CRADA Final Report
for
CRADA Number ORNL94-0287

ADVANCED CERAMICS FOR
LAND-BASED GAS TURBINE APPLICATIONS

J. H. Schneibel
Oak Ridge National Laboratory

E. Ludeman
S. M. Sabol
Westinghouse Power Generation

May 23, 1997

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In order to increase the efficiency of land-based gas turbines, inlet gas temperatures have to be increased, and the amount of air which cools the turbine vanes has to be reduced, to the maximum extent possible. Presently, thermal barrier coatings (TBC’s) are the state of the art in achieving these goals. However, since TBC’s are very thin (typically 100 µm), they have clearly limitations. Since all-ceramic turbine vanes would be a very large and risky development step, Westinghouse is considering to protect the leading edges of turbine vanes with high-performance ceramics. This might be done by either replacing the leading edge with a suitably shaped ceramic part, or by modifying the vanes such that they can accommodate ceramic inserts.

Among the most important criteria for the success of ceramics in such applications are (a) thermodynamic compatibility with the turbine vane alloy, (b) sufficient thermal shock resistance to survive the thermal cycling during operation and in particular during emergency shut-down, and (c) a design considering the thermal expansion mismatch of the metallic and ceramic components. Two of these issues were addressed in the present work:

(1) The thermodynamic compatibility of 6 high-performance ceramics (two silicon nitrides and four SiC whisker-reinforced aluminas) with the Co-base alloy ECY 768 was investigated both by thermodynamic calculations and by experiment. The microstructures of the interfacial reaction zones forming between 1173 and 1423 K were examined, and their thicknesses were measured as a function of time and temperature. Typically, (Cr,Co) carbosilicides formed in the reaction zone. Whereas Si₃N₄ formed a well-defined reaction zone in contact with the Co alloy, SiC whisker toughened Al₂O₃ formed multiple layers of reaction products. The reaction zone widths in this material tended to be erratic. The reaction zone growth in Si₃N₄/ECY 768 couples in vacuum, on the other hand, was well behaved and its kinetics could be well described by semi-empirical equations.

(2) In order to assess the thermal shock resistance of ceramics, Westinghouse provided ORNL with a fluidized bed capable of generating heat transfer coefficients high enough to simulate emergency shut-downs in land-based gas turbines. Six different types of advanced ceramics (two silicon nitrides, two SiC whisker-reinforced aluminas, one SiC particulate-reinforced alumina, and one continuous SiC fiber-reinforced alumina) were tested by quenching them up to 100 times from 1473 K into the previously calibrated fluidized bed. Residual strength measurements showed remarkable differences in the thermal shock capability of the different ceramics. Finite element calculations carried out at Westinghouse predicted the peak tensile stresses during quenching, and, together with microstructural information, predicted the experimentally found strength degradation very well. In particular, the edge-cracking of SiC₆/Al₂O₃ and the successive degradation of continuous SiC fiber-reinforced Al₂O₃ during thermal cycling could be readily understood.

The experimental and theoretical findings in this work form a basis for improved thermal barriers in land-based gas turbines. At the present time, however, there is no economic incentive to carry out the significant development work needed to use advanced ceramics in this application.
The Cyclic Thermal Shock Resistance of Several Advanced Ceramics and Ceramic Composites is Consistent with the Calculated Peak Tensile Stresses

Ceramic specimens were quenched 10 or 100 times from 1200°C (air) into a fluidized bed with a known heat transfer coefficient. Flexure strengths were determined and the results were compared to finite element calculations predicting the maximum tensile stresses caused by thermal shock.

Materials Investigated:
NT154: Si₃N₄ (Norton)
AS800: Si₃N₄ (Allied)
ARtuff CC5500: Al₂O₃-7.5 wt% SiCw, Adv. Comp. Corp.
ARtuff CC7000: Al₂O₃-25 wt% SiCw, Adv. Comp. Corp.
SiCp/Al₂O₃: Du Pont Lanxide
SiCf/Al₂O₃: Du Pont Lanxide

Predicted Peak Tensile Stresses:
Si₃N₄: 57 MPa
SiCp/Al₂O₃: 171 MPa
CC7000: 280 MPa
CC5500: 393 MPa

CRADA 94-0287 with Westinghouse Electric Corporation
The thermodynamics and kinetics of the reaction between ECY 768 and several advanced ceramics (two silicon nitrides and four $\text{Al}_2\text{O}_3/\text{SiC}_w$ ceramics with different $\text{SiC}_w$ contents) were investigated.

- The reaction layer thicknesses varied between 16 and 150 $\mu$m (after 1000 h at 1050°C).
- $\text{Si}_3\text{N}_4$ was more stable in contact with ECY 768 than SiC.
- The two figures illustrate the reaction between NT154 $\text{Si}_3\text{N}_4$ (Norton) and ECY 768.
ABSTRACT

CRADA 94-0287 with Westinghouse Electric Corporation
Advanced Ceramics for Land-Based Gas Turbine Applications

Principal Investigators:
Joachim H. Schneibel, ORNL; Steve M. Sabol, WPG; and Evan Ludeman, WPG

In order to increase the efficiency of land-based gas turbines, inlet gas temperatures have to be increased, and the amount of air which cools the turbine vanes has to be reduced, to the maximum extent possible. Presently, thermal barrier coatings (TBC's) are the state of the art in achieving these goals. However, since TBC's are very thin (typically 100 μm), they have clearly limitations. Since all-ceramic turbine vanes would be a very large and risky development step, Westinghouse is considering to protect the leading edges of turbine vanes with high-performance ceramics. This might be done by either replacing the leading edge with a suitably shaped ceramic part, or by modifying the vanes such that they can accommodate ceramic inserts.

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The experimental and theoretical findings in this work form a basis for improved thermal barriers in land-based gas turbines. At the present time, however, there is no economic incentive to carry out the significant development work needed to use advanced ceramics in this application.
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CRADA 94-0287 with Westinghouse Electric Corporation

Final Report for the Period September 6, 1994, to September 30, 1996

Principal Investigators:
Joachim H. Schneibel, ORNL, Evan Ludeman, WPG, and Steve M. Sabol, WPG

CRADA Objectives

In order to increase the efficiency of land-based gas turbines, inlet gas temperatures have to be increased, and the amount of air which cools the turbine vanes has to be reduced, to the maximum extent possible. Presently, thermal barrier coatings (TBC’s) are the state of the art in achieving these goals. However, since TBC’s are very thin (typically 100 μm), they have clearly limitations. Since all-ceramic turbine vanes would be a very large and risky development step, Westinghouse is considering partial use of ceramics. This might be done by either replacing the leading edge with a suitably shaped ceramic part, or by modifying the vanes such that they can accommodate ceramic inserts. Among the most important criteria for the success of ceramics in such applications are (a) thermodynamic compatibility with the turbine vane alloy, (b) sufficient thermal shock resistance to survive the thermal cycling during operation and in particular during emergency shut-down, and (c) a design considering the thermal expansion mismatch of the metallic and ceramic components. The objective of this CRADA was to address these three issues by both experimental and calculational means.

Meeting the CRADA Objectives

While the design aspect has been addressed only to a limited extent in this work, the thermodynamic compatibility and thermal shock issues have been studied in considerable detail. This work has been carried such that it should be useful to design engineers working with ceramics.

Benefits of the CRADA work

This work is unique in several aspects. First, cyclic thermal shock studies of advanced ceramics are generally not performed under well-controlled heat transfer conditions. Since the heat transfer coefficient was known in the present work, detailed finite element calculations using well-known input parameters could be carried out. The good agreement
between the thermal shock results and the calculations supports the reliability of such calculations. This will enable Westinghouse to screen future applications of ceramics computationally rather than experimentally. Therefore, the process of transferring ceramics into actual applications has become more efficient as a result of this work.

**Work accomplished in this CRADA**

**A. Thermodynamic Compatibility**

The thermodynamic compatibility of 6 high-performance ceramics (two silicon nitrides and four SiC whisker-reinforced aluminas) with the Co-base alloy ECY 768 was investigated both by thermodynamic calculations and by experiment. The microstructures of the interfacial reaction zones forming at temperatures between 1173 and 1423 K were determined, and the thicknesses of the reaction zones were measured as a function of time and temperature. Typically, (Cr,Co) carbosilicides formed in the reaction zone. Whereas Si3N4 formed a well-defined reaction zone in contact with ECY 768, SiC whisker-toughened Al2O3 formed multiple layers of reaction products. Also, the reaction zone widths tended to be erratic. The reaction zone growth in Si3N4/ECY 768 couples in vacuum, on the other hand, was well behaved and could be well described by semi-empirical relations. Detailed results on the thermodynamic compatibility issue are presented in the attached draft document entitled "On the High-Temperature Reactions between Advanced Ceramics and a Cobalt-Base Alloy." This document will be published in a refereed Journal.

**B. Thermal Shock Resistance**

In order to assess the thermal shock resistance of ceramics, Westinghouse provided ORNL with a fluidized bed capable of generating heat transfer coefficients high enough to simulate emergency shut-downs in land-based gas turbines. Six different types of advanced ceramics (two silicon nitrides, two SiC whisker-reinforced aluminas, one SiC particulate-reinforced alumina, and one continuous SiC fiber-reinforced alumina) were tested by quenching them up to 100 times from 1473 K into the previously calibrated fluidized bed. Remarkable differences were found in the thermal shock capability of the different ceramics. Finite element calculations carried out at Westinghouse predicted the peak tensile stresses during quenching, and, together with microstructural information, predicted the experimentally found degradation in the flexure strengths very well. In particular, the edge-cracking of SiCw/Al2O3 and the successive degradation of continuous SiC fiber-reinforced Al2O3 during thermal cycling can be readily understood. Detailed results are presented in the attached draft document entitled "Cyclic Thermal Shock Resistance of
Several Advanced Ceramics and Ceramic Composites." This document will be published in a refereed Journal.

C. Fabrication of Ceramic Inserts by Casting

An idea, which originated at Westinghouse Power Generation, and which was one of the initial motivations for this research, was to place ceramic inserts into a turbine vane mold and to cast an integral alloy-ceramic vane without the need for complicated fabrication procedures. Thermal shock due to the liquid metal impinging on the ceramic during casting was of course a concern. To assess this issue, ceramic pieces with typical sizes 10 x 10 x 3 mm were placed with their smallest side on the bottom of cylindrical 12.5 mm diameter copper chill molds. Pieces of the cobalt-base alloy ECY 768 were arc-melted and dropped onto the ceramic pieces. Due to the high rate of solidification, the filling between the ceramic pieces and the walls of the copper chill mold was usually incomplete. Metallographic cross sections showed that Si₃N₄ survived this experiment reasonably well, with only one crack observed. SiC and Al₂O₃, on the other hand, showed multiple cracks. Due to the rapid cooling of the melt, no reaction with the ceramics was observed.

Table I

<table>
<thead>
<tr>
<th>Log No.</th>
<th>Ceramic</th>
<th>Experimental Details and Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>Si₃N₄</td>
<td>Cobalt alloy ECY 768 drop-cast onto NT154 Si₃N₄ (#188). No visible reaction; the Si₃N₄ had one crack</td>
</tr>
<tr>
<td>194</td>
<td>Co-SiC</td>
<td>Cobalt alloy ECY 768 drop-cast onto piece of Hexoloy SiC. No visible reaction; the SiC had many cracks.</td>
</tr>
<tr>
<td>195</td>
<td>Co-Al₂O₃</td>
<td>Cobalt alloy ECY 768 drop-cast onto piece of AD998 Al₂O₃. The Al₂O₃ had many cracks.</td>
</tr>
</tbody>
</table>

In additional experiments, pieces of the cobalt-base alloy ECY 768 were placed on ceramic pieces (approximately 10 x 10 x 3 mm) previously placed in an Al₂O₃ crucible. After evacuation, the crucible and its contents were heated up to 1450°C over a period of 1.5 hours, held for 6 minutes at this temperature, and then ramped down to room temperature. Table II summarizes the results of this work.
Table II

Response to Prolonged Contact Between Cobalt Melt and Ceramics

<table>
<thead>
<tr>
<th>Log No.</th>
<th>Ceramic</th>
<th>Experimental Findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>197</td>
<td>Si₃N₄</td>
<td>The NT154 Si₃N₄ piece was thrown out of the crucible, presumably due to the vigorous reaction resulting in nitrogen evolution.</td>
</tr>
<tr>
<td>198</td>
<td>Al₂O₃</td>
<td>The AD998 Al₂O₃ was not wetted very well by the cobalt alloy, but it was bonded to the alloy. Several cracks formed in the Al₂O₃, presumably due to thermal expansion mismatch during cool-down.</td>
</tr>
</tbody>
</table>

After these preliminary experiments, the casting approach to fabricating vanes with ceramic inserts was not further pursued.

D. Thermal Barrier Capabilities

A typical ECY 768 vane was assumed to have a 3 mm thick leading edge of Si₃N₄ or whisker-reinforced Al₂O₃, respectively. Finite element calculations were carried out for typical conditions in a land-based gas turbine in order to assess the thermal barrier capabilities of the inserts. The results of this calculation are presented in Table III. For comparison, a typical stabilized zirconia coating is about 100 μm thick and provides a temperature drop of 50°C. Due to its high thermal conductivity, the Si₃N₄ is only a modest thermal barrier. The SiC/Al₂O₃, on the other hand, is an effective thermal barrier. The low thermal conductivity of this material is however associated with a relatively high surface temperature of the insert.

Table III.

Thermal Barrier Capability of 3 mm thick Insert Materials

<table>
<thead>
<tr>
<th>Insert Material</th>
<th>Surface Temperature of Insert, °C</th>
<th>Metal/Ceramic Interface Temperature, °C</th>
<th>Temperature Difference, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄</td>
<td>1020°C</td>
<td>960°C</td>
<td>60°C</td>
</tr>
<tr>
<td>SiC/Al₂O₃</td>
<td>1130°C</td>
<td>820°C</td>
<td>310°C</td>
</tr>
</tbody>
</table>
E. Inventions

No inventions were made during this CRADA work.

F. Commercialization Possibilities

A cost-benefit analysis was carried out for a 1150°C class engine. The savings in cooling air were calculated to be 6 lbs/s and resulted in an increase in power of 0.1% and a fuel saving of 0.1%. Utility cost models were used to estimate the net present value of these enhancements to be $140K. Exclusive of development costs, production of vanes with ceramic inserts was estimated at $4,000/vane or about $200K per engine. This additional cost furthermore covers only the vanes shipped with the engine. Over the life of the engine at least one replacement of these components is anticipated. Additionally, the trend in high-performance land-based engines is toward exceedingly high gas temperatures (1350-1600°C), whereas current engineering ceramics are limited to 1100°C for long-term applications. At the present time, there is therefore no economic incentive for further development of the proposed concept.

G. Future Collaboration

There are no immediate plans for future collaboration.

Conclusions

The concept of vanes containing ceramic inserts, which prompted this research, has been shown to have only marginal viability at the present time. However, this scenario may change if fuel prices rise, and/or if the cost of advanced ceramic components decreases. Our research has focused primarily on two issues, namely, thermodynamic compatibility between advanced ceramics and a cobalt-base alloy, and on the thermal shock resistance of advanced ceramics under well-defined quenching conditions. Both of these issues have been explored in considerable detail, and are likely to be of importance in most hot-section applications of advanced ceramics in land-based turbines. This research forms therefore a basis for future designs involving advanced ceramics in land-based turbines.
On the High-Temperature Reactions between Advanced Ceramics and a Cobalt-Base alloy

Joachim H. Schneibel*, Stephen M. Sabol†, and Deborah L. Joslin*

* Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, TN 37831

† Westinghouse Power Generation
4400 Alafaya Trail MC 303
Orlando, FL 32826-2399

Abstract

The incorporation of advanced ceramics or ceramic composites into land-based turbines may potentially increase their efficiency due to increased gas inlet temperatures and/or reduced cooling requirements. In some proposed designs, incorporation of ceramics would require intimate contact of the ceramic and a metallic structure at elevated temperatures. Since many advanced ceramics contain Si, and since turbines are usually constructed out of Ni or Co-base alloys, the formation of Co or Ni silicides is expected at the ceramic/metalllic interfaces. The goal of the present work is (a) an assessment of the microstructures and reaction products formed at ceramic/metalllic interfaces during annealing at elevated temperatures and (b) a description of the kinetics of the reaction zone formation. Reaction couples consisting of the Co-base alloy E-CY 768 and various advanced ceramics were prepared by hot-pressing in vacuum and subsequent annealing in vacuum or air at temperatures ranging from 1173 to 1323 K and for times ranging between
10 and 1000 h. Two types of silicon nitride (NT154 and AS800) and four whisker-reinforced aluminas containing different weight fractions of SiC whiskers (ARtuff CC5500, S7, SX, and CC7000) were investigated. The reaction zones consisted primarily of (Cr,Co) carbosilicides. The maximum reaction zone thicknesses after 1000 h at 1323 K were in most cases below 50 µm. Whereas the reaction zones were well defined in the case of the silicon nitrides, the Al₂O₃/SiC₆ materials developed multiple silicide layers within the reaction zone. With increasing SiC whisker content, the reaction zones increased in thickness for a given heat treatment. A non-linear fitting procedure was employed to describe the reaction zone thicknesses in terms of apparent activation energies and preexponential factors. Whereas this procedure worked well for the silicon nitrides annealed in vacuum, substantial scatter occurred for anneals carried out in air. The ARtuff materials showed always substantial scatter which is rationalized in terms of their layered reaction microstructure leading to erratic behavior.

I. Introduction

In order to introduce advanced ceramics into land-based gas turbines for power generation, several criteria such as, for example, adequate strength, fracture toughness, thermal shock resistance, and resistance against oxidation and hot corrosion have to be met. Another issue, which may be of importance, is the thermodynamic compatibility between the ceramics and the metallic alloys used in the construction of the turbines. If ceramic/metallic interfaces are exposed to elevated temperatures, reaction products may form and jeopardize the mechanical integrity of the interfaces, even if the mating parts are not bonded, but only mechanically interlocked. Since most advanced ceramics contain significant amounts of Si, reactions with transition elements such as Co and Ni are expected. In this study, we examine the reactions occurring between the Co-base alloy E-CY 768, which is a common high-temperature structural alloy used in land-based turbines, and several advanced ceramics. As representative ceramics we chose two types of silicon
nitride (NT154 and AS800) and four Al2O3/SiCw ceramics with SiC whisker contents ranging from 7.5 to 25 wt%. E-CY 768/ceramic reaction couples were fabricated by hot-pressing, and annealed at temperatures ranging from 1173 to 1323 K for times ranging from 10 to 1000 h. Subsequently, the reaction couples were examined to determine the microstructure, composition, and width of the reaction zones formed during the annealing.

II. Experimental Procedure

Table I shows the composition of the Co-base alloy E-CY 768, and Table II summarizes pertinent information about the investigated ceramics and composites. The NT154 was fabricated by hot isostatic pressing (HIP), whereas the AS800, which contained rare earth sintering aids, was processed by slip-casting and gas pressure sintering (sinter-HIP, i.e. pressures typically ≤ 10 MPa), and was reinforced in-situ with acicular β-

Si3N4 grains [Gasdaska, 1994]. The ARtuff materials CC5500, S7, and SX were sintered and HIPed, whereas the ARtuff CC7000 was hot-pressed.

The ceramic materials were machined into 1×3×10 mm slabs, which were placed into a E-CY 768 slab containing a channel. This assembly was closed at the top with an E-CY 768 cap, as illustrated in Fig. 1, and hot-pressed in vacuum (appr. 10⁻³ Pa). Several preliminary runs showed 1373 K/100 MPa/600 s to be suitable conditions which resulted in complete bonding of the assembly while at the same time minimizing the creep flow of the cobalt alloy. The coupons prepared in this manner were then sliced into 1 mm thick slices, each of which contained a 1×3 mm section of ceramic in its center. The slices were subsequently annealed at temperatures ranging from 1173 to 1323 K and for times ranging from 10 to 1000 hours in vacuum or in air, respectively. The vacuum anneals were either carried out in evacuated quartz capsules or in dynamic vacuum at pressures of 10⁻⁴ - 10⁻³ Pa.

Following the heat treatment, the specimen slices were ground and polished using standard metallographic techniques, and examined by optical and scanning electron
microscopy (SEM), as well as energy dispersive and wave length dispersive microprobe analysis of carbon-coated specimens. Carbon was usually not analyzed directly, but instead indirectly by forming the difference between 100% and the sum of the weight percentages of the remaining elements in the material. The accuracy of the carbon analysis was approximately ±2 wt%. The widths of the reaction zones were estimated by optical metallography in order to describe the reaction kinetics. Limited thermodynamic analysis was carried out using the code ThermoCalc®.

III. Results and Discussion

(1) Thermodynamical Considerations

It is well known that Si$_3$N$_4$ and SiC are thermodynamically not stable in contact with most metals at elevated temperatures. In our case, reactions with the major elements in E-CY 768, namely, Co and Cr, are of particular interest. Weitzer et al. [Weitzer et al., 1987] and Schuster et al. [Schuster et al., 1988] carried out numerous experiments exploring the reactions occurring between Si$_3$N$_4$ and many metals. Turning to cobalt first: after 170 h at 1273 K in vacuum, Si$_3$N$_4$ was found to co-exist with Co, Co$_2$Si, CoSi, or CoSi$_2$. The onset of a major reaction between Si$_3$N$_4$ and Co was found by plotting the logarithm of the pressure in the vacuum system vs. the temperature and by identifying the reaction temperature as that for which the pressure increased substantially due to nitrogen evolution. This reaction temperature was found to be 1423 K, and the reaction products were Co, Co$_2$Si, and N$_2$. For comparison, ThermoCalc® calculations predicted a reaction temperature of 1441 K and the reaction products Co, CoSi, and N$_2$. On the other hand, Co plated Si$_3$N$_4$ films on single crystal silicon studied by Nguyen et al. [Nguyen et al., 1993] show that even at temperatures as low as 873 K copious amounts of nitrogen evolve due to the reaction between Co and Si$_3$N$_4$. In addition to CoSi$_2$, some CoN was also found in that work. There is thus considerable uncertainty with respect to the reaction products, but
it is clearly expected that the Si$_3$N$_4$ materials investigated in our research will react with the E-CY 768 alloy.

E-CY 768 contains not only Co, but also substantial concentrations of Cr, which is also a silicide former. In the Si-N-Cr system, Schuster et al. [Schuster et al., 1988] find, after annealing for 170 h at 1273 K, the phases Cr$_3$Si, Cr$_5$Si$_3$, CrSi, and CrSi$_2$. Pearson's handbook on intermetallic compounds [Villars et al., 1985] lists several mixed Co-Cr silicides such as Co$_x$Cr$_{1-x}$Si ($x=0-1$), (Co,Cr)$_2$Si, Co$_3$Cr$_3$Si$_2$, Co$_5$Cr$_3$Si$_2$, and Co$_3$Cr$_5$Si$_2$. In the reaction zone of Si$_3$N$_4$ in contact with E-CY 768, the formation of mixed (Co,Cr) silicides is thus likely. The question is primarily how fast the reaction will proceed, and also to what extent the other alloying additions in E-CY 768 participate in the reaction.

The ARtuff materials contain different volume fractions of SiC whiskers. While the Al$_2$O$_3$ matrix is not expected to react with the E-CY 768, the SiC whiskers will. Our thermodynamic calculations suggest the formation of C and CoSi, when SiC and Co are in contact at temperatures as low as 773 K. Because of the availability of carbon, phases listed by Villars et al. [Villars et al., 1985] such as (Cr$_5$Si$_3$)$_{1-x}$C$_x$ ($x=0-0.1$) might also form. Chou et al. [Chou et al., 1991] examined the reaction zone formed between SiC and Co after 6 h at 1373 K. An approximately 60 μm wide reaction zone of Co$_2$Si formed. Near the boundary between the reaction zone and the cobalt Kirkendall voids and carbon precipitates were formed. We expect therefore in our experiments the ARtuff materials to react with the E-CY 768 unless the SiC whiskers are completely encapsulated by Al$_2$O$_3$ and therefore not able to react with the alloy.

The above reactions all assumed the absence of oxygen. In the presence of oxygen, SiO$_2$ may form on the Si$_3$N$_4$ or the SiC surfaces. The E-CY 768, in turn, may form a thin layer of Cr$_2$O$_3$. Table III lists some possible reactions as well as the temperatures at which these reactions will occur. Table III suggests that oxide formation on the Si$_3$N$_4$ and the E-CY 768 might inhibit the reactions between Si$_3$N$_4$ or SiC and Co.
(2) Microstructure and Chemical Composition of the Reaction Zones

Figure 2 (a) shows an SEM micrograph of a cross section through an E-CY 768/NT154 reaction couple. The reaction zone with a width of approximately 8 µm is indicated. The dark features between the main reaction zone and the E-CY 768 alloy are thought to be voids. The bright particles adjacent to the voids have the approximate composition 35 Ta-11 Co-8 Cr-5 Ti-13 Si-28 Co (at. %). Villars et al. [Villars et al., 1985] list a Ta₅Si₃C₀.₄₋₀.₆ phase, which contains more Si and less C than the phase found here. In analogy to the known Ti₃SiC₂ phase, the bright particles may very well be related to Ta₃SiC₂.

Figure 2 (b) shows EDS traces for the major elements perpendicular to the reaction zone. Most of the reaction zone consists of a (Cr,Co) silicide, which contains also some carbon (since the cumulative concentration is below 100%). The Cr concentration is higher, and the Co concentration lower than that in the E-CY 768 matrix. The high Cr concentration in the reaction zone is accompanied by Cr depletion at the interface between the E-CY 768 and the main reaction zone [i.e., at a distance of 6 µm in Fig. 2(b)]. This depletion indicates a large driving force for the reaction of the Cr with the Si in the Si₃N₄. Assuming the difference between the cumulative concentration and 100 wt% to be due to carbon, the approximate composition of the reaction zone is 13 Co - 44 Cr - 2 Ni - 15 Si - 26 C (at. %). A precise match with the compounds listed in the previous section is not possible without additional work. Also, the composition found is different from those of the listed compounds. All that can be said is that the reaction zone appears to be a (Cr,Co) carbosilicide, with a composition related to (Cr,Co)₃SiC₂.

Figure 3 (a) shows a cross section through a E-CY 768/AS800 reaction couple. The reaction zone contains significant levels of porosity. The EDS profile for the major elements [Fig. 3 (b)] is similar to that for E-CY 768/NT154. Again, the Cr concentration in the reaction zone is higher than that in the matrix. Both the Co and the Cr concentrations
are particularly low in the region between the E-CY 768 and the reaction zone, indicating again the high driving force for Co and Cr silicide formation.

The reaction zones between the E-CY 768 and the ARtuff materials are very different from those for the E-CY 768/Si₃N₄ couples. The SEM micrograph in Fig. 4 shows their most characteristic feature: a gray layered structure parallel to the reaction front. Occasionally, the gray phase penetrates into the CC7000 material in a direction perpendicular to the interface (arrow in Fig. 4). The most important phases in an E-CY 768/CC7000 reaction couple are indicated in the SEM micrograph in Fig. 5, and the concentrations of the major elements contained in these phases are summarized in Table IV.

The reaction product in the Al₂O₃/SiCₜ precipitate 1 contains substantial amounts of silicon and carbon. Its composition is similar to that of the E-CY 768/Si₃N₄ reaction zones; it is essentially a (Cr,Co) carbosilicide. However, it contains also some oxygen. The presence of Co and Cr in this carbosilicide indicates the diffusion of those elements from the Co alloy into the SiCₜ/Al₂O₃. Similar to the reaction zones in Si₃N₄/E-CY 768, the Cr content is significantly higher than the Co content. This indicates a higher driving force for the reaction of Cr with SiC, as compared to Co. In the E-CY 768 matrix we find (Co,Cr) carbides (precipitate 2) and TaC with some of the Ta replaced by Ti, Co, and Cr (precipitate 3). Precipitates 2 and 3 did however not contain any Si and are therefore representative of the E-CY 768 matrix.

The CC5500 material contains much less SiC than the CC7000, namely, 9 vol. %. This would suggest that the SiC whiskers are separated from each other by the Al₂O₃ matrix, and that the reaction between the E-CY 768 and the CC5500 should be inhibited. However, the CC5500 forms a layer structure similar to that of CC7000. A possible mechanism for the formation of the layered structure is as follows: the SiC whiskers intersecting the surface of the CC5500 react mainly with the Cr and Co in the E-CY 768 to form carbosilicides. This reaction is associated with a volume expansion. In our diffusion couples, the constraint in the direction perpendicular to the reaction interface is much
smaller than in a direction parallel to the interface. The volume expansion is therefore most readily accommodated in a direction perpendicular to the interface. This leads to cracks parallel to the interface, along which further diffusion of Si and reaction with the SiC whiskers occurs. This simple picture helps also to explain why the reaction occurs even for low SiC volume fractions, where the SiC whiskers are not likely to be in contact. Another factor in the formation of the layered morphology is the formation of similar microstructures in reactions between monolithic SiC and transition elements such as Ni, as reported by Backhaus-Ricoult and Chou et al. [Backhaus-Ricoult, 1989; Chou et al., 1991]. Chou attributed the formation of multilayers to discontinuous decomposition of the SiC in contact with Ni.

(3) Kinetics of Reaction Zone Formation

Table V summarizes all the heat treatments, carried out either in vacuum or in air, to study the kinetics of the reaction zone formation. The thickness of the reaction zones was estimated from optical microscopy observations. These measurements required some judgment. As an illustration, the widths of the reaction zones as they were measured are indicated in Figs. 2-4. In the case of the Al₂O₃/SiC₟ materials, the long reaction paths perpendicular to the interface were ignored in the measurement. For these materials, there was considerable scatter of the reaction zone widths even within one and the same specimen. The width measurements refer to the maximum widths found in each specimen. For reference, Table VI lists the maximum widths found for the specimens annealed in air or vacuum, respectively. It should be noted that due to scatter, the maximum reaction zone width for a material was not always observed at the highest temperature and longest annealing time. Table VI shows a trend for increasing reaction zone widths with increasing SiC₟ volume fraction. This is not surprising since the likelihood that SiC whiskers are in contact with each other and provide easy reaction paths increases with the SiC volume fraction. Except for one case, the reaction zones formed in air tend to be smaller than, or
equal to, the corresponding zones in vacuum. This may be related to the inhibiting effect of oxide layers formed at the interfaces during annealing in air.

In an attempt to describe the data more quantitatively, we assumed that, for a given temperature, the thickness of a reaction zone was proportional to the square root of the annealing time. According to Backhaus-Ricoult's data [Backhaus-Ricoult, 1989] for SiC-Ni, this seems reasonable. We assumed also that the temperature dependence of the reaction zone thickness could be described by an Arrhenius function. The initial specimen preparation involved pressing at a high temperature of 1373 K, albeit for a short time. Fitting the reaction zone thicknesses at a lower annealing temperature (for example 1273 K) to a $t^{1/2}$ relationship requires knowledge of the time (at 1273 K) that would be required to generate the same reaction zone thickness as the specimen preparation at 1373 K. For a given annealing temperature $T$ we assume that the reaction zone thickness $d_0$ following immediately the specimen preparation by hot-pressing is given by:

$$d_0 = A \times t_0^{1/2} \times \exp(-\frac{Q}{RT}), \quad \text{(1)}$$

where $A$ is a constant, $Q$ the apparent activation energy for the growth of the reaction zone and $t_0$ the time in hours required to reach the thickness $d_0$.

The reaction zone thickness for annealing a time $t$ following the hot-pressing is then given by:

$$d = A \times (t + t_0)^{1/2} \times \exp(-\frac{Q}{RT}), \quad \text{(2)}$$

Solving eqn. (1) for $t_0$ and inserting into eqn. (2) results in:

$$d = A \times \left[t + A^{-2} \times d_0^2 \times \exp\left(\frac{2Q}{RT}\right)\right]^{1/2} \exp\left(-\frac{Q}{RT}\right).$$

\[21\]
By varying the parameters $A$, $d_0$, and $Q$ such as to minimize the sum of the squared thickness deviations, eqn. (3) was fitted to the experimental data. If the fit to the data resulted in a negative value for $d_0$, $d_0$ was assumed to be zero.

Figure 6 shows an example of such a multivariable least squares fit for the NT154 material. Table VII summarizes the values of the fitting parameters and the regression coefficients for a linear fit through the data points in Fig. 6. Inspection of Table VII shows several trends. First, the apparent activation energies for the two silicon nitrides NT154 and AS800 annealed in vacuum are similar and the regression coefficients are close to one, indicating a good fit. When the silicon nitride/E-CY 768 couples are annealed in air, the quality of the fit decreases dramatically. The (apparent) activation energy of the NT154 in air is only one half of that obtained in vacuum. The data for the AS800 in air is in fact completely meaningless. The pronounced influence of air vs. vacuum annealing may be due to oxidation. Oxidation would result in local volume expansion at the interfaces. It might in this way lead to an inhibition of the interfacial reactions either directly by separating the $\text{Si}_3\text{N}_4$ from the E-CY 768 by oxide layers (see Table III), or by inducing microcracks along the interface. Both of these processes might reduce the reaction between $\text{Si}_3\text{N}_4$ and E-CY 768 in a stochastic manner.

The data for the ARtuff materials shows even more scatter than that for the silicon nitrides. No systematic difference for vacuum anneals vs. air anneals could be found. If only those data with a regression coefficient in excess of 0.8 is considered, then the apparent activation energies vary somewhere between 95 and 160 kJ/mol, considerably lower values than those for the silicon nitrides. In view of the complicated geometry of the reaction zones of the ARtuff materials the scatter in the data is not too surprising. Nevertheless, the data provide an estimate of the extent of the reactions, and rough estimates of expected reaction zone thicknesses may be made using Table VII and eqn. (1) (with the zeros dropped and $t$ in hours). These estimates may help determine whether the extent of the interfacial reaction may be tolerated in a particular application. For more
critical applications, future work should consider preoxidized ceramic and E-CY 768 surfaces in order to reduce the extent of the reactions.

V. Summary and Conclusions

We have examined the reaction products and reaction kinetics for several advanced ceramics in contact with the cobalt-base alloy E-CY 768 at elevated temperatures ranging from 1173 to 1323 K. Since all investigated ceramics contained silicon, interfacial reactions were expected. In the case of Si\textsubscript{3}N\textsubscript{4}, the reaction zones contained (Cr,Co) carbo silicides, with the Cr concentration being much higher than that in the Co alloy matrix. For annealing in vacuum, consistent trends in the reaction zone growth were found. The vacuum data for Si\textsubscript{3}N\textsubscript{4} could be fitted to a simple analytical function describing the time and temperature dependence of the reaction zone growth. This fit is useful for estimating the extent of interfacial reactions in particular service profiles. Air annealing, on the other hand, led to significant scatter, possibly due to oxidation. The reaction zones of the Al\textsubscript{2}O\textsubscript{3}/SiC\textsubscript{w} ceramics exhibited a distinct layered structure consisting of (Cr,Co) carbo silicides. Even for small SiC\textsubscript{w} contents such as 9 vol.\%, the reaction could not be avoided. The widths of the reaction zones showed erratic behavior and, except for the effect of the SiC\textsubscript{w} volume fraction, no systematic trends could be discerned. It is conceivable that the reactions can be inhibited or alleviated by preoxidizing the mating ceramic and E-CY 768 surfaces.

Acknowledgments

We would like to thank Eric Bright from Norton Advanced Ceramics for providing the NT154 silicon nitride for this research. The technical assistance of C. A. Carmichael in many parts of this work is appreciated. This work was supported by a Cooperative Research and Development Agreement with Westinghouse Electric Corporation, sponsored by the U.S. Department of Energy, Office of Energy Research, Laboratory Technology...
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Table I. Composition of E-CY 768

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>W</th>
<th>Ta</th>
<th>C</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min., wt%</td>
<td>22.5</td>
<td>9.0</td>
<td>0.15</td>
<td>6.5</td>
<td>3.0</td>
<td>0.55</td>
<td>0.10</td>
<td></td>
<td></td>
<td>Bal.</td>
</tr>
<tr>
<td>Max., wt%</td>
<td>24.25</td>
<td>11.0</td>
<td>0.30</td>
<td>7.5</td>
<td>4.0</td>
<td>0.65</td>
<td>0.25</td>
<td>1.50</td>
<td>0.4</td>
<td>Bal.</td>
</tr>
<tr>
<td>Average, at.%</td>
<td>26.3</td>
<td>10.1</td>
<td>0.3</td>
<td>2.3</td>
<td>1.1</td>
<td>3.0</td>
<td>0.4</td>
<td>1.6</td>
<td>0.8</td>
<td>54.1</td>
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Table II. Investigated Ceramics and Ceramic Composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Nominal SiC&lt;sub&gt;W&lt;/sub&gt; Content,</th>
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<tr>
<td></td>
<td></td>
<td>wt%</td>
</tr>
<tr>
<td>NT154 Si&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Norton Advanced Ceramics</td>
<td></td>
</tr>
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<td>AS800 Si&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Allied Signal Aerospace</td>
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<td>ARtuff CC5500</td>
<td>Advanced Composite Materials Corp.</td>
<td>7.5</td>
</tr>
<tr>
<td>ARtuff S7</td>
<td></td>
<td>15</td>
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<tr>
<td>ARtuff SX</td>
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<td>20</td>
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<tr>
<td>ARtuff CC7000</td>
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<td>25</td>
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Table III. Reactions between Si₃N₄, SiO₂, and Cr₂O₃ predicted by ThermoCalc

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Reaction Products</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co + SiO₂</td>
<td>Co, SiO₂</td>
<td>≤1600 K</td>
</tr>
<tr>
<td>Cr₂O₃ + Si₃N₄</td>
<td>N₂, Cr, Si₃N₄, SiO₂</td>
<td>1400 K</td>
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<tr>
<td>Cr₂O₃ + Si₃N₄</td>
<td>N₂, Cr₃Si, Si₃N₄, SiO₂</td>
<td>1500 K</td>
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<tr>
<td>Cr₂O₃ + Si₃N₄</td>
<td>N₂, Cr₅Si₃, Si₃N₄, SiO₂</td>
<td>1800 K</td>
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<tr>
<td>SiO₂ + Cr₂O₃</td>
<td>SiO₂, Cr₂O₃</td>
<td>2000 K*</td>
</tr>
</tbody>
</table>

*SiO₂ and Cr₂O₃ are stable up to 1996 K according to Fig. 332 in "Phase Diagrams for Ceramists" [Levin et al., 1964]

Table IV. Typical Compositions (at. %) in E-CY 768/ARtuff CC7000 Reaction Couple (100h/1323 K/Vac)

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Ti</th>
<th>Co</th>
<th>Cr</th>
<th>Ni</th>
<th>W</th>
<th>Ta</th>
<th>Si</th>
<th>C</th>
<th>O</th>
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<td>1</td>
<td>0.2</td>
<td>20.3</td>
<td>37.1</td>
<td>4.8</td>
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<td>12.9</td>
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<tr>
<td>2</td>
<td>0.3</td>
<td>24.7</td>
<td>26.4</td>
<td>5.9</td>
<td>13.2</td>
<td>2.4</td>
<td>0.16</td>
<td>20.8</td>
<td>6.1</td>
</tr>
<tr>
<td>3</td>
<td>6.2</td>
<td>5.5</td>
<td>3.8</td>
<td>0.7</td>
<td>0</td>
<td>30.0</td>
<td>0.15</td>
<td>53.6</td>
<td>0</td>
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Table V. Annealing Schedule

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<tr>
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<th>1173 K</th>
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<th>1323 K</th>
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<tr>
<td>10 h</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>100 h</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>1000 h</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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Table VI. Maximum Reaction Zone Widths observed in Vacuum and in Air

<table>
<thead>
<tr>
<th>SiC Content, vol.%</th>
<th>Vacuum Anneal</th>
<th>Air Anneal</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Anneal</td>
<td>$d_{\text{max}}$, $\mu$m</td>
</tr>
<tr>
<td>NT154</td>
<td>1323 K/1000h</td>
<td>50</td>
</tr>
<tr>
<td>AS800</td>
<td>1323 K/1000h</td>
<td>45</td>
</tr>
<tr>
<td>ARtuff CC5500</td>
<td>9</td>
<td>1273 K/1000h</td>
</tr>
<tr>
<td>ARtuff S7</td>
<td>18</td>
<td>1323 K/1000h</td>
</tr>
<tr>
<td>ARtuff SX</td>
<td>24</td>
<td>1273 K/1000h</td>
</tr>
<tr>
<td>ARtuff CC7000</td>
<td>29</td>
<td>1323 K/1000h</td>
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Table VII. Regression Analysis of Reaction Zones

<table>
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<tr>
<th>Environment</th>
<th>$d_0$, µm</th>
<th>$A$, µm</th>
<th>$Q$, kJ/mol</th>
<th>Regression Coefficient</th>
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</thead>
<tbody>
<tr>
<td>NT154 Vac</td>
<td>0</td>
<td>$4 \times 10^{10}$</td>
<td>263</td>
<td>0.97</td>
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<tr>
<td>NT154 Air</td>
<td>4.6</td>
<td>15800</td>
<td>110</td>
<td>0.82</td>
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<tr>
<td>AS800 Vac</td>
<td>0</td>
<td>$6.7 \times 10^{11}$</td>
<td>296</td>
<td>0.98</td>
</tr>
<tr>
<td>AS800 Air</td>
<td>0</td>
<td>0.34</td>
<td>2.5</td>
<td>0.05</td>
</tr>
<tr>
<td>ARtuff CC5500 Vac</td>
<td>5</td>
<td>7.6</td>
<td>31</td>
<td>0.72</td>
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<tr>
<td>ARtuff CC5500 Air</td>
<td>6</td>
<td>$6.5 \times 10^{5}$</td>
<td>145</td>
<td>0.99</td>
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<tr>
<td>ARtuff S7 Vac</td>
<td>15</td>
<td>6950</td>
<td>91</td>
<td>0.93</td>
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<tr>
<td>ARtuff S7 Air</td>
<td>12</td>
<td>73000</td>
<td>119</td>
<td>0.9</td>
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<tr>
<td>ARtuff SX Vac</td>
<td>2</td>
<td>11500</td>
<td>96</td>
<td>0.84</td>
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<tr>
<td>ARtuff SX Air</td>
<td>13</td>
<td>100</td>
<td>49</td>
<td>0.71</td>
</tr>
<tr>
<td>ARtuff CC7000 Vac</td>
<td>19</td>
<td>53000</td>
<td>110</td>
<td>0.86</td>
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<tr>
<td>ARtuff CC7000 Air</td>
<td>21</td>
<td>$8.6 \times 10^{6}$</td>
<td>160</td>
<td>0.89</td>
</tr>
</tbody>
</table>
Figure Captions

**Fig. 1.** Geometry of reaction couples

**Fig. 2.** Reaction zone between E-CY 768 and NT154 after 100 h at 1323 K in vacuum: (a) backscattered SEM image of section and (b) elemental concentrations across the reaction zone.

**Fig. 3.** Reaction zone between E-CY 768 and AS800 after 100 h at 1323 K in vacuum: (a) backscattered SEM image of section and (b) elemental concentrations across the reaction zone.

**Fig. 4.** SEM micrograph of cross section through E-CY 768/CC7000 reaction couple (100 h/1323 K/Vac).

**Fig. 5.** SEM micrograph depicting the different phases in a E-CY 768/CC7000 couple after 100 h at 1323 K in vacuum (see also Table IV)

**Fig. 6.** Fitted vs. measured reaction zone widths for E-CY 768/NT154 couples annealed in vacuum.
Figure 1
Figure 2 (a)
Figure 2 (b)
Fig. 3 (b)
Figure 5
Figure 6
Cyclic Thermal Shock Resistance of Several Advanced Ceramics and Ceramic Composites

Joachim H. Schneibel*, Stephen M. Sabol†, Jay Morrison‡, Evan Ludeman‡, and Cecil A. Carmichael*

*Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6115

†Westinghouse Power Generation
4400 Alafaya Trail MC 303
Orlando, FL 32826-2399

Abstract

The cyclic thermal shock behavior of two Si₃N₄ ceramics, two SiC whisker-reinforced alumina composites (Al₂O₃/SiCₜ), a SiC particulate-reinforced alumina (SiCₚ/Al₂O₃), and an alumina continuously reinforced with SiC fibers (SiCₙ/Al₂O₃) composite has been studied. Specimens were repeatedly quenched from 1473 K into a fluidized bed with a heat transfer coefficient of 1400 W/(K·m²) [250 Btu/(hr·ft²·F)] maintained at room temperature. The thermal shock degradation after 10 or 100 quenching cycles was assessed by the room temperature flexure strength. Si₃N₄ did not show a substantial decrease in its MOR after 100 cycles. Al₂O₃-7.5 wt% SiCₜ degraded severely after 10 cycles, whereas Al₂O₃-25 wt% SiCₚ retained its flexure strength even after 100 cycles. However, as cycling proceeded, longitudinal cracks started to grow at the ends of the specimens. Two factors are thought to be responsible for this finding. First, finite element calculations showed the
maximum tensile stresses during thermal shock to occur at the ends of the flexure specimens. Second, the fabrication of Al$_2$O$_3$-25 wt% SiC$_w$ by hot-pressing resulted in an anisotropy of the whisker orientation. The SiC$_f$/Al$_2$O$_3$ material containing particulate SiC, on the other hand, retained its flexure strength even after 100 cycles. The flexure strength of continuously reinforced SiC$_f$/Al$_2$O$_3$ decreased continuously during cycling, indicating a cumulative increase in the microcracking introduced during repeated quenching. This would be expected from our calculations which suggest peak tensile stresses higher than those required to introduce microcracking. In all investigated materials, a comparison of the calculated maximum tensile stresses with the flexural strengths of the as-received specimens is consistent with their thermal shock degradation. Also, the calculated peak tensile stresses correlate well with the thermal stress parameter defined by $E\times\alpha/k_{th}$, where $E$ is the Young’s modulus, $\alpha$ the thermal expansion coefficient, and $k_{th}$ the thermal conductivity. This suggests that the thermal shock performance of other material may be estimated from comparisons with the present work.

I. Introduction

In order to introduce advanced ceramics into land-based gas turbines for power generation, many criteria such as sufficient strength, sufficient fracture toughness, thermal shock resistance, and resistance against oxidation and hot corrosion have to be met. In the present work we focus on one of these issues, namely, thermal shock. While thermal shock is not a concern during steady-state operation of gas turbines, it becomes of great importance during emergency shutdowns, during which the temperature of the inlet air drops abruptly by many hundred Kelvin. Since a typical gas turbine undergoes on the order of hundred such shut-downs over its lifetime, ceramic materials may suffer from the formation of cracks, and the associated strength degradation, as a result of thermal shock. In order to assess the effect of thermal shock more closely, we decided to examine a representative selection of advanced ceramics for their thermal shock resistance. In order to
simulate combustion turbine conditions as closely as possible, up to 100 cyclic thermal shocks were carried out for each material. The conditions for each shock were chosen such as to be representative of a forced turbine shut-down. This was achieved by quenching into a suitable, calibrated fluidized bed. Modulus of rupture (MOR) measurements were employed to detect any strength degradation. In order to understand and explain the widely different thermal shock behavior of the various ceramics investigated, finite element calculations were carried out. Using appropriate physical properties, these calculations predict the location and magnitude of the maximum tensile stresses experienced by the specimens during quenching. Knowing the fracture strength, these calculations allow us to assess and interpret the thermal shock sensitivity of the investigated ceramics. Although the thermal shock resistance of advanced ceramics such as Si$_3$N$_4$ and Al$_2$O$_3$/SiC$_w$ has been investigated before (Lee et al., 1989; Hoffmann et al., 1993; Becher et al., 1993; and Case et al., 1993), these investigations employed water as the quenching medium. Since the heat transfer coefficients of water are not well defined (Becher et al., 1993) it was not possible to perform the type of thermal transient stress analysis carried out in our work. Therefore, in previous investigations, the stresses arising during thermal shock could not be compared to the strength of the investigated ceramics. The present work eliminates this shortcoming.

II. Experimental Procedure

The ceramics and ceramic composites investigated in this research are listed in Table I. The weight and volume fractions of the SiC reinforcements in the composites are indicated. The NT154 Si$_3$N$_4$ was processed by hot isostatic pressing (HIP). The AS800, which contained rare earth sintering aids, was processed by slip-casting followed by gas pressure sintering (i.e., pressures ≤ 10 MPa), and was reinforced in-situ with acicular β-Si$_3$N$_4$ grains [Gasdaska, 1994]. The ARtuff CC5500 composite was sintered and hot isostatically pressed, whereas the ARtuff CC7000 was unidirectionally hot-pressed. The
SiCp/Al₂O₃ was fabricated by the Lanxide® process and contained SiC particles in an Al₂O₃ matrix. The SiCp/Al₂O₃ was also fabricated by the Lanxide® process and consisted of alumina reinforced with a woven cloth of continuous SiC (Nicalon) fibers.

Modulus of rupture specimens were machined and ground into bend specimens with chamfered edges. The specimen dimensions were 3×4×50 mm except for the SiCp/Al₂O₃ material which was machined to 3×6×50 mm to minimize specimen to specimen variations expected due to the coarseness of the SiCf weave. The longitudinal edges of all specimens were chamfered. After grinding, the manufacturer gave the SiCp/Al₂O₃ specimens a special heat treatment, which resulted in an Al₂O₃ rich surface layer designed to minimize oxidation of the SiC.

The thermal shock testing was carried out by suspending the specimens in an air furnace at 1473 K for at least 5 minutes, which was long enough for the furnace to recover from a slight drop in temperature (5-10 K), and then dropping them into a fluidized bed. The fluidized bed was operated with room temperature compressed air and contained 100 grit alumina particles. Prior to the quenching experiments, its heat transfer coefficient was determined by means of a heat transfer probe. By supplying a known voltage U and current I to the heat transfer probe, and by measuring the temperature Tₛ on the surface of the probe immersed in the fluidized bed, the bed temperature Tₛ, and the probe surface area A, the heat transfer coefficient h was evaluated according to:

\[ h = \frac{I \times U}{A \times (T_s - T_b)} \]  

(1)

The airflow was selected such that a heat transfer coefficient of approximately 1400 W/(K·m²) [250 Btu/(hr·ft²·F)] was obtained. This value is representative of the heat transfer coefficients encountered in gas turbines. Under these conditions, the Biot numbers \( \beta = d \cdot h/k_{th} \) for the investigated materials are <1. Hereby, d is the specimen thickness and
$k_{th}$ the thermal conductivity. According to Pickles and Field [Pickels et al., 1996], this corresponds to mild thermal shock with a figure of merit criterion given by

$$R = \frac{\sigma(1 - \nu)k_{th}}{\alpha E}$$

(2),

where $\sigma$ is the flexure strength, $\nu$ is Poisson's ratio, $k_{th}$ the thermal conductivity, $\alpha$ the coefficient of thermal expansion, and $E$ is Young's modulus.

The MOR specimens were shocked either 10 or 100 times. The as-received and cyclically shocked specimens were tested in four-point bending with inner and outer spans of 20 and 40 mm, respectively, in order to evaluate their modulus of rupture. For each condition, 5 specimens were tested. Several specimens were also examined by optical as well as scanning electron microscopy (SEM).

III. Finite Element Calculations

Finite element analyses (FEA) were performed for each of the materials (except the SiC/Al$_2$O$_3$) to determine the magnitude, location, and orientation of the thermal stresses induced during quenching. Specimens were modeled by analyzing 1/8 of a specimen (by making use of the 3 planes of symmetry) and including the 45° edge chamfer. Meshing was done with 20-noded brick elements with at least 4 elements in each direction. Thermal (heat transfer) and thermal stress analyses were performed with MSC/Patran’s Advanced FEA code. Thermal boundary conditions consisted of an initial isothermal temperature of 1473 K followed by quenching to ambient temperature (293 K) with a convective heat transfer coefficient of 1400 W/(m$^2$ K). Convection was applied equally to all external surfaces of the specimen.

Transient heat transfer analysis was first conducted to determine the temperature distributions as a function of time. Thermal stress analyses were then conducted at discrete time intervals around the time were maximum temperature gradients occurred. All materials
were assumed to be isotropic. The temperature-dependent properties assumed for the thermal and elastic analyses are shown in Table II for each materials. They were obtained from manufacturer's data and McCluskey et al.'s data (McCluskey et al., 1990).

The transverse temperature differences between the central axis and the edges of the specimens are shown in Fig. 1 as a function of time for each material. These differences were obtained at locations far enough away from the specimen ends in order to preclude specimen end effects. The gage section of the specimen (the inner 40 mm) satisfies this requirement. Since the temperature gradients in the specimens are approximately linear, and since the distance between the specimen central axis and the specimen axes is 2.5 mm, the temperature gradients reach values up to approximately 90 K/mm. Figure 1 shows that all specimens experienced a peak thermal gradient within the first 0.5 s after quenching.

The peak temperature gradient is strongly dependent upon the thermal properties of the material, specifically the thermal diffusivity. The relationship for the present materials is shown in Fig. 2. Here, thermal diffusivities were evaluated from the thermal properties at 1473 K shown in Table II as \( \frac{k_{th}}{c_p \rho} \), where \( c_p \) is the heat capacity and \( \rho \) the density. The relationship in Fig. 2 may be used to predict the performance of new materials with the same geometry, and subjected to the same thermal shock, as ours.

Stresses resulting from the thermal shock temperature gradients are shown for all materials in Table III. Figure 3 illustrates the maximum principle tensile stresses near the end of a CC7000 specimen 0.35 s after the start of a quench. Depending on the location, these stresses may be longitudinal (Point A) or transverse (Point B). The maximum stresses occurred always at the ends of the specimens in the transverse direction, due to the increased three-dimensional heat transfer at the ends. This effect extended only 3 mm from the ends, with temperature gradients and stresses being virtually constant along the center 44 mm of the specimens, as indicated by Fig. 3. The longitudinal stresses in the gage section are most likely to impact the MOR results, since they tend to open up cracks with the same orientations as those leading to flexural fracture.
Equation (2) suggests that the thermal stresses $\sigma_{th}$ scale according to the established correlation:

$$\sigma_{th} \propto \alpha \times E / k_{th} = \text{Thermal Stress Parameter (TSP)} \quad (3).$$

Figure 4 demonstrates that the peak tensile stresses calculated by finite element analysis correlate very well with the above formula. Properties at 1473 K were used, since this is roughly the temperature at which the peak stresses occurred. With the help of Fig. 4, the performance of other materials during thermal shock may be estimated.

It should be noted that the finite element calculations and the above analytical prediction are valid only as long as the thermal and mechanical properties remain the same. As soon as any material thermal or mechanical property changes (e.g., cracking) occur during thermal shock, the peak tensile stresses during subsequent thermal shocks will change. In some materials, this may happen after the first cycle; in others it will happen only after many cycles. Instead of flexural strength, fracture toughness and other measures of crack growth resistance should then be used as the means of comparison.

IV. Experimental Thermal Shock Results, Microstructural Analysis, and Discussion

Figure 5 shows the flexure strengths of the 6 investigated materials in the as-received condition and after 10 and 100 thermal shocks. The two types of silicon nitride behaved quite similar and experienced no or only little degradation within the error of the measurements. According to our finite element analysis for the gage sections, the maximum tensile stress in the longitudinal direction reached only 57 MPa during thermal shock. Since this value is well below the fracture strength of these silicon nitrides, a significant degradation after 100 cycles would not be expected. For comparison, the ratios
of the calculated longitudinal peak stresses and the measured flexure strengths of the as-
received materials are listed in Table IV.

The flexure strength of the ARtuff CC5500 shows a very large error bar after 10
cycles. Out of five specimens tested, two broke at around 700 MPa, whereas the other
three exhibited strengths well below 100 MPa. Substantial fractions of the fracture
surfaces of these three specimens were discolored. This indicates that crack(s) were
introduced at some point during the thermal cycling, whose surfaces discolored due to
oxidation. Those cracks severely degraded the flexure strength. Finite element analysis
predicted this material to experience the highest temperature gradients and thermal stresses
among the analyzed materials. Also, the ratio of the calculated thermal stress and the as-
received flexure strength is almost 0.7. In other words, the maximum stresses occurring
during thermal shock are quite close to the fracture strength of this material. It is therefore
not surprising that repeated thermal shocks introduced macroscopic cracks.

When the SiC<sub>wt</sub> content is raised to 29 vol. % (CC7000), the as-received flexure
strength is not changed noticeably as compared to 9 vol.% (CC5500). However, the
calculated tensile stresses decrease significantly. This is primarily due to the increase in the
thermal conductivity with the increase in the SiC<sub>wt</sub> content. The ratio of the calculated
thermal stresses to the measured flexure strength is lowered substantially, to less than 0.5.
Tiegs and Becher (Tiegs et al., 1987) suggested that the improvement in fracture toughness
due to higher SiC<sub>wt</sub> contents is the most important factor for the resulting improved thermal
shock resistance. Our finite element calculations demonstrate that the reduction in the peak
tensile stresses with increasing SiC<sub>wt</sub> content is also important.

While the CC7000 survived 100 thermal shock cycles without degradation of its flexure
strength, it did nevertheless show distinct thermal shock damage. As thermal cycling
progressed, longitudinal cracks started to grow from the ends of most of the specimens.
These cracks grew to lengths on the order of 10 mm. As shown schematically in Fig. 6,
the cracks occasionally branched out from the main crack. Since the planes of the cracks were,
for the most part, parallel to the longitudinal specimen axis and to the direction of the load applied during the MOR test, and since they did not usually extend into the center section of the MOR bars, they did not cause a degradation in the flexure strength.

The cracks in the CC7000 formed for two reasons. First, the finite element analysis predicts that the maximum tensile stresses during the thermal shocks are transverse stresses occurring at the ends of the specimens, and not the longitudinal stresses in the gage section. Second, the whiskers in the CC7000 material exhibit a preferred orientation since this material was fabricated by hot-pressing. This alignment of the whiskers is illustrated in Fig. 6. It is likely to cause anisotropy in the thermal and mechanical properties. In particular, it is probably easiest to nucleate and propagate cracks in a plane perpendicular to the hot-pressing direction, since the whiskers tend to be oriented parallel to this plane. Therefore, end cracks such as those shown schematically in Fig. 6 form during thermal cycling.

The SiCp/Al2O3 composite retains its flexure strength even after 100 cycles. This material has a much lower as-received flexure strength than the SiCw/Al2O3 materials, and its thermal stresses were also calculated to be considerably lower. In view of its relatively high thermal stress to as-received flexure strength ratio, namely, 0.63, it is somewhat surprising that this material does not degrade even after 100 thermal shocks. The relatively low as-received flexure strength suggests that this material exhibits microcracks to begin with. Because of this, any additional degradation due to thermal shock may not show in the flexure tests.

The SiCp/Al2O3 continuously reinforced composite degraded substantially and in a systematic way as the number of thermal shocks increased. However, its fracture mode remains "graceful," as illustrated in Fig. 7. The non-linearity of the load-displacement curve for the as-received specimen in this figure suggest immediately that this material undergoes irreversible processes at stresses well below the maximum stress. Fareed et al. [Fareed et al., 1992] suggest, on the basis of changes in the slope of tensile stress-strain
curves for this material, that microcracks start to open at stresses as low as 60 MPa. By referring to the thermal stress results for the CC7000 material, which has a comparable SiC volume fraction, the peak tensile stresses in the SiCf/Al2O3 are likely to be substantially higher than 60 MPa. This suggests that thermal cycling will introduce progressively more damage in the SiCf/Al2O3 specimens and in this way degrade their flexure strength. In addition, environmental attack (e.g., oxidation) of the Nicalon fibers in this material during high temperature air exposure may very well play a role in the degradation of this materials system - particularly because of the suspected ongoing crack formation during thermal cycling.

V. Conclusions

A thermal shock test has been devised which simulates combustion turbine shutdown transient effects in a controlled, predictable, and quantifiable manner.

The reductions in flexure strength following thermal shock testing correlate well with analytically predicted thermal stresses in these materials. Observed damage in Al2O3-25 wt% SiCw also correlates well with predicted locations and orientations of high tensile stresses. Finite element analysis has been shown to be an indispensable tool for understanding the results of our thermal shock tests.

In the SiCw reinforced materials the performance improvement offered by higher whisker contents is not only due to the improved fracture toughness, but also the increase in thermal conductivity.

Our data suggests that the thermal shock resistance of linear elastic materials can be readily predicted using established thermal shock resistance parameters and known thermal and mechanical properties.

Thermal and mechanical anisotropy of unidirectional hot-pressed SiCw/Al2O3 materials contributed to initially unexpected modes of failure. Full characterization of these properties would be needed for proper FEA predictions.
Under the conditions examined, both the NT154 and the AS800 silicon nitrides, the \( \text{Al}_2\text{O}_3-29 \text{ vol.\% SiC}_w \), and the \( \text{SiC}_p/\text{Al}_2\text{O}_3 \) performed well, exhibiting little or no strength degradation due to thermal shock. However, the stresses predicted for the \( \text{Al}_2\text{O}_3 \) matrix materials were significantly higher than those in the silicon nitride materials and closer to their as-received fracture strengths. Therefore, on the basis of thermal shock performance alone, the silicon nitride materials would be the best choice, due to their greater design margin. In a final materials selection, however, other design issues, such as corrosion resistance and thermodynamic stability with respect to the environment and to mating parts, must also be considered.

Acknowledgments

We would like to acknowledge Eric Bright, Norton Advanced Ceramics, for providing the NT154 material for this research, and D. Newby and T. Gasparovic from the Westinghouse Science and Technology Center for the design and construction of the fluidized bed. Valuable discussions with P. F. Becher and M. Ferber are gratefully acknowledged. This work was supported by a Cooperative Research and Development Agreement with Westinghouse Electric Corporation, sponsored by the U.S. Department of Energy, Office of Energy Research, Laboratory Technology Research Division under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.
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Table I. Summary of the investigated Ceramics and Ceramic Composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Nominal SiC Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT154 (Si$_3$N$_4$)</td>
<td>Norton Advanced Ceramics</td>
<td>0       wt% 0 vol. %</td>
</tr>
<tr>
<td>AS800 (Si$_3$N$_4$)</td>
<td>Allied Signal Aerospace</td>
<td>0       wt% 0 vol. %</td>
</tr>
<tr>
<td>ARtuff CC5500 (Al$_2$O$_3$/SiC$_w$)</td>
<td>Advanced Composite Materials Corp.</td>
<td>7.5     wt% 9 vol. %</td>
</tr>
<tr>
<td>ARtuff CC7000 (Al$_2$O$_3$/SiC$_w$)</td>
<td>Advanced Composite Materials Corp.</td>
<td>25      wt% 29 vol. %</td>
</tr>
<tr>
<td>SiC$_p$/Al$_2$O$_3$</td>
<td>Du Pont Lanxide Composites Inc.</td>
<td>44      wt% 50 vol. %</td>
</tr>
<tr>
<td>SiC$_f$/Al$_2$O$_3$</td>
<td>Du Pont Lanxide Composites Inc.</td>
<td>30      wt% 35 vol. %</td>
</tr>
</tbody>
</table>
Table II. Materials Properties used for the Finite Element Thermal & Stress Analyses

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Temperature, NT154; SiC\textsubscript{p}/SiC\textsubscript{w}, AS800; Al\textsubscript{2}O\textsubscript{3}</th>
<th>CC5500</th>
<th>CC7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus, ( E )</td>
<td>GPa</td>
<td>293 or 1473</td>
<td>306</td>
<td>320</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion, ( \alpha )</td>
<td>ppm/K</td>
<td>293-1473</td>
<td>3.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Density, ( \rho )</td>
<td>Mg/m\textsuperscript{3}</td>
<td>293-1473</td>
<td>3.31</td>
<td>3.35</td>
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<tr>
<td>Poisson's Ratio, ( \nu )</td>
<td></td>
<td>293-1473</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Thermal Conductivity, ( k_{th} )</td>
<td>W/(m-K)</td>
<td>293</td>
<td>0.63</td>
<td>0.73</td>
</tr>
<tr>
<td>Heat Capacity, ( c_p )</td>
<td>J/(gK)</td>
<td>293</td>
<td>0.67</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table III. Maximum Stresses due to Thermal Shock

<table>
<thead>
<tr>
<th>Materials</th>
<th>Maximum Principle Tensile Stresses, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gage (longitudinal)</td>
</tr>
<tr>
<td>Si\textsubscript{3}N\textsubscript{4} (NT154; AS800)</td>
<td>57</td>
</tr>
<tr>
<td>SiC\textsubscript{p}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>171</td>
</tr>
<tr>
<td>CC5500 SiC\textsubscript{w}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>393</td>
</tr>
<tr>
<td>CC7000 SiC\textsubscript{w}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>280</td>
</tr>
</tbody>
</table>
Table IV. Ratios of calculated Tensile Peak Stresses and Flexure Strengths of as-received Specimens

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated Average MOR, MPa</th>
<th>Ratio of calculated to measured Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT154 Si₃N₄</td>
<td>57</td>
<td>776</td>
</tr>
<tr>
<td>AS800 Si₃N₄</td>
<td>57</td>
<td>704</td>
</tr>
<tr>
<td>Si₃C₇/Al₂O₃</td>
<td>171</td>
<td>270</td>
</tr>
<tr>
<td>CC5500 SiC₆/Al₂O₃</td>
<td>393</td>
<td>577</td>
</tr>
<tr>
<td>CC7000 SiC₆/Al₂O₃</td>
<td>280</td>
<td>586</td>
</tr>
</tbody>
</table>
Figures

1. Maximum predicted transverse temperature differences (gage sections).

2. Maximum temperature difference vs. thermal diffusivity

3. Maximum principle stresses in CC7000 Al$_2$O$_3$/SiC$_w$ at t=0.35 s (stresses in MPa)

4. Correlation between the peak thermal stresses and the thermal stress parameter.

5. Flexure strengths in the as-received condition ("0"), after 10 thermal shocks ("10"), and after 100 shocks ("100") from 1473 K to room temperature.

6. Schematic drawing of end cracks in CC7000 MOR specimen and SEM micrograph of the microstructure showing the whisker alignment due to hot-pressing. The micrograph was obtained with an uncoated specimen at 2 kV and shows the whisker-alumina boundaries as bright lines.

7. Load-displacement curves for 4-point flexure testing of SiCf/Al$_2$O$_3$ in the as-received condition and after 100 thermal shocks.
Thermal Diffusivity at 1473 K, $10^{-6}$ m$^2$/s

Figure 2
Figure 4

Thermal Stress Parameter at 1473 K, $10^3$ s/m$^2$

- CC5500 SiC$_w$/Al$_2$O$_3$
- CC7000 SiC$_w$/Al$_2$O$_3$
- SiC$_p$/Al$_2$O$_3$
- NT154
- AS800

R = 0.99

Peak Tensile Stress, MPa
Figure 6
Figure 7
Distribution

J. H. Schneibel, MS-6115, 4500S
C. A. Valentine, MS-8242, 701SCA
Joyce Shepherd, MS-6416, 5002
C. T. Liu, MS-6115, 4500S
E. E. Bloom, MS-6117, 4500S
D. F. Craig, MS-6132, 4500S
L. L. Horton, MS-6132, 4500S
T. M. Rosseel, MS-6416, 5002
S. M. Sabol, Westinghouse Power Generation, 4400 Alafaya Trail MC 303, Orlando, FL 32826-2399 (5 copies)
W. M. Polansky, Director, Advanced Energy Projects and Technology Research, DOE, 19901 Germantown Road, Germantown, MD 20874-1290
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