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# Table of Contents

22nd Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: B

## Environmental Effects

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Effect of High-Temperature Soaking on the Microstructure and Properties of a Sintered Silicon Nitride</td>
<td>3</td>
</tr>
<tr>
<td>Q. Wei, J. Sankar, V. Vijayrao, and J. Narayan</td>
<td></td>
</tr>
<tr>
<td>Environmentally Induced Time-Dependent Failure Mechatenisms in CFCCs at Elevated Temperatures</td>
<td>11</td>
</tr>
<tr>
<td>C.A. Lewinsohn, C.H. Henager, Jr., and R.H. Jones</td>
<td></td>
</tr>
<tr>
<td>High-Temperature Oxidation and Corrosion of a Porous Si$_3$N$_4$O-ZrO$_2$ Composite Material</td>
<td>19</td>
</tr>
<tr>
<td>Maiken Heim, Jiaxin Chen, Colette O'Meara, Refael Gatt, and Robert Pompe</td>
<td></td>
</tr>
<tr>
<td>Low-Damage, High-Productivity Abrasive Grinding of Advanced Ceramics</td>
<td>29</td>
</tr>
<tr>
<td>Robert Sabia, Victor A. Greenhut, Dale E. Niesz, Ping Tang, Ruilin Zeng, and Ioan Marinescu</td>
<td></td>
</tr>
<tr>
<td>Effect of Crystallization on creep of Clay Bonded SiC Filters</td>
<td>37</td>
</tr>
<tr>
<td>Pirjo H. Pastila, Vesa Helanti, Antti-Pekka Nikkilä, and Tapio A. Mäntylä</td>
<td></td>
</tr>
<tr>
<td>Wear Performance of Monolithic and Composite Mixing Tubes for Abrasive Water Jet Cutting of Ceramics</td>
<td>45</td>
</tr>
<tr>
<td>M. Ramulu, M. G. Jenkins, T.L. Stevens, and J.A. Salem</td>
<td></td>
</tr>
</tbody>
</table>

## Reliability and Life Prediction

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reliability Modeling of Brittle, Anisotropic Materials</td>
<td>57</td>
</tr>
<tr>
<td>Jonathan Salem, Ronald Noebe, and Jane C. Mandersheid</td>
<td></td>
</tr>
<tr>
<td>A Strain-Based Methodology for High-Temperature Lifetime Prediction</td>
<td>65</td>
</tr>
<tr>
<td>Investigations of the Weibull Modulus as a Function of Stressing Rate</td>
<td>79</td>
</tr>
</tbody>
</table>
Exploration of the Weibull Modulus as a Function of Surface Preparation and Flexure Testing Conditions ..........................89
Kristin Breder, Andrew A. Wereszczak, and Mark J. Andrews

Lifetime Prediction for Ceramic Components Subjected to Time-Dependent Loading ..........................................................99
Angelika Brückner-Foit and Christian Ziegler

Prediction of the Load-Bearing Capabilities Based on the First Matrix-Cracking Criterion for Plain-Weave Multilayered Nicalon/SiC Composites with Lay-Ups of [0/20/60] and [0/40/60] ..................................................107
Wei Zhao, Peter K. Liaw, and Niann-i Yu

Life Prediction Tool for Ceramic Matrix Composites at Elevated Temperatures .................................................................117
S. Case, Nirmal Iyengar, and Ken Reifsnider

Experimental Study and Modeling of a Novel Ceramic Composite Hot Gas Candle Filter Material ...............................125
Xinyu Huang, Rob Carter, and Ken L. Reifsnider

**Theoretical Modeling**

Bridging Behavior at Creep Regime .............................................135
S.B. Biner

Oxygen Diffusion and Reaction Kinetics in Continuous Fiber Ceramic Matrix Composites ..................................................143
Michael C. Halbig, Andrew J. Eckel, and James D. Cawley

Prediction of Tension Failure of Textile Composites Using Micromechanics and Statistical Analysis ..............................151
Y. Shi, M.F. Card, V.V. Raman, and R.M.V. Murthi

The Effects of Load, Grain Size, and Grain Boundaries on the Hardness of Alumina ..........................................................159
Andreas Krell

Computational Analysis of Residual Stress in Ceramics Having Heterogeneous Microstructure ..................................169
Yoshihisa Sakaida, Akira Okada, Keisuke Tanaka, Yoshiyuki Yasutomi, and Hiroshi Kawamoto

Finite Element Modeling of Thermal Residual Stress in Tungsten/Tungsten-Carbide Composites .............................177
Kai Wang and Robert R. Reeber
Finite Element Analysis of the Stress Distribution in Silicon Nitride Bearing Balls .................... 185
Y.L. Tsai, J.J. Mecholsky Jr., and H.A. Chin

Finite Element Analysis of Crack Wake Traction in Chevron-Notched Bend Bar .................... 193
G. Reza Sarrafi-Nour, Theo Fett, and Thomas W. Coyle

Analysis of the Bridging Zone Contribution to the R-Curve Behavior of SiC-Platelet-Reinforced Alumina Using the Chevron-Notched Bend Bar Specimen ................ 203
G. Reza Sarrafi-Nour and Thomas W. Coyle

Structural Analysis and Component Design

Fabrication of NZP Ceramic-Metal Composite Diesel Engine Exhaust Port Liners Using Finite Element Analysis as a Guiding Tool .................. 215
R. Nageswaran, J.J. Cassell, S.Y. Limaye, and D. Stinton

Finite Element Modelling and Analysis of a Ceramic Matrix Composite Combustor .......... 225
J. Shi and PD. Andrew

Joint Integrity Issues in a Novel Piezoceramic Actuator Design .......................... 233
T.L. Jessen, R.J. Rayne, B.A. Bender, L.D. Flippen Jr., and C. Kim

Manufacturing of Ceramic Matrix Composite Rotor for Advanced Gas-Generator .............. 241
Takahito Araki, Nobuyuki Suzumura, Shoju Masaki, Tadashi Nasumura, Masakazu Onozuka, Hisaichi Ohnabe, and Koichi Yasuhira

Design and Analysis of a CMC Turbine Blade Tip Seal for a Land-Based Powerturbine ................. 249
J.A. Morrison and K.M. Kauth

Degradation of SiC/Bn/SiC Composites in the Burner Rig ........................................ 257
Linus U. Ogbuji

Rudimentary CFCMC Design and Mechanical Behavior Prediction .......................... 265
T.L. Jessen and A. Kee

Alumina Single-Crystal Fiber Reinforced Alumina Matrix for Combustor Tiles ............... 273
O. Sudre, A.G. Razzell, L. Molliex, and M. Holmquist
High-Performance Coatings
Strength Measurements of Thick Brittle Coatings on Metals ........................................... 283
Ö. Ünal, D. Sordelet, D. Barnard, and A. Akinc

High-Temperature Slow-Crack Growth, Fracture Toughness, and Room-Temperature Deformation Behavior of Plasma-Sprayed ZrO2-8wt % Y2O3 ............. 293
Sung R. Choi, Dongming Zhu, and Robert A. Miller

Dust Erosion Testing of Coated AETB Tile for Aerospace Applications .......................................... 303
Edmund H. Moore and Richard A. Smith

Posters
Thermomechanical Behavior of Plasma Sprayed Zirconia Thermal Barrier Coatings ....................... 313
J.P. Singh, M. Sutaria, and A. Chopra

Damage Behavior and Residual Fatigue Bending Strength of Impact-Induced CFRP Composites .......... 323
Kwang-Hee Im and In-Young Yang

Ultrasonic Nondestructive Evaluation of Carbon/Carbon Brake Disks .............................................. 329
Kwang-Hee Im, David K. Hsu, and Hyunjo Jeong

in situ Observation of Stable Crack Propagation in SENB Specimens for R-Curve Evaluation .......... 335
Kyoji Hiramatsu, Akira Okada, and Matsohiko Usami

Irradiation Creep of Advanced SiC-Based Fibers ............... 341
G.E. Youngblood, R.H. Jones, G.N. Morschel; R. Scholz, and A. Kohyama

Active Metal Brazing of Si3N4 to Metals .................. 347
Maiken Heim, Luiz A.B. Tessarotto, and Victor Greenhut

Uniformity in Microwave Processed Al2O3-ZrO2 Composite Bars ................................................. 355
Greg Darby and David E. Clark

Evolution of Phases in MoSi2-TiB2 Composites Produced by Displacement Reactions ................. 361
L.A. Dempere and M.J. Kaufman
Effects of Silicon Carbide Structure on the Microwave Properties of SiC/Al₂O₃ Cement Composites ............ 367
K.S. Leiser and D.E. Clark

International Symposium on Advanced Synthesis and Processing

Preface .................................................. 375

Advanced Synthesis and Processing

Processing, Deformation, and Fracture of Ni-Al₂O₃ Composites with and without Graded Microstructures .... 379
Andrew N. Winter, Brain A. Corff, Ivar E. Reimanis, and Barry H. Rabin

Functionally Graded Boron Carbide .............................. 387
J.J. Petrovic, K.J. McClellan, C.D. Kise, R.C. Hoover, and W.K. Scarborough

High-Temperature Plasticity in the ZrO₂-Y₂O₃ System ........ 395
Arturo Domínguez-Rodríguez, Diego Gómez-García, and Manuel Jiménez-Melendo

Dynamic Compression Behavior of a Hot Pressed TiB₂-Al₂O₃ Ceramic Composite from SHS-Powders ........ 407
Jean-Marcel Jamet

Synthesis of TiC-Al₂O₃ Composites Using Microwave-Induced Self-Propogating High-Temperature Synthesis (SHS) ...................... 415
Duangduen Atong and D.E. Clark

Mechanical Properties of Melt-Derived Erbium Oxide ......... 423
A.D. Neuman, M.J. Blasic, M. Platero, R.S. Romero, K.J. McClellan, and J.J. Petrovic

Nanotechnology

Amorphous and Nanocrystalline Diamond Synthesized by SCARQ: Shock Compression and Rapid Quenching .......... 433
Ken-Ichi Kondo, Hisako Hirai, and Masatake Yoshida

Effect of Al₂O₃ Phase Transformations on Grain Growth in ZrO₂-Al₂O₃ Nanocomposites ..................... 445
B.M. Smyser and R.D. Sisson Jr.

Effects of Gas Pressure Sintering Conditions in Si₃N₄-Nano-SiC Composites on Tribological Behavior .......... 453
S.W. Lee and S.H. Kim
A Novel Process For Synthesizing Nanostructured Carbides: Mechanically Activated Synthesis .......................... 461
Ruiming Ren, Zhenguo Yang, and Leon L. Shaw

A Preparation of Ceramic Powders by a Solution-Polymerization Route Employing PVA Solutions .................. 469
Sang-Jin Lee and Waltraud M. Kriven

Microstructure-Electrical Transport Correlation in Ceramic Oxide Thin Films ........................................ 477
Igor Kosacki and Harlan U. Anderson

Mechanical Properties of Nanocrystalline MgAl₂O₄ and Its Composites .............................................. 491

Nano-SiC Dispersed Si₃N₄ Composites Sintered by Pulsed Electric Current Method ............................ 499
Yoshiaki Kinemuchi and Kozo Ishizaki

Synthesis of Alkaline Earth Aluminate/Zirconia Composites from Metal Bearing Precursors .................. 507
Kirk A. Rogers, Ramazan Citak, Pragati Kumar, and Ken H. Sandhage

Reaction and Microwave Processing
Microwave Induced Decomposition of Ceramic Oxides to Form Unique Composites .......................... 517
R.R. Di Fiore and David E. Clark

Plasma and Gel Processing Technologies
Effect of Geometry on CVI with RF Heating ..................................... 527
Vikas Midha and Demetre J. Economou

Novel Applications of Atmospheric Pressure Chemically Vapor Deposited Materials and Methods for Control ........................... 535
Terence J. Clark

Thermodynamic Modeling of the Ti-Si-C-H-Cl-Ar System to Determine the Optimum Conditions for Chemical Vapor Deposition of Ti₃SiC₂ ........................................ 541
E. Pickering, W.J. Lackey, and S. Crain

Net-Shape Manufacture of Low-Cost Ceramic Shapes by Freeze-Gelation ........................................ 553
M.J. Statham, F. Hammett, B. Harris, R.G. Cooke, R.M. Jordan, and A. Roche
Al₂TiO₅—New Contributions to Its Preparation via the Sol-Gel Technique ........................................... 559
Stefan Tudyka, Karl Pflanz, Norbert Stroh, Fritz Aldinger, and Herwig Brunner

Design of Self-Diagnosis in/with Composite Materials .... 567
Hiroaki Yanagida

CVD-SiC Manufacturing Process Reproducibility ............. 579
Jitendra S. Goela and Michael A. Pickering
Environmental Effects
THE EFFECT OF HIGH TEMPERATURE SOAKING ON THE MICRO- STRUCTURE AND PROPERTIES OF A SINTERED SILICON NITRIDE

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ABSTRACT

An investigation was carried out to study the effect of high temperature soaking in air on the microstructure and mechanical properties of an AlliedSignal sintered silicon nitride using optical and scanning electron microscopy, energy dispersive spectroscopy and microhardness testing. The Si₃N₄ samples were soaked in air at 1275°C for different periods of time ranging from 16-40 hours. The cross section of the samples were then studied using optical microscope and microhardness measurements. It was found that two distinct white annular rings were formed during thermal soaking. While the outer annular ring stayed relatively stationary with respect to the surface, the inner one advanced towards the center of the sample and expanded simultaneously with time. The position of the inner diameter of the inner ring is roughly a linear function of the time of soaking. Vickers hardness measurements showed strength degradation in both of the annular rings. The results are discussed in combination with the oxygen attacks on the material through fast diffusion along the amorphous grain boundary phases, surface diffusion in the micropores and lattice diffusion of oxygen in silicon nitride grains as revealed by EDS at the edge and in the center of the samples. This would contribute to a better understanding of the high temperature behavior of sintered Si₃N₄.

INTRODUCTION

The β- Si₃N₄ has been synthesized for high temperature applications such as hot turbine engine parts due to its excellent mechanical, chemical and physical properties at elevated temperatures and under severe service conditions[1]. However, since this material is covalently bonded, its densification through sintering has to be facilitated with additives[2]. For this reason, it has become a common practice to add oxide sintering aids in the course of densification which form eutectic phases with the native SiO₂ on the surface of the Si₃N₄ grains and implement liquid phase sintering through a solution-reprecipitation mechanism to achieve a near theoretical density. The liquid eutectic phases will remain in the material as amorphous phases sitting in the multiple junction pockets and along grain boundaries. The residual amorphous or glassy phases and their distribution,
fraction and stability have significant diverse effect on many of the high temperature mechanical properties such as creep resistance, oxidation resistance and fracture resistance. This will largely offset the advantages of the material. Therefore, a good understanding of the material at high temperature and in oxidizing atmosphere will help to make full use of the material. This paper will address the effect of high temperature exposure to air on the microstructure and properties of a sintered silicon nitride.

EXPERIMENTAL
Material
The material for investigation is a sintered silicon nitride, GS44, provided by AlliedSignal. Earlier studies[3] on this material showed that it contains yttria, magnesia and alumina as sintering aids. Transmission electron microscopy showed that the microstructure consists of regularly shaped triple junction phase, low angle grain boundaries, grain boundary phase with atomic ledges or steps along the Si₃N₄ grains, and amorphous grain boundary phase of 1.5 nm in thickness, and dislocation networks in the Si₃N₄ grains. All these features are typical of sintered Si₃N₄ ceramics.

Thermal Soaking Experiment
GS44 samples were soaked at 1275°C in air for 16, 24, 32 and 40 hours to simulate creep condition at no load. Here it must be mentioned that this material's application temperature is around 1000°C and the research is done more for scientific understanding. The thermal soaking was conducted in a creep test setup designed and manufactured by Applied Test Systems, Butler, PA.

Microhardness Measurements
Microhardness profile across the cross section of the thermally soaked samples were carried out. The hardness test measures the resistance to penetration of the surface of a material by a hard object (indentor) and is thus a finger print of the strength of the material studied. We used Vickers hardness test to characterize the mechanical properties of the thermally soaked samples. The Vickers microhardness across the diameter of the polished specimens was measured in 100 μm steps using a microhardness testing machine Model M-400-H1/H2/H3, Leco Co. The polished samples were cleaned in an acetone ultrasonic bath before the measurements.

Microstructural and Compositional Analysis
The cross section of the soaked samples was observed first with an optical microscope at low magnification to study the location of the annular rings formed during the soaking process with changes in time. This is followed by high magnification optical microscopy to study the fine structure of the first annular ring on a well polished sample. Scanning electron microscopy observations were conducted on a microscope with a field emission source with EDS facility in the windowless mode for qualitative compositional analysis.

RESULTS AND DISCUSSION
In practice, the purpose of thermal soaking experiment at high temperatures and in atmospheric environment is to study the oxidation behavior of the material.

Fig.1 is a set of optical micrographs of the cross section of GS44 after thermal soaking for various periods of time. It shows regions of different colors. It can be
observed that the thickness of the first annular ring is relatively unchanged with soaking time. The surface of this ring is nothing but the oxide scale. It can be further observed that the thick white annular ring advances towards the center of the sample with time. Fig. 2 is the position of the inner diameter of the ring relative to the surface of the sample as a function of time.

Fig. 2 Position of the inner diameter of the inner ring relative to the surface of the sample as a function of time

Fig. 3 is a set of high magnification optical micrographs showing the interface between the oxide scale which is rough and loose (Fig. 3a) as compared with the Si₃N₄ matrix and the interior part of the material. Also observed from this micrograph is that some parts of the scale have been spalled off the sample (Fig. 3b).

Similar formation of annular rings during oxidation has been reported by Wereszczak, et al[4] in a HIPed Si₃N₄, with only one annular ring close to the surface. To our knowledge, our observation of two annular rings formed during thermal soaking in air in sintered silicon nitride ceramics is the first one. We expect that the change in color is due to the compositional change during soaking and it is mainly caused by the diffusion of oxygen into the bulk sample. This problem is still under further investigation.

Though a number of investigations have been reported of oxidation of single
Fig. 3 Optical micrographs showing the interface between the oxide scale and the bulk of the soaked GS44 ceramics. (a) shows rough and loose scale and (b) shows that some of the scale is peeled off from the material.

crystal or polycrystalline Si$_3$N$_4$ films prepared by chemical vapor deposition for semiconductor device application[5,6], much less has been known for bulk, sintered or hot-pressed Si$_3$N$_4$ material. As early as 1970s, some researchers started to study the oxidation of HIPed and sintered silicon nitride, but the results reported were based on different additives[7,8]. Only a few references have related oxidation to the high temperature mechanical behavior of Si$_3$N$_4$[5,9]. Tighe, et al[9], reached the conclusion that oxidation at 1200 °C affects the strength and reliability of HIPed, magnesia-doped Si$_3$N$_4$ by modifying the flaw population. Wereszczak, et al.,[4] recognized that the creep resistance of HIPed Si$_3$N$_4$ material is ultimately dictated by its susceptibility to creep enhanced damage(e.g. cavitation) and oxidation induced damage. A few studies[7,8] have been published concerning the oxidation behavior, such as oxidation kinetics, oxidation thermodynamics, etc. of HIPed Si$_3$N$_4$. Both parabolic(Wagner's law) and more complicated kinetics have been observed mainly through approaches such as thermogravity analyses. Most of the microstructural and compositional analyses have been concentrated on the oxide scale region, with much less attention to the interior regions. It could be predicted that the oxidation behavior and the mechanism of oxidation of bulk, polycrystalline silicon nitride would be different from that of single crystal silicon nitride or dense polycrystalline silicon nitride without oxide additives. In the case of the bulk material, either sintered or HIPed, a relatively large number of micropores can be expected along with a considerable amount of amorphous grain boundary phases which can remarkably enhance the diffusion of the reactants such as oxygen. This will lead to a more rapid oxidation process. Studies on a reaction bonded silicon nitride[10] showed that significant oxidation of silicon nitride occurs at temperatures above 900 °C, principally by the formation of silica. On cooling to room temperature, crystalline silica-cristobalite is detected by X-ray diffraction analysis. The bulk of the oxidation occurs throughout the volume of the specimen, presumably round the pores in the material.

To study the effect of thermal soaking on the mechanical properties of the material, we conducted Vickers hardness measurements across the cross section of the soaked samples. The microhardness profile for the sample soaked for 40 hours is shown in Fig. 4. It is seen that corresponding to the color changes across the sample due to thermal soaking, there is a significant modulation of
Microhardness profile across the cross section of the sample soaked at 1275°C for 40 hours.

microhardness. Close to the surface, the strength is seriously degraded, and then it picks up in the region of unchanged color, while in the inner white annular ring, the strength drops again, and gradually restores to the normal value towards the center of the sample. Fig. 5 is the energy dispersive spectra of the cross section of GS44 soaked for 40 hours at 1275°C. Fig. 5a is the EDS from the center of the sample. It shows a large peak of Si and some Al, Mg, oxygen due to the presence of the sintering aids. The peak of nitrogen is small because of the serious absorption of the characteristic lines from nitrogen before reaching the analyzer. Fig. 5b is the EDS from the edge, viz. close to the surface oxide scales of the sample. The depletion of Si and Mg elements in this region is obvious. It is then apparent that material “loss” occurred during thermal soaking in air. This
observation is in agreement with electron microprobe trace analysis of silicon nitride samples oxidized under similar condition[7]. It also agrees with cross sectional composition analysis using x-ray microanalysis (EDAX) [11] and wavelength dispersive spectroscopy (WDS)[12]. A recent report[13] on the CVD Si$_3$N$_4$ presented similar composition profiles.

As for the strength degradation in the inner white annular ring, we still need to do more research to work out a convincing explanation. However, for the time being, this can probably be understood in terms of oxygen attack to the bulk material. Oxygen diffusion could occur during the thermal soaking process through amorphous grain boundary phases[14] which act as rapid diffusion paths, through surface diffusion in the micropores(Knudsen diffusion) and even through volume diffusion in the silicon nitride grains[15]. The diffusion species of oxygen can be either oxygen ions (charged defects, in other words) or molecular oxygen[5,16,17] and the driving force for diffusion is the concentration gradient(or more generally, the chemical potential difference) of oxygen in the material. It is known that grain boundaries, particularly those composed of amorphous structures, facilitate fast diffusion of atoms. Oxygen diffusion through these fast diffusion paths is enhanced at elevated temperatures and this can oxidize the surrounding grains and therefore encroach the grains. More detailed HRTEM studies on this problem will be presented elsewhere[18]. Here we consider the attack of oxygen and its effect on the mechanical properties of the material. From Fig.1, it is seen that with the advancement of the inner white annular ring towards the center of the sample, the ring also expands in size: it becomes thicker, while the position and size of the first ring does not change significantly. It is envisaged that the oxygen attack has two stages. First, it attacks the sample through the pores, the grain boundary phases and the silicon nitride grains that are near the sample surface. An oxide layer of silica would form which might be discontinuous first and at this stage more oxygen could still diffuse into the interior part of the sample through the uncovered areas. Then the silica scale might connect gradually to form a continuous layer, which will act as a barrier for further oxygen diffusion into the sample. As long as the first continuous scale layer of silica (or cristobalite) is formed, the rate of oxidation is reduced radically because of lack of oxidants. However, oxygen species that are already in the material might move forward due to the chemical potential difference between the area close to the surface and inside the sample. This would lead to the expanding of the inner white ring. It can happen through oxygen transport via grain boundary phases or micropores in the material or even through lattice diffusion, since theoretically, there are continuous channels of an equivalent cylindrical radius of 0.145 nm along c axis of β-Si$_3$N$_4$ which may enable large atoms to diffuse readily through the lattice[15]. Oxygen ions might perturb the silicon nitride and make it weaker by forming Si-N-O bonds, or by oxidizing the silicon nitride grains close to the grain boundary phase. As was argued by Ogbuji[19], that the oxidation reaction of silicon nitride could be characterized as the substitutional dissolution of oxygen in the graded oxynitride network. Sheldon[20] argued that the oxidation kinetics of Si$_3$N$_4$ could be modeled by describing the simultaneous diffusion and reaction of interstitial oxygen that is believed to occur inside of the silicon oxynitride interlayer between Si$_3$N$_4$ bulk and the SiO$_2$ layer. Also, it has been recognized that thermodynamically, Si-O bond is
more stable than Si-N bond[21]. This interpretation accounts for the microhardness drop in the inner white annular ring region. It is also in accordance with the observation by other authors [10] for a reaction bonded silicon nitride that the rate of oxidation at elevated temperatures is initially very rapid, approximately 4% cristobalite in 10 minutes. The rate then dropped off rapidly so there is still only about 8% cristobalite in 600 hours.

CONCLUSIONS

Based on the experimental results and brief discussion on the effect of high temperature thermal soaking on the microstructure and mechanical properties of a sintered silicon nitride, the following conclusions have been achieved. Two distinct white annular rings were formed during thermal soaking. While the outer annular ring stayed relatively stationary with respect to the surface, the inner one advanced towards the center of the sample and expanded simultaneously with time. The position of the inner diameter of the inner ring is roughly a linear function of the time of soaking. Vickers hardness measurements showed strength degradation in both of the annular rings. A temporary explanation for the observation was attempted by considering the oxygen attack on the material through fast diffusion along the amorphous grain boundary phases, surface diffusion in the micropores and lattice diffusion of oxygen in silicon nitride grains, as revealed by EDS at the edge and in the center of the samples.

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REFERENCES

ENVIROMENTALLY INDUCED TIME-DEPENDENT FAILURE MECHANISMS IN CFCCS AT ELEVATED TEMPERATURES.


ABSTRACT

The results of several studies suggest that a variety of mechanisms exist for time-dependent failure in CFCCs at elevated temperatures. The failure mechanisms of CFCCs at elevated temperatures when oxidation processes occur during deformation are presented and discussed in the framework of a “Failure Mechanism Map”. In particular, the transition between the oxidation embrittlement mechanism (OEM) and the interfacial removal mechanism (IRM) is discussed with respect to oxygen concentration, exposure temperature, and carbon interphase thickness. Experimental data and modeling from studies, using flexural loading, at PNNL is combined with observations reported by others to produce the map.

INTRODUCTION

Ceramic fiber, ceramic matrix composites (CFCCs), reinforced by small diameter ceramic fibers, offer potential for use in high-temperature structural applications due to their non-catastrophic failure modes. Non-oxide composites are especially promising candidates for increasing the operating temperature of many applications and, hence, increasing fuel conservation due to greater thermodynamic efficiency. In order to obtain the desirable properties of CFCCs it is well known that debonding at the interface between the fiber and matrix must occur during crack propagation. A common method for obtaining interfacial debonding is to incorporate a third constituent, an interphase, between the fiber and the matrix. Appropriate interphase materials promote mode II failure either internally or at the interface between either the fiber and interphase or matrix and interphase. Carbon and boron nitride interphases are currently employed due to their layered structures, which promote mode II failure, and their thermochemical properties. Unfortunately, both of these materials react with oxygen to form volatile gaseous species. Exposure of either carbon or boron nitride interphases to oxygen, therefore, causes removal of the interface and degrades the mechanical properties of the composite component. For different combinations of environmental and microstructural parameters a variety of environmentally induced failure mechanisms may occur in CFCCs.

Four different elevated temperature failure mechanisms have been identified for the non-oxide CFCCs with small diameter (< 50 μm) ceramic fibers with oxidation prone interphases, such as carbon or boron nitride. The first mechanism, referred to as the fiber relaxation mechanism (FRM), involves subcritical crack growth due to a continuous decrease in crack bridging tractions caused by fiber creep. FRM occurs in CFCCs at elevated temperatures under stress in inert atmospheres and a number of models exist to describe crack growth as a function of time. A second mechanism, referred to as the interface recession mechanism (IRM), involves removal of the interphase by oxidation which increases the effective gage length of the bridging fibers. Since the strain due to creep of the fibers is unchanged by interfacial recession the result is a larger crack opening displacement. As the crack opening

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* Operated for the U.S. DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
displacement of the crack increases so does the effective stress intensity at the crack tip. The subcritical crack growth rate increases as the stress intensity at the crack tip increases. Therefore, interphase recession, due to oxidation, accelerates subcritical crack growth. A third mechanism, referred to as the oxidation embrittlement mechanism, involves oxidation of the fiber or the matrix after interphase recession has occurred. It has been proposed that the formation of a brittle oxidation product on the fibers creates Griffith type flaws and decreases the strength of the fibers. The formation of a brittle oxidation product between the fiber and the matrix prohibits matrix sliding and strain accommodation during fracture.

Without matrix sliding and strain accommodation stress builds up in the fibers and they fracture in the plane of the matrix crack. The predominance of OEM or IRM is governed by the competition between interface recession, which is characterized by a low activation energy, and oxidation, which is characterized by a higher activation energy but a faster reaction rate. Therefore, the occurrence of OEM or IRM will be determined by the temperature, oxygen concentration, and interphase thickness. A fourth mechanism, the viscous interface mechanism (VIM), involves the formation of a viscous oxidation product between the fiber and the matrix after interphase recession. Viscous flow of the interphase decreases the crack bridging traction in a manner similar to fiber creep in the FRM mechanism. VIM will only occur at temperatures at which oxidation products are thick enough to connect the fiber to the matrix and have sufficient viscosity to allow deformation.

Failure mechanism maps are a graphical guide to determining the environmental conditions under which each of the four failure mechanisms described above occur. A schematic representation of a failure mechanism map is shown in Figure 1. This type of map plots the range of conditions under which each mechanism controls failure. Since accurate models of all these failure mechanisms do not exist and because the values of required parameters for a specific material may not be known, experimental methods must be employed to allow construction of failure mechanism maps. The aims of this study are to develop techniques for investigating environmentally induced failure mechanisms in CFCCs that allow construction of failure mechanism maps.

**EXPERIMENTAL METHOD**

To reduce the number of experiments required a single CFCC material with fixed interphase thickness and composition, was used. A SiCp/SiC CFCC containing "Ceramic-grade" Nicalon™ fibers was examined in this study (Fig. 2). The material was fabricated from 2-dimensional, plain-weave fiber mats. Before matrix infiltration, a 1.5 x 10⁻⁷ m thick carbon interphase layer was deposited on the fibers by chemical vapor deposition (CVD). A silicon carbide matrix material was also deposited by CVD in a process known as chemical vapor infiltration (CVI). The resulting composites contained approximately 40 volume-percent fibers and 10-15% porosity.

A mixture of fast fracture and subcritical crack growth experiments were conducted to investigate the environmentally induced failure mechanisms of the CFCC material studied.
Figure 2. The microstructure of the CFCC examined. In the cross section, (a), the matrix appears white, fibers appear grey, and voids appear black. A higher magnification image, (b), shows details of the interphase between the fiber and the matrix.

Scanning electron microscopy (SEM) was used to investigate fracture surfaces. All experiments were performed by flexural loading of single-edge-notched beam specimens (SENB) in 1/4 four-point bending in a fully articulated silicon-carbide fixture. Subcritical crack growth was obtained by maintaining a constant load at elevated temperature. The specimen and fixture were incorporated in a vertically oriented mullite tube contained within a high-temperature furnace mounted to an electromechanically controlled mechanical test frame. Loading was provided by a silicon-carbide loading rod, attached to the crosshead of the test frame, that entered the tube through a stainless-steel bellows; the bend fixture was supported by a silicon-carbide tube resting on a standard strain-gauged cantilever-beam load cell. The atmosphere inside the mullite tube was controllable. The deflection of the specimen midpoint was measured by an alumina pushrod, also containing a thermocouple, attached to a strain-gauge extensometer. The displacements were corrected for differences between the load-point and mid-point and for the compliance of the test apparatus. The temperature, load, and deflection were monitored continuously by a personal computer with analog-to-digital conversion software. Since the subcritical crack growth rate was determined from an indirect measurement, which was based on calculating the instantaneous compliance of the specimen, it is also referred to as the effective crack velocity. Details of the testing methods can be found elsewhere.

RESULTS AND DISCUSSION

Three methods were used in this study to investigate the failure mechanisms of a CFCC. The first was investigation of the relationship between the subcritical crack growth rate and time during exposure to different combinations of temperature and atmosphere, measured on SENB specimens loaded in flexure. A second technique was comparison of the fracture toughness, calculated from the peak load of SENB specimens tested in flexure, after exposure to different combinations of temperature and atmosphere to the intrinsic fracture toughness of the same material. The third technique involved investigation of the fracture surfaces via SEM.

Intrinsic Fracture Behavior

The intrinsic fracture toughness of the CFCC was tested at 293, 1073, and 1373 K. At all three temperatures the fracture behavior was similar. The material behaved linearly elastic until failure. Despite the inability to support more than approximately 5% of the peak load after failure, the specimens remained intact and did not fail catastrophically. The toughness values calculated from the peak load were 17.5 ± 0.5, 17.3, and 17.1 MPa-m$^{1/2}$ at 293, 1073, and 1373 K, respectively. The fracture surfaces of these specimens were also similar. Extensive fiber pullout and fracture markings on many of the fibers were readily apparent (Fig. 3).
Identifying the Interface Recession Mechanism

Interface recession causes subcritical crack growth under conditions where oxidation removes the interphase faster than oxidation of the fibers or matrix. In previous studies with a CFCC reinforced by Hi-Nicalon fibers IRM was observed at 1373 K in an environment containing 0.2% of O₂ (by mass). Other experiments conducted previously indicated that, in inert environments, the CFCC reinforced by "Ceramic grade" fibers investigated in this study exhibited the same type of FRM subcritical crack growth as the material reinforced with Hi-Nicalon fibers. Therefore crack growth experiments were performed at 1373 K in an environment containing 0.2% of O₂ using the CFCC investigated in this study.

The subcritical crack growth rate of the specimen tested at 1373 K in an environment containing 2% of O₂ was significantly faster than that of the specimens tested in an inert environment (FRM conditions). The effective crack velocity initially decreased, but then it increased by several orders of magnitude (Fig. 4). The residual toughness of this specimen was 16.4 ± 0.5 MPa-m¹/², which was not significantly lower than the intrinsic toughness of the material measured at 1100°C in an inert atmosphere (<0.2% O₂), 17.1 ± 0.5 MPa-m¹/². Fiber pullout was visible on the fracture surfaces, but the pullout lengths were much less than those for the intrinsic fracture of the material (Fig. 5). Fracture markings were visible on some of the fibers. Although the interphase was too thin to be observed with the microscope used, there were no signs of an oxidation product anywhere on the fracture surface. Oxidation products were also absent from the fracture surfaces of the CFCC with Hi-Nicalon fibers tested under the same conditions. This surprising lack of evidence for fiber weakening or for bonding between the fiber and the matrix combined with accelerated crack growth in oxygen, relative to inert environments, lead to the hypothesis of the IRM mechanism. Comparison
between the activation energy for IRM type subcritical crack growth rates and the activation energy for interface recession support the hypothesis.

Identifying the Oxidation Embrittlement Mechanism

The formation of a brittle oxidation product between a crack-bridging fiber and the matrix prohibits the matrix from sliding along the fiber as the crack opening increases. In this case, as crack opening increases, due to crack propagation, the stress in the fiber increases until the fiber fails. Another possible result of oxygen ingress after interphase recession is the formation of a brittle oxidation product on fiber surfaces. If cracks occur in this oxidation product they may act as Griffith type flaws and lower the stress required for fiber failure. In either case, fiber failure reduces the crack bridging tractions and causes crack propagation., hence the rate of subcritical crack growth continuously increases as a function of time. An insufficient number of experiments has been performed to determine whether the rate of subcritical crack growth initially decreases with increasing normalized crack length for both IRM and OEM.

Several critical experiments were conducted on specimens that were loaded in flexure for approximately 2 hours at 1373 K in an environment containing 2% O₂. Although this IRM pretreatment complicated the analysis of the fracture surfaces it ensured that the crack length and bridging zone size in the specimens were similar. After such a pretreatment one specimen was unloaded, cooled to 1073 K, and exposed to an atmosphere of 50% oxygen for 60 minutes. After this oxidizing exposure, the specimen was loaded to fracture. The residual toughness of the treated specimen was 15 ± 0.5 MPa-m¹/² compared to 17.3 ± 0.5 MPa-m¹/², the intrinsic fracture of the material at 1073 K, and to 17.5 ± 0.5 MPa-m¹/² for the residual toughness at 1073 K for a specimen subject only to the IRM pretreatment.

The fracture surface of the sample treated under oxidizing conditions described above was examined (Fig. 6). The fracture surface was distinctly different from those observed for either intrinsic fracture (Fig. 3) or IRM (Fig. 5). Not only is there very little fiber pullout visible on the fracture surface, but the fibers and the matrix appear to have fractured on almost the same plane. This feature was also noted by other investigators who have examined OEM in more detail. Fracture markings were not visible on any of the fibers, but this may have been due to post-failure oxidation. Surprisingly there are no signs of oxidation products anywhere on the fracture surface.
Figure 6. The fracture surface of a specimen broken at 1073 K after oxidation with 50% O₂.

Figure 7. A Failure Mechanism Map for Nicalon Reinforced CFCCs.

Construction of a Failure Mechanism Map
Several other investigators have tested similar CFCC materials reinforced with Nicalon™ and have reported sufficient information to determine the failure mechanism. These results were combined with the results of this and previous studies in our laboratory (using a CFCC with Hi-Nicalon fibers and a 1-μm-thick carbon interphase) to construct a map describing the conditions under which each failure mechanism has been observed (Fig. 7). Since there are large ranges of values for which experiments have yet to be conducted this failure mechanism map is by no means definitive. This map serves as a basis for choosing critical experiments to determine with more certainty the conditions under which each mechanism operates. Although the failure mechanism map that is presented contains data gathered from slightly different materials, the relationships among the boundaries separating distinct failure mechanisms is expected to be similar for CFCCs with similar constituents.

On the failure mechanism map presented, the range of conditions for which interface recession, without signs of oxidation, was observed in TGA experiments is outlined via a dashed box. Within the range of conditions investigated by TGA data from critical experiments, using fast fracture tests or subcritical crack growth tests, are shown by solid symbols. A significant parameter in determining the precise location of a boundary between two failure mechanism may be the interphase thickness, assuming that similar interphase and matrix compositions have similar oxidation behavior. A thinner interphase will encourage
OEM at lower oxygen concentrations than a thicker interphase of the same composition in the same CFCC. In the failure mechanism map shown, it is not known whether IRM will occur at 1073 K above 1.2% O\textsubscript{2} for the material described in this study with the 1.5 x 10^{-2} m thick carbon interphase. In addition, subcritical crack growth at 1373 K and 0.2% O\textsubscript{2}, using the material described in this study, occurred by FRM. Further experiments will be conducted to determine the boundary conditions among the failure mechanisms observed.

SUMMARY AND CONCLUSIONS

Three techniques were developed to characterize the failure mechanisms of CFCCs under a range of environmental conditions: analysis of the dependence of the subcritical crack growth rate, measurement of residual toughness, and examination of fracture surfaces. FRM was characterized by a continuously decreasing subcritical crack growth rate and no change in residual toughness. IRM was characterized by an initially decreasing subcritical crack growth rate followed by a rapid rate of growth, no change in residual toughness, moderate amounts of fiber pullout, and clearly visible fracture markings on broken fibers. OEM was characterized by a rapid rate of subcritical crack growth, decreased residual toughness, and nearly flat fracture surfaces. A failure mechanism map was constructed that identifies conditions under which each mechanism has been observed.

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REFERENCES

HIGH TEMPERATURE OXIDATION AND CORROSION OF A POROUS Si$_2$N$_2$O-ZrO$_2$ COMPOSITE MATERIAL

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ABSTRACT

The paper presents results concerning the high temperature oxidation and corrosion of a porous Si$_2$N$_2$O-ZrO$_2$ ceramic composite material. It was found that for oxidation at temperatures up to 1100°C only Si$_2$N$_2$O is involved in the reaction, silica is formed and the weight gain obeys a parabolic law. At temperatures >1100°C divergence from pure parabolic regime increases with increasing temperature. At these temperatures SiO$_2$ and ZrO$_2$ start to form a protective zirconium containing silicate layer which inhibits the parabolic oxidation of Si$_2$N$_2$O. The formation of amorphous silica on Si$_2$N$_2$O was found to be faster than on Si. Pre-oxidation treatment at high temperatures significantly improves the oxidation resistance at lower temperatures. Water vapor was found to be a more aggressive oxidizing species than O$_2$ and can significantly enhance oxidation. Wet oxidation with or without salt has been found to enhance oxidation and corrosion at temperatures of ~1250°C. This effect is less profound at higher temperatures. The lowest weight gains have been observed at temperatures >1300°C which might be caused by the protecting effect of the formed zirconium silicate and cristobalite phases, their formation being promoted by the presence of water and salt vapor. At 1000°C oxidation always occurs at all surfaces, while at ≥1200°C, pore closure may or may not occur depending on the gaseous environment.
INTRODUCTION

Nitrogen ceramics have good oxidation, corrosion and thermal shock resistance. This makes them interesting for high temperature applications, where the ceramics are exposed to harsh environments, which may contain excess oxygen, water vapor and salt species. One possible source of component failure in these applications is oxidative/corrosive degradation at high temperatures. It is therefore of great importance to elucidate the oxidation/corrosion mechanism of these ceramics.

Si$_2$N$_2$O-ZrO$_2$, an inexpensive porous ceramic composite material, is a promising candidate for applications in oxidative and corrosive applications due to its good oxidation resistance at high temperatures. Previous study of the material [1-7] showed that the high temperature oxidation resistance of the composite strongly depends on the exposure temperature. This paper summarizes the results concerning the oxidation and corrosion mechanism of Si$_2$N$_2$O-ZrO$_2$ composite material. The high-temperature reactions between Si$_2$N$_2$O and SiO$_2$ and between SiO$_2$ and ZrO$_2$ are also investigated in order to study the relative significance and the role of each reaction.

EXPERIMENTAL

Materials

$Si_2N_2O-ZrO_2$ composite: The material examined in this work is a Si$_2$N$_2$O-ZrO$_2$ composite, fabricated by the nitrided, pressureless sintering technique (NPS) at the Swedish Ceramic Institute with Si and ZrSiO$_4$ as starting materials, according to Eqn (1) [8].

$$3 \text{Si} + \text{ZrSiO}_4 + 2 \text{N}_2 \rightarrow 2 \text{Si}_2\text{N}_2\text{O} + \tau - + m-\text{ZrO}_2$$

(t tetragonal, m monoclinic)

The nominal phase composition of the sintered material is 64 wt% Si$_2$N$_2$O and 36 wt% ZrO$_2$. A residual ZrSiO$_4$ phase in the sample has also been detected.

$Si_2N_2O$ ceramic: The Si$_2$N$_2$O ceramic used in this work was made from Si$_3$N$_4$ and SiO$_2$ powders, without any sintering aid. The material was cold isostatic pressed at 300 MPa and HIPed at 1900°C and 200 MPa for 4 h dwell time. The Si$_2$N$_2$O samples were fully dense. Further information can be found in Ref. [9].

$ZrO_2$ ceramic: ZrO$_2$ ceramic used in this work was Mg-PSZ obtained from Friatec AG, Germany. The material was isostatically pressed, the sample density was ≥5.7 g/cm$^3$, and no open porosity was measured. Samples were ground and polished to grit 4000. After cleaning, a film of highly pure SiO$_2$ was deposited on the surface using a box coater (AVAC) by means of an electron gun at a pressure of 1.3x10$^{-4}$ Pa. The thickness of the SiO$_2$ film was about 500 nm.
Oxidation/Corrosion exposure

Fig. 1 shows the set-up used for the oxidation and corrosion experiments. Samples were oxidized in an alumina tube (99.7% purity) in flowing dry oxygen (4x10^{-2} m/s). For the oxidation of Si,N,O and ZrO, coated with SiO, a high-purity quartz tube was placed as a shelter in the alumina tube in order to avoid any contamination by the alumina tube. The thickness of the formed silica layers was measured by spectroscopic ellipsometry.

Wet oxidation experiments were carried out in the same furnace connected to a steam generator. Oxygen was bubbled through boiling deionized water with a flow rate of 0.012 m/s. The saturated gas was passed through a mantle heater which was connected to a thermostat. The bath temperature was set corresponding to 10, 15 or 20 vol% H_2O. A salt aerosol generator [10] was used to generate a low salt flux in the exposure environment. By dispersing a solution into air and evaporating the solvent, an aerosol of the solute is formed. The aerosol passes from the generator to a diffusion drier. The salt particles were then directly introduced into the hot zone of the furnace so as to avoid any serious interaction with water vapor. The salt concentration in the hot zone was determined to be 25 ± 5 ppm (by volume). All samples were intermittently taken out from the furnace, air cooled and weighed.

The following environments have been investigated:

- a) O_2;
- b) O_2 + H_2O (10, 15, 20 vol%); and
- c) O_2 + NaCl (25 ± 5 ppm) + H_2O (10, 15, 20 vol%)

Phase analysis

X-Ray Diffraction (XRD): The phase composition was determined by XRD using an X-ray powder diffractometer (SIEMENS, D5000) equipped with a position-sensitive detector (PSD).

Transmission Electron Microscopy (TEM): The microstructure of as-received and oxidized samples was characterized by analytical transmission electron microscopy (TEM) in a JEOL 2000 FX TEM/STEM instrument, equipped with a Link System EDX 10.000 spectrometer. Thin sections of oxidized material for TEM analysis were taken from below the external oxide surface and were cut in the longitudinal direction, parallel to the oxide surface. Thinned TEM specimen were dimple ground followed by ion-beam thinning to perforation.

Spectroscopic Ellipsometry: The growth of the oxide film thickness was measured by spectroscopic ellipsometry. A spectroscopic ellipsometer (J.A. Woollam Co.) was used to measure film thicknesses in the wavelength range from 300 to 1000 nm at an angle of incidence of 70°. The error was estimated to be less than ± 10 nm.