Transformation-Toughened Silicon Nitride

Final Report

H. W. Carpenter

CERAMIC TECHNOLOGY FOR ADVANCED HEAT ENGINES

Prepared by
Rockwell International
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, CA 91304
Under Subcontract 86X-22009C

19980123 003
FOREWORD

Work described herein was performed by the Rocketdyne Division of Rockwell International for Martin Marietta, Oak Ridge National Laboratory (ORNL) under the sponsorship of the U.S. Department of Energy, Ceramic Technology for Advanced Heat Engine Program, Contract No. 86X-22009C. This work was performed over the period 1 June 1985 through 31 August 1987. Dr. G. D. Schnitgrund of Rocketdyne Division Advanced Programs was Program Manager and H. W. Carpenter of Rocketdyne's Materials Engineering and Technology was Project Engineer. Major technical contributions were provided by Dr. F. F. Lange, formerly of Rockwell Science Center, Thousand Oaks, CA, and presently on the faculty at the University of California at Santa Barbara. T. N. Tiegs was the ORNL Program Monitor.

The research was sponsored by the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Systems, as part of the Ceramic Technology for Advanced Heat Engines Project of the Advanced Materials Development Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.
## CONTENTS

Abstract ........................................................................................................... 1  
Summary ........................................................................................................... 3  
Technical Background .................................................................................... 9  
Procedure ......................................................................................................... 13  
  Colloidal Power Processing ........................................................................... 13  
  Sample Preparation ....................................................................................... 20  
Evaluation of Samples .................................................................................... 22  
Technical Discussion ....................................................................................... 25  
  ZrO$_2$ (Y$_2$O$_3$) ....................................................................................... 25  
  HfO$_2$ (Y$_2$O$_3$) ....................................................................................... 55  
  ZrO$_2$ (CaO) .............................................................................................. 60  
  Other ............................................................................................................ 79  
  HfO$_2$-ZrO$_2$-TiO$_2$ .................................................................................... 81  
Thermophysical Properties ............................................................................. 83  
  Thermal Diffusivity ..................................................................................... 83  
  Thermal Expansion ....................................................................................... 83  
Injection Molding ............................................................................................. 91  
Conclusions ...................................................................................................... 101  
Recommendations ........................................................................................... 103  
References ...................................................................................................... 105
1. Benefits of Adding Small Amounts of ZrO$_2$ Particles to Si$_3$N$_4$ Matrix
2. Dispersion-Toughened Material Containing Particles with:
   (a) Higher Thermal Expansion Coefficient and (b) Lower Thermal Expansion Coefficient
3. Typical Microstructure Showing Good Dispersion of the Second Phase and Lack of Agglomerates
4. Siphoning the Slurry Containing Less Than 1 Micrometer Particles
5. Pumping Slurry Through the Sonic Mixing Chamber
6. Pressure Filtration Die with Pressed Sample
7. AEM Analysis on a Si$_3$N$_4$ + 45 w/o ZrO$_2$ (9 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$ Sample
8. ZrO$_2$/Y$_2$O$_3$ Phase Diagram
9. Fracture Toughness vs Y$_2$O$_3$ Alloy Content in ZrO$_2$
10. Si$_3$N$_4$ Room-Temperature Strength
11. Effect on Room Temperature Strength of Exposure to an Oxidizing Environment of Si$_3$N$_4$ + ZrO$_2$ (9 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
12. Flexural Strength of Si$_3$N$_4$/ZrO$_2$ (xY$_2$O$_3$) Composites Having 4 w/o Al$_2$O$_3$ as a Sintering Aid
13. Strength of Si$_3$N$_4$ + 45 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) with Y$_2$O$_3$ and SiO$_2$ as Sintering Aid
14. Microstructure of Si$_3$N$_4$/HfO$_2$ Composite
15. Semiquantitative Analysis of Si$_3$N$_4$ + HfO$_2$ (10 m/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
16. Energy Dispersive Analysis of a HfO$_2$ Grain
17. Evidence of Stability at Intermediate Temperatures of Si$_3$N$_4$ + HfO$_2$ Composites
18. Effect of ZrO$_2$ Additions and Post Sintering Heat Treatments on Si$_3$N$_4$ Fracture Toughness
19. Fracture Toughness vs ZrO$_2$ Content
20. Room Temperature Strength vs ZrO$_2$ Particulate Content
21. Room Temperature Strength of Si$_3$N$_4$ + ZrO$_2$ (5 w/o CaO) Composites vs Duration at 700 C in Air
22. Effect of Sintering on Strength and Density
23. Dispersions of 15, 30, and 45 w/o ZrO$_2$ Grains
24. Polished Surface of Sintered Si₃N₄ + 15 w/o ZrO₂ (5 w/o CaO) + 2-1/2 w/o MgO Showing High Porosity Region

25. Strength as a Function of ZrO₂ Content

26. Strength as a Function of Temperature and ZrO₂ Content

27. Aged Composites Show No Microcracking

28. Strength and Density vs Sintering Temperature

29. Fracture Toughness vs CaO Content in the ZrO₂

30. Semiquantitative Analysis Shows Low Ca Content in Monoclinic ZrO₂ Grain

31. Thermal Diffusivity of Si₃N₄ + ZrO₂ Composites at 25 C and 700 C

32. Thermal Diffusivity of Si₃N₄ + ZrO₂ Composites at 1000 C and 1300 C

33. Thermal Expansion Coefficient of Si₃N₄ Composites Comply with Rule of Mixtures

34. Dilatometer Record for NC-132

35. Dilatometer Record for Si₃N₄ + 30 w/o ZrO₂ (12 w/o Y₂O₃) + 4 w/o Al₂O₃

36. Dilatometer Record for Si₃N₄ + 45 w/o ZrO₂ (6.2 w/o CaO) + 2-1/2 w/o MgO

37. Microstructure of Injection Molded Si₃N₄ + 45 w/o ZrO₂ (12 w/o Y₂O₃) + 4 w/o Al₂O₃

38. Photomicrographs of Injection-Molded Bar Surface in the As-Sintered Condition

39. Photomicrographs of Injection-Molded Bar After Grinding

40. Metal Inclusion in Polished Section of Injection-Molded Material

41. Low Density Flaws in Injection-Molded Material

42. Large Pore Fracture Origin in Injection-Molded Sample
TABLES

1. Summary of Results................................................................. 5
2. \( \text{Si}_3\text{N}_4 \) Powder Characteristics........................................ 16
3. Powder Characteristics.............................................................. 18
4. Intermediate-Temperature Stability Results................................. 27
5. Fracture Toughness Measured on Indented MOR Bars...................... 36
6. Test Data for Measuring Fracture Toughness.................................. 37
7. Densities of Hot-Pressed Samples.............................................. 40
8. Properties of \( \text{Si}_3\text{N}_4 \) and \( \text{ZrO}_2 \) for Calculation of \( \text{Si}_3\text{N}_4/\text{ZrO}_2 \)
   Composite Theoretical Density.................................................. 40
9. Density and Room Temperature Flexural Strength............................ 41
10. High-Temperature Strength of \( \text{Si}_3\text{N}_4 + \text{ZrO}_2 \) \( (\text{Y}_2\text{O}_3) \) Composites
    Containing 4 w/o \( \text{Al}_2\text{O}_3 \) as a Sintering Aid.......................... 46
11. Density and High-Temperature Strength of \( \text{Si}_3\text{N}_4 + 45 \) w/o \( \text{ZrO}_2 \)
    \( (12 \) w/o \( \text{Y}_2\text{O}_3 \) ) Containing \( \text{Y}_2\text{O}_3 + \text{SiO}_2 \) Sintering Aid........ 50
12. Strength After Heating in Air at 700 C for Composites of \( \text{Si}_3\text{N}_4 + 45 \) w/o \( \text{ZrO}_2 \)
    \( (12 \) w/o \( \text{Y}_2\text{O}_3 \) ) + \( \text{Y}_2\text{O}_3 + \text{SiO}_2 \).................................................... 53
13. High-Temperature Strength of \( \text{Si}_3\text{N}_4 + \text{ZrO}_2 \) \( (\text{Y}_2\text{O}_3) \) Composites Containing Sintering Aids..................... 54
14. Strength of Hot-Pressed \( \text{Si}_3\text{N}_4 + 45 \) w/o \( \text{ZrO}_2 \) \( (5 \) w/o \( \text{CaO} \) ) \( + 2-1/2 \)
    w/o \( \text{MgO} \)..................................................................... 65
15. Results of 1800 C Sintering....................................................... 69
16. Sintering Results for \( \text{ZrO}_2 \) \( (\text{CaO}) \) Dispersed Phase Composites............... 76
17. Results of Hot Pressed \( \text{Si}_3\text{N}_4 + 45 \) w/o \( \text{ZrO}_2 \) \( (5 \) w/o \( \text{MgO} \) )
    \( + 2-1/2 \) w/o \( \text{MgO} \) Composite........................................... 81
18. Thermal Diffusivity of \( \text{Si}_3\text{N}_4 \)...................................................... 84
19. Coefficients of Thermal Expansion............................................. 84
20. Results of Injection Molding Study............................................ 94
ACKNOWLEDGMENTS

Mr. M. J. Robinson conducted most of the laboratory work and Dr. J. R. Porter provided the TEM/AEM characterization studies.
Composites, consisting of a silicon nitride ($\text{Si}_3\text{N}_4$) matrix containing dispersions of phase-stabilized zirconia ($\text{ZrO}_2$), were prepared by colloidal processing and sintering to near full density. These materials exhibited improved strength and increased fracture toughness relative to the matrix alone. The effects of $\text{ZrO}_2$ content, phase-stabilizer type and amount, and processing conditions on mechanical and thermophysical properties of the resultant composites were determined. The possibility of high-volume, low-cost production was demonstrated by successfully injection molding samples.

Specific systems that appear promising for various alternative applications were developed. A composite containing 45 w/o (~30 v/o) $\text{ZrO}_2$ phase-stabilized with $\text{Y}_2\text{O}_3$ exhibited a 50% improvement in fracture toughness, (6 MPa m$^{1/2}$), high room temperature flexural strength (1000 MPa), low thermal expansion, and low thermal conductivity. Use of $\text{Y}_2\text{O}_3$ plus $\text{SiO}_2$ as sintering aids with this composite was shown to maintain high strength to temperatures of 1400 C. A second system containing from 30 w/o (~20 v/o) to 45 w/o (~30 v/o) $\text{ZrO}_2$ phase-stabilized with CaO also exhibited high fracture toughness and high strength. Further improvements (up to threefold) in fracture toughness were obtained by heat treatment. The CaO-containing system is limited to relatively low use temperatures of less than 700 C.

Probable toughening due to the martensitic tetragonal to monoclinic transition of zirconia has been hypothesized. Potential applications for these toughened systems include cryogenic turbopump bearings, intermediate use temperature applications in diesel engines, and high-temperature turbine uses. Materials will have to be tailored and optimized for each of these areas.
SUMMARY

A family of toughened structural ceramic composites consisting of a Si$_3$N$_4$ matrix plus dispersions of ZrO$_2$ or HfO$_2$ was developed that offers a combination of unique properties which, compared to monolithic Si$_3$N$_4$, include:

- Increased fracture toughness
- Increased strength
- Significantly higher toughness and strength by heat treatment for low and intermediate temperature applications
- Lower thermal conductivity
- Lower thermal expansion

These materials further offer:

- Adaptability to conventional fabrication methods
- Excellent figure of merit for resistance to thermal shock
- Potential as a matrix for whisker- or filament-reinforced composites.

Colloidal processing methods were used in this program to break up soft agglomerates and to eliminate hard agglomerates. Thus, particle size was controlled to provide a homogeneous, fine-grain microstructure free from agglomerates, and one that readily sintered to near full density. Colloidal processing also allowed complete dispersion of the second phase, and it is compatible with conventional low-cost fabrication methods such as slurry casting and injection molding.

Two approaches were successfully used to achieve composite compositions that exhibited increased toughness with concomitant increased strength and that did not exhibit microcracking when oxidized at intermediate temperatures.

The first approach used dispersed ZrO$_2$ particles stabilized with Y$_2$O$_3$. The presence of yttrium cation in the ZrO$_2$ lattice inhibited the formation of zirconium oxynitride, which was determined to be the probable cause of the intermediate temperature cracking problem. The second approach was to use
ZrO₂ particles stabilized with CaO. The CaO stabilization did not prevent
the formation of zirconium oxynitride but the subsequent surface stresses,
that normally caused microcracking, could be controlled by heat treatment to
provide useful structural compositions with increased strength and signifi-
cantly increased apparent toughness. Partial dissolution of CaO and the pre-
sence of CaO in the grain boundaries, however, limits this material to low to
intermediate temperatures, less than 700 C.

Average room temperature strength and fracture toughness values of these com-
posites are listed in Table 1. Values for Si₃N₄ matrix without any toughening
and values for Si₃N₄ toughened with SiC whiskers are provided for comparison.
Room temperature strength of all transformation-toughened composite systems
was higher than 800 MPa and strength could be increased as much as 40% by heat
treatment. The strength gained by heat treatment, however, would not be useful
for high-temperature service. Compositions of Si₃N₄ plus ZrO₂(Y₂O₃) sintered
with selected mixtures of Y₂O₃ and SiO₂ showed no loss of strength at 1400 C.
Room temperature strength was low, however, due to processing difficulties
that were attributed to the character of the starting powders and to metal
inclusions originating from erosion of the sonic mixing equipment. Strength
of the same composition, but prepared using a colloidal processing method and
sintered using 4 w/o Al₂O₃ as a sintering aid, was 700 MPa at 1000 C and
360 MPa at 1200 C, which is a retention of 75 and 60% of room temperature
strength, respectively. Strength decreased above 1200 C for these samples.

Fracture toughness of the Si₃N₄ + 45 w/o (-30 v/o) ZrO₂(Y₂O₃) composite
increased above the level of the Si₃N₄ matrix when the Y₂O₃ alloy content in
the ZrO₂ particles was reduced below 9 w/o. The toughness increased linearly
to 6 MPa m⁰.⁵ at a Y₂O₃ content of 4.5 w/o. The presence of ZrO₂ particles in
the Si₃N₄ matrix also influenced thermal properties. Thermal diffusivity
was significantly lower, which indicates lower thermal conductivity, for these
composites than that predicted by rule of mixtures. A low thermal conductivity
is necessary for some heat engine applications. Thermal expansion, on the
other hand, followed the rule of mixtures, and the resultant low thermal
### Table 1. Summary of Results

<table>
<thead>
<tr>
<th>Toughening Mechanism</th>
<th>Material</th>
<th>Flexural Strength, MPa</th>
<th>Fracture Toughness, MPa m$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Si$_3$N$_4$ matrix</td>
<td>700-965</td>
<td>4</td>
</tr>
<tr>
<td>Whisker reinforcement</td>
<td>Si$_3$N$_4$ + SiC whiskers*</td>
<td>700</td>
<td>5-6</td>
</tr>
<tr>
<td>Transformation toughening</td>
<td>Si$_3$N$_4$ + ZrO$_2$(Y$_2$O$_3$)</td>
<td>800-1000</td>
<td>4-6</td>
</tr>
<tr>
<td>Transformation toughening</td>
<td>Si$_3$N$_4$ + ZrO$_2$(CaO)</td>
<td>900-1200</td>
<td>7-14</td>
</tr>
<tr>
<td>NA</td>
<td>Si$_3$N$_4$ + HfO$_2$(Y$_2$O$_3$)</td>
<td>915</td>
<td>NA</td>
</tr>
</tbody>
</table>

*Typical Properties

expansion contributes favorably to the figure of merit for thermal shock resistance. Thus, additions of 30 and 45 w/o ZrO$_2$(Y$_2$O$_3$) had a synergistic effect on the Si$_3$N$_4$ matrix in that composites exhibited increased strength, a large increase in toughness, a large decrease in thermal diffusivity (Fig. 1), and a high figure of merit for resistance to thermal shock.

HfO$_2$(Y$_2$O$_3$) dispersions were substituted for ZrO$_2$ dispersions to demonstrate that Si$_3$N$_4$ + HfO$_2$ composites could be sintered to near theoretical density with similar properties to the Si$_3$N$_4$ + ZrO$_2$ composites. A composition of Si$_3$N$_4$ + 69 w/o HfO$_2$(10 m/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$ sintered to high density with an average room temperature flexural strength of 915 MPa. High-temperature strength was slightly higher than that of comparable compositions containing ZrO$_2$ dispersions. Transformation toughening was not expected, however, because the HfO$_2$(Y$_2$O$_3$) dispersion was fully stabilized.

The average strength and toughness values for composites composed of Si$_3$N$_4$ matrix containing ZrO$_2$ particles alloyed with CaO also are listed in Table 1. Strength at room temperature was as high as that for the compositions made using ZrO$_2$ dispersions alloyed with Y$_2$O$_3$, but strength began decreasing above 700 C. Toughness of these composites in the as-densified
Figure 1. Benefits of Adding Small Amounts of ZrO₂ Particles to Si₃N₄ Matrix
condition was almost double that of the Si$_3$N$_4$ matrix, and toughness was increased to as high as 14 MPa m$^{1/2}$ by heat treatment. This increase was not an increase in inherent toughness, rather, it was the result of increased surface compressive stresses caused by the oxidation of zirconium oxynitride and the subsequent formation of monoclinic ZrO$_2$. Thermal diffusivity of this composition was higher than that for the composition made with ZrO$_2$ stabilized with Y$_2$O$_3$. Thermal diffusivity values were more in line with results predicted by the rule of mixtures. These composites offer a unique combination of high strength and very high toughness for applications at temperatures less than 700°C.

Injection-molded samples of Si$_3$N$_4$ + 45 w/o ZrO$_2$ (9 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$ were fabricated to demonstrate the feasibility of high-volume, low-cost production. Injection molding characteristics of this composition were the same as for Si$_3$N$_4$ without the ZrO$_2$ dispersion. Average flexural strength values for injection-molded samples were lower than those for colloidal processed material. The bend bar geometry used, pick-up of metallic inclusions during processing, and inhomogeneous distribution of the injection molding plasticizer are all considered sources of the reduced strength.
The fracture toughness of Si₃N₄ can be increased by:

1. The addition of high-strength and elastic modulus, high aspect ratio, small-diameter SiC whiskers
2. The addition of a lower thermal expansion coefficient second phase
3. Heat treatment to grow acicular β-Si₃N₄ grains
4. Inclusion of dispersions that toughen by a phase transformation mechanism.

Toughening by the addition of SiC whiskers occurs principally by crack deflection and whisker pullout which limits toughness increases to about 50% over the matrix. Best results are achieved with high whisker loadings; however, processing becomes more difficult at high loadings. Uniform dispersion of the whiskers becomes increasingly difficult as the concentration increases. There is also a tendency for the whiskers to orient due to shear forces resulting in anisotropic properties. The net result of such processing difficulties is a subsequent inability to maintain strength and isotropy at the high loadings needed to improve toughness.

Toughening by a dispersed second phase having a lower thermal expansion coefficient than the matrix will theoretically result in toughening due to the residual stress fields around the second phase. The hoop tension field, as shown in Fig. 2, attracts passing cracks rather than deflecting them away. There is more dissipation of energy compared to the case in which the thermal expansion coefficient of the particle is higher than the matrix and in which the passing crack is deflected away from, rather than into, the particle. This method has not been demonstrated due to the lack of a suitable second phase that (1) has a lower thermal expansion coefficient than Si₃N₄, (2) is stable, and (3) is compatible with Si₃N₄ at elevated temperatures.
Figure 2. Dispersion-Toughened Material Containing Particles with: 
(a) Higher Thermal Expansion Coefficient and (b) Lower Thermal Expansion Coefficient
The use of transformation toughening in the Si$_3$N$_4$ matrix, on the other hand, increased toughness by as much as threefold over that of the Si$_3$N$_4$ matrix and there is no decrease in strength. In fact, in some cases, strength is 40% higher than that of the matrix material.

Transformation toughening is the basis for a new group of commercial materials based on partially stabilized zirconia (PSZ). Zirconia undergoes a martensitic, athermal phase transformation on cooling over the range from about 1400 to 1000 C. This phase change from the tetragonal phase to the monoclinic phase is accompanied by a 5% volume increase. Toughened materials can be obtained by inhibiting the phase change during fabrication so that the resultant material retains the metastable tetragonal phase at room temperature. When the phase change is triggered by the strain of an advancing crack, compressive loading occurs in the lattice around and ahead of the advancing crack tip. The result is an increase in toughness in the PSZ material from as low as 2 MPa m$^{1/2}$ in the untoughened matrix to as high as 13 MPa m$^{1/2}$ in the toughened composites.

Si$_3$N$_4$ is one desirable matrix material due to its inherent high strength, high modulus, and superior resistance to thermal shock. Although Si$_3$N$_4$ is a leading candidate for heat engine applications, its use is limited in some designs because Si$_3$N$_4$ has high thermal conductivity. Additions of small amounts of ZrO$_2$ to Si$_3$N$_4$ can substantially reduce the thermal conductivity of the composite while yielding significant gains in fracture toughness.

Lange (Ref. 2) reported increased surface toughness in the Si$_3$N$_4$/ZrO$_2$ system resulting from an oxidation-induced phase change. Reactions leading to increased toughness begin with the formation of Zr-oxynitride during the densification process. When the composite is later heated in an oxidizing environment, the surface Zr-oxynitride converts to ZrO$_2$. The formation of ZrO$_2$, which is associated with a volume increase of about 5%, causes compressive surface stresses. These surface stresses can be beneficial, but when the volume content of ZrO$_2$ is more than 10%, severe microcracking and spalling occur.
Gilles (Ref. 3) determined that the Zr-oxynitride structure was associated with an ordered array of oxygen deficiencies in the lattice. Lange et al. (Ref. 4) reasoned that the addition of an alloying agent to the ZrO₂ with a valence different from that of Zr would disrupt the oxygen-deficient lattice structure and thereby reduce or eliminate the formation of Zr-oxynitride. Results of this study indicated that Y₂O₃ alloy additions in the ZrO₂ did reduce or eliminate the Zr-oxynitride phase and inhibited microcracking.
COLLOIDAL POWDER PROCESSING

Silicon nitride composites containing dispersed ZrO₂ must be fine grained, exhibit complete dispersion of the ZrO₂ particles, and be free of large flaws. For these reasons, composites were made using colloidal processing methods. Colloidal processed material produced microstructures that exhibited homogeneity and excellent dispersion of the ZrO₂ particles (Fig. 3). With proper controls, the microstructure can be made with a very low flaw population and very small flaw sizes. The colloidal method can also be compatible with high-volume, low-cost production methods, such as injection molding and slip casting. Another advantage of colloidal processing is that slurry mixtures of two or more powders have long shelf lives. Mixtures can be stored in the flocced state without concern of powder segregation.

Each component, e.g., Si₃N₄, ZrO₂, or selected sintering aids, was separately suspended in dilute water solutions of less than 5 v/o solids to break up soft agglomerates and to remove hard agglomerates by sedimentation. Suspension was achieved by controlling pH. A pH of 10 was used to suspend Si₃N₄ and a pH of 2 was used to suspend ZrO₂ powders. Based on Stoke's Law calculations, the dilute solutions were allowed to settle to remove all particles over 1 micron. Settling duration was typically 24 h for Si₃N₄ and 16 h for ZrO₂ powders. The slurry containing particles less than 1 micron was siphoned into a clean container (Fig. 4), washed, and flocculated so that the excess water could be removed. The coarse sediment left on the bottom of the original container, which was usually a relatively hard cake, was re-suspended. An ultrasonic horn was used to break up the hardened cake and to re-suspend the powder. The suspension was again allowed to settle and the submicron powder was again siphoned off into a clean container. This process was repeated until most of the submicron powder was separated. Usually four separation cycles were sufficient.
Figure 3. Typical Microstructure Showing Good Dispersion of the Second Phase and Lack of Agglomerates
Figure 4. Siphoning the Slurry Containing Less Than 1 Micrometer Particles
The concentration of solids in the slips was determined by measuring the slip specific gravity from which concentration was calculated. The desired quantity of the specified, flocculated slip was then weighed into a separate beaker. Each of the ingredients was then mixed together by manually stirring. The mixture was then pumped back and forth through a small ultrasonic mixing chamber* for a total of four passes (Fig. 5). Controlled parameters included pumping speed and power input to the ultrasonic horn. A photomicrograph of a typical composite (Fig. 3) illustrates the good dispersion of the second phase, good homogeneity, and the lack of inclusions in the microstructure.

High-purity, submicron powders were used whenever possible to make colloidal processing both practical and possible. Exceptions are noted in the text. All composites were based on a single $\text{Si}_3\text{N}_4$ matrix powder source (Table 2). $\text{ZrO}_2$ and $\text{HfO}_2$ were obtained from five different sources to obtain a range of alloying compositions and levels. Characteristics and chemistries of these powders are given in Table 3.

*Fischer Sonic Dismembrator Model 300

Table 2. $\text{Si}_3\text{N}_4$ Powder Characteristics

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\text{Si}_3\text{N}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>UBE Industries, Ltd.</td>
</tr>
<tr>
<td>Grade</td>
<td>SN-E-10</td>
</tr>
<tr>
<td>Lot</td>
<td>A-77</td>
</tr>
<tr>
<td>Particle size</td>
<td>0.1 to 0.3 microns</td>
</tr>
<tr>
<td>Surface area</td>
<td>14 m$^2$/g</td>
</tr>
<tr>
<td>Degree crystallinity</td>
<td>$100%$</td>
</tr>
<tr>
<td>Phase content, $\beta$</td>
<td>$3.5%$</td>
</tr>
<tr>
<td>(alpha + beta)</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Powder Characteristics
(Sheet 1 of 3)

<table>
<thead>
<tr>
<th>Zirconia</th>
<th>TZ-4Y</th>
<th>TZ-6Y</th>
<th>TZ-8Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition - ZrO₂(Y₂O₃)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Source - Toyo Soda Mfg. Co. Ltd., Tokyo</td>
<td>Z405117P</td>
<td>Z605106P</td>
<td>Z805125P</td>
</tr>
<tr>
<td>Grade TZ-4Y</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Lot TZ-4Y</td>
<td>220</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td>Crystallite size (Angstroms)</td>
<td>7.02</td>
<td>10.37</td>
<td>13.25</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>7.02</td>
<td>10.37</td>
<td>13.25</td>
</tr>
<tr>
<td>Chemical analysis (w/o)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.06</td>
<td>0.056</td>
<td>0.007</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.005</td>
<td>0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.003</td>
<td>0.003</td>
<td>0.006</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.003</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Zirconia
Source - Zircoa Products, Corning Glass Works, Solon, OH
Type - Zircoa-B fully stabilized 5 w/o CaO
4.69 μm average particle size (-325 mesh)

| SiO₂                      | 0.68 w/o |
| CaO                      | 5.12     |
| MgO                      | 1.16     |
| Fe₂O₃                    | 0.07     |
| Al₂O₃                    | 0.12     |
| TiO₂                     | 0.11     |

Zirconia
Source - Zircar, Florida, NY

<table>
<thead>
<tr>
<th>Lot</th>
<th>P-298-B</th>
<th>P-298-C</th>
<th>P-301</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-298-B</td>
<td>3.30</td>
<td>6.75</td>
<td>9.93</td>
</tr>
<tr>
<td>P-298-C</td>
<td>6.75</td>
<td>9.74</td>
<td>5.90</td>
</tr>
<tr>
<td>P-301</td>
<td>9.93</td>
<td>5.90</td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Powder Characteristics
(Sheet 2 of 3)

Zirconia
Source - Zircar, Florida, NY
Type - ZYP Stabilized

<table>
<thead>
<tr>
<th></th>
<th>4.5 w/o Y₂O₃</th>
<th>8.0 w/o Y₂O₃</th>
<th>12.0 w/o Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.019</td>
<td>0.019</td>
<td>0.019</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.039</td>
<td>0.039</td>
<td>0.039</td>
</tr>
<tr>
<td>CaO</td>
<td>0.020</td>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>MgO</td>
<td>0.021</td>
<td>0.021</td>
<td>0.021</td>
</tr>
<tr>
<td>Cl</td>
<td>0.10</td>
<td>0.18</td>
<td>0.26</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>LOI</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Agglomerate Size Distribution (%)
- <1 µm: 97
- <0.7 µm: 85
- <0.5 µm: 72
- <0.3 µm: 50
- <0.1 µm: 30

Crystallite size: 0.02-0.03 µm
Surface area: 30-45 m²/gram
### Table 3. Powder Characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Grade</th>
<th>Type</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zirconia</strong></td>
<td>Source - Nippon Shokubai Kagaba Koggo Co., Ltd.</td>
<td>Grade - NS-8Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 8 mol %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Surface area 80 m&lt;sup&gt;2&lt;/sup&gt;/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Particle diameter 130 ångstroms</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Chemical analysis (w/o)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 13.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 0.006</td>
</tr>
<tr>
<td><strong>Hafnium Oxide</strong></td>
<td>Source - Teledyne Wah Chang</td>
<td>Grade - S</td>
<td>Type - K-906</td>
<td>1 to 2 microns powder 10 mole percent Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

**SAMPLE PREPARATION**

Disk-shaped samples, 5 cm in diameter x 1 to 2 cm thick, were prepared by pressing the water out of flocced slurries in a special metal die (Fig. 6). One, or both (at the option of the technician) ends of the plunger was fitted with a porous metal filter to allow the water from the slurry to escape under pressure. A layer of coarse filter paper was placed over the metal filter to keep the fine powder from plugging it. A pressure of about 0.5 MPa (70 psi) was used to force the water out. Lower pressures took too long to remove the water, while higher pressures usually produced samples that cracked during drying.
The samples were air dried slowly then placed in a vacuum oven at 60°C. Green density was typically about 40% of theoretical, but this was increased to about 50% by isostatic pressing to pressures as high as 350 MPa.

Samples were densified by either pressureless sintering or hot pressing. Pressureless sintering was performed under 1 atm of nitrogen in a carbon resistance furnace. Samples were placed in a Si₃N₄ crucible and packed in a seasoned Si₃N₄ powder. Hot pressing was performed under 1 atm of nitrogen using graphite dies and varying compaction pressures from 26 to 52 MPa. The rate of heating and cooling for both densification routes was rapid, typically 1 h from room temperature to the sintering temperature, which ranged from 1700 to 1860°C, hold for 1 h, and furnace cool.

EVALUATION OF SAMPLES

Samples were characterized by the following techniques after densification. Density and porosity were measured by a modified-Archimedes method. X-ray diffraction analyses were performed on diamond-ground or diamond-cut surfaces using a General Electric X-ray diffraction unit with Cu-Kα radiation.

MOR bars with a cross section of 2.0 x 2.5 mm were made by diamond grinding to a surface finish of 10 μinch. MOR bar length ranged from 18 mm to 40 mm and varied depending on stock. All diamond grinding was in the long direction and edges were chamfered. Due to the short length of the average MOR bar and the large number of MOR tests that were required, 3-point bend tests with a span of 15.2 mm were used for most of the initial evaluations. Four-point tests were performed when a large sample population was available and when the sample length was adequate. Two fixtures were used for 4-point bend tests, one with spans of 23 and 8 mm, and one with spans of 32 and 11 mm. The larger fixture was made of SiC and was used for all tests at elevated temperatures. The span on 3-point tests was 15.2 mm. Crosshead rate was 0.05 cm/min.
Fracture toughness was measured by the diamond indentation method after Anstis (Ref. 5) and by breaking pre-indented MOR bars after Cook and Lawn (Ref. 6). Crack length measurements on indented samples were made using a light microscope and a side-angle lighting technique to define the crack tip.

Heat treatments performed on samples were conducted in a resistance heated furnace (SiC heating elements) in static air.
The experimental work in this program was conducted on five families of composites. These composites included an Si₃N₄ matrix, a sintering aid, and from 10 to 30 v/o of one of the following additives as a dispersed phase:

1. ZrO₂(4.0 w/o to 13.5 w/o Y₂O₃)
2. ZrO₂ (3.5 w/o to 10 w/o CaO)
3. ZrO₂ (5 w/o MgO)
4. HfO₂ (10 m/o Y₂O₃)
5. 60 m/o HfO₂ + 20 m/o ZrO₂ + 20 m/o TiO₂.

Each of these five families of compositions is discussed in a separate section of this report. Most of the experimental work was conducted on the first two compositions because of the highly promising early results. The third composition was of interest because it is more refractory, but investigation of this composition was not pursued because the initially densified samples cracked during the hot pressing operation. The fourth composition contained fully stabilized HfO₂ as a dispersed phase. Testing of the fifth composition was discontinued because the oxide alloy reacted with the Si₃N₄ matrix and cracked excessively when oxidized.

ZrO₂(Y₂O₃)

Composites of Si₃N₄ +30 w/o (~20 v/o) or 45 w/o (~30 v/o) ZrO₂(Y₂O₃) with sintering aids offer a combination of unique attributes: (1) as-fabricated toughness 50% higher than the Si₃N₄ matrix, (2) high strength, (3) beneficial surface compressive stresses following oxidation, (4) reduced thermal conductivity, and (5) the absence of Zr-oxynitride phase which is a leading cause of microcracking at intermediate temperatures.
Microcracking at intermediate temperatures (500 to 1000°C) is a problem that has precluded Si₃N₄/ZrO₂ composites from consideration as structural materials in spite of high strength and increased toughness. Three approaches were used in this program to reduce or to eliminate microcracking. The first approach was to alloy the ZrO₂ with a sufficient amount of Y₂O₃ as suggested by Lange (Ref. 4). The second was to preoxidize the sample at an elevated temperature before exposure to the intermediate temperature. The third was to sinter the composite at higher temperatures.

Near-theoretical density values were obtained for samples sintered at 1700°C for 1 h. In this study, samples were sintered at temperatures to 1800°C to determine the effect on oxidation resistance. The Y₂O₃ alloying content and total ZrO₂ content also were varied. Oxidation was carried out at 700°C for periods from 64 to 1008 h. Samples were observed after oxidation for the appearance of microcracks. Results of these studies are summarized in Table 4.

For samples sintered at 1750°C, there was a high incidence of microcracking with only the 12 w/o Y₂O₃ stabilized material not exhibiting microcracks after 1008 h. For samples sintered at 1800°C, results were more encouraging with microcracking observed only for the 8 w/o Y₂O₃ stabilized sample after 255 h exposure.

The longer exposures appeared to result in less observed microcracking. This is not readily explained unless there is an associated crack healing occurring during extended oxidation. Also, since at least part of the Y₂O₃ is believed to enter into the grain boundary phase, it would be expected that the Y₂O₃ content should also affect microcracking and healing mechanisms. From the data available, it appears as if increasing Y₂O₃ content could be inhibiting healing, so that the higher Y₂O₃ content samples require longer oxidation times to eliminate the appearance of microcracks. The possibility of crack healing and the role of Y₂O₃ is speculative at present and would require further study for confirmation.
<table>
<thead>
<tr>
<th>Sintering Temperature, °C</th>
<th>Sample Identification No.</th>
<th>ZrO₂ Content, w/o</th>
<th>Y₂O₃ Content In ZrO₂, w/o</th>
<th>Duration At 700 °C, h</th>
<th>Microcracking Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1750</td>
<td>21</td>
<td>45</td>
<td>9</td>
<td>284</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>45</td>
<td>9</td>
<td>64</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>30</td>
<td>12</td>
<td>1008</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>45</td>
<td>12</td>
<td>1008</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>45</td>
<td>13.5</td>
<td>504</td>
<td>Yes</td>
</tr>
<tr>
<td>1800</td>
<td>51</td>
<td>45</td>
<td>4.5</td>
<td>255</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>51</td>
<td>45</td>
<td>6.9</td>
<td>255</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>45</td>
<td>8</td>
<td>255</td>
<td>Yes</td>
</tr>
<tr>
<td>1800</td>
<td>54</td>
<td>45</td>
<td>6.9</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>45</td>
<td>8</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>1800</td>
<td>34</td>
<td>30</td>
<td>9</td>
<td>1008</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>45</td>
<td>9</td>
<td>1008</td>
<td>No</td>
</tr>
</tbody>
</table>
Preoxidation at an elevated temperature was another method that was successful in reducing or preventing microcracking at intermediate temperatures. The rationale was that microcracking did not occur at elevated temperatures where the body could accommodate the small amount of plastic deformation and, then, when the body was later exposed to oxidation at intermediate temperatures, the oxide layer protected the surface from further oxidation because the oxidation rate through the protective layer was negligible. This approach was used more for compositions containing \( \text{ZrO}_2 \) stabilized with \( \text{CaO} \), and these results are reported later. The limited results for compositions containing \( \text{ZrO}_2 \) stabilized with \( \text{Y}_2\text{O}_3 \) were as follows. Samples of a composition containing 45 w/o \( \text{ZrO}_2 \) stabilized with 13.5 w/o \( \text{Y}_2\text{O}_3 \) exhibited microcracking at 700 °C after 500 h. When samples were preoxidized at 1200 °C for 2 h, however, no microcracking was observed and the strength was retained after exposure in air at 700 °C for 570 h.

An attempt was made to characterize the compositions that did and did not exhibit microcracking at intermediate temperatures. Understanding the difference between these so-called "good" or "bad" materials is essential so that composition and fabrication history can be controlled to ensure that microcracking will not occur. The difference in appearance between these materials was obvious. All diamond-ground samples were dark grey. On heating at intermediate or elevated temperatures in air, the surfaces became white. The difference between the good and bad materials was in the nature of the white surface layers. The white surface layers on samples that did not microcrack were uniform in thickness, exhibited a distinct boundary line from white to grey, and the layers were thin. Layer thickness was about 25 microns after 100 h at 700 °C, and 250 microns after 1000 h.

The white surface layers on samples that microcracked, on the other hand, were nonuniform in thickness, they exhibited a diffuse boundary line between the white and grey areas, and they were much thicker, often penetrating the sample as much as 1000 microns in 200 h.
X-ray diffraction analyses were performed on these materials but no differences between samples that did or did not microcrack were found. Two major phases were present, beta Si$_3$N$_4$ and cubic ZrO$_2$. Sometimes splitting was observed in the major ZrO$_2$ peaks, indicating the presence of tetragonal-prime ZrO$_2$ phase. Tetragonal-prime phase is a nontransformable phase that does not lead to toughening. Occasionally, a minor amount of monoclinic ZrO$_2$ phase was present. In every case, whether it was material sintered at 1750 or 1800 C, the results were similar.

Samples also were characterized using TEM, SEM, and AEM techniques. The analyses were performed on samples made from the same batch of Si$_3$N$_4$ + 45 w/o ZrO$_2$ (9 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$. The differences between samples were that half were sintered at 1750 C and half were sintered at 1800 C. Samples sintered at 1750 C exhibited microcracking after 255 h at 700 C in air, while samples sintered at 1800 C did not microcrack after 1000 h at 700 C in air, the longest duration of exposure.

The purposes of this investigation were to identify the difference in the good and bad samples, to explain the color change between oxidation scale and the unreacted core region, and to provide an explanation of why those samples sintered at the lower temperature microcracked. Three possible mechanisms for microcracking were identified: (1) Si$_3$N$_4$ and ZrO$_2$ could react to form a zirconium oxynitride phase (Zr$_7$O$_{11}$N$_2$ or Zr$_7$O$_8$N$_4$) which would then undergo a destructive volume change on oxidation; (2) Zr metal precipitates, produced during sintering in a reducing environment, could oxidize and generate internal stresses; and (3) undesirable Si$_3$N$_4$:Y$_2$O$_3$ could collect at the grain boundaries (Ref. 12), which could explain the rapid oxidation, or it could precipitate as discrete islands inside the grain boundaries where oxidation would be much slower. Si$_3$N$_4$:Y$_2$O$_3$:SiO$_2$ phases could develop that undergo volume changes on oxidation. In hypothesis (2), for example, Zr metal could (a) collect in the grain boundaries (Ref. 12), in which case the oxidation rate would be high, or (b) precipitate inside the ZrO$_2$ grains, in which case the oxidation would be much slower and, possibly, less destructive. Analyses designed to isolate the actual mechanism(s) were undertaken. Specifically, analytical
electron microscopy (AEM) experiments were performed to identify the presence and location within samples of nitrogen, metallic Zr, and Y₂O₃.

The first direct observation was that scale formation was uniform in thickness only for the good samples while, for the poor quality samples, white material penetrated into the interior of samples nonuniformly with associated cracking. Attempts to prepare transmission electron microscope (TEM) specimens from scale regions by back ion-beam thinning were only partially successful. First, scale samples were poor quality, with little thin area. Second, the thin areas of the back-thinned samples appeared to have darkened, suggesting that they may have transformed back to the unoxidized darker structure in the vacuum of the ion beam thinner. There was insufficient time to overcome the problems of specimen preparation.

AEM characterization identified no significant differences between either the oxidized and unoxidized samples or between the good and bad samples. All samples examined contained a reasonably homogeneous distribution of electron-dense, zirconium-rich grains and electron-transparent, silicon-rich grains, and all grain boundaries and triple points contained a crystalline grain boundary phase.

Energy dispersive X-ray spectrometry (EDS) was performed using an ultra-thin-window detector for light element analysis. Yttria and oxygen were detected in the zirconium-rich grains (0.1 to 0.5 μm diameter), whereas some of the larger silicon-rich grains (5 μ) additionally contained oxygen. Convergent beam diffraction confirmed that the small grains were silicon nitride and that there were a few larger Si₂N₂O grains. The zirconium-rich grains typically contained 7 cation w/o Y and 93 cation w/o Zr. Some internal structure could be imaged by TEM in the Zr-rich grains, possibly consisting of small Zr metal precipitates. Sample thickness prevented analysis of these precipitates by either EDS or diffraction analysis. Monoclinic laths, traversing entire grains, were observed in some zirconia grains. Analysis of the grain boundary phases by EDS identified Si, Al, Y, and O in varying proportions. Although quantitative analysis of the crystalline grain boundary phase would be unreliable (there is
no guarantee that the beam would be contained entirely within the boundary phase), the presence of Y (absent within the Si-rich grains) and elevated levels of Al were confirmed.

Figure 7 shows a scheme of an analyzed area with the results of semiquantitative cation analysis for a number of analyzed points. The shaded grains were zirconia and unshaded grains were silicon nitride. Small pockets of grain boundary phase are also shown shaded.

Although the presence of Si$_2$N$_2$O was confirmed, analysis by thin window EDS is not sufficiently sensitive to detect nitrogen in Zr$_7$O$_{11}$N$_2$. Therefore, the hypothesis that the presence of Si$_2$N$_2$O formation could confirm the presence of Zr$_7$O$_{11}$N$_2$ could not be resolved. Similarly, the hypothesis that the dark color of as-sintered samples is due to the presence of Zr metal precipitates could not be confirmed.

Transformation Toughening

Transformation toughening without microcracking was not achieved for ZrO$_2$ ($Y_2$O$_3$) alloys until near the end of the program and further work is needed to confirm it. Thus, most of the samples made during the program did not exhibit toughening because they contained ZrO$_2$ stabilized with 9 w/o or more $Y_2$O$_3$. Nine weight percent $Y_2$O$_3$ alloy was thought to be necessary to prevent microcracking when these samples were heated in air at intermediate temperatures. Even though some of the $Y_2$O$_3$ comes out of the ZrO$_2$ lattice during sintering, there is enough $Y_2$O$_3$ to keep the composition well within the cubic or tetragonal-prime phase region of the phase diagram (Fig. 8). Tetragonal-prime phase does not undergo a phase transformation (Ref. 6), so there is no toughening mechanism in this composition. Nevertheless, this composition showed enough merit, because of high strength combined with low thermal conductivity, that characterization studies were conducted.
Figure 7. AEM Analysis on a Si₃N₄ + 45 w/o ZrO₂ (9 w/o Y₂O₃) + 4 w/o Al₂O₃ Sample

<table>
<thead>
<tr>
<th>No.</th>
<th>Zr</th>
<th>Y</th>
<th>Si</th>
<th>Al</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>92</td>
<td>5</td>
<td>Si₃N₄ grain</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>94</td>
<td>4</td>
<td>Si₃N₄ grain</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>7</td>
<td>68</td>
<td>19</td>
<td>triple point</td>
</tr>
<tr>
<td>4</td>
<td>93</td>
<td>7</td>
<td>10</td>
<td>triple point</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>83</td>
<td>3</td>
<td>triple point</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0</td>
<td>90</td>
<td>6</td>
<td>Si₃N₄ grain</td>
</tr>
<tr>
<td>7</td>
<td>93</td>
<td>7</td>
<td></td>
<td>ZrO₂ grain</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>0</td>
<td>89</td>
<td>6</td>
<td>triple point</td>
</tr>
</tbody>
</table>

* Numbers signify cation w/o
Figure 8. ZrO₂/Y₂O₃ Phase Diagram
Characterization studies late in the program showed that higher sintering temperatures allowed the use of lower Y$_2$O$_3$ stabilization without the appearance of microcracking and that use of lower Y$_2$O$_3$ stabilization did result in increased toughness. These results are shown in Fig. 9. The toughness for Si$_3$N$_4$-ZrO$_2$ composites containing 45 w/o ZrO$_2$ stabilized with 9 to 13.5 w/o Y$_2$O$_3$ was 4 to 4.5 MPa $m^{1/2}$, about the same as the Si$_3$N$_4$ matrix without ZrO$_2$. However, toughness increased with decreasing Y$_2$O$_3$ stabilizer content to 6.0 MPa $m^{1/2}$ at a Y$_2$O$_3$ content of 4.5 w/o. As shown in the phase diagram (Fig. 9), 4.5 w/o Y$_2$O$_3$ content is near the edge of the region in which transformable tetragonal phase is formed. In practice, the ZrO$_2$ with 4.5 w/o Y$_2$O$_3$ is probably within the transformable region after sintering because a portion of the Y$_2$O$_3$ content will diffuse into the grain boundaries.

A value of 6 MPa $m^{1/2}$ represents a 50% increase in toughness in material in the as-sintered condition. Higher measured toughness values can be expected for heat-treated samples based on the results (which are discussed in a later section) that show significant increases in strength. These increases are due to surface compressive stresses that should also cause an increase in toughness.

Fracture toughness also was measured using bars containing 3 diamond indentations lined up along the length within the constant stress region of a 4-point bend test (Ref. 6). These results (Tables 5 and 6) showed an increase in toughness in the Si$_3$N$_4$ + ZrO$_2$(Y$_2$O$_3$) composites compared to NC-132 control samples, and it showed an increase in toughness when the Y$_2$O$_3$ alloy content was less than 9 w/o. But, it did not show as much increase as was evidenced when toughness was measured by the single indentation method (Fig. 9).

Fracture toughness also was measured by this method at 700 and 1000 C. The Y$_2$O$_3$ alloy content in these bars was 9 w/o so the transformation toughening effect would not be active. Toughness increased 50% at 700 C but it decreased at 1000 C to the level of the NC-132 reference sample.
[COMPOSITION: Si₃N₄ + 45w/o ZrO₂ (xY₂O₃) + 4 w/o A1₂O₃]

*MEASURED BY THE DIAMOND INDENTATION METHOD

Figure 9. Fracture Toughness vs Y₂O₃ Alloy Content in ZrO₂
Table 5. Fracture Toughness Measured on Indented MOR Bars

<table>
<thead>
<tr>
<th>ZrO₂ (Y₂O₃) Content, v/o (w/o)</th>
<th>Y₂O₃ Alloy Content (w/o)</th>
<th>Number of Samples</th>
<th>Test Temperature, C</th>
<th>Fracture Toughness (MPa m₁/²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (45)</td>
<td>13.3</td>
<td>3</td>
<td>25</td>
<td>7.4</td>
</tr>
<tr>
<td>30 (45)</td>
<td>12</td>
<td>5</td>
<td>25</td>
<td>6.7</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>3</td>
<td>25</td>
<td>7.0</td>
</tr>
<tr>
<td>30 (45)</td>
<td>8</td>
<td>7</td>
<td>25</td>
<td>8.2</td>
</tr>
<tr>
<td>30 (45)</td>
<td>6.9</td>
<td>4</td>
<td>25</td>
<td>8.6</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>5</td>
<td>25</td>
<td>5.7*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1</td>
<td>25</td>
<td>6.1</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>2</td>
<td>700</td>
<td>8.9</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1</td>
<td>1000</td>
<td>5.6</td>
</tr>
</tbody>
</table>

*NC-132 material

Sintered Density

Composites of Si₃N₄ + 30 or 45 w/o (20 or 30 v/o) ZrO₂ readily sintered to high densities at 1750 C in 1 h using 4 w/o Al₂O₃ as a sintering aid. Sintered density for 45 w/o ZrO₂ composites was typically 3.90 g/cm³ and that for 30 w/o ZrO₂ composites was 3.50 g/cm³. Sintered densities were estimated to be 96% of theoretical based on theoretical densities of 4.05 g/cm³ and 3.65 g/cm³, respectively. Theoretical values were based on calculations using the rule of mixtures and on measured densities of hot pressed samples (Table 7). Physical properties used for the rule of mixture calculation are listed in Table 8. Calculated values were 4.05 g/cm³ and 3.76 g/cm³. A theoretical density of 4.05 g/cm³ for the 45 w/o ZrO₂ composition was reasonable compared to the average measured value of hot-pressed samples, which was 4.00 g/cm³, but a theoretical value of 3.76 g/cm³ for 30 w/o ZrO₂ compositions seemed high in relation to the results of hot-pressed samples. Therefore, a theoretical value 3.65 g/cm³ was used for the 30 w/o ZrO₂ compositions. This value places the measured densities in agreement with the densities and porosities as determined by the modified Archimedes method.
Table 6. Test Data for Measuring Fracture Toughness
(Sheet 1 of 3)

<table>
<thead>
<tr>
<th>SAMPLE IDENTIFICATION</th>
<th>HEIGHT (INCH)</th>
<th>WIDTH (INCH)</th>
<th>LOAD (LBS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S#54:8Y-4A-117-852-D1-B48-1-1</td>
<td>0.074</td>
<td>0.099</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.099</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td>0.072</td>
<td>0.0985</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>0.073</td>
<td>0.0985</td>
<td>26.8</td>
</tr>
<tr>
<td>S#54:4Y(6.9)-4A-106-852-D2-B47-2-1</td>
<td>0.0735</td>
<td>0.099</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>0.073</td>
<td>0.099</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.099</td>
<td>28.3</td>
</tr>
<tr>
<td>S#53:4Y-4A-117-852-D2-B45-3-1</td>
<td>0.074</td>
<td>0.099</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.0995</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>0.074</td>
<td>0.0995</td>
<td>23.8</td>
</tr>
<tr>
<td>S#51:8Y(13.3)-4-73-852-D1-B44-4-1</td>
<td>0.074</td>
<td>0.0995</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>0.074</td>
<td>0.099</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.099</td>
<td>24.5</td>
</tr>
<tr>
<td>S#39:12*Y-4A-168-795-D2-B26-5-1</td>
<td>0.073</td>
<td>0.099</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.0995</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.099</td>
<td>20.3</td>
</tr>
<tr>
<td>S#34:12*Y-4A-168-795-D1-B22-6-1</td>
<td>0.0725</td>
<td>0.098</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.0735</td>
<td>0.099</td>
<td>20.3</td>
</tr>
<tr>
<td>S#32:12Y(9)-4A-105-795-D3-B29-7-1</td>
<td>0.071</td>
<td>0.099</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>0.072</td>
<td>0.0985</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>0.072</td>
<td>0.095</td>
<td>20.3</td>
</tr>
<tr>
<td>NC132</td>
<td>0.074</td>
<td>0.123</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td>0.074</td>
<td>0.122</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>0.0745</td>
<td>0.115</td>
<td>23.2</td>
</tr>
<tr>
<td></td>
<td>0.0745</td>
<td>0.103</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>0.074</td>
<td>0.114</td>
<td>24.1</td>
</tr>
<tr>
<td>S#32:12T(9)-4A-105-795-D3-B29-9-1</td>
<td>0.073</td>
<td>0.099</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S#32:12Y9-4A-105-795-D3-B29-10-1</td>
<td>0.073</td>
<td>0.099</td>
<td>21.8</td>
</tr>
<tr>
<td>700 C</td>
<td>0.072</td>
<td>0.0985</td>
<td>20.1</td>
</tr>
<tr>
<td>S#32:12Y9(Ø-4A-105-795-D3-B29-11-1</td>
<td>0.0725</td>
<td>0.0985</td>
<td>19.7</td>
</tr>
<tr>
<td>1000 C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 6. Test Data for Measuring Fracture Toughness
(Sheet 2 of 3)

<table>
<thead>
<tr>
<th>4-PT MOR (KSI)</th>
<th>14-PT MOR (MPa)</th>
<th>2Cmax (UNITS)</th>
<th>2Cmin (UNITS)</th>
<th>CVSN FTR (u/UNIT)</th>
<th>Cmax (MICRONS)</th>
<th>Cmin (MICRONS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.8</td>
<td>316</td>
<td>22.8</td>
<td>19.1</td>
<td>22.1</td>
<td>251.94</td>
<td>211.055</td>
</tr>
<tr>
<td>46.6</td>
<td>321</td>
<td>15.5</td>
<td>14.3</td>
<td>22.1</td>
<td>171.275</td>
<td>150.015</td>
</tr>
<tr>
<td>45.7</td>
<td>315</td>
<td>24.4</td>
<td>19.9</td>
<td>22.1</td>
<td>269.62</td>
<td>219.895</td>
</tr>
<tr>
<td>46.0</td>
<td>317</td>
<td>19.8</td>
<td>16.9</td>
<td>22.1</td>
<td>218.79</td>
<td>186.745</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>44.3</td>
<td>305</td>
<td>20.8</td>
<td>16.8</td>
<td>22.1</td>
<td>229.84</td>
<td>185.64</td>
</tr>
<tr>
<td>44.4</td>
<td>306</td>
<td>17.9</td>
<td>16.4</td>
<td>22.1</td>
<td>197.795</td>
<td>181.22</td>
</tr>
<tr>
<td>48.4</td>
<td>334</td>
<td>21</td>
<td>18.1</td>
<td>22.1</td>
<td>232.85</td>
<td>200.005</td>
</tr>
<tr>
<td>47.6</td>
<td>328</td>
<td>22.8</td>
<td>18.3</td>
<td>22.1</td>
<td>251.94</td>
<td>202.215</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>42.7</td>
<td>294</td>
<td>21.9</td>
<td>17.6</td>
<td>22.1</td>
<td>241.995</td>
<td>194.48</td>
</tr>
<tr>
<td>42.4</td>
<td>292</td>
<td>20.5</td>
<td>14.7</td>
<td>22.1</td>
<td>226.525</td>
<td>162.435</td>
</tr>
<tr>
<td>39.3</td>
<td>271</td>
<td>19.3</td>
<td>19.2</td>
<td>22.1</td>
<td>213.265</td>
<td>212.16</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>38.7</td>
<td>266</td>
<td>18</td>
<td>15.3</td>
<td>22.1</td>
<td>198.9</td>
<td>169.065</td>
</tr>
<tr>
<td>41.5</td>
<td>286</td>
<td>20.1</td>
<td>0</td>
<td>22.1</td>
<td>222.105</td>
<td>215.475</td>
</tr>
<tr>
<td>41.2</td>
<td>284</td>
<td>21.1</td>
<td>19.5</td>
<td>22.1</td>
<td>233.135</td>
<td>215.475</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>39.2</td>
<td>270</td>
<td>19.3</td>
<td>0</td>
<td>22.1</td>
<td>213.265</td>
<td>0</td>
</tr>
<tr>
<td>37.3</td>
<td>257</td>
<td>24.7</td>
<td>18.5</td>
<td>22.1</td>
<td>272.935</td>
<td>204.425</td>
</tr>
<tr>
<td>34.2</td>
<td>235</td>
<td>15.6</td>
<td>14.8</td>
<td>22.1</td>
<td>172.38</td>
<td>163.54</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>34.9</td>
<td>241</td>
<td>26.2</td>
<td>20.5</td>
<td>22.1</td>
<td>289.51</td>
<td>226.525</td>
</tr>
<tr>
<td>34.2</td>
<td>235</td>
<td>22.7</td>
<td>22.4</td>
<td>22.1</td>
<td>250.835</td>
<td>247.52</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>35.5</td>
<td>245</td>
<td>23.8</td>
<td>20.9</td>
<td>22.1</td>
<td>262.99</td>
<td>230.945</td>
</tr>
<tr>
<td>37.0</td>
<td>255</td>
<td>25.2</td>
<td>0</td>
<td>22.1</td>
<td>278.46</td>
<td>0</td>
</tr>
<tr>
<td>35.6</td>
<td>245</td>
<td>17</td>
<td>21.7</td>
<td>22.1</td>
<td>187.85</td>
<td>239.785</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>31.0</td>
<td>214</td>
<td>20.6</td>
<td>20.2</td>
<td>22.1</td>
<td>227.63</td>
<td>223.21</td>
</tr>
<tr>
<td>34.1</td>
<td>235</td>
<td>18.5</td>
<td>16.2</td>
<td>22.1</td>
<td>204.425</td>
<td>179.01</td>
</tr>
<tr>
<td>32.7</td>
<td>225</td>
<td>16.4</td>
<td>0</td>
<td>22.1</td>
<td>181.22</td>
<td>0</td>
</tr>
<tr>
<td>32.0</td>
<td>220</td>
<td>17.4</td>
<td>16.6</td>
<td>22.1</td>
<td>192.27</td>
<td>183.43</td>
</tr>
<tr>
<td>34.7</td>
<td>239</td>
<td>16.8</td>
<td>16.2</td>
<td>22.1</td>
<td>185.64</td>
<td>179.01</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>33.3</td>
<td>229</td>
<td>19.6</td>
<td>19.2</td>
<td>22.1</td>
<td>216.58</td>
<td>212.16</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>51.4</td>
<td>354</td>
<td>9.2</td>
<td>7.1</td>
<td>22.1</td>
<td>101.66</td>
<td>78.455</td>
</tr>
<tr>
<td>49.0</td>
<td>338</td>
<td>6.8</td>
<td>6.6</td>
<td>22.1</td>
<td>75.14</td>
<td>72.93</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>47.4</td>
<td>326</td>
<td>20.1</td>
<td>18.1</td>
<td>22.1</td>
<td>222.105</td>
<td>200.005</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td></td>
<td></td>
<td>22.1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 6. Test Data for Measuring Fracture Toughness
(Sheet 3 of 3)

<table>
<thead>
<tr>
<th>Kc max</th>
<th>Kc min</th>
<th>Kc avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MPa m1/2) (MPa m1/2)</td>
<td>(MPa m1/2) (MPa m1/2)</td>
<td></td>
</tr>
<tr>
<td>9.442134</td>
<td>18.584486</td>
<td>19.013310</td>
</tr>
<tr>
<td>7.810435</td>
<td>17.475153</td>
<td>17.642794</td>
</tr>
<tr>
<td>9.752483</td>
<td>18.741484</td>
<td>19.246983</td>
</tr>
<tr>
<td>8.779750</td>
<td>18.059777</td>
<td>18.419663</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>8.658385</td>
<td>17.712565</td>
<td>18.185475</td>
</tr>
<tr>
<td>9.001868</td>
<td>17.653144</td>
<td>17.816006</td>
</tr>
<tr>
<td>9.591676</td>
<td>18.856103</td>
<td>19.223889</td>
</tr>
<tr>
<td>9.840544</td>
<td>18.745325</td>
<td>19.292934</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>8.557422</td>
<td>17.601043</td>
<td>18.079232</td>
</tr>
<tr>
<td>8.193479</td>
<td>16.834077</td>
<td>17.513778</td>
</tr>
<tr>
<td>7.310304</td>
<td>17.289577</td>
<td>17.299400</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>6.906820</td>
<td>16.314703</td>
<td>16.610762</td>
</tr>
<tr>
<td>7.928622</td>
<td>-0.68</td>
<td>13.624311</td>
</tr>
<tr>
<td>8.081766</td>
<td>17.743018</td>
<td>17.912392</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>7.294800</td>
<td>-0.68</td>
<td>13.307400</td>
</tr>
<tr>
<td>7.905188</td>
<td>16.749972</td>
<td>17.327580</td>
</tr>
<tr>
<td>5.562272</td>
<td>15.490107</td>
<td>15.481189</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>7.595091</td>
<td>16.637997</td>
<td>17.117444</td>
</tr>
<tr>
<td>6.849971</td>
<td>16.800048</td>
<td>16.825010</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>7.338572</td>
<td>16.834182</td>
<td>17.086377</td>
</tr>
<tr>
<td>7.916320</td>
<td>-0.68</td>
<td>13.618160</td>
</tr>
<tr>
<td>6.110700</td>
<td>16.992200</td>
<td>16.551450</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>5.829494</td>
<td>15.765986</td>
<td>15.797740</td>
</tr>
<tr>
<td>6.102305</td>
<td>15.666715</td>
<td>15.884510</td>
</tr>
<tr>
<td>5.449058</td>
<td>-0.68</td>
<td>12.384529</td>
</tr>
<tr>
<td>5.497584</td>
<td>15.344132</td>
<td>15.415858</td>
</tr>
<tr>
<td>5.908668</td>
<td>15.789943</td>
<td>15.849305</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>6.135336</td>
<td>16.065433</td>
<td>16.100385</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>6.539224</td>
<td>15.661994</td>
<td>16.100609</td>
</tr>
<tr>
<td>5.232489</td>
<td>15.144892</td>
<td>15.188690</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>9.145917</td>
<td>18.644259</td>
<td>18.895088</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
<tr>
<td>ERR</td>
<td>ERR</td>
<td>ERR</td>
</tr>
</tbody>
</table>
Table 7. Densities of Hot-Pressed Samples

<table>
<thead>
<tr>
<th>ZrO₂ Content, v/o (w/o)</th>
<th>Y₂O₃ Alloy Content, v/o (w/o)</th>
<th>Hot Press Temperature (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (45)</td>
<td>8</td>
<td>1800</td>
<td>4.07*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1700</td>
<td>3.96*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1700</td>
<td>4.05*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1700</td>
<td>4.01*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1700</td>
<td>4.04*</td>
</tr>
<tr>
<td>30 (45)</td>
<td>9</td>
<td>1700</td>
<td>3.88*</td>
</tr>
<tr>
<td>26 (30)</td>
<td>9</td>
<td>1700</td>
<td>3.65</td>
</tr>
</tbody>
</table>

*Avg. = 4.00

Table 8. Properties of Si₃N₄ and ZrO₂ for Calculation of Si₃N₄/ZrO₂ Composite Theoretical Density

<table>
<thead>
<tr>
<th></th>
<th>Si₃N₄</th>
<th>ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.18</td>
<td>6.07</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>3.07</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Compositions of Si₃N₄ + 15 w/o ZrO₂, on the other hand, did not sinter to a high density, even at a temperature of 1860 °C. Sintered samples cracked and had a porosity in excess of 15%. Based on these results, it appears as if the ZrO₂ is acting as a sintering aid which has been previously determined by other researchers.

Room-Temperature Strength

Three-point MOR tests (Table 9) were generally used to obtain the most data from limited material. When there was sufficient material, 4-point MOR tests were performed. Evaluation of these data shows that 4-point flexural strength...
<table>
<thead>
<tr>
<th>Y$_2$O$_3$ Alloy Content (w/o)</th>
<th>Sintering Parameters</th>
<th>Sintered Density (g/cm$^3$)</th>
<th>Porosity (%)</th>
<th>3-Point MOR (MPa)</th>
<th>4-Point MOR (MPa)</th>
<th>Sintered Density (g/cm$^3$)</th>
<th>Porosity</th>
<th>3-Point MOR (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>1750C, 1h</td>
<td>3.93</td>
<td>0.03</td>
<td>782</td>
<td>14</td>
<td>730</td>
<td>6</td>
<td>83</td>
</tr>
<tr>
<td>12</td>
<td>1750C, 1h</td>
<td>3.81</td>
<td>0.00</td>
<td>994</td>
<td>7</td>
<td>3.47</td>
<td>0.16</td>
<td>840</td>
</tr>
<tr>
<td>12</td>
<td>1800C, 1h</td>
<td>3.92</td>
<td>0.01</td>
<td>957</td>
<td>8</td>
<td>3.53</td>
<td>0.02</td>
<td>1009</td>
</tr>
<tr>
<td>12</td>
<td>1860C, 2h</td>
<td>3.89</td>
<td>0.16</td>
<td>812</td>
<td>7</td>
<td>3.48</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1750C, 1h</td>
<td>3.87</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>3.48</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1800C, 1h</td>
<td>3.85</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
<td>3.48</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1800C, 1h</td>
<td>3.92</td>
<td>0.04</td>
<td>860</td>
<td>16</td>
<td>3.65</td>
<td>0.00</td>
<td>916</td>
</tr>
<tr>
<td>8</td>
<td>1800C, 1h</td>
<td>3.96</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1860C, 1h</td>
<td>3.87</td>
<td>0.04</td>
<td>983</td>
<td>11</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>1800C, 1h</td>
<td>3.91</td>
<td>0.22</td>
<td>908</td>
<td>9</td>
<td>840</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6.9</td>
<td>1860C, 1h</td>
<td>3.92</td>
<td>0.19</td>
<td>1003</td>
<td>8</td>
<td>898</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>854</td>
<td>5</td>
<td>806</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

*NC132, Lot 1073, tested for reference

Notes: 3-Point MOR, L$_0$ = 15.2 mm
4-Point MOR, L$_0$ = 23 mm, L$_i$ = 7.2 mm
Composition, Si$_3$N$_4$ + x ZrO$_2$ (y*Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
ranges from 7% to 19% lower than 3-point strength. The strength of a reference material, NC-132, was also measured. NC-132 grade of hot-pressed Si$_3$N$_4$ exhibited a difference of only 6% between 3- and 4-point test data.

The effects of sintering temperature on density and strength can be seen in Table 9 and Figs. 10 and 11. As sintering temperature is increased from 1750 to 1860°C for the 45 w/o ZrO$_2$ sample, there is no significant change in density, but strength decreases. For the 30 w/o ZrO$_2$ samples, there is a slight increase in density with increasing sintering temperatures and a substantial increase in strength. Based on previous considerations of the effect of ZrO$_2$ as a sintering aid, it appears as if the 45 w/o ZrO$_2$ samples could be progressively overfired at temperatures greater than 1750°C, while the lower ZrO$_2$ content materials require a higher sintering temperature of at least 1800°C to achieve their optimum properties.

There was no correlation between strength and Y$_2$O$_3$ stabilizer content in the ZrO$_2$ particles.

Strength increased significantly in samples that were aged in air at 700°C. A temperature of 700°C was an arbitrary temperature selected for evaluating microcracking in the 500°C to 1000°C range. This, of course, applies to material sintered at 1800°C or higher, in which no microcracking occurred. When samples were sintered at 1750°C, the strength of aged samples often decreased due to the microcracking phenomenon. However, when samples were sintered at 1800°C and aged at 700°C, strength increased. Strength in composites containing 45 w/o ZrO$_2$ peaked at 1082 MPa after 240 h, a 26% increase. The increase was even higher for composites containing 30 w/o ZrO$_2$, which peaked at 1254 MPa after 120 h, a 37% increase. Increased strength is due to residual compressive stresses that are formed on the surface. These increased strengths would not be observed at elevated temperatures, of course, as the compressive stresses would be relieved by plastic deformation, but these aged materials would be attractive for low-temperature applications, such as for high wear surfaces.
Figure 10. Si₃N₄ Room-Temperature Strength

- 2 Standard Deviations
- 20 V/O: (30 W/O) ZrO₂
- 30 V/O: (45 W/O) ZrO₂

Sintering Temperature, °C

Average Strength, MPa
Figure 11. Effect on Room Temperature Strength of Exposure to an Oxidizing Environment of Si₃N₄ + ZrO₂ (9 w/o Y₂O₃) + 4 w/o Al₂O₃.
High-Temperature Strength

The purpose of this program was to develop a tough Si₃N₄ composite with high strength at high temperatures. Four weight percent Al₂O₃ was used early in the program as a sintering aid for Si₃N₄ + ZrO₂ (Y₂O₃) systems because it was effective for obtaining dense samples for evaluation and for demonstration of concept. The Al₂O₃ sintering aid additions, however, did not meet the goals of the program because the resultant grain boundary phases are not sufficiently refractory at 1400 °C. Thus, compositional changes were made in an effort to increase the strength at elevated temperatures.

Three approaches were used: (1) the Al₂O₃ was replaced with selected mixtures of Y₂O₃ + SiO₂, (2) the Al₂O₃ content was reduced from 4 w/o to 2 w/o, and (3) an addition of 2 w/o Al₂O₃ + 6 w/o Y₂O₃ was used. The first approach was the most promising. Strengths at elevated temperatures were at the same level as strengths at ambient temperature, although the ambient strength was lower than expected because of processing complications. The second two approaches achieved a small amount of improvement in high-temperature strength compared to the 4 w/o Al₂O₃ reference composition, but the increases were far short of program goals.

Compositions with 4 w/o Al₂O₃—Sintering Aid. The high-temperature strength of compositions containing 4 w/o Al₂O₃ as a sintering aid are presented as a reference level for comparing compositions with sintering aids that were selected to provide more refractory compositions in the grain boundaries.

The results of both 3- and 4-point high-temperature strength measurements are listed in Table 10; 3-point data are plotted in Fig. 12.

Figure 13 shows that strength decreases linearly to 1000 °C where it is 72 to 79% of the room-temperature level. Strength then drops at an increasing rate to between 53 and 57% of the room-temperature level at 1200 °C, which is still at a level above 450 MPa for composites with 45 w/o ZrO₂ and above 524 MPa for composites with 30 w/o ZrO₂. Strength then drops rapidly to 161 MPa at
### Table 10: High-Temperature Strength of Si₃N₄ + ZrO₂ (Y₂O₃)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Test Temperature (°C)</th>
<th>Y₂O₃ Content (w/o)</th>
<th>Si₃N₄ + ZrO₂ (Y₂O₃) Weight (%)</th>
<th>3-Point MOR (L = 15 mm)</th>
<th>4-Point MOR (L₀ = 23 mm, L₁ = 17.6 mm)</th>
<th>Number of Tests</th>
<th>Average Strength (MPa)</th>
<th>Retention of Room Temp. Strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22, 23</td>
<td>25 1000</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>1000</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>1200</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>1400</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>1600</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>1800</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>2000</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>2200</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
<tr>
<td>22, 23</td>
<td>2400</td>
<td>9</td>
<td>9</td>
<td>155</td>
<td>140</td>
<td>1</td>
<td>1749</td>
<td>100</td>
</tr>
</tbody>
</table>

Note: The table provides high-temperature strength data for composites containing 4 w/o Al₂O₃ as a sintering aid.
Figure 12. Flexural Strength of \( \text{Si}_3\text{N}_4/\text{ZrO}_2 (x\text{Y}_2\text{O}_3) \) Composites
Using 4 w/o \( \text{Al}_2\text{O}_3 \) as a Sintering Aid
Figure 13. Strength of $\text{Si}_3\text{N}_4 + 30\text{ v/o ZrO}_2 (12\text{ w/o Y}_2\text{O}_3)$ with $\text{Y}_2\text{O}_3$ and $\text{SiO}_2$ (w/o) as Sintering Aid
1400°C, which is only 19% of the room-temperature level. Thus, these compositions could be useful to 1000°C, or 1200°C at most, but they would not be structurally stable at higher temperatures.

**Composites with Y_2O_3 + SiO_2 Sintering Aid.** Selected mixtures of Y_2O_3 + SiO_2 can be used to sinter Si_3N_4 to near full densities and these compositions have demonstrated very little loss in strength at elevated temperatures (Ref. 8). Rocketdyne used this technology over 10 years ago to develop a composition, Si_3N_4 + 15.5 w/o Y_2O_3 + 7.0 w/o SiO_2, called "SN104", that sintered to near full density and exhibited no loss in strength at 1200°C (Ref. 9). It has been shown that SN104 exhibited excellent resistance to creep (Ref. 9), being second only to a hot-pressed material containing a much lower amount of Y_2O_3 densification aid and no added SiO_2. Studies at Rocketdyne and the Rockwell Science Center showed that high-temperature properties could be improved even more by heat treatment (Ref. 10). Heat treatment is believed to cause (1) undesirable cations to diffuse into the Si_3N_4 grains where they do not affect grain boundary softening or melting, and (2) crystallization of glassy phases in the grain boundary.

With this in mind, mixtures of Y_2O_3 + SiO_2 were selected for evaluation in this program. Compositions were selected based on adding sufficient sintering aid to promote densification while remaining in the Si_3N_4-Si_2N_2O-Si_3Y_2O_7 compatibility phase triangle. Certain compositions outside this triangle, containing Y_2O_3, undergo excessive volume increases on oxidation that lead to cracking and spalling. The oxygen content in the Si_3N_4 powder was taken into account in the calculation of batches, but the reported quantities are only the amount added during fabrication. Selected additions for this study contained as little as 4.04 w/o Y_2O_3 + 1.1 w/o SiO_2 to as high as 15.5 w/o Y_2O_3 + 7.0 w/o SiO_2 (Table 11).

The Y_2O_3 and SiO_2 powders could not be suspended so the colloidal processing method could not be used. These powders were ball-milled then blended with the Si_3N_4 and ZrO_2 powders using the sonic mixing chamber. Large disks 50 mm in diameter were prepared by pressure filtration. Most of the disks cracked on drying even when precautions were exercised, such as slow, controlled humidity
Table 11. Density and High Temperature Strength of Si$_3$N$_4$ + 45 w/o (12 w/o Y$_2$O$_3$) Containing Y$_2$O$_3$ + SiO$_2$ Sintering Aid

<table>
<thead>
<tr>
<th>Sinter Run No.</th>
<th>Sintering Parameter</th>
<th>Sintering Aid</th>
<th>Sintered Density (g/cm$^3$)</th>
<th>Test Temperature (°C)</th>
<th>Strength (3-Point MOR) (MPa)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>1800 C, 1h</td>
<td>Y$_2$O$_3$ (w/o) 4.0</td>
<td>2.18</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ (w/o) 8.0</td>
<td>2.35</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>1860 C, 1h</td>
<td>Y$_2$O$_3$ (w/o) 4.0</td>
<td>3.44</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ (w/o) 8.0</td>
<td>3.40</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>1860 C, 2h</td>
<td>Y$_2$O$_3$ (w/o) 4.0</td>
<td>3.42</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ (w/o) 8.0</td>
<td>3.89</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1860 C, 2h</td>
<td>Y$_2$O$_3$ (w/o) 8.0</td>
<td>4.07</td>
<td>25</td>
<td>$\bar{X} = 455$</td>
<td>n = 8, S.D. = 103 (Process Variation A)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$ (w/o) 3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 516</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 544</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200 618</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200 518</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 526</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000 524</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200 613</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1400 690</td>
<td></td>
</tr>
</tbody>
</table>

$\bar{X}$ = mean  

n = number of samples  

S.D. = standard deviation
Table 11. Density and High Temperature Strength of Si₃N₄ + 45 w/o (12 w/o Y₂O₃) Containing Y₂O₃ + SiO₂ Sintering Aid (Continued)

<table>
<thead>
<tr>
<th>Sinter Run No.</th>
<th>Sintering Parameter</th>
<th>Y₂O₃ (w/o)</th>
<th>SiO₂ (w/o)</th>
<th>Sintered Density (g/cm³)</th>
<th>Test Temperature (°C)</th>
<th>Strength (3-Point MOR) (MPa)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>1860 C, 2h</td>
<td>4.0</td>
<td>3.0</td>
<td>3.78</td>
<td>25</td>
<td>X = 662</td>
<td>n = 4, S.D. = 66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>514</td>
<td>4-Point MOR</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>503</td>
<td>3-Pt. MOR = .89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>4-pt.: 448</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>508</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>8.0</td>
<td>3.6</td>
<td>4.12</td>
<td>25</td>
<td>X = 424</td>
<td>S.D. = 18</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>659</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>666</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>379</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>8.0</td>
<td>5.0</td>
<td>3.82</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.7</td>
<td>8.7</td>
<td>3.9</td>
<td>3.96</td>
<td>25</td>
<td>X = 469</td>
<td>n = 4, S.D. = 16</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>655</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>364</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1400</td>
<td>421</td>
<td></td>
</tr>
</tbody>
</table>
drying schedules and binder additives. For these reasons, large samples for fabricating MOR bars were difficult to obtain. As will be shown below, room-temperature strength levels were much lower than those of the compositions sintered using 4 w/o Al$_2$O$_3$. The reasons for this lower strength are believed to be flaws introduced from ball-milling debris and the lack of uncracked green disks.

High sintered densities were obtained with additions of 8.0 w/o Y$_2$O$_3$ + 3.9 w/o SiO$_2$ and sintering parameters of 1860°C for 2 h (Table 11). These are the same parameters, incidentally, that are required to sinter the SN104 composition. The only phases that were identified on ground surfaces were beta-Si$_3$N$_4$ and cubic ZrO$_2$.

Results of strength tests at ambient and elevated temperatures are listed in Table 11 and plotted in Figure 13. Strengths at 1400°C are the same as those at room temperature. There was no loss in strength at 1400°C.

Only one specimen was tested in 4-point loading because of the scarcity of long MOR bars. The 4-point strength was 11% below that of the 3-point data. Although there was only one sample tested under 4-point loading, an 11% difference is in agreement with other high-temperature tests.

Process variations A and B, shown in Fig. 13, refer to the mixing sequence. The ingredients were mixed sequentially in variation A. That is to say, that Y$_2$O$_3$ and SiO$_2$ powders were ball-milled; these powders were then mixed with the ZrO$_2$ powder in the sonic chamber, and these powders were, in turn, mixed with the Si$_3$N$_4$ powder in the sonic chamber. In variation B, the ball-milled mixture of Y$_2$O$_3$ and SiO$_2$ was mixed with the ZrO$_2$ and Si$_3$N$_4$ powders simultaneously in the sonic chamber. The reason for the increased room temperature strength is unknown, but all strength values measured after any heat treatment or at temperature were in line with the room-temperature strength of samples made by variation B.
Samples were aged in air at 700°C to determine whether microcracking occurred. Based on MOR results (Table 12), none had occurred after exposures as long as 500 h at 700°C.

**Table 12. Strength After Heating in Air at 700°C for Composites of Si₃N₄ + 45 w/o ZrO₂ (12 w/o Y₂O₃) + x Y₂O₃ + y SiO₂**

<table>
<thead>
<tr>
<th>Sinter Run No.</th>
<th>Sintering Aids</th>
<th>Exposure Time at 700°C (h)</th>
<th>Room Temperature Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y₂O₃ (w/o)</td>
<td>SiO₂ (w/o)</td>
<td>n</td>
</tr>
<tr>
<td>40</td>
<td>8.0</td>
<td>3.6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>273</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>517</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>42</td>
<td>8.0</td>
<td>5.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

*n = number of samples

Composites with 2 w/o Al₂O₃ Sintering Aid. Sintered compositions of Si₃N₄ + 45 w/o (~30 v/o) ZrO₂ (12 w/o Y₂O₃) exhibited inconsistent results. Two samples with identical composition and processing history were sintered together at 1800°C for 1 h. The densities were 2.92 g/cm³ and 3.40 g/cm³, which were 72 and 84% of theoretical. A third sample was sintered at 1860°C for 1 h, but the density was 3.11 g/cm³, or 77% of theoretical. Despite the low densities, MOR bars were diamond ground from the latter sample and the results of the tests are listed in Table 13. Results of a similar composition, but containing 4 w/o Al₂O₃ as the sintering aid (Table 13), also are listed for reference (note that the Y₂O₃ content in the ZrO₂ is different, 12 w/o for the composition containing 2 w/o Al₂O₃ and 9 w/o for the composition containing 4 w/o Al₂O₃). The significance of this difference is that the
Table 13. High-Temperature Strength of Si₃N₄ + ZrO₂ (Y₂O₃) Composites Containing Sintering Aids

<table>
<thead>
<tr>
<th>Sintering Aid</th>
<th>Sintered Density (g/cm³)</th>
<th>Test Temperature (°C)</th>
<th>Y₂O₃ Content in ZrO₂ (w/o)</th>
<th>Average 3-Point MOR L = 15 mm (MPa)</th>
<th>Retention of Room Temp. Strength (%)</th>
<th>Average 4-Point MOR L₀ = 30 mm L₁ = 10 mm</th>
<th>Retention of Room Temperature Strength (%)</th>
<th>Strength (4-Point/3-Point)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 w/o Al₂O₃</td>
<td>3.13</td>
<td>25</td>
<td>12</td>
<td>752</td>
<td>100</td>
<td>499</td>
<td>100</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200</td>
<td>12</td>
<td>413</td>
<td>55</td>
<td>418</td>
<td>83</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1400</td>
<td>12</td>
<td>–</td>
<td>–</td>
<td>197</td>
<td>39</td>
<td>–</td>
</tr>
<tr>
<td>6 w/o Y₂O₃ +</td>
<td>3.97</td>
<td>25</td>
<td>12</td>
<td>773</td>
<td>100</td>
<td>707</td>
<td>100</td>
<td>0.91</td>
</tr>
<tr>
<td>2 w/o Al₂O₃</td>
<td></td>
<td>1200</td>
<td>12</td>
<td>477</td>
<td>62</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1400</td>
<td>12</td>
<td>125</td>
<td>16</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4 w/o Al₂O₃</td>
<td>3.85</td>
<td>25</td>
<td>9</td>
<td>860</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200</td>
<td>9</td>
<td>458</td>
<td>53</td>
<td>360</td>
<td>–</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1400</td>
<td>9</td>
<td>161</td>
<td>19</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

[Composition: Si₃N₄ + 45 w/o ZrO₂ (12 w/oY₂O₃) + Sintering Aid Indicated]
grain boundary composition in these composites will be different, one containing more Y₂O₃ dissolved from the ZrO₂ (Y₂O₃) alloy. The grain boundary composition is believed to control high-temperature properties.

Three-point MOR results of tests conducted at 1200 C do not indicate that the lower Al₂O₃ content is of any benefit. The retention of room-temperature strength, 53%, was the same as that for the 4 w/o Al₂O₃ reference material. The 4-point MOR data, on the other hand, indicate that there is some improvement. The retention of room-temperature strength is 83%, but the room-temperature strength appears to be low. Moreover, the strength at 1400 C is very low, 197 MPa, so the approach of simply reducing the Al₂O₃ content did not result in any substantial increase in high-temperature strength.

Composites with 6 w/o Y₂O₃ + 2 w/o Al₂O₃ Sintering Aid. Use of a combination of 6 w/o Y₂O₃ + 2 w/o Al₂O₃ did not produce any better results than that for compositions containing 2 w/o or 4 w/o Al₂O₃. Retention of room-temperature strength at 1200 C was 62%, up from 53%, and at 1400 C it was 12%. These are far below the desired level.

HfO₂ (Y₂O₃)

The use of dispersed HfO₂ in place of, or in combination with, ZrO₂ is attractive because it should allow composites to be used at higher temperatures. It is well documented in the literature that transformation-toughened ZrO₂ materials do not exhibit the toughening mechanism at high temperatures, beginning at about 1000 C. The metastable tetragonal grains tend to transform at the lower end of the transformation temperature range (950 to 1200 C). HfO₂, on the other hand, transforms at a much higher temperature, beginning at 1400 C (Ref. 11). Stabilizer additions may reduce the transformation temperature, but a gain of 500 C in service temperature may be achievable. An increase in service temperature of this magnitude could allow transformation-toughened materials to be used in turbine applications.
Selected stabilizers of HfO$_2$ (Y$_2$O$_3$) and HfO$_2$ (MgO) were ordered but the powders were not received in time to be a part of this program. An Si$_3$N$_4$ + HfO$_2$ composite was made, however, using HfO$_2$ fully stabilized with 10 m/o Y$_2$O$_3$. Naturally, transformation toughening was not anticipated, but samples were made to demonstrate that the composition sintered to near full density and that it exhibited high strength.

The composition of the composite was Si$_3$N$_4$ + HfO$_2$ (10 m/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$ and a batch was prepared using the colloidal method. No differences were noted using HfO$_2$ powder compared to ZrO$_2$ powder. Two disks, 50 mm in diameter, were prepared by pressure filtration, dried and sintered at 1800 C for 1 h. Sintered density was 4.99 g/cm$^3$ in both disks, average weight loss was 0.7%, and the open porosity was 0.1% in one and 0.01% in the other. Ground surfaces were uniform in appearance and dark grey. A photomicrograph showing the good dispersion of the HfO$_2$ grains is shown in Fig. 14. The microstructure was analyzed using TEM and AEM methods as described in the previous section. The microstructure appeared uniform and homogeneous, and similar to that of the comparable Si$_3$N$_4$ + ZrO$_2$ + 4 w/o Al$_2$O$_3$ composites. The size of the Si$_3$N$_4$ grains was 0.2 micrometer, and HfO$_2$ particles consisted of several grains. One difference was that the grain boundaries appeared more glassy than those of compositions containing ZrO$_2$ (Y$_2$O$_3$). Results of a semiquantitative analysis are shown in Fig. 15. The presence of Mg in the HfO$_2$ grains was unexpected. This qualitative observation is valid, although the quantity is uncertain because the dispersive energy of the two elements are adjacent to each other, and because one is a light element and the other is a heavy element (Fig. 16).

The average 4-point MOR at room temperature was 876 MPa with a standard deviation of 34 MPa (4 samples). The average 3-point strength was 917 MPa with a standard deviation of 144 MPa (6 samples).

The 3-point strength of two samples at 1200 C was 555 and 577 MPa, which averages 62% retention of room temperature strength. This is 20% better retention than that for a comparable composition with ZrO$_2$ instead of HfO$_2$. 
Semiquantitative Analysis (cation %)

<table>
<thead>
<tr>
<th>No.</th>
<th>Hf</th>
<th>Mg</th>
<th>Y</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89</td>
<td>2</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>88</td>
<td>3</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>86</td>
<td>4</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>86</td>
<td>2</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>89</td>
<td>3</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>87</td>
<td>3</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>9</td>
<td>21</td>
<td>57</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>

Grain boundary triple point

Figure 15. Semiquantitative Analysis of Si$_3$N$_4$ + HfO$_2$
(10 m/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
Figure 16. Energy Dispersive Analysis of a HfO$_2$ Grain

ELEMENTAL WEIGHT (%)

TYPICAL ANALYSIS:
Hf 89%
Mg 3%
Y 8%
The strength at 1400 C was 220 and 203 MPa. While this was higher than comparable ZrO₂ composites, the use of a more refractory sintering aid, such as Y₂O₃ + SiO₂, will be necessary to improve strength at 1400 C.

Samples were aged in air at 700 C to determine whether there was any microcracking at intermediate temperatures. Results showed no indication of degradation; in fact, strength increased at each duration that was tested (Fig. 17). The average room-temperature strengths of bars aged at 700 C in air are listed in Table 12. The average strength after aging 500 h was 20% higher than that of unaged samples.

ZrO₂ (CaO)

Hot-Pressed Composites

Early in the program, increased toughness could not be obtained in Si₃N₄/ZrO₂ (Y₂O₃) composites without microcracking, so a ZrO₂ alloying agent with a divalent cation was evaluated. The only two available ZrO₂ powders were alloyed with CaO or MgO. Success was immediate with the CaO-alloyed composition and the results are reported in this section. Results of the MgO-alloyed composition are reported in the next major section of this report.

The ZrO₂ powder*, which contained 5 w/o CaO, was too coarse for colloidal suspension processing. Batches containing Si₃N₄ plus 15, 30, and 45 w/o ZrO₂ (5 w/o CaO) were prepared by ball-milling using ZrO₂ milling media and polyethylene jars. Initial samples were densified by hot pressing and near full density was achieved at 1700 C, 1 h. Two and one-half percent MgO was added as a sintering aid and to keep the CaO in the ZrO₂ grains from diffusing to the grain boundaries during densification. The results showed significant increases in both fracture toughness and strength.

*Zircoa Grade B
Figure 17. Evidence of Stability at Intermediate Temperatures of $\text{Si}_3\text{N}_4 + \text{HfO}_2$ Composites
The fracture toughness of all samples was substantially higher than that of the Si$_3$N$_4$ matrix. The baseline matrix toughness is 4.1 MPa m$^{1/2}$. Toughness was measured and calculated by the same diamond indentation technique (Ref. 5) on NC-132 samples. Toughness values measured on as-hot-pressed samples and samples subjected to selected heat treat conditions are shown in Fig. 18. All of these samples, except the NC132, were composed of Si$_3$N$_4$ + 45 w/o ZrO$_2$ (5 w/o CaO) + 2.5 w/o MgO.

A large portion of the high measured toughness in the aged samples is due to surface compressive stresses that develop as Zr-oxynitride oxidizes to form monoclinic ZrO$_2$ on the surface. Toughness was measured at 12.5 MPa m$^{1/2}$ on the surface of a specimen aged at 1350°C for 2 h. Toughness was measured after 0.25 mm of the surface was removed by polishing, and this was repeated until the toughness level reached the level of the material in the as-hot pressed condition, which was 8.9 MPa m$^{1/2}$. This level of toughness was reached 1 mm below the original surface. Toughness was not affected by annealing at an intermediate temperature of 700°C for 120 h.

Toughness for the three loadings of ZrO$_2$ (5 w/o CaO) and for the matrix material without the ZrO$_2$ is shown in Fig. 19. Toughness increases from that of NC-132 Si$_3$N$_4$, 4.1 MPa m$^{1/2}$, to 6.3 MPa m$^{1/2}$ with a loading of only 15 w/o. Toughness then increases nearly linearly to 7 MPa m$^{1/2}$ at the highest loading of 45 w/o. Thus, even a small amount of ZrO$_2$ results in substantial increases in fracture toughness.

Flexural strengths of Si$_3$N$_4$ composites with 45 w/o ZrO$_2$ modified with 5 w/o CaO are given in Table 14. These samples were tested in either the as-hot-pressed or after-heat-treatment conditions. Heat treatment consisted of 1350°C for 2 h followed by 700°C for 261 h exposure in an air environment.

The 4-point modulus of rupture was measured as a function of (1) volume loading of ZrO$_2$ and (2) exposure to oxidation at 700°C for durations to 250 h. The strength of these compositions is degraded by microcracking at moderate temperatures, and a temperature of 700°C was selected to study this microcracking phenomenon. The degree of strength degradation for volume loadings
Figure 19. Fracture Toughness vs ZrO₂ Content
Table 14. Strength of Hot-Pressed Si₃N₄ + 45 w/o ZrO₂  
(5 w/o CaO) + 2-1/2 w/o MgO

<table>
<thead>
<tr>
<th>HOT PRESS RUN (NO.)</th>
<th>MOR (MPa) AS HOT PRESSED</th>
<th>MOR (MPa) HEAT TREATED 1350°C, 2 HR + 700°C, 261 HR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4-POINT</td>
<td>3-POINT</td>
</tr>
<tr>
<td>4</td>
<td>118</td>
<td>–</td>
</tr>
<tr>
<td>15</td>
<td>115</td>
<td>132</td>
</tr>
<tr>
<td>16</td>
<td>118</td>
<td>130</td>
</tr>
<tr>
<td>17</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>18</td>
<td>124</td>
<td>147</td>
</tr>
</tbody>
</table>

NOTE: HEAT TREATING AT ELEVATED TEMPERATURES ELIMINATES INTERMEDIATE - TEMPERATURE DEGRADATION
of 15, 30, and 45 w/o ZrO₂ is plotted in Fig. 20. Reduction in MOR at a volume loading of 45 w/o ZrO₂ is substantial, but the degradation can be reduced by pre-aging at an elevated temperature. A temperature of 1350 C was selected for evaluation. The strength of samples aged at 1350 C for 2 h and then exposed at 700 C for selected periods is plotted in Fig. 21. There is no apparent reduction in strength at volume loadings of 15 and 30 w/o ZrO₂. The strength of the 45 w/o ZrO₂ composite, on the other hand, decreased about 33% as a result of heating at 700 C in air. Densification at higher temperatures reduced the occurrence of this when using Y₂O₃ alloyed ZrO₂ additions. XRD analyses showed that the major phases in the as-hot-pressed material were beta-Si₃N₄, cubic, and sometimes tetragonal ZrO₂. Monoclinic ZrO₂ was a minor phase and it increased to a major phase during heat treatment. Monoclinic phase was seldom observed in the composites containing ZrO₂ alloyed with Y₂O₃.

Large black inclusions and agglomerated microporosity were observed in the microstructure of these materials. The agglomerated microstructure created a mottled appearance to the unaided eye.

**Sintered Material Using Coarse ZrO₂**

Samples of the same compositions, 15, 30, and 45 w/o ZrO₂ (5 w/o CaO), + 2-1/2 w/o MgO, were sintered at 1800 C, 1 h. The 15 and 30 w/o compositions sintered to near theoretical densities but not as high as the densities of hot-pressed material (Table 15). The 45 w/o ZrO₂ composition, on the other hand, was extremely porous when sintered at 1800 C. It also lost weight during sintering, while the 15 and 30 w/o compositions gained small amounts of weight. Another batch of material was prepared and sintered with results in line with the other two compositions. This 45 w/o composition was sintered at five different temperatures from 1700 C to 1825 C (Fig. 22). Comparable behavior was not observed.
Figure 20. Room Temperature Strength vs ZrO₂ Particulate Content

Figure 21. Room Temperature Strength of Si₃N₄ + ZrO₂ (5 w/o CaO) Composites vs Duration at 700°C in Air
Figure 22. Effect of Sintering on Strength and Density
Table 15. Results of 1800 C Sintering

<table>
<thead>
<tr>
<th>ZrO₂ Content* (w/o)</th>
<th>Wt. Change (%)</th>
<th>Density (g/cm³)</th>
<th>Strength (3-Pt. MOR) (MPa)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>+0.03</td>
<td>3.15</td>
<td>668</td>
<td>Considerable Agglomerated Porosity</td>
</tr>
<tr>
<td>30</td>
<td>+0.06</td>
<td>3.56</td>
<td>779</td>
<td>Considerable Agglomerated Porosity</td>
</tr>
<tr>
<td>45</td>
<td>NA</td>
<td>3.73</td>
<td>730</td>
<td>Excessive Porosity</td>
</tr>
</tbody>
</table>

*Zircoa Grade B powder

The microstructures of the three compositions, 15, 30, and 45 w/o, are shown in Fig. 23. All of the compositions exhibited agglomerated microporosity (Fig. 24), much more than was observed in the hot-pressed materials. The data in Fig. 22 show that sintered density increased with temperature to 1750 C. Increased sintering temperatures resulted in little density change but decreased strength. Even at a sintering temperature of 1825 C, the density remained below that of hot-pressed material, which was 3.83 g/cm³.

In spite of the agglomerated microporosity and the black inclusions, the room-temperature strength was over 700 MPa. Average strength of the 45 w/o composite also is shown in Fig. 22. The density increased only slightly above 1750 C, and the strength peaked at 1750 C, then decreased with increasing sintering temperature. As was the case for the ZrO₂ (Y₂O₃) composites, the compositions containing 30 w/o were the strongest (Fig. 25). Strengths were 670, 780, and 730 MPa for the compositions 15, 30, and 45 w/o, respectively. The decrease in strength observed for sintering temperatures above 1750 C for the 45 w/o ZrO₂ loading agrees with results for the Y₂O₃ alloyed ZrO₂ additions.

The strength at elevated temperatures was relatively low because an appreciable amount of CaO diffuses into the grain boundaries during sintering. Strengths of these materials to 1200 C are shown in Fig. 26. Strength dropped rapidly after 600 C.
Figure 23. Dispersions of 15, 30, and 45 w/o ZrO₂ Grains
Figure 24. Polished Surface of Sintered $\text{Si}_3\text{N}_4 + 15$ w/o $\text{ZrO}_2$ (5 w/o CaO) + 2-1/2 w/o MgO Showing High Porosity Region
Figure 25. Strength as a Function of ZrO$_2$ Content
Figure 26. Strength as a Function of Temperature and ZrO₂ Content
Intermediate-temperature oxidation degradation was not observed in the sintered material, but aging was carried out only to 250 h (Fig. 27). This is, however, in agreement with results with material containing \( \gamma_2 \text{O}_3 \) as the alloying agent, as reported in the preceding section. Degradation was pronounced in the hot-pressed materials, which were densified at 1700°C, while it was not observed in the material that was sintered at 1800°C. The composites were more stable when densified at 1800°C or above.

Fracture toughness of the sintered materials was at the same high level as that of the hot-pressed material. The toughness, measured according to the Anstis relationship (Ref. 5), of the 45 w/o composition was 7.5 MPa m\(^{1/2}\). When aged in air at 1200°C for 2 h, it increased to 11.8 MPa m\(^{1/2}\).

**Sintered Composite with Submicron \( \text{ZrO}_2 \)-(CaO)**

Submicron, high-purity \( \text{ZrO}_2 \) powders containing 3.5, 6.2, and 10 w/o CaO were obtained. Batches of \( \text{Si}_3\text{N}_4 + 45 \text{ w/o ZrO}_2 \) (xCaO) + 2.5 w/o MgO were colloidally prepared, and disk-shaped samples were prepared by pressure filtration. These disks were then dried and sintered at 1800°C, 1860°C, and 1900°C for 1 h. Properties of the sintered samples are presented in Table 16. A sintering temperature of 1860°C was required to obtain a high density for the composition containing 10 w/o CaO; a temperature of 1900°C was required for the composition containing 6.2 w/o CaO, while the composition containing 3.5 w/o did not sinter to a high density, even at 1900°C.

Examination under a high-power light microscope showed that these samples did not exhibit the agglomerated microporosity as the previous samples made with the coarse, less pure powder. A secondary phase that appeared as black inclusions was observed in the new samples made from the high-purity, submicron \( \text{ZrO}_2 \), however. The black inclusions were found to be composed of Fe and Ti. Subsequent investigation of the Ti-alloy ultrasonic horn showed signs of wear.
Figure 27. Aged Composites Show No Microcracking

45w/o ZrO₂ (5w/o CaO)
SINTERED AT 1800°C
Table 16. Sintering Results for ZrO₂ (CaO) Dispersed Phase Composites

<table>
<thead>
<tr>
<th>Sinter Temperature (°C)</th>
<th>CaO Alloy (w/o)</th>
<th>Wt Loss (%)</th>
<th>Porosity (%)</th>
<th>Density (g/cm³)</th>
<th>Room-Temperature Strength (Avg. 3-Pt. MOR) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>3.5</td>
<td>3.3</td>
<td>21</td>
<td>2.89</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>2.5</td>
<td>14</td>
<td>3.29</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.8</td>
<td>10</td>
<td>3.48</td>
<td>-</td>
</tr>
<tr>
<td>1860</td>
<td>3.5</td>
<td>4.5</td>
<td>6.9</td>
<td>3.40</td>
<td>682</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>1.2</td>
<td>0.2</td>
<td>3.66</td>
<td>792</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.8</td>
<td>0.1</td>
<td>3.83</td>
<td>723</td>
</tr>
<tr>
<td>1900</td>
<td>3.5</td>
<td>7.1</td>
<td>8.9</td>
<td>3.44</td>
<td>675</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>1.3</td>
<td>0.2</td>
<td>3.80</td>
<td>772</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.1</td>
<td>1.7</td>
<td>3.78</td>
<td>655</td>
</tr>
</tbody>
</table>

*Si₃N₄ + 45 w/o ZrO₂ (CaO) + 2-1/2 MgO

Note: All fracture origins were at metal inclusions (Fe, Ni, Cr, Ti)

Room-temperature strength is also presented in Table 16. Maximum strength, 792 MPa, was obtained for the 6.2 w/o CaO composition sintered at 1860 C. All failures originated at large, black metal inclusions. The sintered density and strength are plotted in Fig. 28 as a function of sintering temperature. The highest density was exhibited by the 10 w/o CaO composition because there is more CaO in the grain boundaries. However, the strength of the 10 w/o composition was lower than that of the 6.2 w/o composition. Strength decreased for each composition when the sintering temperature was raised from 1860 C to 1900 C.

Toughness was measured (Ref. 5) and the results are plotted in Fig. 29. Toughness was highest, 8.5 MPa m¹/², for the composition containing 6.2 w/o CaO alloy, while the toughness was lowest, 6.8 MPa m¹/², for the composition containing 10 w/o CaO alloy. These toughness values represent a 100 and a 60% increase, respectively. The composite with 6.2 w/o CaO alloy did not respond
Figure 28. Strength and Density vs Sintering Temperature
Composition: $\text{Si}_3\text{N}_4 + \text{ZrO}_2 \times \text{CaO} + 2.5 \text{ w/o MgO}$
Figure 29. Fracture Toughness vs CaO Content in the ZrO₂

COMPOSITION: Si₃N₄ + 45 w/o ZrO₂ (xCaO) + 2½ w/o MgO
to heat treatment at 1350 C as did the composite made with the coarse 5 w/o CaO powder. In fact, toughness decreased slightly after the heat treatment.

TEM studies of the composite microstructure were conducted. The presence of monoclinic phase was confirmed by convergent beam diffraction and the monoclinic laths extended across the entire zirconia grain. The ZrO$_2$ grains were depleted of CaO (Fig. 30).

OTHER DISPERSED PHASES

ZrO$_2$ (5 w/o MgO)

MgO as an alloying agent for ZrO$_2$ or HfO$_2$ offers potential advantages over CaO. An appreciable amount of the alloying constituent will diffuse out of the ZrO$_2$ grains during sintering and react with the other compounds in the grain boundaries. MgO would be expected to form more refractory and oxidation-resistant compositions than would CaO. However, the ZrO$_2$ (MgO) system was not pursued because the first samples that were made cracked. The results of the Si$_3$N$_4$/ZrO$_2$ (MgO) samples are presented to show that this system did indicate high fracture toughness.

The only powder that could be obtained for evaluation early in the program was a relatively coarse powder, average particle size of 22 micrometers, containing 5 w/o MgO*. Due to the particle size, the colloidal processing method could not be used. A water slurry of the composition Si$_3$N$_4$ + 45 w/o ZrO$_2$ (5 w/o MgO) plus 2.5 w/o MgO as a sintering aid was prepared by milling for 16 h using ZrO$_2$ milling material. Disks, 3.8 cm in diameter, were prepared by pressure filtration, dried, and hot-pressed at 1550 C for 1/4 h; at 1600 C for 1 h; and at 1700 C for 1 h. Fracture toughness was exceptionally high (Table 17), 7.6 MPa m$^{1/2}$ in the as-hot-pressed condition, and as high as 13.4 MPa m$^{1/2}$ after aging at 1350 C for 2 h. This apparent toughness is double and triple that of the Si$_3$N$_4$ matrix.

*SCMG5 Grade, Magnesium Electron, Inc., Flemington, NJ
Figure 30. Semiquantitative Analysis Shows Low Ca Content in Monoclinic ZrO$_2$ grain
Table 17. Results of Hot Pressed Si₃N₄ + 45 w/o ZrO₂
(5 w/o MgO) + 2-1/2 w/o MgO Composite

<table>
<thead>
<tr>
<th>Properties</th>
<th>Hot-Pressing Temperature (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1700</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td></td>
</tr>
<tr>
<td>Fracture Toughness* (MPa m¹/²)</td>
<td></td>
</tr>
<tr>
<td>As-Hot-Pressed Condition</td>
<td>7.6</td>
</tr>
<tr>
<td>Aged at 1350 C, 2 h in air</td>
<td>10.1</td>
</tr>
<tr>
<td>3-Point MOR (MPa)</td>
<td></td>
</tr>
<tr>
<td>As-Hot Pressed</td>
<td>138</td>
</tr>
<tr>
<td>Aged at 700 C, 64 h in air</td>
<td>103</td>
</tr>
<tr>
<td>Aged at 1350 C, 2 h in air</td>
<td>-</td>
</tr>
<tr>
<td>Aged at 1350 C, 2 h + 700 C, 64 h in air</td>
<td>-</td>
</tr>
</tbody>
</table>

*Diamond indentation per Anstis (Ref. 5)

Strength, on the other hand, was low and erratic. These low and erratic results were believed to be due to microcracking that occurred during hot pressing. The sample hot pressed at 1600 C cracked audibly into two pieces while at temperature. Density was highest at the lowest hot-pressing temperature.

HfO₂-ZrO₂-TiO₂

A composite with a zero thermal expansion coefficient to 1800 C was developed and patented (Ref. 12) at Rocketdyne for rocket nozzle applications in the mid 1960s. The intent of this experiment was to use this composition, 60 m/o HfO₂-20 m/o ZrO₂-20 m/o TiO₂, as a dispersion in Si₃N₄ to cause toughening. Submicron powder was obtained and a composition of Si₃N₄ + 30 v/o dispersion + 4 w/o Al₂O₃ was prepared by the colloidal processing method. A 3.8 cm diameter disk was prepared by pressure filtration, dried, and hot pressed to near full density. The material was very dark and appeared to be uniform. The fracture toughness, however, was low, only 2.7 MPa m¹/², and samples turned into powder when oxidized in air at 700 C. For these reasons, investigation of this composition was abandoned.

*Wah Chang, Albany, OR
THERMOPHYSICAL PROPERTIES

Thermal diffusivity and thermal expansion were measured and are reported in this section.

THERMAL DIFFUSIVITY

Thermal diffusivity of four samples was measured by the laser flash method* from room temperature to 1300 C. Results are listed in Table 18. Sample composites included Si$_3$N$_4$ + 30 and 45 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$ and Si$_3$N$_4$ + 30 and 45 w/o ZrO$_2$ (6.2 w/o CaO) + 2.5 w/o MgO. Data for the Y$_2$O$_3$ alloyed composites are plotted in Fig. 31 and 32, along with data for both single-phase Si$_3$N$_4$ and ZrO$_2$ (Y$_2$O$_3$). The Si$_3$N$_4$ data were measured on grade NC132 material (Ref. 14) and the ZrO$_2$ data were measured on ZrO$_2$ material alloyed with 5.3 w/o Y$_2$O$_3$ (Ref. 13). The thermal diffusivity values for the composites show a significant deviation from the rule of mixtures. The 30 and 45 w/o additions of ZrO$_2$ result in significant reductions of thermal diffusivity. Thermal diffusivity values for the CaO alloyed compositions, on the other hand, fall on or near the straight line connecting the Si$_3$N$_4$ and ZrO$_2$ end members.

THERMAL EXPANSION

Thermal expansion was measured** on samples of three different compositions, using an Orton Automatic Recording Dilatometer. Total sample length was 51 mm. Samples were made in two end-to-end bars. A single bar, 51 mm long, could not be produced due to the limited diameter of the pressure filtration die. NC-132 material, supplied by Norton Co. (lot 3931), was one of the three samples and it, also, was in two pieces. The measured coefficients are summarized in Table 19. The measured expansion value for the NC-132 reference

*Dr. D. P. H. Hasselman, Virginia Polytechnic Institute and State University, Blacksburg, VA
**Measurements performed at Emhart Corp., Windsor, CT
Table 18. Thermal Diffusivity of Si$_3$N$_4$

<table>
<thead>
<tr>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. ($^\circ$C)</td>
<td>$T_a D_\perp$ (cm$^2$s$^{-1}$)</td>
<td>Temp. ($^\circ$C)</td>
<td>$T_a D_\perp$ (cm$^2$s$^{-1}$)</td>
</tr>
<tr>
<td>25</td>
<td>0.0658</td>
<td>25</td>
<td>0.0628</td>
</tr>
<tr>
<td>300</td>
<td>0.0466</td>
<td>304</td>
<td>0.0428</td>
</tr>
<tr>
<td>404</td>
<td>0.0431</td>
<td>400</td>
<td>0.0356</td>
</tr>
<tr>
<td>505</td>
<td>0.0414</td>
<td>505</td>
<td>0.0308</td>
</tr>
<tr>
<td>609</td>
<td>0.0390</td>
<td>600</td>
<td>0.0281</td>
</tr>
<tr>
<td>706</td>
<td>0.0361</td>
<td>705</td>
<td>0.0252</td>
</tr>
<tr>
<td>803</td>
<td>0.0325</td>
<td>807</td>
<td>0.0237</td>
</tr>
<tr>
<td>906</td>
<td>0.0298</td>
<td>905</td>
<td>0.0223</td>
</tr>
<tr>
<td>1004</td>
<td>0.0277</td>
<td>1002</td>
<td>0.0208</td>
</tr>
<tr>
<td>1100</td>
<td>0.0258</td>
<td>1100</td>
<td>0.0192</td>
</tr>
<tr>
<td>1200</td>
<td>0.0239</td>
<td>1200</td>
<td>0.0176</td>
</tr>
<tr>
<td>1300</td>
<td>0.0220</td>
<td>1300</td>
<td>0.0172</td>
</tr>
</tbody>
</table>

Density (g/cm$^3$) | Composition
--- | ---
A | 3.53 Si$_3$N$_4$ + 30 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
B | 3.91 Si$_3$N$_4$ + 45 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$
C | 3.50 Si$_3$N$_4$ + 30 w/o ZrO$_2$ (6.2 w/o CaO) + 2-1/2 w/o MgO
D | 3.66 Si$_3$N$_4$ + 45 w/o ZrO$_2$ (6.2 w/o CaO) + 2-1/2 w/o MgO

Table 19. Coefficient of Thermal Expansion

<table>
<thead>
<tr>
<th>Coefficient (10$^{-6}$/C)</th>
<th>(25 to 725 C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-132</td>
<td>2.90</td>
</tr>
<tr>
<td>Si$_3$N$_4$ + 30 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$</td>
<td>4.20</td>
</tr>
<tr>
<td>Si$_3$N$_4$ + 45 w/o ZrO$_2$ (6.2 w/o CaO) + 2-1/2 w/o MgO</td>
<td>4.20</td>
</tr>
</tbody>
</table>
Figure 31. Thermal Diffusivity of $\text{Si}_3\text{N}_4 + \text{ZrO}_2$ ($\text{Y}_2\text{O}_3$) Composites at 25°C and 700°C
Figure 32. Thermal Diffusivity of Si$_3$N$_4$/ZrO$_2$ ($Y_2$O$_3$) Composites at 1000 C and 1300 C
sample (Fig. 34) agreed closely with published data. The other two sample compositions were $\text{Si}_3\text{N}_4 + 30\% \text{ZrO}_2$ (12 w/o $\text{Y}_2\text{O}_3$) + 4 w/o $\text{Al}_2\text{O}_3$ and $\text{Si}_3\text{N}_4 + 45\% \text{ZrO}_2$ (6.2 w/o CaO) + 2-1/2 w/o MgO. The thermal expansion coefficients, 25 to 725°C, were calculated from Fig. 35 and 36. The composite values followed the rule of mixtures (Fig. 33). The 30 w/o ZrO$_2$ composite in Fig. 33 was alloyed with 12 w/o $\text{Y}_2\text{O}_3$ and X-ray diffraction analysis showed that the ZrO$_2$ particles were cubic phase. The 30 w/o ZrO$_2$ composition in Fig. 33 was alloyed with 6.2 w/o CaO and X-ray diffraction showed that the ZrO$_2$ particles were mostly cubic with a minor amount of monoclinic phase present. Thus, the expansion coefficient was below the line connecting NC132 and cubic ZrO$_2$ end point compositions, and it was closer to the line connecting the NC132 and monoclinic-ZrO$_2$ end points.

The fact that the thermal expansion for the composites is relatively low for a structural ceramic material indicates that these composites have potentially excellent resistance to thermal shock. These composites have an exceptionally high figure of merit for thermal shock resistance due to their combination of low thermal expansion, high strength, and high toughness compared with monolithic $\text{Si}_3\text{N}_4$, which exhibits, by far, the best resistance to thermal shock of high-temperature monolithic ceramics (Ref. 15).
Figure 33. Thermal Expansion Coefficient of Si₃N₄ Composites Comply with Rule of Mixtures
Figure 34. Dilatometer Record for NC-132

Figure 35. Dilatometer Record for $\text{Si}_3\text{N}_4 + 30 \text{ w/o ZrO}_2$
(12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$

Figure 36. Dilatometer Record for $\text{Si}_3\text{N}_4 + 45 \text{ w/o ZrO}_2$
(6.2 w/o CaO) + 2-1/2 w/o MgO
One of the primary objectives of this program was to demonstrate fabrication using a high-volume, low-cost process. The colloidal processing methods used in this program are compatible with two conventional fabrication methods, injection molding and slip casting plus sintering. The injection molding method was selected for this program because Rocketdyne has been active in injection molding of $\text{Si}_3\text{N}_4$ for a decade and has been successful in producing a number of demonstration shapes of $\text{Si}_3\text{N}_4$ such as turbine blades and vanes.

Ideally, a water soluble plasticizer/binder system should be used so that it can be mixed directly with the $\text{Si}_3\text{N}_4$/ZrO$_2$ powders which are suspended in water. However, a water-base system was not available so the suspended slurries of $\text{Si}_3\text{N}_4$/ZrO$_2$ had to be dried before mixing with the plasticizer/binder systems. Mixing was performed in a heated sigma blade-type machine. The maximum volume loading that could be attained was 50% solids. A higher loading would be preferred. The green bodies sintered to near full density but the shrinkage would have been less had the starting green density been higher.

The material molded well, and no major problems were encountered in making MOR bars. Binder removal was normal, and MOR bars sintered to an average density of 3.89 g/cm$^3$, which is 96% of theoretical. Average weight loss was 1.5%, and the average measured open porosity was less than 0.1%. Examination of polished sections showed that the microstructure was homogeneous and the ZrO$_2$ grains were well dispersed (Fig. 37).

MOR bars were made with an existing die which was designed for making metal tensile specimens shaped like flat, thin, dog bones. The dumbbell ends were cut off in the green state, and the center section was used for MOR bars. The resultant MOR specimen is satisfactory, and Rocketdyne has used it for a decade to generate strength data. A disadvantage of this bar is that it is not a standard geometry that can be directly compared to data reported by other laboratories. The typical size of these injection molded bars is 2.2 mm x
Figure 37. Microstructure of Injection Molded Si3N4 + 45 w/o ZrO2 (12 w/o Y2O3) + 4 w/o Al2O3
6.4 mm x 50 mm long. Thus, they are a slab rather than a beam. Unpublished data generated by the author using NC430 grade SiC bars, one-half having been diamond ground to the injection-molded slab geometry and one-half having been diamond ground to a similar size but having a cross section more like a conventional MOR bar; showed that the flexural strength of the same material when measured in a slab configuration was 20% lower.

The 4-point MOR data are listed in Table 20. The strength of samples densified in sintering runs No. 36 and 41 were similar, and they were grouped together. The strengths of samples densified in sintering run No. 45, however, were lower and are listed separately. The reason for the difference in strength is unknown. Samples tested in the as-sintered condition were covered with a very thin film of zirconium nitride. Four-point MOR was 429 MPa and 356 MPa, respectively. When the surfaces were tested in the ground condition, the strength increased to 595 MPa and 538 MPa. Figures 38 and 39 show the texture of the surface of injection-molded MOR bars in the as-sintered and ground conditions.

Analyses were conducted on fractured and polished surfaces of injection-molded bars using the scanning electron microscope to identify the source of fracture-causing flaws. Few flaws were found but the population was enough that one or more would always be found within the high-stress region of the test bar, and these flaws were large. One category of flaws was metal inclusions composed of Fe and Ti (Fig. 40), which probably originated from the titanium alloy ultrasonic mixing horn. Other metal surfaces were coated with a hard abrasion-resistant layer of chromium. A second category of flaws was low-density regions caused by incomplete mixing of the powder and plasticizer (Fig. 41). This was verified by inspecting the powder/plasticizer before injection molding under low-power magnification. White inclusions were analyzed by energy-dispersive X-ray analyses which showed that the composition was the same as that of the composite mixture. In other words, these were plasticizer-rich nodules that left a pore-like structure after the plasticizer was removed. The third category of flaws was worm-like pores caused by dust contamination during processing (Fig. 42).
<table>
<thead>
<tr>
<th>Sinter Run No.</th>
<th>Procedure</th>
<th>Surface Condition</th>
<th>Number of Samples</th>
<th>Average Strength (4-Point MOR) $^3$ (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Weight Loss During Sintering (%)</th>
<th>Sintered Density (g/cm$^3$)</th>
<th>Open Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 and 41</td>
<td>Standard</td>
<td>As-sintered</td>
<td>9</td>
<td>429</td>
<td>47</td>
<td>1.1</td>
<td>3.89</td>
<td>0.01</td>
</tr>
<tr>
<td>36 and 41</td>
<td>Standard</td>
<td>Ground</td>
<td>8</td>
<td>595</td>
<td>96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>Standard</td>
<td>As-sintered</td>
<td>4</td>
<td>356</td>
<td>51</td>
<td>1.6</td>
<td>3.90</td>
<td>0.1</td>
</tr>
<tr>
<td>45</td>
<td>Isopressed$^1$</td>
<td>As-sintered</td>
<td>8</td>
<td>354</td>
<td>56</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>Isopressed</td>
<td>Ground$^2$</td>
<td>5</td>
<td>538</td>
<td>41</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Notes: 1. The MOR bars were isostatically pressed at 345 MPa after binder removal and before sintering.
2. Grinding exposed a few large surface pores.
3. Typical sample size 2.2 mm x 6.4 mm x 50 mm

Outer span = 31.6 mm
Inner span = 10.3 mm

Composition: Si$_3$N$_4$ + 45 w/o ZrO$_2$ (12 w/o Y$_2$O$_3$) + 4 w/o Al$_2$O$_3$

Sintering parameters: 1800 $^\circ$C 1 h
Figure 38. Photomicrographs of Injection-Molded Bar in the As-Sintered Condition
Figure 39. Photomicrographs of Injection-Molded Bar After Grinding
Figure 40. Metal Inclusion in Polished Section of Injection-Molded Material
Figure 41. Low-Density Flaws in Injection-Molded Material
Figure 42. Large Pore Fracture Origin in Injection-Molded Sample
Low-power examination of samples after burnout of the plasticizer indicated that some pores might be created during the burnout operation. It was postulated that these, as well as other types of pores, could be eliminated by isostatically pressing the green flexure test bars after the burnout operation and before the sintering operation. The strengths of sintered bars prepared by this modification are listed in Table 20. No improvement was indicated as a result of the isopressing operation.
CONCLUSIONS

Two composite systems composed of Si$_3$N$_4$ plus a dispersion of ZrO$_2$ particles were shown to exhibit improved properties over those of the Si$_3$N$_4$ matrix:

1. Colloidal processing produced composites with excellent dispersion and homogeneity.

2. Compositions of Si$_3$N$_4$ + 30 and 45 w/o ZrO$_2$ stabilized with Y$_2$O$_3$ exhibited:
   a. An increase in toughness to 6 MPa m$^{1/2}$ over the untoughened Si$_3$N$_4$ value of 4.1 MPa m$^{1/2}$.
   b. Room-temperature strengths as high as 1000 MPa.
   c. High strength to 1000 C with Al$_2$O$_3$ as the sintering aid, and no loss in strength to 1400 C with a mixture of Y$_2$O$_3$ + SiO$_2$ as the sintering aid.
   d. Significantly lower thermal diffusivity (lower than predicted by rule of mixtures).
   e. Capability of increasing strength another 40% by heat treatment for low to moderate temperature applications.
   f. Injection molding possibilities.

3. Compositions of Si$_3$N$_4$ + 15, 30, or 45 w/o ZrO$_2$ stabilized with CaO exhibited:
   a. Increases in apparent toughness to 7 MPa m$^{1/2}$ without post-heat treatment.
   b. Potential toughness increases to 14 MPa m$^{1/2}$ with heat treatment.
   c. Room-temperature strength as high as 780 MPa.
   d. Potential for low-temperature (<700 C) application.

4. Successful substitution of HfO$_2$ (Y$_2$O$_3$) for ZrO$_2$ (Y$_2$O$_3$) with associated strength gain.
RECOMMENDATIONS

1. Ensure Long-Term Stability. Composites of Si₃N₄ and ZrO₂ stabilized with Y₂O₃ and sintered at 1750°C and 1800°C must be completely characterized by TEM and SEM analyses. Differences in microcompositions must be determined to understand the microcracking mechanism that is present in material sintered at the lower temperature. This information is essential to ensure formulation and fabrication of composites that will demonstrate long-term stability at intermediate temperatures. The possibility of crack healing needs further evaluation.

2. Optimize Toughness. The Y₂O₃ stabilizer content in ZrO₂ and sintering conditions should be optimized to yield maximum toughness with long-term stability.

3. Develop Improved High-Temperature Toughness. Optimize HfO₂ additions for use in place of, or in combination with, ZrO₂.

4. Increase High-Temperature Strength. Submicron powders of Y₂O₃ and SiO₂ must be obtained so that these oxides can be added by colloidal processing rather than by ball-milling.

5. Demonstrate High-Volume, Low-Cost Fabrication. The colloidal processing method lends itself to slip casting. Slip casting of the colloidal suspensions should be developed.


7. Confirm existence of transformation toughening mechanism in samples containing dispersions of partially stabilized zirconia, e.g., having less than 9 w/o Y₂O₃ in the Y₂O₃ stabilized system.
REFERENCES


### INTERNAL DISTRIBUTION

1-2. Central Research Library  
3. Document Reference Section  
4-5. Laboratory Records Department  
6. Laboratory Records, ORNL RC  
7. ORNL Patent Section  
8. L. F. Allard, Jr.  
9. B. R. Appleton  
10. R. L. Beatty  
11. P. F. Becher  
12. T. M. Besmann  
13. P. J. Blau  
14. A. Bleier  
15. E. E. Bloom  
16. K. W. Boling  
17. R. A. Bradley  
18. C. R. Brinkman  
19. V. R. Bullington  
20. A. J. Caputo  
21. R. S. Carlsmith  
22. P. T. Carlson  
23. J. V. Cathcart  
24. G. M. Caton  
25. R. H. Cooper  
26. S. A. David  
27. J. H. DeVan  
28. W. P. Eatherly  
29. J. I. Federer  
30. W. Fulkerson  
31. R. L. Graves  
32. D. L. Greene  
33. M. A. Janney  
34-43. D. R. Johnson  
44. R. R. Judkins  
45. M. A. Karnitz  
46. H. D. Kimrey, Jr.  
47. T. G. Kollie  
48. T. B. Lindemer  
49. K. C. Liu  
50. E. L. Long, Jr.  
51. W. D. Manly  
52. R. W. McClung  
53. D. L. McElroy  
54. J. R. Merriman  
55. A. J. Moorhead  
56. T. A. Nolan  
57. J. L. Rich  
58. C. R. Richmond  
59. J. M. Robbins  
60. M. W. Rosenthal  
61. M. L. Santella  
62-80. A. C. Schaffhauser  
81. G. M. Slaughter  
82. W. B. Snyder, Jr.  
83. E. J. Soderstrom  
84. D. P. Stinton  
85. R. W. Swindeman  
86. V. J. Tennery  
87-89. P. T. Thornton  
90. T. N. Tiegs  
91. J. R. Weir, Jr.  
92. F. W. Wiffen  
93. R. K. Williams  
94. S. G. Winslow  
95. C. S. Yust

### EXTERNAL DISTRIBUTION

96. Donald F. Adams  
    University of Wyoming  
    Laramie, WY 82071  
97. Jane W. Adams  
    Corning Glass Works  
    Corning, NY 14831  
98. Donald J. Adrian  
    High Velocity Corporation  
    701 Scarboro Road  
    Oak Ridge, TN 37830  
99. Bruce J. Agle  
    Sundstrand Corporation  
    Turbomach Division  
    4400 Ruffin Road  
    PO Box 85757  
    San Diego, CA 92138-5757  
100. Richard L. Allor  
    Ford Motor Company  
    20000 Rotunda Drive  
    PO Box 2053  
    Dearborn, MI 48121-2053
101. Richard T. Alpaugh  
U.S. Department of Energy  
Forrestal Building CE-151  
1000 Independence Avenue  
Washington, DC 20585

102. H. Arbabi  
Brunel University  
Uxbridge Middlesex  
UNITED KINGDOM UB8 3PH

103. V. S. Avva  
North Carolina Agricultural and Technical State University  
Greensboro, NC 27411

104. John M. Bailey  
Caterpillar Inc.  
Technical Center  
Post Office Box 1875  
Peoria, IL 61656-1875

105. Murray Bailey  
NASA Lewis Research Center  
21000 Brookpark Road  
MS: 77-6  
Cleveland, OH 44135

106. R. R. Baker  
Ceradyne, Inc.  
3169 Red Hill Avenue  
Costa Mesa, CA 92626

107. J. Gary Baldoni  
GTE Laboratories, Inc.  
40 Sylvan Road  
Waltham, MA 02254

108. A. L. Bement, Jr.  
TRW, Inc.  
23555 Euclid Avenue  
Cleveland, OH 44117

109. M. Bentele  
Xamag, Inc.  
259 Melville Avenue  
Fairfield, CT 06430

110. Clifton G. Bergeron  
University of Illinois  
105 South Goodwin Avenue  
204 Ceramics Building  
Urbana, IL 61801

111. William D. Bjorndahl  
TRW, Inc.  
One Space Park  
Building 01, Room 2060  
Redondo Beach, CA 90278

112. James A. Black  
American Matrix, Inc.  
118 Sherlake Drive  
Knoxville, TN 37922

113. Dan Blake  
Solar Energy Research Institute  
1617 Cole Boulevard  
Golden, CO 80401

114. Keith Blandford  
Boride Products, Inc.  
2879 Aero Park Drive  
Traverse City, MI 49684

115. John Blum  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

116. Paul N. Blumberg  
Integral Technologies Inc.  
415 East Plaza Drive  
Westmont, IL 60559

117. Wolfgang D. G. Boecker  
Standard Oil Engineered Materials Company  
Post Office Box 832  
Niagara Falls, NY 14302
<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Company/Institution</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>Han Juergen Bossmeyer</td>
<td>BMW Technologies, Inc.</td>
<td>800 South Street</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Waltham, MA 02154</td>
</tr>
<tr>
<td>119</td>
<td>J.A.M. Boulet</td>
<td>University of Tennessee</td>
<td>310 Perkins Hall</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Knoxville, TN 37996</td>
</tr>
<tr>
<td>120</td>
<td>Raymond J. Bratton</td>
<td>Westinghouse Electric Corporation</td>
<td>1310 Beulah Road</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pittsburgh, PA 15235</td>
</tr>
<tr>
<td>121</td>
<td>Catherine E. Brown</td>
<td>E. I. DuPont de Nemours &amp; Company</td>
<td>Wilmington, DE 19898</td>
</tr>
<tr>
<td>122</td>
<td>J. J. Brown</td>
<td>Virginia Polytechnic Institute and State University</td>
<td>Blacksburg, VA 24061</td>
</tr>
<tr>
<td>123</td>
<td>W. Bryzik</td>
<td>U.S. Army Tank Automotive Command</td>
<td>Warren, MI 48090</td>
</tr>
<tr>
<td>124</td>
<td>S. T. Buljan</td>
<td>GTE Laboratories, Inc.</td>
<td>40 Sylvan Road</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Waltham, MA 02254</td>
</tr>
<tr>
<td>125</td>
<td>John M. Byrne, Jr.</td>
<td>PPG Industries, Inc.</td>
<td>One PPG Place</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pittsburgh, PA 15272</td>
</tr>
<tr>
<td>126</td>
<td>Donald J. Campbell</td>
<td>Air Force Wright Aeronautical Laboratory</td>
<td>AFWAL/POX</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Wright-Patterson AFB</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>OH 45433</td>
</tr>
<tr>
<td>127</td>
<td>Roger Cannon</td>
<td>Rutgers University</td>
<td>Post Office Box 909</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bowser Road</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Piscataway, NJ 08855-0909</td>
</tr>
<tr>
<td>128-132</td>
<td>Harry W. Carpenter</td>
<td></td>
<td>19945 Acre Street</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Northridge, CA 91324</td>
</tr>
<tr>
<td>133</td>
<td>David Carruthers</td>
<td>Allied-Signal Aerospace Company</td>
<td>Garrett Engine Division</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>111 South 34th Street</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Post Office Box 5217</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phoenix, AZ 85010</td>
</tr>
<tr>
<td>134</td>
<td>Jere G. Castor</td>
<td>Allied-Signal Aerospace Company</td>
<td>Garrett Engine Company</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>111 South 34th Street</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Post Office Box 5217</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Phoenix, AZ 85010</td>
</tr>
<tr>
<td>135</td>
<td>Se-Tak Chang</td>
<td>Sundstrand Corporation</td>
<td>Turbomach Division</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4400 Ruffin Road</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>San Diego, CA 92138-5757</td>
</tr>
<tr>
<td>136</td>
<td>R. J. Charles</td>
<td>General Electric Company</td>
<td>Post Office Box 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Schenectady, NY 12301</td>
</tr>
<tr>
<td>137</td>
<td>En-sheng Chen</td>
<td>B&amp;C Engineering Research</td>
<td>13906 Dentwood Drive</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Houston, TX 77014</td>
</tr>
<tr>
<td>138</td>
<td>Albert A. Cheynes</td>
<td>U.S. Department of Energy</td>
<td>Forrestal Building CE-151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000 Independence Avenue</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Washington, DC 20585</td>
</tr>
<tr>
<td>139</td>
<td>Frank Childs</td>
<td>EG&amp;G, Inc.</td>
<td>Post Office Box 1625</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Idaho Falls, ID 83415</td>
</tr>
</tbody>
</table>
140. Gilbert Y. Chin  
Bell Telephone Laboratories  
Murray Hill, NJ 07974

141. Melvin H. Chiogioji  
U.S. Department of Energy  
Forrestal Building CE-15  
1000 Independence Avenue, SW  
Washington, DC 20585

142. William J. Chmura  
The Torrington Company  
59 Field Street  
Torrington, CT 06790

143. Eugene V. Clark  
Turbine Metal Technology, Inc.  
7327 Elmo Street  
Tujunga, CA 91042-2204

144. William L. Cleary  
ORI, Inc.  
1375 Piccard Drive  
Rockville, MD 20850

145. Jack L. Clem  
J. M. Huber Corporation  
PO Box 2831  
Borger, TX 79008-2831

146. Philip R. Compton  
National Aeronautics and  
Space Administration  
Washington, DC 20546

147. Harry E. Cook  
Chrysler Motors Corporation  
1200 Chrysler Drive  
Highland Park, MI 48288-1118

148. Stephen Copley  
University of  
Southern California  
Los Angeles, CA 90089-0241

149. John A. Coppola  
Standard Oil Engineered  
Materials Company  
Structural Ceramics Division  
PO Box 1054, Bldg 91-2  
Niagara Falls, NY 14302

150. Normand D. Corbin  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

151. Charles H. Craig  
Defense Technology Security  
Administration  
400 Army-Navy Drive  
Suite 300  
Arlington, VA 22202

152. William J. Croft  
U.S. Army Materials  
Technology Laboratory  
Arsenal Street  
Watertown, MA 02172

153. Gary M. Crosbie  
Ford Motor Company  
20000 Rotunda Drive  
PO Box 2053, Room S-2079  
Dearborn, MI 48121-2053

154. Floyd W. Crouse, Jr.  
U.S. Department of Energy  
PO Box 880  
Morgantown, WV 26505

155. Raymond Cutler  
Ceramatec, Inc.  
163 West 1700 South  
Salt Lake City, UT 84115

156. David A. Dalman  
The Dow Chemical Company  
Midland, MI 48640

157. James I. Dalton  
Reynolds Metals Company  
Fourth and Canal Streets  
PO Box 27003  
Richmond, VA 23261

158. Stephen C. Danforth  
Rutgers University  
Post Office Box 909  
Bowser Road  
Piscataway, NJ 08854
159. Stanley J. Dapkunas  
National Bureau of Standards  
Gaithersburg, MD 20899

160. Robert F. Davis  
North Carolina State University  
232 Riddick Laboratory  
Box 7907  
Raleigh, NC 27695

161. Evelyn M. DeLiso  
Rutgers University  
PO Box 909  
Bowser Road  
Piscataway, NJ 08854

162. Alan L. Dragoo  
National Bureau of Standards  
Gaithersburg, MD 20899

163. Keith F. Dufrane  
Battelle Columbus Laboratories  
505 King Avenue  
Columbus, OH 43201

164. Edmund M. Dunn  
GTE Laboratories Inc.  
40 Sylvan Road  
Waltham, MA 02254

165. Jeremy D. Dunning  
Indiana Memorial Union 662  
Indiana University  
Bloomington, IN 47405

166. Dr. Sunil Dutta  
NASA Lewis Research Center  
21000 Brookpark Road  
MS: 49-3  
Cleveland, OH 44135

167. Paul N. Dyer  
Air Products and Chemicals, Inc.  
PO Box 538  
Allentown, PA 18105

168. Robert J. Eagan  
Sandia National Laboratories  
Department 1840  
PO Box 5800  
Albuquerque, NM 87185

169. Christopher A. Ebel  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

170. J. J. Eberhardt  
U.S. Department of Energy  
Forrestal Building CE-12  
1000 Independence Avenue, SW  
Washington, DC 20585

171. E. E. Ecklund  
U.S. Department of Energy  
Forrestal Building CE-151  
1000 Independence Avenue  
Washington, DC 20585

172. William A. Ellingson  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, IL 60439

173. Graydon A. Elliott  
U.S. Army Research and  
Technology Laboratory  
(AVSCOM)  
Fort Eustis, VA 23604

174. A. Erdely  
26 Av. Gore des Eaux-Vives  
1208 Geneva  
SWITZERLAND

175. Charles D. Estes  
U.S. Senate  
Washington, DC 20510

176. Peggy Evanich  
National Aeronautics and  
Space Administration  
Washington, DC 20546

177. Anthony G. Evans  
University of California  
Santa Barbara, CA 93106

178. Robert C. Evans  
NASA Lewis Research Center  
21000 Brookpark Road  
MS: 77-6  
Cleveland, OH 44135
179. Katherine T. Faber  
Ohio State University  
2041 College Road  
Columbus, OH 43210

180. John W. Fairbanks  
U.S. Department of Energy  
Forrestal Building CE-151  
1000 Independence Avenue  
Washington, DC 20585

181. Larry Farrell  
Babcock and Wilcox  
Old Forrest Road  
Lynchburg, VA 24505

182. H. W. Foglesong  
Dow Corning Corporation  
3901 South Saginaw Road  
Midland, MI 48686

183. Thomas F. Foltz  
Avco Corporation  
Two Industrial Avenue  
Lowell, MA 01851

184. Robert G. Frank  
Technology Assessment Group  
10793 Bentley Pass Lane  
Cincinnati, OH 45140

185. Douglas W. Freitag  
LTV Aerospace and Defense Company  
PO Box 225907  
MS: TH-85  
Dallas, TX 75265

186. George E. Gazza  
U.S. Army Materials Technology Laboratory  
405 Arsenal Street  
Watertown, MA 02172

187. Charles M. Gilmore  
The George Washington University  
Washington, DC 20052

188. Paul Glance  
Concept Analysis  
950 Stephenson Highway  
Troy, MI 48007-7013

189. Fred M. Glaser  
U.S. Department of Energy  
Washington, DC 20545

190. Joseph W. Glatz  
Naval Air Propulsion  
Test Center  
Box 7176, PE 34  
Trenton, NJ 08628

191. W. M. Goldberger  
Superior Graphite Company  
2175 East Broad Street  
Columbus, OH 43209

192. Stephen T. Gonczi  
Allied Signal Research Center  
50 UOP Plaza  
Des Plaines, IL 60016-6187

193. Robert J. Gottschall  
U.S. Department of Energy  
MS: G-256  
Washington, DC 20545

194. Dr. Earl Graham  
Cleveland State University  
Uclid Ave East 24th Street  
Cleveland, OH 44115

195. Kenneth Green  
Coors Ceramics Company  
17750 West 32nd Street  
Golden, CO 80401

196. Robert E. Green, Jr.  
Center for Nondestructive Evaluation  
Maryland Hall 107  
The Johns Hopkins University  
Baltimore, MD 21218
| 197. | Lance E. Groseclose  
General Motors Corporation  
PO Box 420  
Indianapolis, IN 46206-0420 |
| 198. | T. D. Gulden  
GA Technologies, Inc.  
PO Box 81608  
San Diego, CA 92138 |
| 199. | P. Ulf Gummeson  
Hoeganaes  
River Road and Taylors Lane  
Riverton, NJ 08077 |
| 200. | Bimleshwar P. Gupta  
Solar Heat Research Division  
Solar Energy Research Institute  
1617 Cole Boulevard  
Golden, CO 80401 |
| 201. | M. D. Gurney  
NIPER  
PO Box 2128  
Bartlesville, OK 74005 |
| 202. | John P. Gyekenyesi  
NASA Lewis Research Center  
2100 Brookpark Road  
Cleveland, OH 44135 |
| 203. | J. J. Habeeb  
Esso Petroleum Canada  
PO Box 3022  
Sarina, Ontario  
CANADA N7T 7MI |
| 204. | H. T. Hahn  
Pennsylvania State University  
227 Hammond Building  
University Park, PA 16802 |
| 205. | Nabil S. Hakim  
General Motors Corporation  
36880 Ecorse Road  
Romulus, MI 48174 |
| 206. | John W. Halloran  
Ceramic Process Systems  
840 Memorial Drive  
Cambridge, MA 02139-3758 |
| 207. | Kay Hardman-Rhyne  
DARPA  
1400 Wilson Boulevard  
Arlington, VA 22209 |
| 208. | R. A. Harmon  
25 Schalren Drive  
Latham, NY 12110 |
| 209. | Stephen D. Hartline  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545 |
| 210. | Willard E. Hauth  
Dow Corning Corporation  
3901 South Saginaw Road  
Midland, MI 48640 |
| 211. | Kevin L. Haynes  
McDonnell Douglas  
Astronautics Company  
Box 516 E456/HQ/3N/MS329  
Saint Louis, MO 63166 |
| 212. | Norman L. Hecht  
University of Dayton  
Research Institute  
300 College Park  
Dayton, OH 45469-0001 |
| 213. | S. S. Hecker  
Los Alamos National Laboratory  
PO Box 1663  
Los Alamos, NM 87545 |
| 214. | Peter W. Heitman  
General Motors Corporation  
PO Box 420, W-5  
Indianapolis, IN 46206-0420 |
| 215. | Richard L. Helferich  
The Duriron Company, Incorporated  
PO Box 1145  
Dayton, OH 45401 |
216. H. E. Helms  
General Motors Corporation  
PO Box 420  
Indianapolis, IN 46206-0420

217. Thomas L. Henson  
GTE Products Corporation  
Hawes Street  
Towanda, PA 18848-0504

218. Thomas P. Herbell  
NASA Lewis Research Center  
21000 Brookpark Road  
MS: 49-3  
Cleveland, OH 44135

219. Hendrik Heystek  
Bureau of Mines  
Tuscaloosa Research Center  
PO Box L  
University, AL 35486

220. Robert V. Hillery  
General Electric Company  
One Neumann Way  
PO Box 156301  
Cincinnati, OH 45215

221. Jonathan W. Hinton  
Standard Oil Engineered Materials Company  
Structural Ceramics Division  
PO Box 1054  
Niagara Falls, NY 14302

222. George Hsu  
Jet Propulsion Laboratory  
4800 Oak Grove Drive  
MS: 512-103  
Pasadena, CA 91109

223. Stephen M. Hsu  
National Bureau of Standards  
Gaithersburg, MD 20899

224. Harold A. Huckins  
Princeton Advanced Technology, Inc.  
56 Finley Road  
Princeton, NJ 08540

225. Fred Huettic  
Advanced Ceramic Technology, Inc.  
17 Deerfield Road  
East Brunswick, NJ 08816

226. O. Richard Hughes  
Celanese Research Company  
86 Morris Avenue  
Summit, NJ 07901

General Motors Corporation  
12 Mile and Mound Roads  
Warren, MI 48090-9055

228. Louis C. Ianniello  
U.S. Department of Energy  
Washington, DC 20545

229. Robert H. Insley  
Champion Spark Plug Company  
20000 Conner Avenue  
Detroit, MI 48234

230. D. M. Jacques  
Norton Company  
HPC Library  
Goddard Road  
Northboro, MA 01532-1545

231. Curt A. Johnson  
General Electric Company  
PO Box 8  
Schenectady, NY 12301

232. Douglas C. Johnson  
Sundstrand Corporation  
4400 Ruffin Road  
PO Box 85757  
San Diego, CA 92138-5757

233. Larry Johnson  
Argonne National Laboratory  
9700 South Cass Avenue  
Bldg 362  
Argonne, IL 60439

234. R. A. Johnson  
General Motors Corporation  
PO Box 420  
Indianapolis, IN 46206-0420
235. L. A. Joo
Great Lakes Research Corporation
Post Office Box 1031
Elizabethton, TN 37643

236. A. David Joseph
Sealed Power Corporation
100 Terrace Plaza
Muskegon, MI 49443

237. Roy Kamo
Adiabatics, Inc.
630 South Mapleton
Columbus, IN 47201

238. Allan Katz
Air Force Wright Aeronautical Laboratory
Materials Laboratory, AFWAL/MLLM
Wright-Patterson AFB, OH 45433

239. R. N. Katz
U.S. Army Materials Technology Laboratory
405 Arsenal Street
Watertown, MA 02172

240. Mr. Kawaguchi
Tokai Carbon
375 Park Avenue
Suite 3802
New York, NY 10152

241. P. Victor Kelsey
Aluminum Company of America
Alcoa Technical Center B
Alcoa Center, PA 15061

242. Frederick L. Kennard, III
General Motors Corporation
1300 North Dort Highway
Flint, MI 48556

243. J. R. Kidwell
Allied-Signal Aerospace Company
Garrett Engine Division
111 South 34th Street
Post Office Box 5217
Phoenix, AZ 85010

244. Max Klein
Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, IL 60631

245. C. E. Knapp
Norton Company
8001 Daly Street
Niagara Falls, Ontario
CANADA

246. A. S. Kobayashi
University of Washington
Seattle, WA 98195

247. David M. Kotchick
AiResearch Manufacturing Company
2525 West 190th Street
Torrance, CA 90509

248. Bruce Kramer
George Washington University
Washington, DC 20052

249. Saunders B. Kramer
U.S. Department of Energy
Forrestal Building CE-151
1000 Independence Avenue
Washington, DC 20585

250. D. M. Kreiner
Allied-Signal Aerospace Company
Garrett Engine Division
111 South 34th Street
PO Box 5217
Phoenix, AZ 85010

251. Pieter Krijgsman
Ceramic Design Int. Hold., Ltd.
PO Box 68
8050 AB Hattem
THE NETHERLANDS

252. W. J. Lackey
Georgia Tech Research Institute
Atlanta, GA 30332
253. Everett A. Lake  
Air Force Wright  
Aeronautical Laboratory  
AFWAL/POOS  
Wright-Patterson AFB  
OH 45433

254. Hari S. Lamba  
General Motors Corporation  
Electro-Motive Division  
LaGrange, IL 60525

255. James Lankford  
Southwest Research Institute  
6220 Culebra Road  
PO Drawer 28510  
San Antonio, TX 78284

256. John G. Lanning  
Corning Glass Works  
Corning, NY 14831

257. David C. Larsen  
Corning Glass Works  
Sullivan Park, FR-51  
Corning, NY 14831

258. Dr. S. K. Lau  
Standard Oil Engineered  
Materials Company  
Technology Division  
Box 832  
Niagara Falls, NY 14302

259. Harry A. Lawler  
Standard Oil Engineered  
Materials Company  
Structural Ceramics Division  
PO Box 1054, Bldg 91-2  
Niagara Falls, NY 14302

260. Alan Lawley  
Drexel University  
Philadelphia, PA 19104

261. Daniel Lee Temescon  
2850 7th Street  
Berkeley, CA 94710

262. June-Gunn Lee  
Korea Advanced Institute of  
Science and Technology  
PO Box 131  
Dong Dac Mun, Seoul  
KOREA

263. E. M. Lenoe  
Air Force Office of Scientific  
Research  
APO San Francisco  
CA 96503-0110

264. Stanley R. Levine  
NASA Lewis Research Center  
21000 Brookpark Road  
Cleveland, OH 44135

265. David Lewis  
Naval Research Laboratory  
4555 Overlook Avenue, SW  
Washington, DC 20375

266. Winston W. Liang  
AMERCOM, Inc.  
8948 Fullbright Avenue  
Chatsworth, CA 91311

267. Bill Long  
Babcock and Wilcox  
PO Box 1260  
Lynchburg, VA 24505

268. L. A. Lott  
EG&G, Inc.  
PO Box 1625  
Idaho Falls, ID 83415

269. Bryan K. Luftglass  
Chem Systems, Inc.  
303 South Broadway  
Tarrytown, NY 10591

270. Robert Lundberg  
Svenska Silikatforsknings-  
institutet  
Swedish Institute for  
Silicate Research  
Box 5403  
S-402 29 Gothenburg  
SWEDEN
271. Michael J. Lynch  
   General Electric Company  
   PO Box 414, 7B-36  
   Milwaukee, WI 53201

272. James W. MacBeth  
   Standard Oil Engineered Materials Company  
   Structural Ceramics Division  
   Box 1054  
   Niagara Falls, NY 14302

273. Vincent L. Magnotta  
   Air Products and Chemicals, Inc.  
   PO Box 538  
   Allentown, PA 18105

274. Tai-il Mah  
   Universal Energy Systems  
   4401 Dayton-Xenia Road  
   Dayton, OH 45432

275. L. Manes  
   Commission of the European Communities  
   Ispra Establishment  
   I-21020 Ispra (Varese)  
   ITALY

276. Gerald R. Martin  
   Fleetguard, Inc.  
   Cookeville, TN 38501

277. Dr. John L. Mason  
   Allied-Signal Aerospace Company  
   AiResearch Los Angeles Division  
   2525 West 190th Street  
   Torrance, CA 90509

278. J. McCauley  
   U.S. Army Materials Technology Laboratory  
   DRXMR-MC  
   Arsenal Street  
   Watertown, MA 02172-0001

279. William J. McDonough  
   Keramont  
   4233 South Fremont Avenue  
   Tucson, AZ 85714

280. Bryan J. McEntire  
   Norton Company  
   TRW Ceramics  
   Goddard Road  
   Northboro, MA 01532-1545

281. Thomas D. McGee  
   Iowa State University  
   Ames, IA 50011

282. H. Christopher McGowan  
   Advanced Ceramic Technology, Inc.  
   17 Deerfield Road  
   East Brunswick, NJ 08816

283. Malcolm G. McLaren  
   Rutgers University  
   PO Box 909  
   Bowser Road  
   Piscataway, NJ 08854

284. Arthur F. McLean  
   6225 N Camino Almonte  
   Tucson, AZ 85718

285. Brian L. Mehosky  
   Standard Oil Engineered Materials Company  
   4440 Warrensville Center Road  
   Cleveland, OH 44128

286. P. K. Mehrotra  
   Kennametal, Inc.  
   PO Box 639  
   Greensburg, PA 15601

287. Joseph J. Meindl  
   Reynolds International, Inc.  
   PO Box 27002  
   6603 West Broad Street  
   Richmond, VA 23261

288. D. Messier  
   U.S. Army Materials Technology Laboratory  
   DRXMR-MC  
   Arsenal Street  
   Watertown, MA 02172
289. Arthur G. Metcalfe  
Solar Turbines, Inc.  
2200 Pacific Highway  
PO Box 80966  
San Diego, CA 92138

290. Thomas N. Meyer  
Aluminum Company of America  
Alcoa Technical Center  
Alcoa Center, PA 15069

291. W. Miloscia  
Standard Oil Engineered Materials Company  
4440 Warrensville Center Road  
Cleveland, OH 44128

292. Bill Moehle  
Ethyl Corporation  
451 Florida Avenue  
Ethyl Tower  
Baton Rouge, LA 70801

293. Helen Moeller  
Babcock and Wilcox  
PO Box 11165  
Lynchburg, VA 24506-1165

294. Frederick E. Moreno  
Turbo Energy Systems, Inc.  
350 Second Street, Suite 5  
Los Altos, CA 94022

295. Peter E. D. Morgan  
Rockwell International  
1049 Camino Dos Rios  
PO Box 1085  
Thousand Oaks, CA 91360

296. Lawrence M. Murphy  
Thermal Systems Research Branch  
Solar Energy Research Institute  
1617 Cole Boulevard  
Golden, CO 80401

297. Solomon Musikant  
General Electric Company  
PO Box 8555  
MS: U-1219  
Philadelphia, PA 19101

298. Pero Nannelli  
Pennwalt Corporation  
900 First Avenue  
PO Box C  
King of Prussia, PA 19406-0018

299. Robert M. Neilson, Jr.  
EG&G Idaho, Inc.  
PO Box 1625  
Idaho Falls, ID 83415

300. William D. Nix  
Stanford University  
Stanford, CA 94305

301. Richard D. Nixdorf  
American Matrix, Inc.  
118 Sherlake Drive  
Knoxville, TN 37922

302. Brian M. O'Connor  
The Lubrizol Corporation  
29400 Lakeland Boulevard  
Wickliffe, OH 44092

303. W. Richard Ott  
Alfred University  
Alfred, NY 14802

304. Muktesh Paliwal  
GTE Products Corporation  
Hawes Street  
Towanda, PA 18848-0504

305. Hayne Palmour III  
North Carolina State University  
2158 Burlington Engineering Laboratories  
PO Box 5995  
Raleigh, NC 27607

306. Joseph N. Panzarino  
Norton Company  
Goddard Road  
Northboro, MA 01532-1545

307. Pellegrino Papa  
Corning Glass Works  
Corning, NY 14831
308. James G. Paschal  
Reynolds Metals Company  
PO Box 76154  
Atlanta, GA 30358

309. Arvid E. Pasto  
GTE Laboratories, Inc.  
40 Sylvan Road  
Waltham, MA 02254

310. Donald O. Patten  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

311. James W. Patten  
Cummins Engine Company, Inc.  
Box 3005, Mail Code 50183  
Columbus, IN 47202-3005

312. Timothy M. Pattison  
Textron Lycoming  
MS: LSM1  
550 Main Street  
Stratford, CT 06497

313. Robert A. Penty  
Eastman Kodak Company  
901 Elmgrove Road  
Rochester, NY 14650

314. Gary R. Peterson  
U.S. Department of Energy  
785 DOE Place  
Idaho Falls, ID 83402

315. R. Byron Pipes  
University of Delaware  
2001 Spencer Laboratory  
Newark, DE 19716

316. Robert C. Pohanka  
Office of Naval Research  
800 North Quincy St, Code 431  
Arlington, VA 22217

317. Stephen C. Pred  
ICD Group, Inc.  
1100 Valley Brook Avenue  
Lyndhurst, NJ 07071

318. Karl M. Prewo  
United Technologies Corporation  
Silver Lane, MS: 24  
East Hartford, CT 06108

319. Hubert B. Probst  
NASA Lewis Research Center  
21000 Brookpark Road  
Cleveland, OH 44135

320. Carr Lane Quackenbush  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

321. Brian Quigy  
National Aeronautics and Space Administration  
Washington, DC 20546

322. George Quinn  
U.S. Army Materials Technology Laboratory  
Arsenal Street  
Watertown, MA 02172

323. Dennis T. Quinto  
Kennametal, Inc.  
PO Box 639  
Greensburg, PA 15601

324. S. Venkat Raman  
Air Products and Chemicals, Inc.  
PO Box 538  
Allentown, PA 18105

325. Dennis Readey  
Ohio State University  
2041 College Road
326. Robert R. Reeber  
U.S. Army Research Office  
PO Box 12211  
Research Triangle Park  
NC 27709

327. K. L. Reifsnider  
Virginia Polytechnic Institute and State University  
Blacksburg, VA 24061

328. Paul Rempes  
Williams International  
2280 West Maple  
MS: 6-5  
Walled Lake, MI 48088

329. T. M. Resetar  
U.S. Army Materials Technology Laboratory  
DAXMA-MC  
Arsenal Street  
Watertown, MA 02172

330. K. T. Rhee  
Rutgers University  
PO Box 909  
Bowser Road  
Piscataway, NJ 08854

331. Roy W. Rice  
W. R. Grace and Company  
7379 Route 32  
Columbus, MD 21044

332. David W. Richerson  
Ceramatec, Inc.  
163 West 1700 South  
Salt Lake City, UT 84115

333. Paul Rieth  
Ferro Corporation  
661 Willet Road  
Buffalo, NY 14218-9990

334. Michael A. Rigdon  
Institute for Defense Analyses  
1801 Beauregard Street  
Alexandria, VA 22311

University of Massachusetts  
Amherst, MA 01003

336. Giulio A. Rossi  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

337. Barry R. Rossmo  
Lanoxide Corporation  
Tarae Industrial Park  
Newark, DE 19711

338. David J. Rowcliffe  
SRI International  
333 Ravenswood Avenue  
Menlo Park, CA 94025

339. Donald W. Roy  
Coors Ceramics Company  
17750 West 32nd Street  
Golden, CO 80401

340. Bruce Rubinger  
Gobal  
50 Milk Street, 15th Floor  
Boston, MA 02109

341. Robert Ruh  
Air Force Wright Aeronautical Laboratory  
Materials Laboratory  
AFWAL/M LLM  
Wright-Patterson AFB, OH 45433

342. Robert J. Russell, Sr.  
Norton Company  
High Performance Ceramics  
Goddard Road  
Northboro, MA 01532-1545

343. George P. Safol  
Westinghouse Electric Corporation  
Pittsburgh, PA 15235
344. J. Sankar  
North Carolina Agricultural and Technical State University  
Greensboro, NC 27411

345. Maxine L. Savitz  
Garrett Processing Company  
Ceramic Components Division  
19800 South Van Ness Avenue  
Torrance, CA 90509

346. Richard Schapery  
Texas A&M University  
College Station, TX 77843

347. J. L. Schienle  
Allied-Signal Aerospace Company  
Garrett Auxiliary Power Division  
2739 East Washington Street  
PO Box 5227  
Phoenix, AZ 85010

348. Liselotte J. Schioler  
Aerojet Tech Systems Company  
PO Box 13222  
Dept. 9990, Bldg. 2019-A2  
Sacramento, CA 95813

349. Richard A. Schmidt  
Battelle Columbus Laboratories  
505 King Avenue  
Columbus, OH, 43201-2693

350. Arnie Schneck  
Deere and Company Technical Center  
PO Box 128  
Wood-Ridge, NJ 07075

351. Matthew Schreiner  
Gas Research Institute  
8600 West Bryn Mawr Avenue  
Chicago, IL 60631

352. John Schudtles  
Industrial Ceramic Technology, Inc.  
37 Enterprise Drive  
Ann Arbor, MI 48103

353-363. R. B. Schulz  
U.S. Department of Energy  
Forrestal Building CE-151  
1000 Independence Avenue  
Washington, DC 20585

364. Murray A. Schwartz  
Bureau of Mines  
2401 Eye Street, N.W.  
Washington, DC 20241

365. Douglas B. Schwarz  
The Dow Chemical Company  
52 Building  
Midland, MI 48674

366. Thomas M. Sebestyen  
U.S. Army Tank Automotive Command  
AMSTA-RGRT  
Warren, MI 48397-5000

367. Brian Seegmiller  
Coors Ceramics Company  
17750 West 32nd Street  
Golden, CO 80401

368. S. G. Seshadri  
Standard Oil Engineered Materials Company  
PO Box 832  
Niagara Falls, NY 14302

369. Peter T. B. Shaffer  
Advanced Refractory Technologies, Inc.  
699 Hertel Avenue  
Buffalo, NY 14207

370. Maurice E. Shank  
United Technologies Corporation  
East Hartford, CT 06108

371. Laurel M. Sheppard  
Advanced Materials and Processes  
Route 87  
Metals Park, OH 44073

372-376. Dinesh K. Shetty  
The University of Utah  
Salt Lake City, UT 84112
377. Wesley J.C. Shuster  
Thermo Electron Corporation  
115 Eames Street  
PO Box 340  
Wilmington, MA 01887

378. Jack D. Sibold  
Coors Ceramics Company  
17750 West 32nd Street  
Golden, CO 80401

379. Neal Sigmon  
U.S. House of Representatives  
Rayburn Building, Room B308  
Washington, DC 20515

380. Richard Silberglitt  
Quest Research Corporation  
1651 Old Meadow Road  
McLean, VA 22102

381. Maurice J. Sinnott  
University of Michigan  
438 West Engineering Building  
Ann Arbor, MI 48109-2136

382. S. R. Skaggs  
Los Alamos National Laboratory  
PO Box 1663  
Los Alamos, NM 87545

383. J. Thomas Smith  
GTE Laboratories, Inc.  
40 Sylvan Road  
Waltham, MA 02254

384. Jay R. Smyth  
Allied-Signal Aerospace Company  
Garrett Auxiliary Power Division  
2739 East Washington Street  
PO Box 5227  
MS: 93-172/1302-2K  
Phoenix, AZ 85010

385. Rafal Sobotowski  
Standard Oil Engineered Materials Company  
3092 Broadway Avenue  
Cleveland, OH 44115

386. Thomas M. Sopko  
Lubrizol Enterprises, Inc.  
29400 Lakeland Boulevard  
Wickliffe, OH 44092

387. Boyd W. Sorenson  
Du Pont Company  
Experimental Stat, Bldg 304  
Wilmington, DE 19898

388. Dr. Richard M. Spriggs  
Center for Advanced Ceramic Technology  
New York State College of Ceramics at Alfred University  
Alfred, NY 14802

389. M. Srinivasan  
Standard Oil Engineered Materials Company  
PO Box 832  
Niagara Falls, NY 14302

390. Gordon L. Starr  
Cummins Engine Company, Inc.  
Box 3005, Mail Code 50183  
Columbus, IN 47202-3005

391. Harold L. Stocker  
General Motors Corporation  
PO Box 420, T-23  
Indinapolis, IN 46206-0420

392. Paul D. Stone  
The Dow Chemical Company  
1801 Building  
Midland, MI 48674

393. Roger Storm  
Standard Oil Engineered Materials Company  
PO Box 832  
Niagara Falls, NY 14302

394. E. E. Strain  
Allied-Signal Aerospace Company  
Garrett Engine Division  
111 South 34th Street  
PO Box 5217  
MS: 301-2N  
Phoenix, AZ 85010
<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Company/Institution</th>
<th>Address</th>
</tr>
</thead>
<tbody>
<tr>
<td>395</td>
<td>Thomas N. Strom</td>
<td>NASA Lewis Research Center</td>
<td>21000 Brookpark Road, 77-6 Cleveland, OH 44135</td>
</tr>
<tr>
<td>396</td>
<td>Jerry Strong</td>
<td>Albright &amp; Wilson</td>
<td>PO Box 26229 Richmond, VA 23260</td>
</tr>
<tr>
<td>397</td>
<td>Richard Suddeth</td>
<td>Boeing Motor Airplane Company</td>
<td>PO Box 7730 MS: K-76-67' Wichita, KS 67277</td>
</tr>
<tr>
<td>398</td>
<td>Paul Sutor</td>
<td>Midwest Research Institute</td>
<td>425 Volker Boulevard Kansas City, MO 64116</td>
</tr>
<tr>
<td>399</td>
<td>J. J. Swab</td>
<td>U.S. Army Materials Technology Laboratory</td>
<td>405 Arsenal Street Watertown, MA 02172</td>
</tr>
<tr>
<td>400</td>
<td>John W. Swain, Jr.</td>
<td>Kollmorgen Corporation PCK Technology Division</td>
<td>15424 Garrison Lane Southgate, MI 48915</td>
</tr>
<tr>
<td>401</td>
<td>Lewis Swank</td>
<td>Ford Motor Company</td>
<td>20000 Rotunda Drive PO Box 2053 Dearborn, MI 48121-2053</td>
</tr>
<tr>
<td>402</td>
<td>Stephen R. Tan</td>
<td>ICI Advanced Materials</td>
<td>PO Box 11 The Heath, Runcorn Cheshire ENGLAND WA7 4QE</td>
</tr>
<tr>
<td>403</td>
<td>Anthony C. Taylor</td>
<td>U.S. House of Representatives</td>
<td>Rayburn Building, Room 2321 Washington, DC 20515</td>
</tr>
<tr>
<td>404</td>
<td>W. H. Thielbahr</td>
<td>U.S. Department of Energy</td>
<td>550 2nd Street Idaho Falls, ID 83401</td>
</tr>
<tr>
<td>405</td>
<td>John K. Tien</td>
<td>Columbia University</td>
<td>1137 S.W. Mudd Building New York, NY 10027</td>
</tr>
<tr>
<td>406</td>
<td>T. Y. Tien</td>
<td>University of Michigan</td>
<td>Dow Building Ann Arbor, MI 48109-2136</td>
</tr>
<tr>
<td>408</td>
<td>Louis E. Toth</td>
<td>National Science Foundation</td>
<td>1800 G Street, N.W. Washington, DC 20550</td>
</tr>
<tr>
<td>409</td>
<td>Richard E. Tressler</td>
<td>Pennsylvania State University</td>
<td>201 Steidle Building University Park, PA 16802</td>
</tr>
<tr>
<td>410</td>
<td>Donald R. Uhlmann</td>
<td>Massachusetts Institute of Technology</td>
<td>77 Massachusetts Avenue Cambridge, MA 02139</td>
</tr>
<tr>
<td>411</td>
<td>Edward C. Van Reuth</td>
<td>Technology Strategies, Inc.</td>
<td>10722 Shingle Oak Court Burke, VA 22015</td>
</tr>
<tr>
<td>412</td>
<td>Thomas Vasilos</td>
<td>Avco Corporation</td>
<td>201 Towell Street Wilmington, MA 01887</td>
</tr>
<tr>
<td>413</td>
<td>V. Venkateswaran</td>
<td>Standard Oil Engineered Materials Company</td>
<td>PO Box 832 Niagara Falls, NY 14302</td>
</tr>
</tbody>
</table>
414. John B. Wachtman, Jr.
Rutgers University
PO Box 909
Bowser Road
Piscataway, NJ 08854

415. Richard B. Wallace
36880 Ecorse Road
Romulus, MI 48174

416. Harlan L. Watson
U.S. House of Representatives
Rayburn Building, Suite 2321
Washington, DC 20515

417. John D. Watson
BHP Research & New Technology
Melbourne Research Laboratories
245 Wellington Road
Mulgrave, Vic. 3170
AUSTRALIA

418. Albert R. C. Westwood
Martin Marietta Laboratories
1450 South Rolling Road
Baltimore, MD 21227

419. Thomas J. Whalen
Ford Motor Company
20000 Rotunda Drive
PO Box 2053
Dearborn, MI 48121-2053

420. Sheldon M. Wiederhorn
National Bureau of Standards
Gaithersburg, MD 20899

421. James C. Williams
Carnegie-Mellon University
Schenley Park
Pittsburgh, PA 15213

422. Roger R. Wills
TRW, Inc.
Valve Division
1455 East 185th Street
Cleveland, OH 44110

423. J. M. Wimmer
Allied-Signal Aerospace Company
Garrett Engine Division
111 South 34th Street
Post Office Box 5217

424. David Wirth
Coors Ceramics Company
17750 West 32nd Street
Golden, CO 80401

425. Thomas J. Wissing
Eaton Corporation
26201 Northwestern Highway
Post Office Box 766
Southfield, MI 48037

426. Dale Wittmer
Southern Illinois University at Carbondale
Department of Mechanical Engineering and Energy Processes
Carbondale, IL 62901

427. George W. Wolter
Howmet Turbine Components Corporation
699 Benston Road
Whitehall, MI 49461

428. James C. Wood
NASA Lewis Research Center
21000 Brookpark Road
MS: 500-210
Cleveland, OH 44135

429. Roger P. Worthen
Eaton Corporation
26201 Northwestern Highway
PO Box 766
Southfield, MI 48076
430. Thomas M. Yonushonis
Cummins Engine Company, Inc.
Box 3005, Mail Code 50183
Columbus, IN 47202-3005

431. Don Zabierek
Air Force Wright
Aeronautical Laboratory
AFWAL/POTC
Wright-Patterson AFB
OH 45433

432. Charles Zeh
U.S. Department of Energy
PO Box 880
Morgantown, WV 26505

433. Anne Marie Zerega
U.S. Department of Energy
Forrestal Building CE-15
1000 Independence Avenue
Washington, DC 20585

434. Martin Zlotnick
Nichols Research Corporation
8618 Westwood Center Dr.
Suite 200
Vienna, VA 22180-2222

435. Klaus M. Zwilsky
National Research Council
2101 Constitution Avenue
Washington, DC 20418

436. Department of Energy
Oak Ridge Operations Office
Assistant Manager for Energy
Research and Development
PO Box 2001
Oak Ridge, TN 37831

437-446. Department of Energy
Office of Scientific and
Technical Information
Office of Information Services
PO Box 62
Oak Ridge, TN 37831

For distribution by microfiche
as shown in DOE/TIC-4500,
Distribution Category UC-95.