Task 8.8 - Low Cost Ceramic Materials

**Topical Report
June 30, 1997**

**RECEIVED
JAN 26 1998
OSTI**

Work Performed Under Contract No.: DE-AC21-93MC30246

**For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
Morgantown Site
P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
Solar Turbines, Inc.
2200 Pacific Highway
San Diego, California 92186-5376**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DTIC QUALITY INSPECTED 3

19980327 026

Disclaimer

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

CONTENTS

<u>Paragraph</u>		<u>Page</u>
1.0	INTRODUCTION	1
2.0	MODIFICATION OF PROGRAM	2
3.0	MATERIAL SELECTION AND PROPERTIES	3
3.1	LoTec BZP	3
3.2	SAIC CMC-8	5
3.3	International Thermoproducts Altra KVS 16 With Ceramic Fabric Reinforcement	6
4.0	SUBSCALE RIG TESTING	7
4.1	LoTec BZP Liner Subscale Rig Test	7
4.2	SAIC CMC-8 Liner Subscale Rig Test	8
4.3	ITP CF3000 Liner Subscale Rig Test	8
5.0	CONCLUSIONS AND RECOMMENDATIONS	10

FIGURES

<u>Figure</u>		<u>Page</u>
1	Coefficient of Thermal Expansion Variation With BZP Composition	3
2	Metallic Housing for Combustor Liner	7
3	LoTEC Subscale Combustor Liner Used for Rig Testing	8
4	Fracture Surface of Small Fragment SAIC CMC-8	9

TABLES

<u>Table</u>		<u>Page</u>
1	Candidate Ceramic Materials for the Combustor Application	1
2	BZP Material Properties	4
3	Stresses for BZP Liner With $cte = 0.5 \times 10^{-6}/^{\circ}F$	4
4	Stresses for BZP Liner With $cte = 1.7 \times 10^{-6}/^{\circ}F$	5
5	Material Properties of SAIC S2 Glass Reinforced CMC-8	5
4	Physical Properties of CF 3000 Vacuum Formed Ceramic Fiber	6

1.0 INTRODUCTION

This subtask was originally titled "Reheat Combustor Materials" and was proposed in anticipation of the addition of a reheat combustor to the ICR gas turbine cycle. When the emphasis of ATS became the optimized recuperated cycle, the goal of the subtask was changed to the evaluation of low cost materials for gas turbine combustor liners. It now supplements similar work being conducted by Solar under DOE Contract No.DE-AC02-92-CE40960, titled "Ceramic Stationary Gas Turbine (CSGT) Development." The use of a ceramic combustor liner in gas turbines contributes to emissions reductions by freeing cooling air for use as primary combustion air and by allowing higher wall temperatures, which contribute to more complete combustion of hydrocarbons.

Information from a literature's survey, manufacturer's data, and Solar experience was used to select three materials for testing. In addition to material properties requirements for selection, subscale combustor liner cost was required to be at least half of the high modulus continuous fiber reinforced composite part cost. The three materials initially selected for evaluation are listed in Table 1. Four hour subscale rig tests were planned for eight inch diameter liners made from each material. Upon successful completion of each four hour test, a fifty hour test was planned.

Table 1. Candidate Ceramic Materials for the Combustor Application

Material Name	Type	Supplier
B-30	Barium Zirconia Phosphate	LoTEC
Altra KVS 16	High Alumina Fiber Reinforced Composite	International Thermoproducts
System 2.2 High Temperature Composite	Glass-Ceramic Fiber Reinforced Composite	AEA Technologies

In addition to rig testing, cyclic thermal/erosion testing at ITP was planned for comparative analysis of different fiber blends in the Altra KVS material. The test apparatus consists of a gas burner that automatically cycles on and off for 695 cycles per day. Test specimens are soaked to about 2350°F (1288°C) at the end of the test cycle.

2.0 MODIFICATION OF PROGRAM

AEA Technologies, formerly a U.K. government organization, was privatized after being selected for participation in this program. After reorganizing, they were unable to use their subcontractor for HIPing the System 2.2 glass ceramic composite in the eight inch subscale combustor size. Therefore, AEA Technologies was dropped from the program, and a relatively low cost Nextel 440 fiber reinforced glass-ceramic composite from Scientific Applications International Corporation (SAIC) was chosen as a replacement (CMC-SAIC-8).

3.0 MATERIAL SELECTION AND PROPERTIES

The CSGT program tested 8 inch subscale combustor liners of silicon carbide composite (SiC/SiC) from DuPont Lanxide Corporation and B.F. Goodrich Aerospace - Supertemp as well as aluminum oxide ($\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$) liners from Babcock & Wilcox. These materials are relatively expensive; a typical 8 inch subscale liner costs about \$30K. Under Task 8.8, a major requirement for material selection was substantially lower cost than the CSGT structural composites. The three materials selected for evaluation in subtask 8.8 were as follows:

- B-30 BZP (Barium Zirconia Phosphate) supplied by LoTEC. This material features a near zero coefficient of thermal expansion, eliminating most thermal stresses, and the potential to reduce the \$30,000 per liner cost of SiC/SiC by 94%.
- CMC SAIC-8 (Nextel 440/ Al_2O_3 - SiO_2) offers the toughness and strength of a CFCC material at a cost 60% lower than that of SiC/SiC. This material is supplied by SAIC.
- Altra KVS 16 (Al_2O_3 fibers/ Al_2O_3 - SiO_2) from International Thermoproducts with temperature capability to 3000°F (1649°C) at a cost 90% lower than that of SiC/SiC.

3.1 LoTEC BZP

The Barium Zirconia Phosphate (BZP) material properties are listed in Table 2. The thermal expansion coefficient can be changed by varying the barium, phosphorous, silicon ratio in the material, as shown in Figure 1.

Figure 1. Coefficient of Thermal Expansion Variation with BZP Composition

Table 2. BZP Material Properties

Property	
Flexural Strength (MOR)	10ksi (70MPa)
Flexural Strength at 2732°F (1500°C)	9ksi (65MPa)
Young's Modulus	10Msi (70GPa)
Poissons Ratio	0.2
Fracture Toughness	1.5 to 2 Mpam ^{1/2} (1.4 to 1.8ksi in ^{1/2})
Density	211lb/ft ³ (3.39g/cm ³)
Thermal Expansion	1ppm/°C (1.7ppm/°F) or lower
Thermal Expansion Anisotropy	≤1ppm/°C (1.7ppm/°F) or lower
Thermal Conductivity	1 W/mK (7 Btu.in/ft ² hr°F)
Thermal Shock Resistance	ΔT> 2300°F (1250°C)
Use Temperature	Up to 2732°F (1500°C)

The impact of coefficient of thermal expansion on thermal stress was illustrated by a one dimensional stress analysis for the subscale combustor liner running at a 2200°F (1204°C) wall temperature. Results of that analysis, which was done under Solar APDM funding, are in Tables 3 and 4. Increasing the cte from $0.5 \times 10^{-6}/^{\circ}\text{F}$ to $1.7 \times 10^{-6}/^{\circ}\text{F}$ caused a corresponding increase in the stress values. Assuming that the modulus and temperature conditions are constant, the stresses in Table 4, based on the maximum cte value for BZP ($1.7 \times 10^{-6}/^{\circ}\text{F}$), are the maximum stresses for the application. Therefore, the strength of the material was assumed to be adequate.

Table 3. Stresses for BZP Liner with cte = $0.5 \times 10^{-6}/^{\circ}\text{F}$

Stress Direction	Maximum Stress psi (MPa)	Minimum Stress psi (MPa)
S1 [r]	869 (5.99)	-48 (-.33)
S2 (θ)	290 (1.99)	-212 (-1.46)
S3 (z)	67 (0.46)	-855 (-5.89)
SEQV	892 (6.15)	57 (.39)

Table 4. Stresses for BZP Liner with $\text{cte} = 1.7 \times 10^{-6}/^{\circ}\text{F}$

Stress Direction	Maximum Stress psi (MPa)	Minimum Stress psi (MPa)
S1 [r]	2956 (20.4)	-162 (-1.12)
S2 (θ)	986 (6.79)	-720 (-4.96)
S3 (z)	227 (1.56)	-2907 (-20.0)
SEQV	3033 (20.9)	194 (-1.34)

3.2 SAIC CMC-8

SAIC supplied the only continuous fiber reinforced ceramic composite (CFCC) that was investigated under this program. The material is manufactured using a pre-ceramic polymer impregnated fabric which can be processed using polymer based composite autoclave techniques. The combustor part was laid up by hand on a mandrel and autoclaved on a female tool. Using this method to process the part allowed SAIC to price their liner 60% less than other CFCC materials. The material system used was Nextel 440 fabric with a proprietary silica based matrix. Since this material was in its infancy, mechanical property data was not available. Therefore, mechanical data (Table 5) generated on a similar composite reinforced with S2 glass was used for evaluation. The strength and modulus values were expected to be greater for the liner than for the data given, since the part fiber volume was about 60% instead of 50%. Based on a tensile strength of 20.9 ksi (144MPa), the material was assumed to have adequate strength for the combustor application. Also, the relatively low modulus was expected to reduce thermal stresses developed in the part at temperature. The matrix was expected to devitrify around 1800 to 2200°F (982 to 1204°C). The effects of devitrification were not known, but the material was expected to return to its original state after going through devitrification.

The main advantages of this system include low cost for good thermal performance, good thermal shock resistance, and an expected graceful CFCC failure mode. Thermal shock resistance for this material was demonstrated in a rocket launch pad application at 3200°F (1760°C) for 1 hour. This material was also tested as a fire door for 4 hours at 2500°F (1371°C).

Table 5. Material Properties of SAIC S2 Glass Reinforced CMC-8

Property	Room Temperature	550°F (288°C)
Tensile Strength, ksi (MPa)	20.9 (144)	na
Tensile Modulus, Msi (GPa)	3.2 (22)	na
Tensile Strain, $\mu\text{in/in}$ ($\mu\text{m/m}$)	6614	na
Short Beam Shear, ksi (MPa)	1.6 (11)	0.790 (5.44)
Flexural Strength, ksi (MPa)	26.5 (183)	15.1 (104)
Flexural Modulus, Msi (GPa)	3.0 (21)	2.7 (19)

3.3 INTERNATIONAL THERMOPRODUCTS ALTRA KVS 16 WITH CERAMIC FABRIC REINFORCEMENT

The liner from International Thermoproducts was fabricated using a vacuum forming and firing technique which bonds micron size fibers into a fibrous ceramic structure. CF3000, a blend of ultra pure bulk aluminosilicate ceramic fibers and inorganic binders, was used for the Task 8.8 part. This refractory based material, rated to 3000°F (1649°C), is used primarily for high temperature industrial furnace applications and is not a structural ceramic. Advantages of using this low density material include high thermal shock resistance and low thermal conductivity. Also, unlike dense ceramics, spalling of the CF3000 does not pose a threat to downstream components. In the combustor application, it is intended to act as a thermal barrier and not as a structural, mechanical stress carrying member. Therefore, mechanical property data was not generated under this task. Physical property data is listed in Table 6.

This material is much softer than the other materials, but a proprietary method was used to increase its erosion resistance for the combustor application. To qualify it in terms of erosion and thermal shock resistance, thermal cycle testing was performed by ITP. The sample configuration for these tests is half of an eight inch diameter liner. Heat is applied to the inner wall of the cylinder. Initially, two fibers blends, one rated at 2300°F (1260°C) and one rated at 3000°F (1649°C) were tested. Both were cycled about every two minutes for 695 cycles per day. Natural gas was used to heat the samples to between 2200°F (1204°C) and 2400°F (1316°C). Cold cycle temperatures were estimated to be between 600°F (316°C) and 800°F (427°C). Both samples survived 17,000 cycles and showed no evidence of surface cracking or wear. The implication from these results is that the lower cost 2300°F rated material may be sufficient for the combustor application.

Currently, ITP is testing samples of the fiber blend rated at 2300°F (1260°C), one without ceramic fabric reinforcement and one with ceramic fabric reinforcement. The sample with fiber only has survived over 75,000 cycles. The sample with fabric reinforcement has survived over 53,000 cycles. Neither shows signs of cracking or erosion.

Table 6. Physical Properties of CF3000 Vacuum Formed Ceramic Fiber

Property	
Color	White
Continuous Use Temperature	3000°F (1649°C)
Melting Point	3392°F (1867°C)
Nominal Density	20lb/ft ³ (.32g/cm ³)
Mean Fiber Diameter	2-3μm (79μin)
Fiber Lengths	0.25in to 4in (6.4mm to102mm)
Chemical Composition	80% Al ₂ O ₃ , 20% SiO ₂

4.0 SUBSCALE RIG TESTING

The liners were tested in Solar's high pressure single can subscale rig using a SoLoNOx fuel injector. This facility has the capability to achieve engine rated pressure and temperature while maintaining a single injector's mass flow into the rig. It is fully instrumented for temperature, pressure, flow, and emissions measurement. A fuel shut-off system is activated at the beginning of each test. It is triggered whenever the wall temperature at any measured location exceeds a predetermined maximum. All data are captured via a Daytronics data acquisition system and VAX workstation which uses a Real Time Engine Test System (RETS) software package. Exhaust emissions are taken with a state of the art Rosemount Analytical continuous emission monitoring system (CEMS). Natural gas was used for fuel in all of the tests.

Each liner was instrumented with fifteen thermocouples attached to the outside with an alumina based adhesive. The thermocouples were arranged in three axial rows of five. Axial and circumferential spacing were about 1.25 inches and 120°, respectively. Nextel 440 is used to insulate the liner and as a compliant layer between the ceramic liner and the metallic housing of the rig. The metallic housing is shown in Figure 2. The insulation layer is typically 0.125 inch thick.

Figure 2. Metallic Housing for Combustor Liner

Each liner was approximately eight inches in outer diameter, and eight inches in length. The thickness of the LoTEC and ITP liners was approximately 0.375 inch. Thickness of the SAIC liner was about 0.125 inch. The LoTEC liner is shown in Figure 3 as an example of the part configuration.

4.1 LoTEC BZP LINER SUBSCALE RIG TEST

In the BZP liner test, the rig was lit successfully, and main fuel was introduced slowly to increase wall temperature to the target of 1925° F (1052°C). When the maximum wall temperature was

Figure 3.

LoTEC Subscale Combustor Liner Used for Rig Testing

approximately 1500°F (816°C), a change in the sound of the rig was heard. Seconds later, one of the thermocouples overtemped and caused an automatic shutdown of the rig. The thermocouple was exposed to the combustion gases due to catastrophic failure of the liner, eight minutes into the test. Post-test examination of the liner pieces indicated that the liner probably failed from thermal shock. Also, the fracture

pattern suggested that failure originated from a large inclusion in the material. Even though the coefficient of thermal expansion is extremely low in this material, some thermal stress is still generated. The strength of this material is very low, and the presence of large inclusions drops the critical failure stress even lower. Therefore, it is assumed that the stresses generated were high enough to cause failure of the liner.

4.2 SAIC CMC-8 LINER SUBSCALE RIG TEST

The SAIC liner was lit successfully, and main fuel was introduced slowly to increase the wall temperature to 1925°F (1052°C). While trying to increase the wall temperature, the wall color changed to yellow/orange, and the material sparked. Nine minutes into the test, the wall temperature raced to 1995°F (1091°C) and the rig shut down automatically. The rig was opened and the liner was found in pieces. Post-test evaluation revealed that the composite exhibited extremely brittle failure with no fiber pullout. Figure 4 shows the smoothness of the failure surface in one piece of the failed part. The fracture pattern was indicative of thermal shock. The nature of this failure indicates that SAIC did not obtain adequate fiber/matrix interface properties to provide composite behavior in this part. Also, the material was easily broken apart by hand and did not have mechanical properties similar to those listed in Table 5.

4.3 ITP CF3000 LINER SUBSCALE RIG TEST

In addition to the fifteen exterior thermocouples, three thermocouples were embedded through the thickness to the interior wall, spaced about 120° apart at the mid-plane of the liner. The ITP liner was lit successfully on pilot fuel, and main fuel was added slowly to increase the wall temperature to 2000°F (1093°C). However, only a few minutes into the test, several wall temperatures went over

Figure 4. Fracture Surface of Small Fragment SAIC CMC-8

2000°F (1093°C). The liner was found in the rig in large and small pieces. The nature of the failure is not entirely clear. Since this material is a refractory and is not dense, thermal shock is not a likely cause of failure. One possible cause of failure includes mechanical stress induced by a slight difference in pressure between the outside diameter and the inside of the liner. This material is very fibrous, has little mechanical strength and can be crushed by very low levels of stress. Another possible cause is stress induced by vibration.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The LoTEC BZP and SAIC CMC-8 liners failed due to a lack adequate strength and thermal shock resistance. Although these materials are very low cost, it is not feasible to continue investigation of their use in combustor liner applications.

The ITP CF3000 liner does not have adequate strength to be used in the integral combustor liner configuration. However, because of its thermal insulating capability, thermal shock resistance, and thermal cycling durability, the ITP material warrants further investigation. Solar will work with ITP engineers to develop new concepts that will take advantage of the material's thermal properties while protecting it from mechanically induced failures. Three concepts that have been identified for study include the following:

- A CF3000 with ceramic fabric liner press fit into a high temperature metallic liner backing for strength.
- A CF3000 with ceramic fabric liner in a concentric ring configuration for stress relief.
- An CF3000 with ceramic fabric liner in a half cylinder configuration for stress relief.

ITP will produce drawings of these concepts for Solar's review. Solar will then decide whether to pursue any or all of the concepts using internal funding.

M98002020

Report Number (14) DOE/MC/30246-- 5812

Publ. Date (11) 1997

Sponsor Code (18) DOE/FE, XF

JC Category (19) UC-101, DOE/ER

DOE