigate an as-sintered specimen and a very highly polished Hexoloy SA specimen. It is anticipated that the spectra from these two Hexoloy SA specimens should provide a better basis for evaluating residual strain in the machined specimens.

Table 5. Raman Microprobe Results for the Change in Line Position and Line Width for the Three Primary Hexoloy SA Peaks

A. Hexoloy SA SiC 767.55 Raman Line

Specimen	Change in Position	Width
Baseline #1	767.55 ± 0.03	5.72 ± 0.09
Baseline #2	767.44 ± 0.02	5.27 ± 0.08
15° Bias #1	767.47 ± 0.02	5.20 ± 0.08
15° Bias #2	767.34 ± 0.02	5.32 ± 0.08
Creep Feed 88.9 mm/min	767.12 ± 0.01	4.44 ± 0.05
Creep Feed 88.9 mm/min	767.19 ± 0.02	4.59 ± 0.06
Creep Feed 24.5 mm/min	767.16 ± 0.02	4.57 ± 0.06
Creep Feed 24.5 mm/min	767.14 ± 0.02	4.43 ± 0.06

B. Hexoloy SA SiC 788.334 Raman Line

Specimen	Change in Position	Width
Baseline #1	788.334 ± 0.004	5.27 ± 0.01
Baseline #2	788.367 ± 0.004	5.27 ± 0.01
15° Bias #1	788.364 ± 0.004	5.20 ± 0.01
15° Bias #2	788.260 ± 0.004	5.31 ± 0.01
Creep Feed 88.9 mm/min	788.141 ± 0.002	4.597 ± 0.008
Creep Feed 88.9 mm/min	788.144 ± 0.003	4.78 ± 0.01
Creep Feed 24.5 mm/min	788.239 ± 0.003	4.68 ± 0.01
Creep Feed 24.5 mm/min	788.086 ± 0.003	4.64 ± 0.01

Table 5. Raman Microprobe Results for the Change in Line Position and Line Width for the Three Primary Hexoloy SA Peaks (concluded)

C. Hexoloy SA SiC 797.67 Raman Line

Specimen	Change in Position	Width
Baseline #1	797.67 $\pm$ 0.01	4.74 $\pm$ 0.04
Baseline #2	797.68 $\pm$ 0.01	4.64 $\pm$ 0.04
15° Bias #1	797.67 $\pm$ 0.01	4.54 $\pm$ 0.04
15° Bias #2	797.61 $\pm$ 0.01	4.52 $\pm$ 0.04
Creep Feed 88.9 mm/min	797.431 $\pm$ 0.007	3.88 $\pm$ 0.02
Creep Feed 88.9 mm/min	797.396 $\pm$ 0.009	4.07 $\pm$ 0.03
Creep Feed 24.5 mm/min	797.3424 $\pm$ 0.008	4.00 $\pm$ 0.03
Creep Feed 24.5 mm/min	797.370 $\pm$ 0.008	3.91 $\pm$ 0.03

The effects of transverse grinding, grinding at a 15° bias, and creep feed grinding at 88.9 mm/min feed rate were also investigated on the flexural strength of specimens from a Kyocera SN-252 spin disc. The average flexural strength measured for the different machining methods are presented in Table 6.

Table 6. Flexural Strength Measured for SN-252 Specimens Machined by Different Methods

Machining Methods/ Treatments	Loading Rate (MPa/s)	Specimens Tested	Average Flexural Strength (MPa)	Standard Deviation (MPa)	Weibull Modulus
Baseline grind (320 grit)*	100	14	750	$\pm$ 48	17
Baseline grind (320 grit)*	0.1	10	698	$\pm$ 83	9
Perpendicular grind (320 grit)	100	15	753	$\pm$ 58	14
Bias Grind 15°	100	4	816	$\pm$ 39	27
Bias Grind 15°	0.1	4	683	$\pm$ 44	19
Creep feed grind 88.9 mm/min	100	5	773	$\pm$ 57	14
Creep feed grind 88.9 mm/min	0.1	5	742	$\pm$ 81	10

3.4 FRACTURE MECHANICS

TESTING AND EVALUATION OF ADVANCED CERAMICS AT HIGH TEMPERATURE

J. Sankar, A. D. Kelkar, V. Vijayrao, and S. Sudarshan (Department of Mechanical Engineering, North Carolina A & T State University, Greensboro, NC 27406).

Objective/Scope

Technical Highlights

During this reporting period, creep tests were performed on GS-44 silicon nitride material. The testing temperatures were 1100 °C and 1200 °C. The test was also performed for different loading conditions, namely 80mpa, 100MPa and 120MPa. Creep curves were generated from the tests for this material system (creep strain vs time for the given load). The creep curves are shown in Figure 1. Further, some tests were stopped during the secondary creep stage and were tested for tensile residual strength. All the residual strength tests were carried out at room temperature.

During this reporting period, some samples were thermally soaked at 1200°C. The samples were soaked for the same time as the creep tests. After the completion of the thermal soaking, the samples were tested for tensile residual strength at room temperature. The above process allows us to study the effect of creep at high temperature on the residual tensile strength of the material. The soaking time was varied between 32hrs and 217hrs. Stress vs Strain plots were generated from the data obtained. The test conditions and the residual strengths at room temperature are shown in Table 1. The stress vs strain tensile residual strength plots of both, thermally soaked and creep tested samples are shown in Figure 2.

Comparison Of Residual Strengths For GS-44(Si₃N₄) Under Different Conditions		
Room Temp Strength		= 631MPa
Strength @ 1200C		= 450MPa
Condition		Residual Strength @ Room Temp(MPa)
1	Creep : 1100C, 100MPa - 217hrs	472.121
2	Creep : 1200C, 100MPa - 32hrs	525.781
3	Thermal Soaking : 1200C -32hrs	487.488
4	Thermal Soaking : 1200C -108hrs	531.372

Microstructural Characterization

The microstructure of the tensile tested, creep tested, and thermally soaked tensile tested specimens were studied using field emission scanning electron microscopy (SEM) and optical microscopy. The sections of tested material were polished and then etched in a molten Sodium Hydroxide (NaOH) bath at 673K for 15-25 seconds. This etching procedure removes the grain boundaries, so that the grains can be seen clearly in the SEM. For SEM analysis the specimens were cut and polished in a Buheler Minimet Polisher using 3,1, and 0.5 μm diamond paste. The micrograph of a polished and etched surface of a creep tested specimen at 1200 °C and 100 MPa is shown in Figure 3a . The TEM analysis of the samples are due to be performed.

RESULTS AND DISCUSSION

Creep tests were performed at different loads. Figure 1 shows the creep strain vs time at 1200 °C and 120 MPa, 100 MPa, and 80 MPa of GS44. As can be seen from the graph one of the specimen which was tested at 1200 °C and 100 MPa broke in 5hrs. This clearly shows that the properties of GS44 varies from specimen to specimen. The fracture surface of the creep tested sample at 100 MPa and 1200 °C is shown in Figure 3b . As can be seen from figure 3b, due to a slower strain rate the fracture surface is smooth and even. The fracture initiation site of GS44 which was tested at 1200 °C and 100 MPa can be clearly seen from Figure 3c . The GS-44 sample which was exposed to a constant load of 120 MPa at 1200 °C exhibited a much higher strain rate than the one at 100MPa. Thermal soaking of the samples at the same temperature and time allows us to study the effect of creep on the room temperature residual strength. Based on the few tests performed, it was observed that the sample that had undergone creep (1200 °C, 32hrs, 100MPa) had a higher room temperature residual strength than the thermally soaked sample (1200 °C, 32hrs). More tests need to be performed to verify the above.

Status of Milestones

On schedule

Communications/Visitors/Travel

None

Publications**Accepted for publication:**

J.Sankar, A.D.Kelkar, J.Neogi. "Fatigue, Creep and Fracture Behavior of Silicon Nitride Ceramics." ASME Winter Annual Meeting, San Francisco, Nov. 1995.

Problems Encountered

1. Some difficulties were encountered in accessing the data (time vs elongation) generated by the existing creep test program. This problem was however modified to provide easy access to the data.

Figure 1
Creep Strain ($\mu\text{m/m}$) Vs Time (hrs), at 1200 C for GS44

Figure 2

Figure 3a. Micrograph (400X) of a polished and etched cross-section of a creep tested specimen at 1200 °C and 100 Mpa.

Figure 3b. Fracture surface of a creep tested specimen at 1200 °C and 100 Mpa

Figure 3c. Fracture initiation site of a creep tested specimen at 1200 °C and 100 MPa

Standard Tensile Test Development

S. M. Wiederhorn, R. F. Krause, Jr., W.E. Luecke and J.D. French
(National Institute of Standards and Technology)

Objective/Scope:

This project is concerned with the development of test equipment and procedures to determine the tensile strength and creep resistance of ceramic materials at elevated temperatures. Inexpensive techniques for measuring the creep behavior and strength of structural ceramics have been developed and are being used to characterize the mechanical behavior of these materials. The ultimate goal of the project is to help develop a data base and a test methodology for the structural design of heat engines for vehicular applications.

Technical Highlights:

Small Specimen Development - As structural ceramics enter the marketplace for components in heat engines, it will be necessary to test their high-temperature mechanical properties to assure quality control and ascertain remaining lifetime. This work introduces three different flat, single-reduction tensile specimens suitable for high-temperature creep-testing of material from ceramic components. The overall lengths of these specimens are 30 mm, 50.8 mm and 76.2 mm, which we designate as SR30, SR51 and SR76, SR signifying the single-reduction, or uniform thickness, design. The two smaller specimens are improvements in design over earlier geometries used in our laboratory [1, 2, 3, 4]. The SR51 is designed for creep and static fatigue tests of experimental grades of material and larger ceramic components. The SR30 specimen is small enough to be cut from very small batches of material, or from complex ceramic components, such as turbine blades and stator vanes. The SR76 specimen is a modification of a specimen developed earlier at Norton Company [5] for creep and strength measurements of silicon nitride. We have used the SR76 for strength, static fatigue and creep behavior studies [6]. Specimen validation was carried out on a single lot of a commercial grade of silicon nitride, SN88 (NGK Insulator, Japan), that, in our experience, gives very reproducible creep results on an individual specimen type. This grade of Si_3N_4 also is relatively unaffected by long exposures in air at high temperatures.

Experimental Details - The three specimen geometries, illustrated in Figure 1, are compromises between the longest possible gauge length, which decreases the gauge length measurement uncertainty [7], and the shortest possible specimen length, which maximizes the number of specimens. The SR76 specimen has a 19 mm gauge length and can be used for tensile strength, static fatigue and creep measurements. Frequently, however, experimental batches of material are not large enough to accommodate the SR76 specimen. The SR51 is a compromise between a long gauge length, 12 mm versus 19 mm, and a large number of specimens. We designed a small

specimen, the SR30, with which to measure creep and static fatigue of materials from ceramic components and very small batches of experimental materials.

dimensions are in millimeters

Figure 1 The three single-reduction, flat tensile specimens.

Table I. Characteristics of the three tensile specimen geometries.

Specimen	Gauge length (mm)	Gauge area (mm ²)	Gauge volume (mm ³)	Specimen length (mm)	Neck stress concentration [§] (%)
SR30	8.0	3.0	24	30	8.2
SR51	12.0	5.0	60	50.8	6.1
SR76	19.0	6.5	123	76.2	3.7

[§]Neck stress concentration = [(maximum stress in neck)/(stress in gauge)] - 1

Two-dimensional finite element modelling (FEM) was used to optimize the designs for the SR51 and SR30 specimens, using a PC-based, commercial software package (Strand6, G+D Computing, Ultimo NSW, Australia). A database already existed on the SR76 specimen, so we made no modifications to that design. Simply scaling the SR76 specimen smaller to arrive at the SR51 and SR30 specimens made the gauge cross-section prohibitively small from both machining and handling standpoints. We fixed gauge width of the SR51 at 2.0 mm the SR30 specimen at 1.5 mm in the 2-D FEM simulations and used the following constraints for the optimization: maximum gauge length, fixed specimen length, and minimum stress concentrations at the ends of the

gauge length and at the loading holes. The specimen thickness was also increased, from a square cross-section, to increase the load-bearing capacity of the heads. The gauge dimensions and stress concentration at the ends of the gauge (the "neck") are shown in Table I. The results of the FEM calculations were verified by successively refining the mesh size. A convergence test on the mesh resulted in <1% change in the calculated stress in the neck.

Creep Tests - Two experimental conditions were chosen for the specimen comparison: 1400 °C and 150 MPa; 1300 °C and 250 MPa. Each test condition was replicated five times with each specimen geometry. Single experiments were also performed at higher stresses to test the limits of the specimen geometries. Each specimen was equilibrated in the testing furnace for 20 hours prior to the application of the load to attain thermal stability in the testing furnace. For each experiment, the minimum creep rate was determined graphically from the strain versus time data.

Table II. Creep parameters and their standard deviations generated from the five tests at each condition with each of the three tensile specimen geometries.

Condition, Specimen	$\dot{\epsilon}_{min}$ (1/s)	(ϵ_p) (%)	t_f (hr)	$t_{1\%}$ (hr)
1400 °C				
150 MPa				
SR30	$(7.12 \pm 0.42) \times 10^{-3}$	2.73 ± 0.36	84.3 ± 10.1	29.7 ± 3.2
SR51	$(7.85 \pm 0.52) \times 10^{-3}$	2.59 ± 0.26	76.8 ± 10.1	26.1 ± 1.3
SR76	$(7.29 \pm 0.32) \times 10^{-3}$	2.60 ± 0.28	83.6 ± 8.4	28.3 ± 1.9
1300 °C				
250 MPa				
SR30	$(4.15 \pm 0.37) \times 10^{-3}$	1.78 ± 0.15	89.8 ± 6.2	53.5 ± 2.8
SR51	$(3.67 \pm 0.38) \times 10^{-3}$	1.68 ± 0.10	98.6 ± 11.5	59.0 ± 6.0
SR76	$(3.47 \pm 0.50) \times 10^{-3}$	1.56 ± 0.23	95.2 ± 6.4	61.7 ± 7.3

Creep tests were performed using test procedures described earlier [2, 7]. The specimen is gripped in the hot zone using a pin-and-clevis arrangement. The 3.5 mm diameter pins for the SR30 specimens were made from silicon nitride, either NCX-5102 (Saint Gobain/Norton Industrial Ceramics Corp., Northboro, MA) or SN88. The 4.7 mm diameter pins for the SR51 and SR76 specimens were Hexoloy-SA SiC (Carborundum Co., Niagara Falls, NY) for the 1400 °C tests and NCX-5102 silicon nitride for the 1300 °C tests. At 1400 °C the Si₃N₄ pins deformed during the test, which prevented their reuse.

Figure 2 Creep curves generated at 1400 EC, 150 MPa with the three specimens, five replicated tests with each specimen geometry.

Figure 3 Creep curves generated at 1300 EC, 250 MPa with the three specimens, five replicated tests with each specimen geometry.

Results & Discussion - The results of the two test conditions are presented graphically in Figures 2 and 3. The creep curves are plotted together to illustrate the consistency of the data. Important creep parameters, minimum creep rate ($\dot{\epsilon}_{min}$), failure strain (ϵ_f), failure time (t_f), time to 1% strain ($t_{1\%}$), and their respective standard deviations are given in Table II. An analysis of variance (ANOVA) for a 95% confidence level using a commercially available software package (QUATTRO Pro 5.0, Borland International, Inc, Scotts Valley, CA) shows that the creep parameters do not depend on the specimen geometry, see Table III. Unreplicated tests at higher stresses, such as 300 MPa or 350 MPa, indicated that the agreement between the three specimens at the higher stresses was similar to that of the replicate tests at 250 MPa and 150 MPa.

This study and other studies in our laboratory have shown that the stress limits of these specimens at any temperature were determined by the strength or slow crack growth resistance of the loading pins, and not by the failure at the loading holes. The 250 MPa experiments on the SR30 specimens had to be done with SN88 pins, because the NCX-5102 was too susceptible to slow crack growth, which lead to failure of the pin during the creep test. We conducted successful creep tests at 350 MPa on the SR30 with SN88 pins and 400 MPa on the SR51 and SR76 with NCX-5102 pins. We conducted successful strength tests as high as 710 MPa at room temperature using the SR76 specimen with steel pins, and static fatigue tests at 525 MPa at 800 °C with MAR-M246 Superalloy pins and pullrods without failure of the loading holes. For creep and static fatigue test at higher temperatures (>800 °C) where the Superalloy pins deform, it is necessary to enlarge the loading hole and the pin diameter to 6.35 mm (1/4 inch), to decrease the stress in the loading pins, and use silicon nitride or silicon carbide pins. Because we have conducted successful strength, static fatigue and creep tests at the full range of temperatures and stresses, we have adopted the 6.35 mm diameter loading holes for all tensile testing with the SR76 specimen.

Table III. ANOVA results for the creep parameters generated from the three different specimen geometries for a 95% confidence interval.

Creep Parameter	1400 °C, 150 MPa		1300 °C, 250 MPa		F-critical
	P-value [†]	F statistic [‡]	P-value	F statistic	
$\dot{\epsilon}_{min}$	0.060	3.594	0.067	3.411	3.885
ϵ_f	0.746	0.300	0.147	2.263	3.885
t_f	0.414	0.950	0.288	1.382	3.885
$t_{1\%}$	0.076	3.221	0.109	2.687	3.885

[†]P-value is the observed significance level of the F statistic. If the P-value is greater than the 0.05 set for the significance test (95% confidence), the data sets are statistically indistinguishable.

[‡]F statistic is the ratio of the between-samples variation to the within-sample variation. If the F-statistic is less than F-critical, the data sets are statistically indistinguishable.

Summary - The SR30, SR51 and SR76 tensile specimens have been validated using a well-behaved grade of silicon nitride. We have shown that useful creep and creep rupture data can be generated with small tensile specimens. Such tests are useful for characterizing small batches of experimental materials or for quality control and life assessment of ceramic components.

References:

1. D.F. Carroll and S.M. Wiederhorn, "High Temperature Creep Testing of Ceramics," *Int. J. High Technology Ceramics*, **4**, 227-241 (1988).
2. D.F. Carroll, S.M. Wiederhorn and D.E. Roberts, "Technique for Tensile Creep Testing of Ceramics," *J. Am. Ceram. Soc.*, **72**, 1610-14 (1989).
3. S.M. Wiederhorn, R.J. Gettings, D.E. Roberts, C. Ostertag and J.J. Petrovic, "Tensile Creep of Silicide Composites," *Mat. Sci. Engr.*, **A155**, 209-215 (1992).
4. J.D. French, S.M. Wiederhorn and J.J. Petrovic, "Creep Rupture of $\text{MoSi}_2/\text{SiC}_p$ Composites," *Mat. Res. Soc. Symp. Proc.*, **322**, 203-208 (1994).
5. J.A. Wade, C.S. White and F.J. Wu, "Predicting Creep Behavior of Silicon Nitride Components Using Finite Element Techniques," pp. 360 - 373 in **Life Prediction Methodologies and Data for Ceramic Materials**, ASTM STP 1201, Eds. C.R. Brinkman and S.F. Duffy, ASTM, Philadelphia, 1994
6. J.D. French, R.F. Krause, W.E. Luecke and S.M. Wiederhorn, unpublished work.
7. W.E. Luecke and J.D. French, "Sources of Strain Measurement Uncertainty in Flag-Based Extensometry," *J. Am. Ceram. Soc.*, Submitted, 1995.

Lectures Presented and Meetings Attended:

W.E. Luecke, "Creep and Cavitation of Structural Ceramics," presented at General Electric Central Research and Development Laboratory, Schenectady, NY, April 10, 1995.

Sheldon M. Wiederhorn, William E. Luecke, B.A. Fields and J.D. French, National Institute of Standards and Technology, Gaithersburg, MD 20899, "Damage Generation in Ceramics at High Temperature," Presented at the Institute for Mechanics and Materials Workshop on Rational Design and Processing of Advanced Ceramics, June 21-23, 1995, University of California San Diego, La Jolla, CA

S.M. Wiederhorn and W.E. Luecke, National Institute of Standards and Technology, Gaithersburg, MD 20899, "Dilational Creep Silicon Nitride and Silicon Carbide,"

presented at the 97th Annual Meeting of the American Ceramic Society, April 30-May 3, 1995.

Visits:

Solar Turbines - June 20, 1995, to discuss their ceramic turbine program. I presented a discussion of the work for the Department of Energy.

Publications:

S.M. Wiederhorn and W.E. Luecke, "The importance of cavitation to the creep of structural ceramics," to be published in the proceedings of the symposium on *Plastic Deformation of Ceramics*, Sponsored by the Engineering Foundation, Snowbird, Utah, August 7-12, 1994.

Sheldon M. Wiederhorn, Jonathan D. French and William E. Luecke, "High-Temperature Reliability of Structural Ceramics," pp. 145-155 in 5th International Symposium on *Ceramic Materials and Components for Engines*, D.S. Yan, X.R. Fu and S.X. Shi eds., World Scientific Publishing Co., Singapore (1995).

S.M. Wiederhorn, J.D. French and W.E. Luecke, "A Comparison of Fracture Mechanism Maps with the Larson-Miller Method of Predicting Lifetime," *Ceram. Eng. and Sci. Proc.* **16**[5] 691-8 (1995).

W.E. Luecke, S.M. Wiederhorn, B.J. Hockey, R. Krause, Jr. and G.G. Long, "Cavitation Contributes Substantially to Tensile Creep in Silicon Nitride," *J. Am. Ceram. Soc.* **78**[8] 2085-96 (1995).

B.A. Fields and S.M. Wiederhorn, "Creep Cavitation in a Siliconized Silicon Carbide Tested in Tension and Flexure," *J. Am. Ceramic Soc.*, Submitted.

W.E. Luecke and J.D. French, "Sources of Strain Measurement Uncertainty in Flag-Based Extensometry," *J. Am. Ceramic Soc.*, Submitted.

J.D. French and S.M. Wiederhorn, "Tensile Specimens from Ceramic Components," *J. Am. Ceram. Soc.*, Submitted.

3.5 NONDESTRUCTIVE EVALUATION DEVELOPMENT

Nondestructive Characterization

S. A. David (Oak Ridge National Laboratory)

Objective/Scope

The purpose of this program is to conduct nondestructive evaluation (NDE) development directed at identifying approaches for quantitative determination of conditions (including both properties and flaws) in ceramics that affect the structural performance. Those materials that have been seriously considered for application in advanced heat engines are all brittle materials whose fracture is affected by structural features whose dimensions are on the order of the dimensions of their microstructure. This work seeks to characterize those features using high-frequency ultrasonics and radiography to detect, size, and locate critical flaws and to measure nondestructively the elastic properties of the host material.

Technical Progress

Ultrasonics - W. A. Simpson, Jr.

We continue to receive requests from various manufacturers of ceramic parts to assist in evaluating the quality of their product. One recent request involved a number of ceramic disks fabricated from alumina and having slightly different chemistries and processing history. The concern was for cracking in the disks; accordingly, the specimens were evaluated using high-frequency (50-MHz) surface acoustic waves. Such a wave is extremely sensitive to cracks regardless of their orientations on the part. The samples were examined visually before testing to determine whether gross cracking might be present. No such defects were found, but it was noted that many of the samples had slightly different colors and surface appearance, presumably because of the fabrication differences.

Figure 1 shows the result obtained on thirty-three of the disks scanned in a single batch. The dark features near the edge of many of the disks are numerical identification etched into the disk for identification purposes. Many of these numbers were very difficult to detect visually but were easily discernable in the ultrasonic surface wave image. The dark semicircular features at the edges of some of the disks - e.g., the first in the third row, the first and third in the fourth row, and the first and last in the last row - are cracked areas, regions where conchoidal fractures occurred, probably as a result of beveling of the edge. In some cases, material had actually broken from the sample, leaving the rough fracture surface. Many of the disks also had smaller areas of edge fracture on one or both faces. No evidence of body cracking was seen.

The missing upper portion in the image of the fourth sample in the top row was traced to a manufacturing defect; this sample had an anomalous thickening in the affected area, causing the surface wave to be lost because of nonnormal incidence of the ultrasonic energy.

One interesting characteristic of all of the images was the varying intensity displayed for the different samples. All the specimens in a given row have undergone the same processing history and presumably have the same chemistry. The samples of rows two, three, and six produced very bright images, while those in rows one and four were noticeably darker. This difference is not simply a result of changing acoustic impedance in these samples, nor is it caused by changes in the surface wave velocity, for this wave was seen to occur at the same point in time

for all samples. The surface wave amplitude was simply smaller for these samples. This behavior is consistent for differing surface roughnesses, but no such difference could be detected visually. It may also be attributable to grain size or microvoid density, but we have no data to support this conjecture. At this point, we do not know the cause of differing sample brightness.

Figure 2 shows an enlargement of one of the samples (last on the right in the second row) and shows more detail. The dark pointlike indication, which can just be seen in figure 1, is a subsurface void. The other indications appear to be surface grinding marks, though we could not see these marks visually.

These disks appear to be of very high quality, having very few detectable voids and no discernable cracking. Other than the average image brightness produced by a given disk, which in this case cannot be correlated with detectable flaws, there were no observable differences in sample quality.

We continue to press the development of nonlinear elastic wave techniques for the characterization of damage in structural ceramics. Although extremely promising, nonlinear techniques are difficult to implement because of the high power levels involved. This makes it necessary to couple as much of the available power as possible into the transducer. At or near resonance, piezoelectric devices have complex impedances which are poorly matched to the output circuitry of the high-power exciter and therefore require matching networks for maximum transfer of power. Operation at greatly reduced power is therefore necessary to prevent damage to the exciter when the load is improperly matched. In order to construct an efficient system for excitation of elastic wave harmonic energy, considerable additional hardware had to be ordered. This equipment included, among other items, two matching networks (one for the fundamental driving transducer and another for the harmonic receiving transducer) capable of handling the full output power of the exciter.

As the nonlinear response of materials increases quadratically with driving power,¹ the use of as high a power as possible is indicated. When we first received our high-power (3.6 kW) exciter, the output power had to be limited to approximately 250 watts when driving an ultrasonic transducer. However, we have measured a maximum output power of over 5000 watts when operating into a 50 ohm resistive load. This means that the second-harmonic content is more than 400 times smaller than could be obtained if the transducer were properly matched to the driving source. Nevertheless, we have observed measurable levels of second-harmonic energy in several materials, including alumina, when excited at this low level. Furthermore, the harmonic content decreased approximately in the predicted manner (quadratically) when the power was reduced to 100 watts.

In addition to the rapid increase of harmonic generation with driving power, the nonlinear response also increases quadratically with operating frequency and linearly with specimen thickness.¹ In many applications the ceramic thickness will be fixed at a value of a few millimeters, which is a very thin specimen for nonlinear studies. Consequently, there is strong incentive to use as high a frequency and driving power as possible. The high-power exciter consists of a broadband amplifier and frequency-selectable plugins. The original plugin operates over the range 1-30 MHz, which is adequate but well below the maximum useable frequency for structural ceramics. Therefore, a 20- to 120-MHz plugin was also ordered. At the highest operating frequency, this unit should produce 16 times the harmonic content of the 30-MHz plugin. Also ordered was a high-power stepped attenuator. This hardware is desirable for accurate measurement of the sample response to power changes.

The additional hardware has now been received for high-power excitation of elastic wave harmonic energy in structural ceramics. Two high-power impedance matching networks, a high-power stepped attenuator (0-47 dB in 1-dB steps), and a 20-120-MHz exciter were obtained. The matching networks were tested using undamped (tuned) quartz transducers, which exhibit high impedance, even at resonance. The networks performed very well, properly matching the transducers to provide dramatically improved signal levels and revealing the high Q of the quartz units. We have been using damped PZT transducers - primarily because of availability - which are inherently broadband (low Q) devices having good response at half the marked center frequency, a poor attribute for a receiving transducer used in the measurement of second-harmonic generation.

During these tests, we noted that the quartz transducers tended to arc at power levels in excess of 1800 watts. This corresponds to a potential of only about 425 volts peak, well below the breakdown voltage in quartz for the specified thickness at the operating frequency. These are commercial units with integral grounding pins, however, and the source of the problem may reside in this design, or in poor routing of the contact conductors. Accordingly, we have contacted two manufacturers of special-order transducers and are negotiating a design for new units.

We are also examining different transducer materials in an attempt to determine which might be optimum for nonlinear measurements. Quartz has traditionally been the material of choice because of its very high Q, but the sensitivity of quartz is considerably below that of most modern materials. Lithium niobate also appears to be a good choice, but the mechanical strength of elements in the 5-10 MHz range and higher is rather poor. We have also obtained several PZT-5A transducer elements, but even unbacked the Q of this material is low. Best results to date have been obtained with quartz and lithium niobate, in that order.

We continue to seek new applications for the 2-GHz acoustic microscope. Several gel-cast silicon nitride samples have been examined for near-surface carbide precipitates. Because these precipitates have significantly different acoustic properties than the silicon nitride matrix, they are easily detected by the surface-wave component of the microscope. Consequently, we could easily image the precipitate distribution in the samples studied. Several of the precipitate regions produced a much stronger indication than normal, and these areas were found to be associated with porosity. Comparison of the acoustic results with visual examination revealed that those precipitate regions which could be detected visually (i.e., they were surface-breaking) were very often accompanied by pores or pitting. Additional studies will be conducted using the low-frequency (100-MHz) acoustic system.

We also continue to employ the high-frequency acoustic microscope for characterization of ceramic surface and near-surface machining damage. Currently the greatest interest in this technology appears to be coming from research groups responsible for developing thin (<10 μm) ceramic coatings. We have previously demonstrated² the ability to detect extremely small cracks not found by either visible or electron microscopy in such coatings.

Computed Tomography (CT) - D. J. McGuire and W. A. Simpson, Jr

Last fall, in collaboration with Professor Dale Wittmer of Southern Illinois University, we made a series of CT scans of two experimental silicon nitride engine valves. The valves were in a bisque-fired pre-sintered state, and the object of the experiments was to try to determine distribution of density and porosity that might lead to causes for previously observed warping in the finished valves. The valves were carefully marked at each CT slice location for later

comparative scanning after final processing.

During this reporting period we received the finished valves which had warped during the firing process. We rescanned them at the previously identified locations. CT scans and X-ray density plots have been made for comparison of the pre-sintering and post-sintering material conditions. It is interesting to note that the post-sintering density increase, whose values have been obtained by forcing the CT reconstruction algorithms to a constant scale, compares favorably with the measured decrease in linear dimensions of the valves. The display programs of the CT system are capable of computing density values for either numerical or graphical output over a given region of interest, and a cross-sectional slice of one of the valves along with a displayed profile of its X-ray density is shown in Figure 3. Analysis of the CT scan information relative to observed warping of the valves and other process variables will be done by Dr. Wittmer.

Semi-annual maintenance procedures for the CT system were performed during May by a factory engineer. We addressed several minor problems and preventive maintenance, but the system continues to perform to design capabilities. Recent additions such as the Sun workstation, area detector and video printer are valuable assets and continue to perform well.

We are making a series of CT scans of ceramic engine exhaust valves submitted by A. A. Wereszczak of ORNL. The valves are being scanned in 1 mm thick slices over two identified regions of interest. After experimenting with X-ray and machine scanning parameters including some purely rotational scans, we finalized on use of translate-rotate scans with an X-ray peak voltage of 420KV and 125 detectors in a linear array with 1 mm vertical by 0.25 mm horizontal apertures. Rayspacing was at 0.1 mm with 0.015 second exposure times. The resulting images are being analyzed for density inhomogeneity, porosity, agglomeration and cracking. To date the valves have shown uniformly good quality with evidence only of some distributed 100 micrometer porosity. In a few images we noted some serial porosity that might possibly be a precursor to inservice cracking. Figure 4 shows a CT image of a cross-section of a ceramic engine exhaust valve.

We have now made several hundred 1mm wide cross-sectional scans in the exhaust valves and have found very few flaw indications other than some distributed porosity. In the shaft area of one of the valves we did image a crack-like indication about 0.5 mm long. This indication can be seen near the center of the cross-section shown in figure 5. Note also several large pore-like indications in this image.

References

1. W. A. Simpson, Jr., "Nondestructive Evaluation Development," *Ceramic Technology Project Bimonthly Progress Report*, June-July, 1993, p. 69.
2. W. A. Simpson, Jr., "Nondestructive Evaluation Development," *Ceramic Technology Project Bimonthly Progress Report*, February-March, 1995, p. 73.

Milestones

On schedule.

Publications

P. J. Blau and W. A. Simpson, Jr., "Applications of Scanning Acoustic Microscopy in Analyzing Wear and Single-Point Abrasion Damage," to be published in *Wear*.

Figure 1. (YP-21643) Ultrasonic surface-wave image of several alumina disks having differing chemistries and processing histories.

Figure 2. (YP-21644) Enlargement of the image of an alumina disk showing detection of a subsurface void and possible grinding marks.

Figure 3. CT cross-section of the shaft of a silicon nitride engine valve. Series of dots at the top of the figure shows a computed X-ray density profile of the material.

Figure 4. A CT image of a cross-section of a ceramic exhaust valve.

Figure 5. A CT image of a cross-section of the shaft of a ceramic exhaust valve. Note the dark crack-like indication near the center.

NDE STANDARDS FOR ADVANCED CERAMICS

R. W. McClung (Oak Ridge National Laboratory)

The development of standards is important for the establishment of reliability and acceptance of advanced structural materials. Committee C-28 on Advanced Ceramics is organized in the American Society for Testing and Materials (ASTM) to address this issue. One of the activities of the C-28 committee is nondestructive examination (NDE). The Section on NDE (SNDE) is reviewing existing standards on NDE (primarily developed for metals) to determine potential applicability for ceramics as well as preparing original standards. Use of existing or modified standards is more efficient than generation of new documents and will assure the input of a large body of NDE expertise. Close liaison is established with ASTM Committee E-7 on Nondestructive Testing and documents are in various stages of review, recommendations for modification, and balloting. R. W. McClung is a member of both committees and the official liaison.

Liaison and technical support have been continued between ASTM Committees C-28 and E-7. To date, thirty-six E-7 NDE standards have been reviewed in detail with recommendations made to E-7 for modifications to identified documents. Successful action is complete on thirty-one documents; the others require action by C-28.

A draft standard on "Ceramics Reference Specimens Containing Seeded Inclusions," was revised to accommodate comments received during a concurrent ballot of subcommittee and committee levels and was approved for another concurrent ballot. A draft standard for making precise measurements of ultrasonic velocity in advanced ceramics (one application is determination of porosity in ceramics) has been significantly revised in response to comments received from concurrent subcommittee and committee ballots. The revised draft standard has been balloted at the C28.02 subcommittee level with a concurrent advisory ballot in Subcommittee E-7.06 on Ultrasonic Examination Methods. A new revision has been prepared to accommodate comments received and it was approved at the June 1995 meeting for concurrent subcommittee/committee ballot. C-1175, the standard guide for existing NDE standards, was revised to enter five additional E-7 standards and successfully balloted at subcommittee/committee levels. It is now ready for Society ballot. A new draft standard on measurement of ultrasonic attenuation in advanced ceramics was balloted at the subcommittee level. A revision has been prepared to accommodate comments received and it was approved at the June meeting for concurrent subcommittee/committee ballot. McClung served on an E-7 Task Group (TG) to revise E-1324, *Standard Guide for Measuring Some Electronic Characteristics of Ultrasonic Examination Instruments*, to accommodate higher frequencies (e.g., to 100 MHz) needed for advanced ceramics. The technical changes were successfully balloted through E-7 and a Society ballot will complete the approval. Further action is planned on requesting data for "radiographic equivalence factors" from members of the section and other potential sources of data. Other work in progress includes an amplified outline for a draft standard for reference specimens containing laser-drilled holes and a possible standard on determination of porosity in ceramics using ultrasonic velocity. The latter standard will be delayed until the standard on ultrasonic velocity is completed. Preparation of a list of facilities and expertise for NDE of advanced ceramics at government laboratories is planned.

During meetings of Committee E-7, also in June, participation by McClung as C-28 liaison included meetings of the subcommittees on radiology and ultrasonics. Significant activity is ongoing in both subcommittees that will result in standards of interest and value for advanced ceramics. Among the work items in the subcommittee on radiology are draft standards on image quality indicators, image-quality response of film at low X-ray energy, index of performance of film, determining contrast sensitivity in radioscopy, and performance of computed tomography systems (several standards).

The E-7 subcommittee on ultrasonics has several action items on standards on both contact and immersion methods of examination, as well as methods for evaluation of ultrasonic search units and instrumentation (including the item noted earlier on standard E-1324. Several E-7 standards on computed tomography and ultrasonics with potential application to ceramics were reviewed and comments prepared as part of the E-7 ballot process.

X-Ray Computed Tomographic Imaging

W. A. Ellingson, E. R. Koehl, E. A. Sivers, J. B. Stuckey (Argonne National Laboratory), J. P. Pollinger, and H. C. Yeh (AlliedSignal Inc.)

Objective/Scope

The original objectives of the Phase III work of this project were to: (1) study the utilization of high-spatial-resolution 3-D X-ray micro computed tomography techniques to study density distributions in composite green-state (as cast) pressure slip-cast ATTAP rotors; and (2) correlate destructive density analysis (to be conducted by Allied-Signal Ceramic Components) of the as-cast ATTAP rotors with the 3-D microtomography density data. Because the large ATTAP rotors are no longer of technical interest, a change is being made to refocus the work to the AS-800 Si₃N₄ Series 85 nozzles being produced by Allied-Signal Ceramic Components.

Technical HighlightsATTAP Rotor Density Studies

The original objective of this project was to explore 3D Xray CT as a nondestructive method to map density variations within pressure slip-cast ATTAP rotors to assist Allied Signal Ceramic Components (ASCC) in maintaining quality control. We have been trying to push the limits of microfocus X-ray CT to examine these rotors and we have experienced several difficulties. However, the large ATTAP rotors are no longer of technical interest and we started, this period, to change this work to focus on AS-800 Si₃N₄ "Series 85" nozzles being developed by ASCC. We will report here on the last of our ATTAP efforts.

The first of two specially made ATTAP rotors has been analyzed, via multi-scan X-ray CT. The most recent X-ray CT data of the first ATTAP rotor have been taken in the L/5 and 2L/5 planes as shown in Fig. 1. The 3D X-ray CT system used to obtain these data still consists of a microfocus X-ray source (155 kVp) with an image intensifier (II) coupled to a 14 bit CCD camera as the detector. Because of the pronounced taper of the body and blades of the rotor, the L/5 plane was imaged with a slice width of 0.02 cm and the 2L/5 plane was imaged with a slice-width of 0.01 cm. Figure 2 shows the 2-dimensional (2D) in-plane image data of the L/5 plane and Fig. 3 shows the 2D in-plane image data of the 2L/5 plane. In both images, the pixel width is 0.025 cm.

Figure 2. A 3-D X-ray CT reconstruction of the L/5 slice of the first ATTAP rotor.

Figure 3 A 3D X-ray CT reconstruction of the 2L/5 slice of the first ATTAP rotor.

Qualitatively, these images are very informative. They are of sufficient quality to perform dimensional analysis and allow visualization detection of any voids or inclusions of a size on the order of the pixel width, i.e. 250 μm . In contrast to earlier images made with thicker slice widths, the edges of the body and blades of the rotor are sharp and there are no "windmill" artifacts around the blades. These image data also permit a general determination of the density of the rotor. Line plots in Fig. 4 and Fig. 5 show superimposed, radial line profiles from both L/5 and 2L/5 slices through blades 1 and 7 and through the body of the rotor between blades 1 and 23. Experimental evidence thus far leads us to expect that both of these profiles should resemble "top-hat" functions. The fact that they do not resemble this function suggests that there is residual error in the data. The effect of this error can be assessed by noting that the CT data have been normalized to a monochromatic energy of 78 KeV so that density is determined by dividing the reconstructed CT number (in units of 1/cm) by the mass attenuation coefficient of Si_3N_4 at 78 KeV ($0.186 \text{ cm}^2/\text{g}$). Simple calculation shows that the density of the rotor varies between 3.4 g/cm^3 and 2 g/cm^3 . This determination is adequate to obtain a general estimate of the rotor density, but may not be good enough to differentiate density variations on the order of 5%.

Figure 4 Superimposed line profiles through blades 1 and 7 from reconstructed images of the L/5 and 2L/5 slices of the ATTAP rotor.

Figure 5 Superimposed line profiles between blades 1 and 12 from reconstructed images of the 1L/5 and 2L/5 slices of the ATTAP rotor.

The conclusion we have reached is that the beam attenuation of the large ATTAP rotor exceeds the design parameters of the present Argonne 3D CT system. That does not mean that the microfocus/II/CCD system cannot be used to obtain accurate density determinations of less attenuating objects or that the ATTAP rotor cannot be imaged using 3D X-ray CT.

Difficulties in this case are due to a combination of the poor (low) penetration of the highest-energy X-rays available (155K_eV) and the scatter/veiling glare offset in the II detector. The longest path length through both blades and body in the slices in this case is about 10.3 cm. Thus, the attenuation of the mean X-ray intensity through the longest path is about $\exp(0.186 \times 3.4 \times 10.3) = 0.0015$. Figure 6 illustrates the degree to which X-ray scatter and veiling glare corrupt the X-ray attenuation readings of one row of one exposure through the center section of the rotor. The solid line in Fig. 6 is the raw projection recorded by the detector. The dashed line is the raw projection when

thick lead strips are interposed between the X-ray source and the rotor during a duplicate scan. The solid curve connecting the square dips in the "lead" scan is a low-order polynomial fit used to estimate the combination of the X-ray scatter that enters the detector plus the light scattered in the exit phosphor of the II (veiling glare). A scaled version of this fit is subtracted from the raw projection to produce the corrected, raw data, which is shown as the bold curve. Comparison of the bold curve and the raw curve shows that, for the lowest reading, the scatter plus veiling glare contribution to the signal is more than 10 times higher than the signal itself.

Figure 6 Superimposed row plots from identical raw exposures of the center section of the rotor with and without lead. The polynomial fit to the lead dips and the corrected data are also shown

The use of duplicate "lead" scans to remove scatter/veiling glare in an II detector is very successful when the offset is only a few percent of the true signal. However, when the offset is more than 10 times the value of the signal, the correction can be approximate only. A very small change in the offset subtracted can cause a large change in the reconstructed density. Figures 7 and 8 show the effect on the L/5 slice when the magnitude of the offset subtracted from the raw data is reduced by 5%. In both radial line profiles, the reconstructed linear attenuation in the center of the rotor is correspondingly reduced by about 17%.

Figure 7 Superimposed line profiles through blades 1 and 7 from reconstructed images of the L/5 slice of the ATTAP rotor. Dashed line is profile with 95% of scatter/veiling glare fit subtracted. Bold line is profile with 100% of scatter/veiling glare fit subtracted.

Figure 8 Superimposed line profiles between blades 1 and 12 from reconstructed images of the L/5 slice of the ATTAP rotor. Dashed line is profile with 95% of scatter/veiling glare fit subtracted. Bold line is profile with 100% of scatter/veiling glare fit subtracted.

Additional problems are caused by a characteristic of the CsI crystal in the II known as "afterglow", which is a kind of hysteresis. Not all excited states in CsI decay and emit light "immediately" after absorbing X-rays. For instance, "ghosts" of the lead strips can still be seen in exposures of the II taken more than an hour after they have been removed. Thus, regions of the II exposed to high flux in a previous scan will produce a higher signal than regions obscured by the rotor in that previous scan. Figures 9 and 10 illustrate the anomalies that afterglow can introduce into "lead" scan readings. Since each curve is recorded in the duration of a few microseconds, the intensity of the X-ray source is effectively constant during acquisition. The solid curve in Fig. 9 is the raw data from the right-of-center scan of the 2L/5 section of the rotor. The dashed line is the corresponding lead scan taken somewhat later. Regions of the plot that are not blocked by lead should receive the same flux, possibly scaled by a constant.

Figure 9 Superimposed row plots from identical raw exposures of the right-of-center section of the rotor with and without lead. The polynomial fit to the lead dips and the correct data are also shown

However, the less attenuating region of the lead scan between the first and second lead pieces is higher than the corresponding region in the unblocked scan, but the highly attenuating region between the third and fourth pieces is lower than its corresponding region. This discrepancy is not the result of a change in the spatial distribution of the x-ray intensity profile between scans because examination of the left-left-of-center scan shown in Figure 10 shows the same effect spatially reversed. Thus, "lead" scan correction profiles will not be exact and the "wagon-wheel" streaks in the images of Figs. 2 and 3 are almost certainly due to residual offset.

Fig. 10 Superimposed row plots from identical raw exposures of the left-of-center section of the rotor with and without lead. The polynomial fit to the lead dips and corrected data are also shown.

It thus has been concluded that we will not be able to further improve the images of these ATTAP rotors with data taken on the Argonne 3D X-ray CT system because of signal-to-noise limitations. However, it is still highly likely that accurate densitometry can be performed on the ATTAP rotors using 3D X-ray CT. For such rotors, if of interest in the future, it is recommended that both a higher-energy X-ray source (e.g., a new 225 or 320 KVP system) and a different X-ray detector be used (e.g., new fiber optic scintillator). A higher-energy source will permit better penetration of the rotor so that higher signal is available. In addition however, a more attenuating detector that does not suffer from afterglow and veiling glare is needed to obtain "clean" readings. Data will still be corrupted by X-ray scatter and "beam hardening" due to the polychromatic energy spectrum of the X-ray source, but duplicate lead scans can be used to estimate X-ray scatter alone fairly accurately and the one-material polychromaticity can be used to remove beam hardening.

Because of these limitation, we again decided, this period, to study potential use of new "spiral scan" medical X-ray CT systems for the large ATTAP rotors. A Siemens Somatom was used at Mallinckrodt Institute of Radiology in St. Louis, Missouri. Both ATTAP rotors were shipped. Rotor 0170 with a drilled hole in the upstream shaft, and rotor 0482 with no upstream drilled hole in the shaft.

Figures 11 and 12 show respectively the topogram of rotor 0170 and the topogram with locators of the CT scans.

*Figure 11. Topogram
(digital projection radiograph)
of rotor 0170. Data taken on
Siemens medical CT scanner*

*Figure 12. Topogram of rotor 0170
showing location of CT scans.*

Figures 13,14 and 15 show, respectively, the CT scans obtained at locations 3,4 and 5. The wagon wheel artifacts are present in locations 3 and 4 just as in the micro-focus CT scans. An internal low-density "flaw" is detected at the eleven o'clock position of the CT data from locations 4 and 5. We will compare the data from the two scanners and report on the observations in future reports.

0170 Rotor Slice 3

*Figure 13. 1mm thick CT cross section of rotor 0170 taken at location 3.
CT image obtained on medical scanner*

0170 Rotor Slice 4

*Figure 14. 1mm thick CT cross-section of rotor 0170 taken at location 4.
CT image obtained by medical CT spiral scanner.*

0170 Rotor Slice 5

*Figure 15. 1mm thick CT cross-section of rotor 0170 taken at location 5.
CT image obtained by medical CT spiral scanner.*

As noted earlier, in discussions with Allied-Signal Ceramic Components, the ATTAP rotors being currently studied are no longer of industrial interest and we have made initial steps to change to a smaller turbine component which is of interest. This is discussed below.

A so-called "Series 85" nozzle is being developed by ASCC. This is shown in Figures 16 and 17 below.

Figure 16. Photograph of "Series 85" nozzle planned for use in future X-ray CT densitometry work.

Figure 17. Photograph of "Series 85" nozzle planned for use in future X-ray CT densitometry work.

The ceramic processing methods are still under development and the ability to map density variation by each process is planned to be established by X-ray CT. We will discuss this in more detail in subsequent reports. A new work statement is being prepared by ASCC and Argonne jointly.

MILESTONE SCHEDULE 3.5.1.5

		<u>DATE DUE</u>	<u>STATUS</u>
351510	Obtain region-of-interest image of large Si ₃ N ₄ rotors as-cast	12/15/92	Completed
351511	Complete fabrication of calibration wedges	2/28/94	Completed
351512	Complete 3-D X-ray CT images of calibration wedges	5/30/94	Completed
351513	Complete fabrication of first rotor	3/31/94	Completed
351514	Complete 3-D X-ray CT study of first rotor with destructive analysis	12/30/94	Revised date
351515	Complete fabrication of second rotor	10/31/94	Completed
351516	Complete 3-D X-ray CT study of second rotor with destructive analysis	4/30/96	Revised date
351517	Submit report on correlation between X-ray CT data and destructive analysis	6/30/96	Revised date
351518	Complete fabrication of initial gel-cast cylindrical specimens	5/30/96	New
351519	Complete initial nondestructive analysis of first gel-cast components	8/34/96	New

Task Identification:

WBS 3.5.1.6¹

 April - September, 1995

Nuclear Magnetic Resonance Imaging

S. L. Dieckman, S. Ahuja, O. O. Omatete*, A. C. Raptis, and W. A. Ellingson
(Argonne National Laboratory; *Metals and Ceramics Division, Oak Ridge
National Laboratory)

Objective/Scope

The purpose of this work is to evaluate the potential of NMR imaging to impact the development and process control of near-net-shape gel-cast ceramic composites. The specific objectives of this work are to determine the utility of NMR imaging for: (1) 3D mapping of polymerization homogeneity; (2) real-time imaging of the polymerization process; (3) nondestructive evaluation of voids and flaws in the resultant components; and (4) measurement of physical properties such as degree of polymerization, viscosity, and specimen strength via correlation of these properties with measurable NMR parameters (T_1 , $T_{1\rho}$, and T_2). This work will be performed in conjunction with Dr. Ogbeml O. Omatete from the Materials and Ceramics Division at Oak Ridge National Laboratory.

Technical Highlights

In previous reporting periods experimental NMR studies have been conducted on the methacrylamide-N,N'-methylene bisacrylamide (MAM-MBAM) copolymer system. These studies have included both spectroscopic and imaging experiments. The results have shown that NMR relaxation times are directly indicative of polymerization extent, and can therefore be used as an imaging modality showing polymerization rate and homogeneity. Experiments to date were performed on the spectrometer system in chemistry. This system however had distinct geometric and experimental operating constraints that has limited the utility of this system for applications to small specimens.

During this and several recent reporting periods, the Energy Technology Division at ANL has installed a commercial NMR spectrometer and imaging system, see Figure 1. This system is capable of imaging large ceramic gelcast specimens with high resolution and speed. During this period several custom circuits have been designed to permit the operation of this system with ANL's custom amplifier and probe accessories. This system is thus nearly complete and should be performing imaging in the up coming reporting period. Experimental studies to be performed with Dr. Omatete are planned for the November/December time-frame.

Fig. 1: NMR Imaging and spectroscopy system facilities recently installed at ANL.

4.0 TECHNOLOGY TRANSFER

4.1 TECHNOLOGY TRANSFER

4.1.1 Technology Transfer

Technology Transfer

D. R. Johnson (Oak Ridge National Laboratory)

Technology transfer in the Propulsion System Materials Program is accomplished by a number of mechanisms including the following:

Trade Shows - A portable display describing the program has been built and has been used at numerous national and international trade shows and technical meetings.

Newsletter - A Ceramic Technology Newsletter is published regularly and sent to a large distribution.

Reports - Semiannual technical reports, which include contributions by all participants in the program, are published and sent to a large distribution. Informal bimonthly management and technical reports are distributed to the participants in the program. Open-literature reports are required of all research and development participants.

Direct Assistance - Direct assistance is provided to subcontractors in the program via access to unique characterization and testing facilities at the Oak Ridge National Laboratory.

Workshops - Topical workshops are held on subjects of vital concern to the ceramics community.

International Cooperation - This program is actively involved in and supportive of the cooperative work being done by researchers in West Germany, Sweden, the United States, Japan, and, most recently, Belgium under an agreement with the International Energy Agency. This effort is ultimately aimed at development of international standards and includes physical, morphological, and micro-structural characterization of ceramic powders and dense ceramic bodies, and mechanical characterization of dense ceramics.

Semi-Annual -- April 1, 1995-September 30, 1995

IEA ANNEX II Management

M. K. Ferber and K. Breder (Oak Ridge National Laboratory)

Objective/scope

The purpose of this task is to organize, assist, and facilitate international research cooperation on the characterization of advanced structural ceramic materials. A major objective of this research is the evolution of measurement standards. This task, which is managed in the United States by ORNL, now includes a formal IEA Annex agreement identified as Annex II between the United States, Germany, Sweden, Japan, and Belgium. Annex II has been extended until June 30, 1997. The original annex included four subtasks: (1) information exchange, (2) ceramic powder characterization, (3) ceramic chemical and physical characterization, and (4) ceramic mechanical property measurements. In the United States, a total of 13 industrial and government laboratories have participated and contributed their resources to this research. The research in Subtasks 2, 3, and 4 is now complete. In 1990, research in two new subtasks was initiated. These included, Subtask 5, Tensile and Flexural Properties of Ceramics, and Subtask 6, Advanced Ceramic Powder Characterization and were completed in 1993. Two new tasks, Subtask 7, on Ceramic Machining and, Subtask 8, on Ceramic Powder Characterization were proposed in late FY 1993, and the research is ongoing. Subtask 7 in the United States includes ten companies and two federal laboratories. Subtask 8 includes six companies.

Recent Developments

A Subtask 7 Working Group Meeting with the International Participants was held at Alfred University, Alfred, New York, on July 9, 1995, in conjunction with the "Fractography of Glasses and Ceramics III," conference. The minutes have been compiled and sent to the participants. A summary of the major points which were discussed and decided upon is given below. A representative from each of the participating countries made two presentations. The first discussion session was on the fractography round robin exercise; this was followed by a report from each country on the status of their machining work. Future research was also discussed.

1. Fractography Round Robin Discussions

Dr. Mizuno presented the status of the fractography work in Japan. He remarked that this was a challenging project and he hoped that the results could be unified. There were two phases of the work in Japan: (1) the work at JFCC on fractography on material from Japan, Sweden, and the United States; and (2) six Japanese laboratories evaluating the fractography pictures generated at the JFCC. The Japanese work clearly demonstrated that the locations of the fracture origins were easy to identify, while the exact nature of the flaw was more difficult. Large discrepancies between the countries were seen at that point. Better agreement was seen in the work performed and then shown in the domestic

Japanese pictures. However, it was clear that the person looking at pictures, rather than a specimen, is biased by the opinion of the person who took the picture.

Dr. Carlsson presented a summary of the fractography work in Sweden. He noted that only Sweden and Germany used EDX while evaluating the fracture origins. There was some confusion on how different researchers identify the flaw.

Dr. Hollstein stated that the German work was in agreement with Dr. Carlsson's findings.

Dr. Erauw said that the Belgian work was in good agreement with Carlsson's comments. He also remarked on the problems related to identifying the flaw size especially for machining damage.

Dr. Breder briefly summarized the U.S. results from the fractography round robin by saying that the findings in the United States are the same as already presented. Flaw location and fracture mirror are well identified, flaw types of volume origin such as porous regions were well agreed upon, while the surface-located machining flaws were difficult to identify and measure.

In summarizing this portion of the meeting, several points were agreed upon: On the issue of looking at need for fractography, there was discussion of looking at mirrors as alternative and the need to tilt specimens for best examination. Dr. Hollstein remarked that in some materials the failure origins were hard to determine, and too much time could be spent to no use. This differs from material to material and would also differ with the intent of the research. Dr. Breder discussed the importance of knowing the origin of failure. Is it due to machining, or some other factor? How detailed should we be in fractography work? The purpose of the fractography is to explain the differences seen in samples due to machining.

Dr. Breder agreed to take individual fractography reports from each country and to compile them into one comprehensive report.

2. Status Of Machining Work

Each speaker gave an account of the time schedule for the machining work in their country, which is given here with comments from the general discussion which followed their presentations.

Japan: Has sent to all participants the conditions for grinding; should finish grinding by end of August 1995.

Sweden: Will not be able to start until beginning of August 1995.

Germany: Can start with machining when they get specimens from Belgium.

Belgium: Billets will be sent out by August 15, 1995. They are now doing correlation of work; but would like to do more and analyze results before sending procedures. Belgium should be able to send procedures in mid-August 1995. Dr. Erauw indicated that he had compared the instructions received so far from other countries on the machining procedures and found several omissions.

United States: Dr. Breder's presented the status of the U.S. work. They are about half way through the U.S. participant work of grinding specimens; and should finish by end of August. All specimens have been distributed.

In the discussion on the machining procedures, several of the participants indicated that clarification is needed in these instructions. It was then agreed that Drs. Ferber and Breder will distribute to each participant a table comparing all machining instructions for comment.

Dr. Ferber suggested that maybe the five highest and five lowest strength specimens should be looked at more closely. After some discussion in which it was brought out that the lower end was of more importance, the group agreed to perform SEM on ten specimens, taking seven from the lower end of the Weibull distribution and three from the higher end as a minimum requirement. It was also agreed that if the flaw can be identified, try to measure it.

Dr. Ferber suggested that after breaking the specimens, each country would return them to the originating country for fractography. This was well received and agreed to after some discussion on how to avoid contamination of specimens during transit. Dr. Ferber agreed to supply packaging instructions which would minimize the contamination problem.

Although the ideal schedule for finishing the machining work would be by the time of the Executive Committee Meeting in October, problems with obtaining grinding wheels may prohibit this. The group did agree that all machining will be done by the end of December 1995, and all specimens returned to the originating country for fractography.

Each country will do their own report on machining.

3. Future Research

Plans for future work, identified as Subtask 9, were discussed. Sweden proposed to perform oxidation studies. Germany and Japan each presented proposals with a strong endorsement for thermal shock research. Japan included their current standard practice for oxidation testing which they felt was sufficiently detailed to address their needs in this area. Belgium and the United States agree with the need for the thermal shock research. The Fractography Reports from Belgium, Germany, and Sweden were sent to the International Participants and the U.S. participants (July 28, 1995) as part of the information exchange.

Technical Highlights

Subtask 7, Machining Effects on Strength of Structural Ceramics

United States

The replication run of 150 specimens was fractured in a randomized set. About half of this set was strain gaged. The results have been analyzed in terms of Weibull statistics, and statistical analysis of the experimental design has been performed. The replication run gave indications as to the reproducibility of the machining conditions as well as to the reproducibility of the grinding forces. The factor analysis showed that the grit size is the single strongest factor influencing the strength. Within each grit size the wheel speed had some effect on strength, i.e., higher surface wheel speed resulted in higher strengths. Expressing the experimental conditions in terms of grit depth of cut it was seen that the strength decreased with increasing grit depth of cut. The grinding forces have been analyzed and no direct correlation between the measured grinding forces and the resulting strength was found. However, re-analyzing the grinding forces in terms of force per cutting grit, a correlation between increased force per grit and decreasing strength was seen. Further analysis of the entire data set as well as fractography is ongoing.

All but one of the U.S. participants has now completed the work in the HTML. Each participant has machined and fracture tested thirty specimens. Valuable information has been obtained on some of the machining and wheel dressing procedures. Also, further insights into possible uses of the force data gathered during the machining has been acquired. The participation of all these experienced researchers has resulted in valuable information regarding interpretation of machining data, surface finish, and quality results.

The grinding data produced by the U.S. participants have been analyzed at ORNL. The grinding forces have been analyzed and compared to the two previous runs performed in the HTML, and for the most part good reproducibility was obtained. Weibull analyses of the strength data have been completed, and surface roughness data have been collected on all the participants' specimens. Some fractography have been completed. The strength results from the participants' runs lie well within the range observed for the two HTML runs. Due to the size of the billets being ground, each participant ground one and a half billet in order to obtain 30 specimens. The strength distribution within each billet was very tight, i.e., the Weibull modulus was high, but in most cases there was significant difference in the average strength for the two billets prepared under the exact same conditions. The fractography did not indicate any obvious differences in the specimen sets, and also, since the machined billets in many cases originally came from the same larger hot-pressed billet, material differences seem to be an unlikely reason for the strength differences. Although the wheel truing and dressing schedules were kept constant throughout the experiments, it is likely that some of the variability is due to the conditions of the grinding wheels. One participant had considerable experience in wheel characterization, and was very meticulous in the truing and dressing, and as a result, this participant's results did not exhibit such a billet to billet variation. Similar experience was reported from the Belgian laboratory, and it clearly indicates that the understanding of the wheel conditions is very important. A report containing the machining characteristics, the

strength and Weibull data, roughness values, and preliminary fractography will be sent to each participant for comments and feedback. The results for the participants will also be compared to the work performed previously in the HTML, and an evaluation of the overall data to this point will be assembled.

The international round robin fractography results have been summarized in a draft report which has been distributed to the international partners for feed-back and comments.

The grinding instructions from the international partners have been received at ORNL, and a summary sheet containing all the grinding variables has been prepared. This sheet was faxed to all the participating countries, and comments, questions, and clarifications have been received and sent back out. All questions regarding the international grinding conditions have been coordinated through ORNL to ensure that all participants receive the same information. All international billets and grinding instructions have been exchanged at this point.

Subtask 8, Ceramic Powder Characterization

Major responsibility for this subtask in the United States is at NIST, and a detailed report of progress on this subtask is provided in the section of this report submitted by NIST.

Status of Milestones - Milestone 411517 - Complete flexure strength measurements - completed April 30, 1995.

Additional change made to Milestone 411518 - completion date changed from August 31, 1995, to November 30, 1995, due to one U.S. participant (NIST) coming in November to complete the machining measurements.

Other Milestones are on schedule.

Communications/Visits/Travel - Dr. Mineo Mizuno (Japanese Technical Leader of Subtask 7), Japan Fine Ceramics Center, and Mr. H. Ogiyama (Japanese Alternate Executive Committee Member), New Energy and Industrial Technology Development Organization, visited (July 5, 1995) and presented a seminar on the "Research and Development of the CGT Programs Ongoing in Japan."

Matt Ferber, Kristin Breder, and Felicia Foust attended IEA Subtask 7 Working Group Meeting, Alfred University, Alfred, New York (July 9, 1995).

Publications and Presentations - Carlsson, Lennart, "A Round Robin 1994 on Fractography of Silicon Nitride, Swedish Specimens," Swedish National Testing and Research Institute, Materials Technology, Technical Note 1995:21, 1995. (Sweden)

Drüsedau, K. A. and Hollstein, T., "A Round Robin on Fractography of Silicon Nitride, German Results," IWM-Report V 26/95, April 1995. (Germany)

Hendrix, W. and Erauw, J. P., "Round Robin on Fractography of Silicon Nitride, Belgian Results," VITO - Materials Division, MAT/95/R.108, June 1995. (Belgium)

Breder, Kristin and Ferber, Matt K., "IEA Annex II, Subtask 7 - Status of U.S. Machining Work," presented at Subtask 7 Working Group Meeting, Alfred, University, July 9, 1995.

Breder, Kristin and Ferber, Mattison K., "Effect of Different Machining Parameters on the Strength of a Silicon Nitride. An International Collaboration Under IEA," presented at Cost-Effective Ceramic Machining Workshop, Oak Ridge, Tennessee, September 20, 1995.

Characterization of Ceramic Powders

S. G. Malghan and L.-S. Lum

(National Institute of Standards and Technology)

Objective/Scope

Ceramics have been successfully employed in engines on a demonstration basis. The successful manufacture and use of ceramics in advanced engines depends on the development of reliable materials that will withstand high, rapidly varying thermal stress loads. Improvement in the characterization of ceramic starting powders is a critical factor in achieving reliable ceramic materials for engine applications. The production and utilization of such powders require characterization methods and property standards for quality assurance.

The objectives of the NIST program are: (1) to assist with the division and distribution of ceramic starting powders for an international round-robin on powder characterization; (2) to provide reliable data on physical (dimensional), chemical and phase characteristics of powders; and (3) to conduct statistical assessment, analysis and modeling of round-robin data. This program is directed toward a critical assessment of powder characterization methodology and toward establishment of a basis for the evaluation of fine powder precursors for ceramic processing. This work will examine and compare by a variety of statistical means the various measurement methodologies employed in the round-robin and the correlations among the various parameters and characteristics evaluated. The results of the round-robin are expected to provide the basis for identifying measurements for which Standard Reference Materials are needed and to provide property and statistical data which will serve the development of internationally accepted standards.

Technical Progress

During this period, the primary activities in progress were on analysis of powders, development of data entry formats, entry and analysis of data, and communications with the technical leaders.

We completed testing of the two primary powders--silicon nitride and silicon carbide--on selected procedures. In addition, occasionally, we have experimented with the alumina powder. Data on particle size distribution by x-ray sedimentation and interface chemistry by electroacoustic techniques have been obtained. In addition, settling rate of as-received powders and flow rate of spray dried powders have also been obtained. Preliminary analysis of these data show no surprises.

During July-August period, we completed the analysis of silicon nitride, silicon carbide and alumina powders for all secondary properties of interest. In addition, aluminum nitride powder has been tested for several selected secondary properties. The flowability of the spray dried form of this powder was excellent. Thanks to Dow Chemical Company for providing this powder to the round robin activity.

Data from over 75% of the participants has arrived. Both Japan and Germany decided that their technical leaders will collect data from all participants and send it to NIST in July-August as a single package. The participants in these countries have started sending the data to their respective technical leaders. They plan to hold a meeting of the participants to discuss data before sending the data to NIST. We are experiencing some delay in the overall project due to extra time involved in completing the analysis at all participating laboratories. This is primarily due to more than anticipated analysis time, and delay experienced in the participating laboratories due to lack of technical staff availability. We are expecting to receive most of the data before the end of October. Our goal was to compile all data and develop tables for statistical analysis. At the executive meeting in Italy on October 2, 1995, the technical leaders plan to meet and develop preliminary conclusions based on the Subtask 8 data. Formats for entry of data from secondary properties of powders have been developed for most properties.

We have been in contact with the technical leaders in Japan, Germany, and Sweden to monitor progress and resolve any issues with respect to procedures. During August, we completed entry of most of the data from Japan. Dr. Naito, Technical Leader, visited NIST to describe the data. Prior to his visit, he had organized a meeting of the Japanese participants to discuss the data. Therefore, the primary purpose of his visit was to convey the discussions of their meeting. In addition, we discussed the technical areas for the continuation project to be proposed at the upcoming executive committee meeting in Italy. The Japanese participants are very eager to continue this program. However, they suggest, the primary thrust should be on reduced number of powders and on selected number of secondary properties. In addition, as agreed by all other participants, more emphasis should be placed on ruggedness testing of the procedures before the final round robin. This will ensure better quality of the powder. Most likely, the next subtask will be the last to be conducted under the IEA umbrella. Therefore, we need to take sufficient measures to ensure that the quality of the data will be high enough to pass these procedures to standards setting bodies.

Complete data from Belgium has been received. Also, Sweden and Norway have sent most of their data. We are continuing to input these data as we receive it.

In the ASTM activities, final revisions on the procedure for particle size distribution by gravity sedimentation were completed, and the final draft has been returned for concurrent subcommittee and society ballot. In the ASTM-related activities, at the Denver meeting, Dr. R. Newman, Dow Chemical Company, presented the revised versions of procedures for C, N, and O analysis. The data from IEA Subtask 6 were used in these procedures for establishing repeatability and reproducibility.

Status of Milestones

On target

Publications/Presentations

None

Communications/Visits

None

Ceramic Mechanical Property Test Method Development

George D. Quinn

(National Institute of Standards and Technology)

Objective/Scope

This task is to develop mechanical test method standards in support of the Ceramic Technology Project and Advanced Turbine Technology Applications Programs. Test method development should meet the needs of the DOE engine community but should also consider the general USA structural ceramics community as well as foreign laboratories and companies. Emphasis will be placed on the needs of the DOE community.

Draft recommendations for practices or procedures shall be developed based upon the needs identified above and circulated within the DOE ceramics heat engine community for review and modification. Round robins will be conducted as necessary, but shall be well-focussed, limited in scope, and not interfere with ongoing IEA round-robins. Procedures developed in this program will be advanced for final standardization by ASTM.

Technical Highlights and Results

Earlier work in this project has contributed to the following completed standards:

1. ASTM C-1198-91 "Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Sonic Resonance," by S. Gonczy, Allied-Signal; G. Quinn, NIST; and J. Helfinstine, Corning.
2. ASTM C-1161-90 "Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature," G. Quinn, NIST.
3. ASTM C-1211-92 "Standard Test Method for Flexural Strength of Advanced Ceramic at Elevated Temperature," by G. Quinn in cooperation with Mr. M. Foley, Norton; Mr. T. Richerson, Allied-Signal; and Dr. M. Farber, ORNL.
4. MIL HDBK 790 "Fractography and Characterization of Fracture Origins in Advanced Structural Ceramics," with J. Swab and M. Slavin, U. S. Army, ARL.
5. ASTM C-1239-93 "Standard Practice for Reporting Strength Data and Estimating Weibull Distribution Parameters," by S. Duffy, NASA-Lewis; G. Quinn, NIST; and C. Johnson, G.E.

In addition, work on this task has contributed to the following draft standards which are now being balloted in ASTM Committee C-28:

1. ASTM C-xxxx "Standard Test Methods for the Determination of Fracture Toughness of Advanced Ceramics," in cooperation with Prof. Isa Var-on, WPI; and M. Jenkins and J. Salem of University of Washington."
2. ASTM C-xxxx "Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics."
3. ASTM C-xxxx "Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics."

4. ASTM C-xxxx "Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics," in cooperation with Mr. J. Swab, U.S. ARL.

Fracture Toughness

A draft fracture toughness standard was balloted twice ASTM committees C-28, Advanced Ceramics and E-08, Fracture and Fatigue in April, 1995. The document was balloted simultaneously by the appropriate subcommittees in the two ASTM committees. Negative ballots and constructive comments were received in the first ballot and the document was withdrawn for remedial actions. The revisions that are necessary are refinements. The general framework and the three specific procedures in it (SEPB, CN, SCF) were accepted by the voters. At the time this semiannual report was prepared, ballot results from the second ballot were being received suggesting that a few additional revisions may be needed. Professor Isa Bar-on of Worcester Polytechnic Institute is the overall coordinator of this activity as well as the C-28/E-8 committee liaison.

Work in this task has focussed on refining the surface crack in flexure (SCF) method which is one of the three in the draft standard. We have also contributed to elements of the main body of the draft standard, particularly the error and uncertainty statements, and the specimen orientation scheme. The uncertainty statements for the SCF and SEPB procedures were prepared on the basis of two VAMAS round robin projects and the numerical analysis of ASTM standard E 591, "Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method." Numbers were adjusted in April when outlier results were deleted and the new numbers have been used in the latest version of the draft standard.

In this semiannual period, two papers were written on the SCF method. The first, presented at the fracture mechanics of ceramics conference in Karlsruhe, Germany in July 1995, discussed the numerical results in some detail, particularly the remarkable consistency in results obtained on NC 132 hot-pressed silicon nitride. This material, a staple of mechanical test studies in the 1970's-1980's, has a fracture toughness of $4.6 \text{ MPa}\sqrt{\text{m}}$ as measured by any one of several reputable methods over the course of twenty years by many different laboratories. It is gratifying that the three methods in the ASTM draft standard all yield the same outcome for this material. The consistency is due in large part to the consistency in manufacture of this material, and the fact that it has little or no R-curve behavior. The second paper prepared was for the conference on fractography of glasses and ceramics at Alfred University in July. This paper emphasized the fractographic techniques that can be used to find and measure the precracks.

The data base of fracture toughness values by the SCF method has been expanded to 26 advanced ceramics. We are accumulating and acquiring new ceramics for additional studies, particularly ceramics with fracture toughnesses >8 and $<3 \text{ MPa}\sqrt{\text{m}}$. Studies are underway regarding the apparent results obtained by this method for materials with suspected R-curve behavior. We welcome inquiries from other Ceramic Technology Project participants who have materials for NIST to measure fracture toughness by this method.

A round robin on the SCF method may be starting in Europe.

Hardness

Work continued at NIST on developing hardness standards for advanced ceramics. This is a two pronged program which has an effort performed under this task to prepare ASTM Knoop and Vickers standard test methods as well as a separate NIST program to develop two standard reference materials (SRM's). Figure 1 illustrates the two SRM's.

SRM 2830, Knoop Indentation Hardness was fabricated in the Spring and Summer of 1995. At the time this semiannual report was prepared, all artifact preparation work had been completed, and the final, exhaustive statistical analysis of the data was underway. We project that the NIST Knoop blocks will have hardnesses certified to within 1% at a 95% confidence level. This is extraordinary and the SRM's will be eminently suitable to support the ASTM standard which requires users to verify their hardness test equipment within $\pm 5\%$. The blocks should be available for sale in December, 1995.

SRM 2830, Vickers Indentation Hardness has been delayed since the vender of the material has delivered two unacceptable batches. The material is a tungsten carbide, and was chosen since it had a hardness of 1500 kg/mm², had clean, crisp indentations, and was very uniform. A new batch is in preparation.

The draft Knoop and Vickers hardness standards were balloted in ASTM in the Spring of 1995 at the C28.01 subcommittee level. They received one negative ballot apiece as well as a few constructive suggestions on affirmative-with-comment ballots. The negative ballot pertained to a single word in the drafts: "should". The word was used in the context of whether a polished surface was mandatory or not. "Should" was used in one clause, and "shall" in another. The latter is mandatory, the former recommended. Unfortunately, ASTM is strict about wording changes such as this, and it was not possible to make a simple editorial revision. The drafts have been corrected and the opportunity was taken to make a few additional "polishing-up" revisions to the drafts. A new figure showing acceptable and unacceptable Knoop indents has been added to the Knoop standard.

Mr. Quinn continued to exchange detailed correspondence with Mr. Sakaguchi of NIRIN, Nagoya on questions pertaining to a proposed ISO standard for Vickers and Knoop hardness. Mr. Sakaguchi proposes to clone a rudimentary ISO standard for the Vickers hardness of metals. We feel that this is a mistake. The ASTM ceramic standards, when properly used, will have hardness precision and bias of less than 5%. Such levels of precision will not be achievable by cloning the metal ISO standard. The ISO ceramic draft standard also includes both 1 kg and 10 kg as loads for Vickers indentation. It is our experience that the higher load is unreasonable for many ceramics, since the indents will be badly cracked or chipped. Extensive communications were relayed to NIRIN about this, but ultimately it was decided that NIST will make a series of 10 kg and 1 kg indents into a range of 10 or more ceramics. We will assess the quality of the indentations and formulate a recommendation for a USA stance (to be determined at the next C-28 meeting) on the ISO draft standard.

Several inquiries have been received regarding the applicability of the new NIST SRM's for instrumented hardness or nanoindentation testing.

Figure 1

The two NIST hardness standard reference materials. #2830 is a silicon nitride which will have Knoop indents. #2831 is a tungsten carbide with Vickers indents.

A prototype SRM silicon nitride specimen was sent to Germany where Dr. Christian Ullner of BAM studied it with "recording hardness" testing. The disk was suitable and now a new VAMAS round robin is being set up which will study this method. Prototype Knoop-silicon nitride and Vickers-tungsten carbide disks were also sent to Dr. Stephen Webb of Wilson-Instron in Massachusetts for similar evaluation. The NIST SRM's were not prepared for these purposes, but they may be found to be satisfactory.

Fractography

This work is focussing on creating a standard practice for fractographic characterization of fracture origins in advanced structural ceramics. Military Handbook (MIL HBK) 790, which was completed in June 1992, is in widespread use in the United States and Europe, and serves as the basis of this work. This work is a collaboration between G. Quinn of NIST and J. Swab of U. S. Army Research Laboratory (ARL).

The draft ASTM standard "Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics," which is an improvement on MIL HBK 790, was balloted by subcommittee C-28.05, in November, 1994. Mr. Quinn and Mr. Swab made a number of changes to the document and it was resubmitted to ASTM in August for a Fall, 1995 ballot.

Papers on the results of the recently completed VAMAS round robin were presented by Mr. Swab at the conference on Fractography at Alfred University in July, 1995. This conference was a marvelous forum for the key participants in the IEA and VAMAS projects to come together and discuss the draft standards and the round robins.

Diametral Compression

Information has been accumulated on the diametral compression test, illustrated in Figure 2, and approval to form a task group in C28.01 for this method was obtained. Mr. Quinn and Mr. Swab of the U. S. ARL will collaborate on a project to evaluate this method and prepare a draft standard. Materials are being accumulated and specimens are being prepared. Emphasis will be on applying sound fractographic techniques to the fractured disks. This may help clear up the question of why diametral compression strength often does not agree with results from other methods.

Other Activities

Al Segal of the Center of Advanced Materials at Pennsylvania State University requested help in revising his C-ring strength standard.

G. Quinn helped Chuck Brinkman of ORNL write a paper about the activities of ASTM Committee C-28 for the Annual Meeting of the American Ceramic Society in April, 1995. We collaborated again in writing a chapter on mechanical test method standards for a new book on Mechanical Testing of Ceramics which David Crammer of NIST is editing for Marcel Dekker.

As a result of new work on machining of several silicon nitrides, Dr. S. Jahanmir of NIST requested clarification on the specifications for machining bend bars in the ASTM and MIL STD flexure standards. The specifications call for rather low removal rates per pass (.0002 mm) in

Figure 2
Diametral Compression Strength Testing

the final longitudinal grinding stages. The rationale for this rate was reviewed and a survey made of current world standards. Bomas and Chand Kare were contacted for further information. The rates of removal were intentionally chosen in 1982 to be conservative, and were intended for a wide range of materials, not merely silicon nitrides. No changes to the machining specifications are planned at this time, but this topic may come up when the new ISO draft flexure standard is proposed.

Status of Milestones

412125 Prepare a draft of "Standard Practice for Size Scaling of Uniaxial Strengths Using Weibull Statistics for Advanced Ceramics"

Ongoing, (Task group led by S. Duffy, NASA-Lewis)

The following are all on schedule:

412126 Prepare a draft ISO flexure strength standard
 412127 Review fracture mirror literature, and plan a program for mirror constant evaluation
 412128 Write a comprehensive paper on hardness testing of ceramics
 412129 Fabricate and Test diametral compression specimens
 41230 Evaluate the fracture toughness of ceramics with high or low low fracture toughnesses by SCF

Publications/Presentations

1. R. Gettings and G. Quinn, "Surface Crack in Flexure (SCF) Measurements of the Fracture Toughness of Advanced Ceramics," Ceram. Eng. and Sci. Proc., Vol. 16, No.4 (1995) pp. 539-547.
2. J. Swab and G. Quinn, "Fractography of Advanced Structural Ceramics: Results from Topic #2 of the VAMAS Round Robin Exercise," Ceram. Eng. and Sci. Proc., Vol. 16, No. 5, (1995) pp. 929-938.
3. J. Swab and G. Quinn, "Fractography of Advanced Structural Ceramics: Results from the VAMAS Round Robin Exercise," U.S. ARL Technical Report TR 656, Dec. 1994.
4. J. J. Swab and G. D. Quinn, "Fractography of Advanced Structural Ceramics, Results from the VAMAS Round Robin Exercise," VAMAS Report #19, June 1995.)
5. C. R. Brinkman, G. D. Quinn, and R. W. McClung, "Overview of ASTM Standard Activities in Support of Advanced Structural Ceramics Development," to be publ. Ceram. Eng. and Sci. Proc., 1995.
6. R. J. Gettings, G. D. Quinn, A. W. Ruff, and L. K. Ives "Hardness Standard Reference Materials (SRM's) for Advanced Ceramics," submitted to the 9th International Symposium on Hardness Testing in Theory and Practice," Dusseldorf, Nov. 1995.
7. G. D. Quinn, R. J. Gettings, and J. J. Kübler, "Fracture Toughness of Ceramics by the Surface Crack in Flexure (SCF) Method," submitted to the 6th International Symposium on Fracture Mechanics of Ceramics, Karlsruhe, July, 1995.
8. G. D. Quinn and R. J. Gettings, "Fractography and the Surface Crack in Flexure (SCF) Method for Evaluating Fracture Toughness of Ceramics," submitted to the Third Alfred Conference on Fractography of Glasses and Ceramics," July, 1995.
9. J. J. Swab and G. D. Quinn, "Findings of the VAMAS Fractography Round Robin Exercise," *ibid.*

Communications/Visits

1. G. Quinn attended the ASTM Committee C-28 meeting in Denver in June, 1995.
2. T. Ohji of NIRIN Nagoya met G. Quinn at Karlsruhe in July to talk about fracture toughness and tension standards for ISO.
3. M. Sakaguchi of NIRIN, Nagoya repeatedly contacted NIST regarding hardness standards. Sakaguchi met Quinn at the Karlsruhe meeting.
4. J. Swab of the U.S. ARL came to work at NIST as an exchange scientist.
5. An instrumented hardness program was set up for VAMAS in cooperation with the German Lab, BAM. Christian Ullner of BAM will organize this project.
6. G. Quinn had extensive contact and communications with I. Bar-on, WPI regarding the preparation of the draft fracture toughness standard.
7. G. Quinn contacted Dr. Herman Vettters, the German leader of CEN TC 184, Working Group #2, to learn more about CEN standards for ceramic coatings.
8. Jurgen Rödel of the Technical Hochschule Darmstadt visited NIST and discussed details of SCF fracture toughness testing. He uses this method routinely now. A new round robin is being organized in Europe on the method, and G. Quinn will inquire further about this.
9. Golden Ceramics inquired about methods to test for edge chip sensitivity. Details about a test method and a dedicated machine to measure this were sent to Golden.
10. Michael Gardos of Hughes sent extensive information about fracture toughness and hardness test data on silicon nitride bearing ball materials to G. Quinn. One set of results was on NC 132. Fracture toughness results by the so called "indentation fracture" method (indent and measure the surface traces) could be made to agree with other data only if a correction factor was applied. Discrepancies in hardness data generated at Hughes were noted.
11. G. Quinn contacted C. Breder and M. Perber of ORNL in order to coordinate VAMAS and IEA programs. IEA and VAMAS meetings at Alfred University in July helped coordinate the fractography work in each program.

INTERNAL DISTRIBUTION

Central Research Library (2)	M. A. Janney
Document Reference Section	D. R. Johnson (5)
Laboratory Records Department (2)	D. Joslin
Laboratory Records, ORNL RC	R. R. Judkins
ORNL Patent Section	M. A. Karnitz
M&C Records Office (3)	B. L. Keyes
L. F. Allard, Jr.	H. D. Kimrey, Jr.
L. D. Armstrong	R. J. Lauf
P. F. Becher	W. Y. Lee
R. F. Bernal	K. C. Liu
T. M. Besmann	E. L. Long, Jr.
P. J. Blau	W. D. Manly
R. A. Bradley	R. W. McClung
K. Breder	D. J. McGuire
C. R. Brinkman	T. A. Nolan
V. R. Bullington	A. E. Pasto
G. M. Caton	K. P. Plucknett
S. J. Chang	M. H. Rawlins
A. Choudhury	M. L. Santella
D. D. Conger	A. C. Schaffhauser
R. H. Cooper, Jr.	E. J. Soderstrom
S. A. David	D. P. Stinton
J. L. Ding	R. W. Swindeman
M. K. Ferber	T. N. Tiegs
R. L. Graves	B. H. West
D. L. Greene	S. G. Winslow
H. W. Hayden, Jr.	J. M. Wyrick
C. R. Hubbard	R. E. Ziegler

EXTERNAL DISTRIBUTION

Pioneering Research Info. Ctr.
E.I. Dupont de Nemours & Co.
Experimental Station
P.O. Box 80302
Wilmington DE 19880-0302

Jeffrey Abboud
U.S. Advanced Ceramics Assoc.
1600 Wilson Blvd., Suite 1008
Arlington VA 22209

James H. Adair
University of Florida
Materials Science & Engineering
317 MAE Bldg.
Gainesville FL 32611-2066

Donald F. Adams
University of Wyoming
Mechanical Engineering Dept.
P.O. Box 3295
Laramie WY 82071

Andrzej Aeamski
Materials Conversion Group
236-B Egidi Drive
Wheeling IL 60090

Jalees Ahmad
AdTech Systems Research Inc.
Solid Mechanics
1342 N. Fairfield Road
Dayton OH 45432-2698

Yoshio Akimune
NISSAN Motor Co., Ltd.
Materials Research Laboratory
1 Natsushima-Cho
Yokosuka 237
JAPAN

Mufit Akinc
Iowa State University
322 Spedding Hall
Ames IA 50011

Ilhan A. Aksay
Princeton University
A313 Engineering Quadrangle
Princeton NJ 08544-5263

Charles Aldridge
Heany Industries, Inc.
249 Briarwood Lane
Scottsville NY 14546

Joseph E. Amaral
Instron Corporation
Corporate Engineering Office
100 Royale Street
Canton MA 02021

Edward M. Anderson
Aluminum Company of America
N. American Industrial Chemical P.O.
Box 300
Bauxite AR 72011

Norman C. Anderson
Ceradyne, Inc.
Ceramic-to-Metal Division
3169 Redhill Avenue
Costa Mesa CA 92626

Don Anson
BCL
Thermal Power Systems
505 King Avenue
Columbus OH 43201-2693

Thomas Arbanas
G.B.C. Materials Corporation
580 Monastery Drive
Latrobe PA 15650-2698

Frank Armatís
3M Company
Building 60-1N-01
St. Paul MN 55144-1000

Everett B. Arnold
 Detroit Diesel Corporation
 Mechanical Systems Technology
 13400 Outer Drive West
 Detroit MI 48239-4001

Bertil Aronsson
 Sandvik AB
 S-12680
 Stockholm Lerkrogsvagen 19
 SWEDEN

Dennis Assanis
 University of Michigan
 Dept. of Mechanical Engineering
 321 W.E. Lay, N.C.
 Ann Arbor MI 48109

V. S. Avva
 North Carolina A&T State Univ.
 Dept. of Mechanical Engineering
 Greensboro NC 27411

Patrick Badgley
 Sky Technologies, Inc.
 2815 Franklin Drive
 Columbus IN 47201

Sunggi Baik
 Pohang Institute Sci. & Tech.
 P.O. Box 125
 Pohang 790-600
 KOREA

Bob Baker
 Ceradyne, Inc.
 3169 Redhill Avenue
 Costa Mesa CA 92626

Frank Baker
 Aluminum Company of America
 Alcoa Technical Center
 Alcoa Center PA 15069

Clifford P. Ballard
 AlliedSignal Aerospace Company
 Ceramics Program
 P.O. Box 1021
 Morristown NJ 07962-1021

B. P. Bandyopadhyay
 University of North Dakota
 Box 8359 University Station
 Grand Forks, ND 58202-8359

P. M. Barnard
 Ruston Gas Turbines Limited
 P.O. Box 1
 Lincoln LN2 5DJ
 ENGLAND

Harold N. Barr
 Hittman Corporation
 9190 Red Branch Road
 Columbia MD 21045

Renald D. Bartoe
 Vesuvius McDanel
 510 Ninth Avenue
 Box 560
 Beaver Falls PA 15010-0560

David L. Baty
 Babcock & Wilcox - LRC
 P.O. Box 11165
 Lynchburg VA 24506-1165

Donald F. Baxter, Jr.
 ASM International
 Advanced Materials & Processes
 Materials Park OH 44073-0002

M. Brad Beardsley
 Caterpillar Inc.
 Technical Center Bldg. E
 P.O. Box 1875
 Peoria IL 61656-1875

John C. Bell
 Shell Research Limited
 Thornton Research Centre
 P.O. Box 1
 Chester CH1 3SH
 ENGLAND

Larry D. Bentsen
 BFGoodrich Company
 R&D Center
 9921 Brecksville Road
 Brecksville OH 44141

Tom Bernecki
 Northwestern University
 1801 Maple Avenue
 Evanston IL 60201-3135

Charles F. Bersch
 Institute for Defense Analyses
 1801 N. Beauregard Street
 Alexandria VA 22311

Ram Bhatt
 NASA Lewis Research Center
 21000 Brookpark Road
 Cleveland OH 44135

William D. Bjorndahl
 TRW, Inc.
 One Space Park, MS:R6-2188
 Building 01, Room 2040
 Redondo Beach CA 90278

Keith A. Blakely
 Advanced Refractory Technologies, Inc.
 699 Hertel Avenue
 Buffalo NY 14207

Edward G. Blanchard
 Netzsch Inc.
 119 Pickering Way
 Exton PA 19341

Bruce Boardman
 Deere & Company Technical Ctr.
 3300 River Drive
 Moline IL 61265

Lawrence P. Boesch
 EER Systems Corp.
 1593 Spring Hill Road
 Vienna VA 22182-2239

Donald H. Boone
 Boone & Associates
 2412 Cascade Drive
 Walnut Creek CA 94598-4313

Tom Booth
 AlliedSignal, Inc.
 AiResearch Los Angeles Division
 2525 West 190th Street
 Torrance CA 90509-2960

Raj Bordia
 University of Washington
 Roberts Hall
 Box 35212
 Seattle WA 98195-2120

Tibor Bornemisza
 Energy Technologies Applications, Inc.
 5064 Caminito Vista Lujo
 San Diego CA 92130-2846

J.A.M. Boulet
 University of Tennessee
 Engineering Science & Mechanics
 Knoxville TN 37996-2030

Leslie J. Bowen
 Materials Systems
 53 Hillcrest Road
 Concord MA 01742

Steven C. Boyce
 Air Force Office of Scientific
 Research
 AFOSR/NA Bldg. 410
 Bolling AFB DC 20332-6448

Steve Bradley
UOP Research Center
50 E. Algonquin Road
Des Plaines IL 60017-6187

Michael C. Brands
Cummins Engine Company, Inc.
P.O. Box 3005, Mail Code 50179
Columbus IN 47201

Raymond J. Bratton
Westinghouse Science & Technology
1310 Beulah Road
Pittsburgh PA 15235

John J. Brennan
United Technologies Corporation
Silver Lane, MS:24
East Hartford CT 06108

Gunnar Broman
317 Fairlane Drive
Spartanburg SC 29302

Alan Brown
P.O. Box 882
Dayton NJ 08810

Jesse J. Brown
VPI & SU
Ctr. for Adv. Ceram. Mater.
Blacksburg VA 24061-0256

Sherman D. Brown
University of Illinois
Materials Science & Engineering
105 South Goodwin Avenue
Urbana IL 61801

S. L. Bruner
Ceramatec, Inc.
2425 South 900 West
Salt Lake City UT 84119

Walter Bryzik
U.S. Army Tank Automotive
Command
R&D Center, Propulsion Systems
Warren MI 48397-5000

Curt V. Burkland
AMERCOM, Inc.
8928 Fullbright Avenue
Chatsworth CA 91311

Bill Bustamante
AMERCOM, Inc.
8928 Fullbright Avenue
Chatsworth CA 91311

Oral Buyukozturk
Massachusetts Institute of
Technology
77 Massachusetts Ave., Rm 1-280
Cambridge MA 02139

David A. Caillet
Ethyl Corporation
451 Florida Street
Baton Rouge La 70801

Roger Cannon
Rutgers University
P.O. Box 909
Piscataway NJ 08855-0909

Scott Cannon
P.O. Box 567254
Atlanta GA 30356

Harry W. Carpenter
1844 Fuerte Street
Fallbrook CA 92028

David Carruthers
Kyocera Industrial Ceramics
P.O. Box 2279
Vancouver WA 98668-2279

Calvin H. Carter, Jr.
Cree Research, Inc.
2810 Meridian Parkway
Durham NC 27713

J. David Casey
35 Atlantis Street
West Roxbury MA 02132

Jere G. Castor
J. C. Enterprise
5078 N. 83rd Street
Scottsdale AZ 85250

James D. Cawley
Case Western Reserve University
Materials Science & Engineering
Cleveland OH 44106

Thomas C. Chadwick
Den-Mat Corporation
P.O. Box 1729
Santa Maria CA 93456

Ronald H. Chand
Chand Kare Technical Ceramics
2 Coppage Drive
Worcester MA 01603-1252

William Chapman
Williams International Corp.
2280 W. Maple Road
Walled Lake MI 48390-0200

Ching-Fong Chen
LECO Corporation
3000 Lakeview Avenue
St. Joseph MI 49085

William J. Chmura
Torrington Company
59 Field Street
Torrington CT 06790-4942

Tsu-Wei Chou
University of Delaware
201 Spencer Laboratory
Newark DE 19716

R. J. Christopher
Ricardo Consulting Engineers
Bridge Works
Shoreham-By-Sea W. Sussex
BN435FG ENGLAND

Joel P. Clark
Massachusetts Institute of
Technology
Room 8-409
Cambridge MA 02139

Giorgio Clarotti
Commission of the European Comm
DGXII-C3, MO75, 1-53;
200 Rue de la Loi
B-1049 Brussels
BELGIUM

W. J. Clegg
ICI Advanced Materials
P.O. Box 11, The Heath
Runcorn Cheshire WA7 4QE
ENGLAND

William S. Coblentz
Adv. Research Projects Agency
3701 N. Fairfax Drive
Arlington VA 22203

Gloria M. Collins
ASTM
1916 Race Street
Philadelphia PA 19103

William C. Connors
Sundstrand Aviation Operations
Materials Science & Engineering
4747 Harrison Avenue
Rockford IL 61125-7002

Shawn Cooper
FEV Engine Technology
2285 Opdyke Road, Suite F
Auburn Hills, MI 48326

John A. Coppola
Carborundum Company
Niagara Falls R&D Center
P.O. Box 832
Niagara Falls NY 14302

Normand D. Corbin
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

Douglas Corey
AlliedSignal, Inc.
2525 West 190th Street, MS:T52
Torrance CA 90504-6099

Keith P. Costello
Chand/Kare Technical Ceramics
2 Coppage Drive
Worcester MA 01603-1252

Ed L. Courtright
Pacific Northwest Laboratory
MS:K3-59
Richland WA 99352

Anna Cox
Mitchell Market Reports
20 St. James Street
Monmouth Gwent NP5 3DL
UNITED KINGDOM

J. Wesley Cox
BIRL
1801 Maple Avenue
Evanston IL 60201-3135

Art Cozens
Instron Corporation
3414 Snowden Avenue
Long Beach CA 90808

Mark Crawford
New Technology Week
4604 Monterey Drive
Annandale VA 22003

Richard A. Cree
Markets & Products, Inc.
P.O. Box 14328
Columbus OH 43214-0328

Les Crittenden
Vesuvius McDanel
Box 560
Beaver Falls PA 15010

M. J. Cronin
Mechanical Technology, Inc.
968 Albany-Shaker Road
Latham NY 12110

Gary M. Crosbie
Ford Motor Company
20000 Rotunda Drive
MD-3182, SRL Building
Dearborn MI 48121-2053

Floyd W. Crouse, Jr.
U.S. Department of Energy
Morgantown Energy Tech. Ctr.
P.O. Box 880
Morgantown WV 26505

John Cuccio
AlliedSignal Engines
P.O. Box 52180, MS:1302-2Q
Phoenix AZ 85072-2180

Raymond A. Cutler
Ceramatec, Inc.
2425 South 900 West
Salt Lake City UT 84119

Stephen C. Danforth
Rutgers University
P.O. Box 909
Piscataway NJ 08855-0909

Sankar Das Gupta
Electrofuel Manufacturing Co.
9 Hanna Avenue
Toronto Ontario MGK-1W8
CANADA

Frank Davis
AlliedSignal Aerospace Company
7550 Lucerne Drive, #203
Middleburg Heights OH 44130

Robert F. Davis
North Carolina State University
Materials Engineering Department
P.O. Box 7907
Raleigh NC 27695

George C. DeBell
Ford Motor Company
Scientific Research Lab
P.O. Box 2053, Room S2023
Dearborn MI 48121-2053

Michael DeLuca
RSA Research Group
1534 Claas Ave.
Holbrook NY 11741

Gerald L. DePoorter
Colorado School of Mines
Metallurgical & Materials Engr
Golden CO 80401

J. F. DeRidder
Omni Electro Motive, Inc.
12 Seely Hill Road
Newfield NY 14867

Nick C. Dellow
Materials Technology Publications
40 Sotherton Road
Watford Herts WD1 2QA
UNITED KINGDOM

L. R. Dharani
University of Missouri-Rolla
224 M.E.
Rolla MO 65401

Douglas A. Dickerson
Union Carbide Specialty Powders
1555 Main Street
Indianapolis IN 46224

John Dodsworth
Vesuvius Research & Development
Technical Ceramics Group
Box 560
Beaver Falls PA 15010

B. Dogan
Institut für Werkstofforschung
GKSS-Forschungszentrum Geesthacht
Max-Planck-Strasse
D-2054 Geesthacht
GERMANY

Alan Dragoo
U.S. Department of Energy
ER-131, MS:F-240
Washington DC 20817

Jean-Marie Drapier
FN Moteurs S.A.
Material and Processing
B-4041 Milmort (Herstal)
BELGIUM

Kenneth C. Dreitlein
United Technologies Res. Ctr.
Silver Lane
East Hartford CT 06108

Robin A.L. Drew
McGill University
3450 University Street
Montreal Quebec H3A 2A7
CANADA

Winston H. Duckworth
BCL
Columbus Division
505 King Avenue
Columbus OH 43201-2693

Ernest J. Duwell
3M Abrasive Systems Division
3M Center
St. Paul MN 55144-1000

Robert J. Eagan
Sandia National Laboratories
Engineered Mater. & Proc.
P.O. Box 5800
Albuquerque NM 87185-5800

Harry E. Eaton
United Technologies Corporation
Silver Lane
East Hartford CT 06108

Harvill C. Eaton
Louisiana State University
240 Thomas Boyd Hall
Baton Rouge LA 70803

J. J. Eberhardt
U.S. Department of Energy
Office of Transportation Technologies
EE-33, Forrestal Building
Washington DC 20585

Jim Edler
Eaton Corporation
26201 Northwestern Highway
P.O. Box 766
Southfield MI 48037

G. A. Eisman
Dow Chemical Company
Ceramics and Advanced Materials
52 Building
Midland MI 48667

William A. Ellingson
Argonne National Laboratory
Energy Technology Division
9700 S. Cass Avenue
Argonne IL 60439

Anita Kaye M. Ellis
Machined Ceramics
629 N. Graham Street
Bowling Green KY 42101

Glen B. Engle
Nuclear & Aerospace Materials
16716 Martincoit Road
Poway CA 92064

Art Erdemir
Argonne National Laboratory
9700 S. Cass Avenue
Argonne IL 60439

E. M. Erwin
Lubrizol Corporation
17710 Riverside Drive
Lakewood OH 44107

W. L. Everitt
Kyocera International, Inc.
8611 Balboa Avenue
San Diego CA 92123

Gordon Q. Evison
332 S. Michigan Avenue
Suite 1730
Chicago IL 60604

John W. Fairbanks
U.S. Department of Energy
Office of Transportation Technologies
EE-33, Forrestal Building
Washington DC 20585

Tim Fawcett
Dow Chemical Company
Advanced Ceramics Laboratory
1776 Building
Midland MI 48674

Robert W. Fawley
Sundstrand Power Systems
Div. of Sundstrand Corporation
P.O. Box 85757
San Diego CA 92186-5757

Jeff T. Fenton
Vista Chemical Company
900 Threadneedle
Houston TX 77079

Raymond R. Fessler
BIRL
1801 Maple Avenue
Evanston IL 60201

Ross F. Firestone
Ross Firestone Company
188 Mary Street
Winnetka IL 60093-1520

Sharon L. Fletcher
Arthur D. Little, Inc.
15 Acorn Park
Cambridge MA 02140-2390

Michael Foley
Norton Company
Goddard Road
Northboro MA 01532-2527

Thomas F. Foltz
Textron Specialty Materials
2 Industrial Avenue
Lowell MA 01851

Renee G. Ford
Materials and Processing Report
P.O. Box 72
Harrison NY 10528

Edwin Frame
Southwest Research Institute
P.O. Drawer 28510
San Antonio TX 78284

Armanet Francois
French Scientific Mission
4101 Reservoir Road, N.W.
Washington DC 20007-2176

R. G. Frank
Technology Assessment Group
10793 Bentley Pass Lane
Loveland OH 45140

David J. Franus
Forecast International
22 Commerce Road
Newtown CT 06470

Marc R. Freedman
NASA Lewis Research Center
21000 Brookpark Road, MS:49-3
Cleveland OH 44135

Douglas Freitag
Bayside Materials Technology
17 Rocky Glen Court
Brookeville MD 20833

Brian R.T. Frost
Argonne National Laboratory
9700 S. Cass Avenue, Bldg. 900
Argonne IL 60439

Lawrence R. Frost
Instron Corporation
100 Royall Street
Canton MA 02021

Xiren Fu
Shanghai Institute of Ceramics
1295 Ding-xi Road
Shanghai 200050
CHINA

J. P. Gallagher
University of Dayton Research
Institute
300 College Park, JPC-250
Dayton OH 45469-0120

Richard Gates
NIST
Materials Bldg., A-256
Gaithersburg MD 20899

L. J. Gauckler
ETH-Zurich
Sonneggstrasse 5
CH-8092 Zurich 8092
SWITZERLAND

D. Gerster
CEA-DCOM
33 Rue De La Federation
Paris 75015
FRANCE

John Ghinazzi
Coors Technical Ceramics Co.
1100 Commerce Park Drive
Oak Ridge TN 37830

Robert Giddings
General Electric Company
P.O. Box 8
Schenectady NY 12301

A. M. Glaeser
University of California
Lawrence Berkeley Laboratory
Hearst Mining Building
Berkeley CA 94720

Joseph W. Glatz
510 Rocksville Road
Holland PA 18966

W. M. Goldberger
Superior Graphite Company
R&D
2175 E. Broad Street
Columbus OH 43209

Allan E. Goldman
U.S. Graphite, Inc.
907 W. Outer Drive
Oak Ridge TN 37830

Stephen T. Gonczy
Allied Signal Research
P.O. Box 5016
Des Plaines IL 60017

Robert J. Gottschall
U.S. Department of Energy
ER-131, MS:G-236
Washington DC 20585

Earl Graham
Cleveland State University
Dept. of Chemical Engineering
Euclid Avenue at East 24th St.
Cleveland OH 44115

John W. Graham
Astro Met, Inc.
9974 Springfield Pike
Cincinnati OH 45215

G. A. Graves
U. of Dayton Research Institute
300 College Park
Dayton OH 45469-0001

Robert E. Green, Jr.
Johns Hopkins University
Mater. Sci. and Engineering
Baltimore MD 21218

Alex A. Greiner
Plint & Partners
Oaklands Park
Wokingham Berkshire RG11 2FD
UNITED KINGDOM

Lance Groseclose
Allison Engine Company
P.O. Box 420, MS:W-5
Indianapolis IN 46206

Thomas J. Gross
U.S. Department of Energy
Office of Transportation Technologies
EE-30, Forrestal Building
Washington DC 20585

Mark F. Gruninger
Union Carbide Corporation
Specialty Powder Business
1555 Main Street
Indianapolis IN 46224

Ernst Gugel
Cremer Forschungsinstitut
GmbH&Co.KG
Oeslauer Strasse 35
D-96472 Roedenta
GERMANY

John P. Gyekenyesi
NASA Lewis Research Center
21000 Brookpark Road, MS:6-1
Cleveland OH 44135

Nabil S. Hakim
Detroit Diesel Corporation
13400 Outer Drive West
Detroit MI 48239

Philip J. Haley
Allison Engine Company
P.O. Box 420, MS:T12A
Indianapolis IN 46206-0420

Judith Hall
Fiber Materials, Inc.
Biddeford Industrial Park
5 Morin Street
Biddeford ME 04005

Y. Hamano
Kyocera Industrial Ceramics
5713 E. Fourth Plain Blvd.
Vancouver WA 98661-6857

Y. Harada
IIT Research Institute
10 West 35th Street
Chicago IL 60616

Norman H. Harris
Hughes Aircraft Company
P.O. Box 800520
Saugus CA 91380-0520

Alan M. Hart
Dow Chemical Company
1776 Building
Midland MI 48674

Pat E. Hart
Battelle Pacific Northwest Labs
Ceramics and Polymers Development
P.O. Box 999
Richland WA 99352

Michael H. Haselkorn
Caterpillar Inc.
Technical Center, Building E
P.O. Box 1875
Peoria IL 61656-1875

Deborah A. Haught
U.S. Department of Energy
Off. of Transportation Technologies
EE-32, Forrestal Bldg.
Washington DC 20585

N. B. Havewala
Corning Inc.
SP-PR-11
Corning NY 14831

John Haygarth
Teledyne WAA Chang Albany
P.O. Box 460
Albany OR 97321

Norman L. Hecht
U. of Dayton Research Institute
300 College Park
Dayton OH 45469-0172

Peter W. Heitman
Allison Engine Company
P.O. Box 420, MS:W-5
Indianapolis IN 46206-0420

Robert W. Hendricks
VPI & SU
210 Holden Hall
Blacksburg VA 24061-0237

Thomas P. Herbell
NASA Lewis Research Center
21000 Brookpark Road, MS:49-3
Cleveland OH 44135

Robert L. Hershey
Science Management Corporation
1255 New Hampshire Ave., N.W.
Suite 1033
Washington DC 20036

Hendrik Heystek
Bureau of Mines
Tuscaloosa Research Center
P.O. Box L
University AL 35486

Robert V. Hillery
GE Aircraft Engines
One Neumann Way, M.D. H85
Cincinnati OH 45215

Arthur Hindman
Instron Corporation
100 Royall Street
Canton MA 02021

Shinichi Hirano
Mazda R&D of North America
1203 Woodridge Avenue
Ann Arbor MI 48105

Tommy Hiraoka
NGK Locke, Inc.
1000 Town Center
Southfield MI 48075

Fu H. Ho
5645 Soledad Mtn. Road
San Diego, CA 92037-7256

John M. Hobday
U.S. Department of Energy
Morgantown Energy Tech. Ctr.
P.O. Box 880
Morgantown WV 26507

Thomas Hollstein
Fraunhofer-Institut für
Werkstoffmechanik
Wohlerstrasse 11
D-79108 Freiburg
GERMANY

Richard Holt
Natl. Research Council Canada
Structures and Materials Lab
Ottawa Ontario K1A 0R6
CANADA

Woodie Howe
Coors Technical Ceramics
1100 Commerce Park Drive
Oak Ridge TN 37830

Stephen M. Hsu
NIST
Quince Orchard & Clopper Road
Bldg. 223, Rm A256
Gaithersburg MD 20899

Hann S. Huang
Argonne National Laboratory
9700 S. Cass Avenue
Argonne IL 60439-4815

Gene Huber
Precision Ferrites & Ceramics
5576 Corporate Drive
Cypress CA 90630

Fred R. Huettig
Advanced Magnetics Inc.
45 Corey Lane
Mendham NJ 07945

Brian K. Humphrey
 Lubrizol Petroleum Chemicals
 3000 Town Center, Suite 1340
 Southfield MI 48075-1201

Robert M. Humrick
 Dylon Ceramic Technologies
 3100 Edgehill Road
 Cleveland Heights OH 44118

Michael S. Inoue
 Kyocera International, Inc.
 8611 Balboa Avenue
 San Diego CA 92123-1580

Joseph C. Jackson
 U.S. Advanced Ceramics Assoc.
 1600 Wilson Blvd., Suite 1008
 Arlington VA 22209

Osama Jadaan
 U. of Wisconsin-Platteville
 1 University Plaza
 Platteville WI 53818

Said Jahanmir
 NIST
 Materials Bldg., Room A-237
 Gaithersburg MD 20899

Curtis A. Johnson
 General Electric Company
 P.O. Box 8
 Schenectady NY 12301

Sylvia Johnson
 SRI International
 333 Ravenswood Avenue
 Menlo Park CA 94025

Thomas A. Johnson
 Lanxide Corporation
 P.O. Box 6077
 Newark DE 19714-6077

Walter F. Jones
 AFOSR/NA
 110 Duncan Ave., Ste. B115
 Washington DC 20332-0001

Jill E. Jonkouski
 U.S. Department of Energy
 9800 S. Cass Avenue
 Argonne IL 60439-4899

L. A. Joo
 Great Lakes Research Corporation
 208 Chickasaw Street
 Johnson City TN 37604-1409

Adam Jostsons
 Australian Nuclear Science &
 Technology
 New Illawarra Road
 Lucas Heights New South Wales
 AUSTRALIA

Lyle R. Kallenbach
 Phillips Petroleum
 Mail Drop:123AL
 Bartlesville OK 74004

Nick Kamiya
 Kyocera Industrial Ceramics Corp. 25 NW
 Point Blvd., #450
 Elk Grove Village IL 60007

Roy Kamo
 Adiabatics, Inc.
 3385 Commerce Park Drive
 Columbus IN 47201

Chih-Chun Kao
 Industrial Technology Research
 Institute
 195 Chung-Hsing Road, Sec. 4
 Chutung Hsinchu 31015 R.O.C.
 TAIWAN

Keith R. Karasek
AlliedSignal Aerospace Company
50 E. Algonquin Road
Des Plaines IL 60017-5016

Robert E. Kassel
Ceradyne, Inc.
3169 Redhill Avenue
Costa Mesa CA 92626

Allan Katz
Wright Laboratory
Metals and Ceramics Division
Wright-Patterson AFB OH 45433

R. Nathan Katz
Worcester Polytechnic Institute
100 Institute Road
Worcester MA 01609

Tony Kaushal
GE Transportation Systems
2902 East Lake Road
Building 14-0008
Erie, PA 16531

Ted Kawaguchi
Tokai Carbon America, Inc.
375 Park Avenue, Suite 3802
New York NY 10152

Noritsugu Kawashima
TOSHIBA Corporation
4-1 Ukishima-Cho
Kawasaki-Ku Kawasaki, 210
JAPAN

Lisa Kempfer
Penton Publishing
1100 Superior Avenue
Cleveland OH 44114-2543

Frederick L. Kennard, III
Delphi Energy & Engine Mgmt. Systems
Division of General Motors
1300 N. Dort Highway
Flint MI 48556

David O. Kennedy
Lester B. Knight Cast Metals
549 W. Randolph Street
Chicago IL 60661

George Keros
Photon Physics
3175 Penobscot Building
Detroit MI 48226

Thomas Ketcham
Corning, Inc.
SP-DV-1-9
Corning NY 14831

Pramod K. Khandelwal
Allison Engine Company
P.O. Box 420, MS:T10B
Indianapolis IN 46206

Jim R. Kidwell
AlliedSignal Engines
P.O. Box 52180
Phoenix AZ 85072-2180

Shin Kim
The E-Land Group
19-8 ChangJeon-dong
Mapo-gu, Seoul 121-190
KOREA

W. C. King
Mack Truck, Z-41
1999 Pennsylvania Avenue
Hagerstown MD 21740

Carol Kirkpatrick
MSE, Inc.
P.O. Box 3767
Butte MT 59702

Tony Kim
Caterpillar Inc.
Defense Products Dept., JB7
Peoria IL 61629

James D. Kiser
NASA Lewis Research Center
21000 Brookpark Road, MS:49-3
Cleveland OH 44135

Max Klein
900 24th Street, N.W., Unit G
Washington DC 20037

Stanley J. Klima
NASA Lewis Research Center
21000 Brookpark Road, MS:6-1
Cleveland OH 44135

Albert S. Kobayashi
University of Washington
Mechanical Engineering Dept.
Mail Stop: FU10
Seattle WA 98195

Shigeki Kobayashi
Toyota Central Research Labs
Nagakute Aichi, 480-11
JAPAN

Richard A. Kole
Z-Tech Corporation
8 Dow Road
Bow NH 03304

Joseph A. Kovach
Eaton Corporation
32500 Chardon Road
Willoughby Hills OH 44094

Kenneth A. Kovaly
Technical Insights Inc.
P.O. Box 1304
Fort Lee NJ 07024-9967

Edwin H. Kraft
Kyocera Industrial Ceramics
5713 E. Fourth Plain Boulevard
Vancouver WA 98661

Arthur Kranish
Trends Publishing Inc.
1079 National Press Building
Washington DC 20045

A. S. Krieger
Radiation Science, Inc.
P.O. Box 293
Belmont MA 02178

Pieter Krijgsman
Ceramic Design International
Holding B.V.
P.O. Box 68
Hattem 8050-AB
THE NETHERLANDS

Waltraud M. Kriven
University of Illinois
105 S. Goodwin Avenue
Urbana IL 61801

Edward J. Kubel, Jr.
ASM International
Advanced Materials & Processes
Materials Park OH 44073

Dave Kupperman
Argonne National Laboratory
9700 S. Cass Avenue
Argonne IL 60439

Oh-Hun Kwon
North Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

W. J. Lackey
GTRI
Materials Science and Tech. Lab
Atlanta GA 30332

Jai Lala
 Tenmat Ltd.
 40 Somers Road
 Rugby Warwickshire CV22 7DH
 ENGLAND

Hari S. Lamba
 General Motors Corporation
 9301 West 55th Street
 LaGrange IL 60525

Richard L. Landingham
 Lawrence Livermore National Lab
 P.O. Box 808, L-369
 Livermore CA 94550

James Lankford
 Southwest Research Institute
 6220 Culebra Road
 San Antonio TX 78228-0510

Stanley B. Lasday
 Business News Publishing Co.
 1910 Cochran Road, Suite 630
 Pittsburgh PA 15220

S. K. Lau
 Carborundum Company
 Technology Division
 P.O. Box 832, B-100
 Niagara Falls NY 14302

J. Lawrence Lauderdale
 Babcock & Wilcox
 1525 Wilson Blvd., #100
 Arlington VA 22209-2411

Jean F. LeCostaouec
 Textron Specialty Materials
 2 Industrial Avenue
 Lowell MA 01851

Benson P. Lee
 Technology Management, Inc.
 4440 Warrensville Rd., Suite A
 Cleveland OH 44128

Burtrand I. Lee
 Clemson University
 Olin Hall
 Clemson SC 29634-0907

June-Gunn Lee
 KIST
 P.O. Box 131, Cheong-Ryang
 Seoul 130-650
 KOREA

Stan Levine
 NASA Lewis Research Center
 21000 Brookpark Road, MS:49-3
 Cleveland OH 44135

David Lewis, III
 Naval Research Laboratory
 Code 6370
 Washington DC 20375-5343

Ai-Kang Li
 Materials Research Labs., ITRI
 195-5 Chung-Hsing Road, Sec. 4
 Chutung Hsinchu 31015 R.O.C.
 TAIWAN

Robert H. Licht
 Norton Company
 SGNICC/NRDC
 Goddard Road
 Northboro MA 01532-1545

E. Lilley
 Norton Company
 SGNICC/NRDC
 Goddard Road
 Northboro MA 01532-1545

Chih-Kuang Lin
 National Central University
 Dept. of Mechanical Engineering
 Chung-Li 32054
 TAIWAN

Laura J. Lindberg
AlliedSignal Aerospace Company
Garrett Fluid Systems Division
P.O. Box 22200
Tempe AZ 85284-2200

Hans A. Lindner
Cremer Forschungsinstitut
GmbH&Co.KG
Oeslauer Strasse 35
D-8633 Rodental 8866
GERMANY

Ronald E. Loehman
Sandia National Laboratories
Chemistry & Ceramics Dept. 1840
P.O. Box 5800
Albuquerque NM 87185

Bill Long
Babcock & Wilcox
P.O. Box 11165
Lynchburg VA 24506

L. A. Lott
EG&G Idaho, Inc.
Idaho National Engineering Lab
P.O. Box 1625
Idaho Falls ID 83415-2209

Raouf O. Loutfy
MER Corporation
7960 S. Kolb Road
Tucson AZ 85706

Lydia Luckevich
Ortech International
2395 Speakman Drive
Mississauga Ontario L5K 1B3
CANADA

James W. MacBeth
Carborundum Company
Structural Ceramics Division
P.O. Box 1054
Niagara Falls NY 14302

George Maczura
Aluminum Company of America
3450 Park Lane Drive
Pittsburgh PA 15275-1119

David Maginnis
Tinker AFB
OC-ALC/LIIRE
Tinker AFB OK 73145-5989

Frank Maginnis
Aspen Research, Inc.
220 Industrial Boulevard
Moore OK 73160

Tai-il Mah
Universal Energy Systems, Inc.
4401 Dayton-Xenia Road
Dayton OH 45432

L. E. Mains
Deco-Grande
4850 Coolidge Highway
Royal Oak MI 48073-1023

Kenneth M. Maillar
Barbour Stockwell Company
83 Linskey Way
Cambridge MA 02142

S. G. Malghan
NIST
I-270 & Clopper Road
Gaithersburg MD 20899

Lars Malmrup
United Turbine AB
Box 13027
Malmo S-200 44
SWEDEN

John Mangels
Ceradyne, Inc.
3169 Redhill Avenue
Costa Mesa CA 92626

Murli Manghnani
University of Hawaii
2525 Correa Road
Honolulu HI 96822

Russell V. Mann
Matec Applied Sciences, Inc.
75 South Street
Hopkinton MA 01748

William R. Manning
Champion Aviation Products Div
P.O. Box 686
Liberty SC 29657

Ken Marnoch
Amercom, Inc.
8928 Fullbright Avenue
Chatsworth CA 91311

Robert A. Marra
Aluminum Company of America
Alcoa Technical Center
Alcoa Center PA 15069

Steve C. Martin
Advanced Refractory Technologies
699 Hertel Avenue
Buffalo NY 14207

Kelly J. Mather
William International Corp.
2280 W. Maple Road
Walled Lake MI 48088

James P. Mathers
3M Company
3M Center, Bldg. 201-3N-06
St. Paul MN 55144

Ron Mayville
Arthur D. Little, Inc.
15-163 Acorn Park
Cambridge MA 02140

F. N. Mazadarany
General Electric Company
Bldg. K-1, Room MB-159
P.O. Box 8
Schenectady NY 12301

James W. McCauley
Alfred University
Binns-Merrill Hall
Alfred NY 14802

Colin F. McDonald
McDonald Thermal Engineering
1730 Castellana Road
La Jolla CA 92037

B. J. McEntire
Norton Company
10 Airport Park Road
East Granby CT 06026

Thomas D. McGee
Iowa State University
110 Engineering Annex
Ames IA 50011

James McLaughlin
Sundstrand Power Systems
4400 Ruffin Road
P.O. Box 85757
San Diego CA 92186-5757

Matt McMonigle
U.S. Department of Energy
Office of Industrial Technologies
EE-234, Forrestal Building
Washington DC 20585

J. C. McVickers
AlliedSignal Engines
P.O. Box 52180, MS:9317-2
Phoenix AZ 85072-2180

D. B. Meadowcroft
 "Jura," The Ridgeway
 Oxshott
 Leatherhead Surrey KT22 OLG
 UNITED KINGDOM

Joseph J. Meindl
 Reynolds International, Inc.
 6603 W. Broad Street
 P.O. Box 27002
 Richmond VA 23261-7003

Michael D. Meiser
 AlliedSignal, Inc.
 Ceramic Components
 P.O. Box 2960, MS:T21
 Torrance CA 90509-2960

George Messenger
 National Research Council of
 Canada
 Building M-7
 Ottawa Ontario K1A 0R6
 CANADA

Arthur G. Metcalfe
 Arthur G. Metcalfe & Assoc.
 2108 East 24th Street
 National City CA 91950

R. Metselaar
 Eindhoven University
 P.O. Box 513
 Eindhoven 5600 MB
 THE NETHERLANDS

David J. Michael
 Harbison-Walker Refractories
 P.O. Box 98037
 Pittsburgh PA 15227

Ken Michaels
 Chrysler Motors Corporation
 P.O. Box 1118, CIMS:418-17-09
 Detroit MI 48288

D. E. Miles
 Commission of the European
 Community
 rue de la Loi 200
 B-1049 Brussels
 BELGIUM

Carl E. Miller
 AC Rochester
 1300 N. Dort Highway, MS:32-31
 Flint MI 48556

Charles W. Miller, Jr.
 Harper International
 West Drullard Avenue
 Lancaster NY 14086-1698

R. Mininni
 Enichem America
 2000 Cornwall Road
 Monmouth Junction NJ 08852

Michele V. Mitchell
 AlliedSignal, Inc.
 Ceramic Components
 P.O. Box 2960, MS:T21
 Torrance CA 90509-2960

Howard Mizuhara
 WESGO
 477 Harbor Boulevard
 Belmont CA 94002

Helen Moeller
 Babcock & Wilcox
 P.O. Box 11165
 Lynchburg VA 24506-1165

Francois R. Mollard
 Concurrent Technologies Corp.
 1450 Scalp Avenue
 Johnstown PA 15904-3374

Phil Mooney
 Panametrics
 221 Crescent Street
 Waltham MA 02254

Geoffrey P. Morris
3M Company
3M Traffic Control Materials
Bldg. 209-BW-10, 3M Center
St. Paul MN 55144-1000

Joel P. Moskowitz
Ceradyne, Inc.
3169 Redhill Avenue
Costa Mesa CA 92626

Brij Moudgil
University of Florida
Material Science & Engineering
Gainesville FL 32611

Christoph J. Mueller
Sprechsaal Publishing Group
P.O. Box 2962, Mauer 2
D-8630 Coburg
GERMANY

Thomas W. Mullan
Vapor Technologies Inc.
345 Route 17 South
Upper Saddle River NJ 07458

Theresa A. Mursick-Meyer
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

M. K. Murthy
MkM Consultants International
10 Avoca Avenue, Unit 1906
Toronto Ontario M4T 2B7
CANADA

David L. Mustoe
Custom Technical Ceramics
8041 W I-70 Service Rd. Unit 6
Arvada CO 80002

Curtis V. Nakaishi
U.S. Department of Energy
Morgantown Energy Tech. Ctr.
P.O. Box 880
Morgantown WV 26507-0880

Yoshio Nakamura
Faicera Research Institute
3-11-12 Misono
Sagamihara, Tokyo
JAPAN

K. S. Narasimhan
Hoeganaes Corporation
River Road
Riverton NJ 08077

Robert Naum
Applied Resources, Inc.
P.O. Box 241
Pittsford NY 14534

Malcolm Naylor
Cummins Engine Company, Inc.
P.O. Box 3005, Mail Code 50183
Columbus IN 47202-3005

Dale E. Niesz
Rutgers University
Center for Ceramic Research
P.O. Box 909
Piscataway NJ 08855-0909

Paul W. Niskanen
Lanxide Corporation
P.O. Box 6077
Newark DE 19714-6077

David M. Nissley
United Technologies Corporation
Pratt & Whitney Aircraft
400 Main Street, MS:163-10
East Hartford CT 06108

Daniel Oblas
50 Meadowbrook Drive
Bedford MA 01730

Don Ohanehi
Magnetic Bearings, Inc.
1908 Sussex Road
Blacksburg VA 24060

Hitoshi Ohmori
ELID Team
Itabashi Branch
1-7 13 Kaga Itabashi
Tokyo 173
JAPAN

Robert Orenstein
General Electric Company
55-112, River Road
Schenectady NY 12345

Richard Palicka
Cercom, Inc.
1960 Watson Way
Vista CA 92083

Joseph N. Panzarino
379 Howard Street
P. O. Box 652
Northboro MA 01532-1545

Pellegrino Papa
Corning Inc.
MP-WX-02-1
Corning NY 14831

Terry Paquet
Boride Products Inc.
2879 Aero Park Drive
Traverse City MI 49684

E. Beth Pardue
MPC
8297 Williams Ferry Road
Lenoir City TN 37771

Soon C. Park
3M Corporate Research
3M Center, Bldg. 251-3B-13
St. Paul MN 55144-1000

Vijay M. Parthasarathy
Caterpillar/Solar Turbines
2200 Pacific Highway
P.O. Box 85376
San Diego CA 92186-5376

Harmut Paschke
Schott Glaswerke
Christoph-Dorner-Strasse 29
D-8300 Landshut
GERMANY

Pandit G. Patil
Department of Energy
Ofc. of Transportation Technologies
EE-32, Forrestal Bldg.
Washington, DC 20585

James W. Patten
Cummins Engine Company, Inc.
P.O. Box 3005, Mail Code 50183
Columbus IN 47202-3005

Robert A. Penty
Penty & Associates
38 Oakdale Drive
Rocester NY 14618

Robert W. Pepper
Textron Specialty Materials
2 Industrial Avenue
Lowell MA 01851

John J. Petrovic
Los Alamos National Laboratory
Group MST-4, MS:G771
Los Alamos NM 87545

Frederick S. Pettit
University of Pittsburgh
Pittsburgh PA 15261

Richard C. Phoenix
Ohmtek, Inc.
2160 Liberty Drive
Niagara Falls NY 14302

Bruce J. Pletka
Michigan Technological Univ.
Metallurgical & Materials Engr.
Houghton MI 49931

John P. Pollinger
AlliedSignal, Inc.
Ceramic Components
P.O. Box 2960, MS:T21
Torrance CA 90509-2960

P. Popper
High Tech Ceramics Int. Journal 22
Pembroke Drive - Westlands
Newcastle-under-Lyme
Staffs ST5 2JN
ENGLAND

F. Porz
Universitat Karlsruhe
Institut für Keramik Im
Maschinendau
Postfach 6980
D-76128 Karlsruhe
GERMANY

Harry L. Potma
Royal Netherlands Embassy
Science and Technology
4200 Linnean Avenue, N.W.
Washington DC 20008

Bob R. Powell
General Motors Corporation
Metallurgy Department
Box 9055
Warren MI 48090-9055

Stephen C. Fred
Biesterfeld U.S., Inc.
500 Fifth Avenue
New York NY 10110

Karl M. Prewo
United Technologies Res. Ctr.
411 Silver Lane, MS:24
East Hartford CT 06108

Vimal K. Pujari
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

Fred Quan
Corning Inc.
Sullivan Park, FR-02-08
Corning NY 14831

George Quinn
NIST
Quince Orchard & Clopper Road
Ceramics Division, Bldg. 223
Gaithersburg MD 20899

Ramas V. Raman
Ceracon, Inc.
1101 N. Market Blvd., Suite 9
Sacramento CA 95834

Charles F. Rapp
Owens Corning Fiberglass
2790 Columbus Road
Granville OH 43023-1200

Dennis W. Readey
Colorado School of Mines
Metallurgy and Materials Engr.
Golden CO 80401

Wilfred J. Rebello
PAR Enterprises, Inc.
12601 Clifton Hunt Lane
Clifton VA 22024

Harold Rechter
Chicago Fire Brick Company
7531 S. Ashland Avenue
Chicago IL 60620

Robert R. Reeber
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park NC
27709-2211

K. L. Reifsnider
VPI & SU
Engineering Science and Mechanics
Blacksburg VA 24061

Paul E. Rempes
McDonnell Douglass Aircraft Co.
P.O. Box 516, Mail Code:0642263
St. Louis MO 63166-0516

Gopal S. Revankar
John Deere Company
3300 River Drive
Moline IL 61265

K. Y. Rhee
Rutgers University
P.O. Box 909
Piscataway NJ 08854

Roy W. Rice
W. R. Grace and Company
7379 Route 32
Columbia MD 21044

David W. Richerson
2093 E. Delmont Drive
Salt Lake City UT 84117

Tomas Richter
J. H. France Refractories
1944 Clarence Road
Snow Shoe PA 16874

Michel Rigaud
Ecole Polytechnique
Campus Universite De Montreal
P.O. Box 6079, Station A
Montreal, P.Q. Quebec H3C 3A7
CANADA

John E. Ritter
University of Massachusetts
Mechanical Engineering Department
Amherst MA 01003

W. Eric Roberts
Advanced Ceramic Technology
990 "F" Enterprise Street
Orange CA 92667

Y. G. Roman
TNO TPD Keramick
P.O. Box 595
Eindhoven 5600 AN
HOLLAND

Michael Rossetti
Arthur D. Little, Inc.
15 Acorn Park
Cambridge MA 01240

Barry Rossing
Lamde Corporation
P.O. Box 6077
Newark DE 19714-6077

Steven L. Rotz
Lubrizol Corporation
29400 Lakeland Boulevard
Wickliffe OH 44092

Robert Ruh
Wright Laboratory
WL/MLLM
Wright-Patterson AFB OH 45433

Robert J. Russell
Riverdale Consulting, Inc.
24 Micah Hamlin Road
Centerville MA 02632-2107

Jon A. Salem
NASA Lewis Research Center
21000 Brookpark Road
Cleveland OH 44135

J. Sankar
North Carolina A&T State Univ.
Dept. of Mechanical Engineering
Greensboro NC 27406

Yasushi Sato
NGK Spark Plugs (U.S.A.), Inc.
1200 Business Center Dr., #300
Mt. Prospect IL 60056

Maxine L. Savitz
AlliedSignal, Inc.
Ceramic Components
P.O. Box 2960, MS:T21
Torrance CA 90509-2960

Ashok Saxena
GTRI
Materials Engineering
Atlanta GA 30332-0245

David W. Scanlon
Instron Corporation
100 Royall Street
Canton MA 02021

Charles A. Schacht
Schacht Consulting Services
12 Holland Road
Pittsburgh PA 15235

Robert E. Schafrik
Nat'l Materials Advisory Board
2101 Constitution Ave., N.W.
Washington DC 20418

James Schienle
AlliedSignal Engines
P.O. Box 52180, MS:1302-2P
Phoenix AZ 85072-2180

Gary Schnittgrund
PyroPacific Processes
16401 Knollwood Drive
Granada Hills, CA 91344

Mark Schomp
Lonza, Inc.
17-17 Route 208
Fair Lann NJ 07410

Joop Schoonman
Delft University of Technology
P.O. Box 5045
2600 GA Delft
THE NETHERLANDS

Robert B. Schulz
U.S. Department of Energy
Office of Transportation Technologies
EE-33, Forrestal Building
Washington DC 20585

Murray A. Schwartz
Materials Technology Consulting 30
Orchard Way, North
Potomac MD 20854

Peter Schwarzkopf
SRI International
333 Ravenswood Avenue
Menlo Park CA 94025

William T. Schwessinger
Multi-Arc Scientific Coatings
1064 Chicago Road
Troy MI 48063-4297

W. D. Scott
University of Washington
Materials Science Department
Mail Stop:FB10
Seattle WA 98195

Nancy Scoville
Thermo Electron Technologies
P.O. Box 9046
Waltham MA 02254-9046

Thomas M. Sebestyen
U.S. Department of Energy
Office of Transportation Technologies
EE-32, Forrestal Building
Washington DC 20585

T. B. Selover
AICRE/DIPPR
3575 Traver Road
Shaker Heights OH 44122

Charles E. Semler
Semler Materials Services
4160 Mumford Court
Columbus OH 43220

Thomas Service
Service Engineering Laboratory
324 Wells Street
Greenfield MA 01301

Kish Seth
Ethyl Corporation
P.O. Box 341
Baton Rouge LA 70821

William J. Shack
Argonne National Laboratory
9700 S. Cass Avenue, Bldg. 212
Argonne IL 60439

Richard K. Shaltens
NASA Lewis Research Center
21000 Brookpark Road, MS:302-2
Cleveland OH 44135

Robert S. Shane
1904 NW 22nd Street
Stuart FL 34994-9270

Ravi Shankar
Chromalloy
Research and Technology
Blaisdell Road
Orangeburg NY 10962

Terence Sheehan
Alplex Wheel Company
727 Berkley Street
New Milford NJ 07646

Dinesh K. Shetty
University of Utah
Materials Science and Engineering
Salt Lake City UT 84112

Masahide Shimizu
New Ceramics Association
Shirasagi 2-13-1-208, Nakano-ku
Tokyo, 165
JAPAN

Thomas Shreves
American Ceramic Society, Inc.
735 Ceramic Place
Westerville OH 43081-8720

Johann Siebels
Volkswagen AG
Werkstofftechnologie
Postfach 3180
Wolfsburg 1
GERMANY

George H. Siegel
Point North Associates, Inc.
P.O. Box 907
Madison NJ 07940

Richard Silbergliitt
FM Technologies, Inc.
10529-B Braddock Road
Fairfax VA 22032

Mary Silverberg
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

Gurpreet Singh
U.S. Department of Energy
Office of Transportation Technologies
EE-33, Forrestal Building
Washington DC 28505

Maurice J. Sinnott
University of Michigan
5106 IST Building
Ann Arbor MI 48109-2099

John Skildum
3M Company
3M Center
Building 224-2S-25
St. Paul MN 55144

Richard H. Smoak
Smoak & Associates
3554 Hollislope Road
Altadena CA 91001-3923

Jay R. Smyth
AlliedSignal Engines
111 S. 34th Street, MS:503-412
Phoenix AZ 85034

Rafal A. Sobotowski
British Petroleum Company
Technical Center, Broadway
3092 Broadway Avenue
Cleveland OH 44115

S. Somiya
Nishi Tokyo University
3-7-19 Seijo, Setagaya
Tokyo, 157
JAPAN

Boyd W. Sorenson
DuPont Lamxide Composites
1300 Marrows Road
Newark DE 19711

Charles A. Sorrell
U.S. Department of Energy
Office of Industrial Technologies
EE-232, Forrestal Building
Washington DC 20585

C. Spencer
EA Technology
Capenhurst Chester CH1 6ES
UNITED KINGDOM

Allen Spizzo
Hercules Inc.
Hercules Plaza
Wilmington DE 19894

Richard M. Spriggs
Alfred University
Ctr. for Advanced Ceramic Tech.
Alfred NY 14802

Charles Spuckler
NASA Lewis Research Center
21000 Brookpark Road, MS:5-11
Cleveland OH 44135-3191

Gordon L. Starr
Cummins Engine Company, Inc.
P.O. Box 3005, Mail Code:50182
Columbus IN 47202-3005

Tom Stillwagon
AlliedSignal, Inc.
Ceramic Components
P.O. Box 2960, MS:T21
Torrance CA 90509-2960

H. M. Stoller
TPL Inc.
3754 Hawkins, N.E.
Albuquerque NM 87109

Paul D. Stone
Dow Chemical USA
1776 "Eye" Street, N.W., #575
Washington DC 20006

F. W. Stringer
Aero & Industrial Technology
P.O. Box 46, Wood Top
Burnley Lancashire BB11 4BX
UNITED KINGDOM

Thomas N. Strom
NASA Lewis Research Center
21000 Brookpark Road, MS:86-6
Cleveland OH 44135

M. F. Stroosnijder
Institute for Advanced Materials
Joint Research Centre
21020 Ispra (VA)
ITALY

Karsten Styhr
30604 Ganado Drive
Rancho Palos Verdes CA 90274

T. S. Sudarshan
Materials Modification, Inc.
2929-P1 Eskridge Center
Fairfax VA 22031

M. J. Sundaresan
University of Miami
P.O. Box 248294
Coral Gables FL 33124

Patrick L. Sutton
U.S. Department of Energy
Office of Transportation Technologies
EE-32, Forrestal Building
Washington DC 20585

Willard H. Sutton
United Technologies Corporation
Silver Lane, MS:24
East Hartford CT 06108

Robert E. Swanson
Metalworking Technology, Inc.
1450 Scalp Avenue
Johnstown PA 15904

Yo Tajima
NGK Spark Plug Company
2808 Iwasaki
Komaki-shi Aichi-ken, 485
JAPAN

Fred Teeter
5 Tralee Terrace
East Amherst NY 14051

Victor J. Tennery
113 Newell Lane
Oak Ridge TN 37830

David F. Thompson
Corning Glass Works
SP-DV-02-1
Corning NY 14831

T. Y. Tien
University of Michigan
Materials Science & Engineering
Dow Building
Ann Arbor MI 48103

D. M. Tracey
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

Marc Tricard
Norton Company, WGTC
1 New Bond Street, MS-413-201
Worcester MA 01615-0008

L. J. Trostel, Jr.
Box 199
Princeton MA 01541

W. T. Tucker
General Electric Company
P.O. Box 8, Bldg. K1-4C35
Schenectady NY 12301

Masanori Ueki
Nippon Steel Corporation
1618 Ida
Nakahara-Ku Kawasaki, 211
JAPAN

Filippo M. Ugolini
ATA Studio
Via Degli Scipioni, 268A
ROMA, 00192
ITALY

Donald L. Vaccari
Allison Gas Turbines
P.O. Box 420, Speed Code S49
Indianapolis IN 46206-0420

Carl F. Van Conant
Boride Products, Inc.
2879 Aero Park Drive
Traverse City MI 49684

John F. Vander Louw
3M Company
3M Center, Bldg. 60-1N-01
Saint Paul MN 55144

Marcel H. Van De Voorde
Commission of the European
Community
P.O. Box 2
1755 ZG Petten
THE NETHERLANDS

O. Van Der Biest
Katholieke Universiteit Leuven
Dept. Metaalkunde en Toegepaste
de Croylaan 2
B-3030 Leuven
BELGIUM

Michael Vannier
Washington University,
St. Louis
510 S. Kings Highway
St. Louis MO 63110

Stan Venkatesan
Southern Coke & Coal Corp.
P.O. Box 52383
Knoxville TN 37950

V. Venkateswaran
Carborundum Company
Niagara Falls R&D Center
P.O. Box 832
Niagara Falls NY 14302

Theodore Vojnovich
U.S. Department of Energy
Laboratory Technology Applications
ER-32, Forrestal Bldg.
Washington DC 20585

John B. Wachtman
Rutgers University
P.O. Box 909
Piscataway NJ 08855

Shigetaka Wada
Toyota Central Research Labs
Nagakute Aichi, 480-11
JAPAN

Janet Wade
AlliedSignal Engines
P.O. Box 52180, MS:1303-2
Phoenix AZ 85072-2180

Richard L. Wagner
Ceramic Technologies, Inc.
537 Turtle Creek South Dr.
Indianapolis IN 46227

J. Bruce Wagner, Jr.
Arizona State University
Center for Solid State Science
Tempe AZ 85287-1704

Daniel J. Wahlen
Kohler, Co.
444 Highland Drive
Kohler WI 53044

Ingrid Wahlgren
Royal Institute of Technology
Studsvik Library
S-611 82 Nykoping
SWEDEN

Ronald H. Walecki
AlliedSignal, Inc.
Ceramic Components
P.O. Box 2960, MS:T21
Torrance CA 90509-2960

Michael S. Walsh
Vapor Technologies Inc.
6300 Gunpark Drive
Boulder CO 80301

Chien-Min Wang
Industrial Technology Research
Institute
195 Chung-Hsing Road, Sec. 4
Chutung Hsinchu 31015 R.O.C.
TAIWAN

Robert M. Washburn
ASMT
11203 Colima Road
Whittier CA 90604

Kevin Webber
Toyota Technical Center, U.S.A.
1410 Woodridge, RR7
Ann Arbor MI 48105

James K. Weddell
Du Pont Lanxide Composites Inc.
P.O. Box 6100
Newark DE 19714-6100

R. W. Weeks
Argonne National Laboratory
MCT-212
9700 S. Cass Avenue
Argonne IL 60439

Ludwig Weiler
ASEA Brown Boveri AG
Eppelheimer Str. 82
D-6900 Heidelberg
GERMANY

James Wessel
127 Westview Lane
Oak Ridge TN 37830

Robert D. West
Therm Advanced Ceramics
P.O. Box 220
Ithaca NY 14851

Thomas J. Whalen
1845 Cypress Pointe Court
Ann Arbor MI 48108

Ian A. White
Hoeganaes Corporation
River Road
Riverton NJ 08077

Sheldon M. Wiederhorn
NIST
Building 223, Room A329
Gaithersburg MD 20899

John F. Wight
Alfred University
McMahon Building
Alfred NY 14802

D. S. Wilkinson
McMaster University
1280 Main Street, West
Hamilton Ontario L8S 4L7
CANADA

James C. Williams
General Electric Company
Engineering Materials Tech.
One Neumann Way, Mail Drop:H85
Cincinnati OH 45215-6301

Steve J. Williams
RCG Hagler Bailly, Inc.
1530 Wilson Blvd., Suite 900
Arlington VA 22209-2406

Thomas A. Williams
National Renewable Energy Lab
1617 Cole Boulevard
Golden CO 80401

Craig A. Willkens
Norton Company
SGNICC/NRDC
Goddard Road
Northboro MA 01532-1545

Roger R. Wills
Ohio Aerospace Institute (OAI)
22800 Cedar Point Road
Brook Park OH 44142

David Gordon Wilson
Massachusetts Institute of
Technology
77 Massachusetts Ave., Rm 3-455
Cambridge MA 02139

J. M. Wimmer
AlliedSignal Ceramic Components
Department 27000, MS:T21
2525 W. 190th Street
Torrance CA 90509

Matthew F. Winkler
Seaworthy Systems, Inc.
P.O. Box 965
Essex CT 06426

Gerhard Winter
Hermann C. Starck Berlin GmbH
P.O. Box 25 40
D-3380 Goslar 3380
GERMANY

Thomas J. Wissing
Eaton Corporation
Engineering and Research Center
P.O. Box 766
Southfield MI 48037

James C. Withers
MER Corporation
7960 S. Kolb Road
Building F
Tucson AZ 85706

Dale E. Wittmer
Southern Illinois University
Mechanical Engineering Dept.
Carbondale IL 62901

Warren W. Wolf
Owens Corning Fiberglass
2790 Columbus Road, Route 16
Granville OH 43023

Egon E. Wolff
Caterpillar Inc.
Technical Center
P.O. Box 1875
Peoria IL 61656-1875

George W. Wolter
Howmet Turbine Components Corp.
Technical Center
699 Benston Road
Whitehall MI 49461

Wayne L. Worrell
University of Pennsylvania
3231 Walnut Street
Philadelphia PA 19104

John F. Wosinski
Corning Inc.
ME-2 E-5 H8
Corning NY 14830

Ruth Wroe
ERDC
Capenhurst Chester CH1 6ES
ENGLAND

Bernard J. Wrona
Advanced Composite Materials
1525 S. Buncombe Road
Greer SC 29651

Carl C. M. Wu
Naval Research Laboratory
Ceramic Branch, Code 6373
Washington DC 20375

David C. Wu
AlliedSignal Engines
P.O. Box 52181, MS:301-227
Phoenix AZ 85072-2181

John C. Wurst
U. of Dayton Research Institute
300 College Park
Dayton OH 45469-0101

Neil Wyant
ARCH Development Corp.
9700 S. Cass Avenue, Bldg. 202
Argonne IL 60439

Roy Yamamoto
Texaco Inc.
P.O. Box 509
Beacon NY 12508-0509

John Yamanis
AlliedSignal Aerospace Company
P.O. Box 1021
Morristown NJ 07962-1021

Harry C. Yeh
AlliedSignal, Inc.
Ceramic Components
P.O. Box 2960, MS:T21
Torrance CA 90509-2960

Hiroshi Yokoyama
Hitachi Research Lab
4026 Kuji-Cho
Hitachi-shi Ibaraki 319-12
JAPAN

Thomas M. Yonushonis
Cummins Engine Company, Inc.
P.O. Box 3005, Mail Code 50183
Columbus IN 47202-3005

Jong Yung
Sundstrand Aviation Operations
4747 Harrison Avenue
Rockford IL 61125

A. L. Zadoks
Caterpillar Inc.
Technical Center, Building L
P.O. Box 1875
Peoria IL 61656-1875

Avi Zangvil
University of Illinois
104 S. Goodwin Avenue
Urbana IL 61801

Charles H. Zenuk
Transtech
6662 E. Paseo San Andres
Tucson AZ 85710-2106

Zhenqi Zhu
University of Connecticut
Precision Manufacturing Center
Storrs, CT 06269-5119

Carl Zweben
General Electric Company
P. O. Box 8555, VFSC/V4019
Philadelphia PA 19101

Department of Energy
Oak Ridge Operations Office
Assistant Manager for Energy
Research and Development
P. O. Box 2001
Oak Ridge TN 37831-8600

Department of Energy (2)
Office of Scientific and Technical
Information
Office of Information Services
P. O. Box 62
Oak Ridge TN 37831

For distribution by microfiche
as shown in DOE/OSTI-4500,
Distribution Category UC-332
(Ceramics/Advanced Materials).