

TECHNICAL PROGRESS REPORT
FOR
"HIGH PERFORMANCE MATERIALS IN COAL CONVERSION UTILIZATION"

FOR THE PERIOD
JULY 1, 1995 THROUGH SEPTEMBER 30, 1995

OCTOBER 1995
Work Performed Under Grant No. DE-FG22-93PC93225

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.

Prepared for:
The United States Department of Energy

Prepared by:
The University of Tennessee Space Institute
B. H. Goethert Parkway
Tullahoma, Tennessee 37388-8897

US/DOE Patent Clearance is Not required prior to publication of this document.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

Table of Contents

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 DISCUSSION	1
2.1 Objective and Scope of Work	1
2.2 Task 1-Materials (Lanxide Corporation)	1
2.3 Task 2-Pre and Post Test Material Characterization	2
2.3.1 Subtask 2A-Strength of Materials Testing and Analysis (UTSI)	2
2.3.2 Subtask 2B-Corrosion Thermodynamic Analysis (U of Pa)	2
2.4 Task 3-Exposure Testing	6
2.4.1 Subtask 3A-Bench Scale Lab Tests (UTSI)	6
2.4.2 Subtask 3B-Field Exposure Tests (UTSI)	6
2.5 Task 4-Project Management	7
3.0 SCHEDULE	7
4.0 CONCLUSION	7
5.0 REFERENCES	7
APPENDIX A LASER INDUCED SURFACE MODIFICATION OF CERAMICS COATED CERAMIC COMPOSITE FOR HIGH TEMPERATURE CORROSION PROTECTION	A-1

List of Figures

	<u>Page</u>
Figure 1. Temperature dependence of DIMOX strength (Lanxide Brochure)	4
Figure 2. Temperature dependence of DIMOX strength (P. LaRue M.S. Thesis, UTSI)	5
Figure 3. Effect of High Temperature Oxidation on Room Temperature Strength of the DIMOX material.	6

1.0 INTRODUCTION

This is the eighth quarterly report on a three year grant regarding "High Performance Materials in Coal Conversion Utilization." The grant is for a joint university/industry effort under the US Department of Energy (DOE) University Coal Research Program. The University of Tennessee Space Institute (UTSI) is the prime contractor and The University of Pennsylvania and Lanxide Corporation are subcontractors.

UTSI has completed all the initially planned laboratory exposure tests involving pulverized coal slag on the production Lanxide DIMOX™ ceramic composite material. In addition, the strength testing (at temperature) and analysis of C-ring sections of the exposed production composite are complete.

2.0 DISCUSSION

2.1 Objective and Scope of Work

The object of this grant is to test, analyze, and improve the heat and coal-slag corrosion resistance of a $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ ceramic composite tubular material. The material will be evaluated for its ability to withstand the pressures, temperatures and corrosion attack which would be encountered within a coal-fired high-temperature, high pressure air heater. The evaluation includes strength testing at elevated temperatures of production tubes as well as one manufactured with an innovative new technology. The feasibility of several joining and coating techniques are also being investigated.

2.2 Task 1-Materials (Lanxide Corporation)

In the previous quarterly report, the development of an alternate preforming technique that can potentially overcome the limitations of slip casting was described. The new approach utilizes the principles of centrifugal casting. Using this approach, a cylindrical mold cavity is first filled with a flowable mixture of SiC particles and Lanxide's novel preceramic polymer, CERASET™ SN. During the spinning of the mold the SiC particles are forced radially outward. The spaces between the particles are at this point filled with the preceramic polymer. Upon heating of the spinning mold, the preceramic polymer cures to form a rigid material. Upon cooling of the mold, a hard and strong preform can be taken from the mold. Further heating of the preform converts the cured preceramic polymer into a ceramic.

The CERASET™ SN preceramic polymer is considerably more advantageous to use than other known commercial or developmental preceramic polymers in that it is solvent free and thermosetting, and features low viscosity, high purity, and excellent stability in ambient atmospheres. Further, the CERASET™ SN polymer is inexpensive and available in large quantities.

In the previous reporting period, the design of a centrifugal tube casting machine was completed. In this period the casting machine was installed and casting trials commenced. The machine consists of a laboratory bench top lathe and an arrangement of three heat guns that blow hot air through a manifold onto the exterior surfaces of the rotating mold. Initial trials indicated the need to identify a satisfactory debond coating that would allow for the demolding of the cast preforms from the mold. A coating that provides for excellent mold release was identified and deposited onto the inner mold surface. Several preforms were successfully cast. It was noted that an increase in the mold revolutions per minute was essential for removing porosity in the preforms. It was determined that the SiC/polymer mix had to be flowable in order to make preforms with uniform wall thickness. Too high a particle loading in the starting mix leads to too high a viscosity, resulting in nonuniform preforms. Several preforms measuring 5 cm (two inch) OD by 30.5 cm (12 inch) long have been prepared. An attempt will now be made to grow an alumina matrix into these preforms using the DIMOX™ directed metal oxidation process. The results of these experiments will be described in the next progress report.

2.3 Task 2-Pre and Post Test Material Characterization

2.3.1 Subtask 2A-Strength of Materials Testing and Analysis (UTSI)

Current plans call for strength testing of approximately 20 each C ring sections of a polymer based DIMOX™ tube. This should occur during the June-March 1996 quarter.

2.3.2 Subtask 2B-Corrosion Thermodynamic Analysis (U of Pa)

Analysis of the UTSI strength data [1] and microstructural information [2] has demonstrated the difficulties of modeling the DIMOX system. Thus, the PENN group has shifted focus from global thermodynamic and kinetic modeling to the analysis of local failure mechanisms. This role supports the experimental work at UTSI and will provide realistic answers rather than hypothetical models.

Figure 1, from the Lanxide brochure on the DIMOX material, shows the temperature dependence of the strength behavior for the SiC-Al₂O₃-Al composite. The decrease in strength with increasing temperature correlates with the melting of the residual (3-5%) Al-Si alloy. As shown in the last quarterly, report, the residual metal pockets may be as large as 30 microns. Thus, when these regions lose their load bearing capability, they become critical flaws. Figure 2 summarizes the characteristic strength behavior from the present study [1]. The difficulty in separating the temperature effects from the slag effects becomes obvious. While the 1400°C

slagged samples reacted significantly with the liquid slag phase, the slag effects at lower temperatures are still unclear.

It seems that the effects of slag at 1100°C are negligible, and the difference in strength is representative of the varying microstructures of different tubes. The statistical information on phase content (from the previous quarterly report) supports this conclusion. Different samples of the DIMOX material had variations in phase content that may have led to the differences in characteristic strengths. Lanxide's development of the centrifugal casting process using a preceramic polymer may reduce much of the microstructural variability.

The data from the 1260°C slag tests have not been included because of the anomalous strength effects. The adherent layer of slag had two effects: 1) increased apparent strength, and 2) decreased Weibull modulus. The increase in strength can be attributed to the load bearing capability of the slag during the stress tests at these temperatures. The decrease in Weibull modulus is representative of the defect concentration and non R-curve behavior of the low toughness slag outer layer. Thus, the slag layer has significant effects on the strength at 1260 °C. However, the actual target application of this material - long periods of moderate stress at high temperature, implies that a creep type of test may be useful for augmenting the extensive strength data performed to date. This tests the material's ability to support moderate loads for long times.

The reasons for this are twofold. First, the viscous nature of the slag implies that while it supports loads for high strain rate tests (as were done in this study), it may flow during a creep test. This flow would remove its load bearing capability. Additionally, the effects of the liquid Al-Si alloy on creep are unclear, but it is reasonable to assume that the liquid would enhance creep.

The phase stability of the DIMOX material during exposure has also been analyzed. Although the scatter in the data is large, there is a general trend toward increasing porosity with exposure time. This can be attributed to the gradual oxidation of the residual Al-Si alloy at high temperatures. This oxidation is expected to have an effect on the room temperature strength of the DIMOX material, since the residual alloy is a load bearing phase at room temperature. This effect is seen in Figure 3, also taken from the Lanxide information data. High temperature oxidation results in loss of residual alloy, leading to reduced room temperature strength.

Although the room temperature strength is not critical for the target coal applications, this information supports the conclusions that the preferential oxidation of the residual Al-Si alloy has significant effects on the mechanical behavior of the DIMOX material.

Thus, work this quarter has expanded to include assessment of the UTSI experimental data, and support for the continued UTSI goals. Although not reported, thermodynamic and kinetic modeling work continues, although the difficulties mentioned in previous reports have proven challenging.

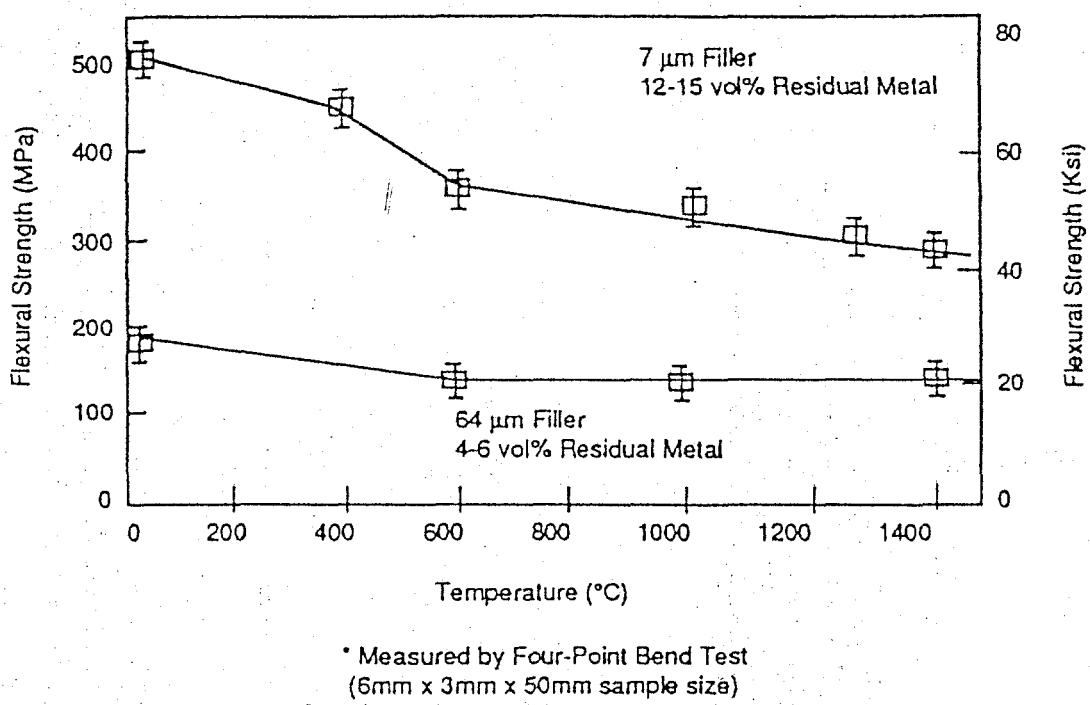


Figure 1: Temperature dependence of DIMOX strength (Lanxide Brochure)

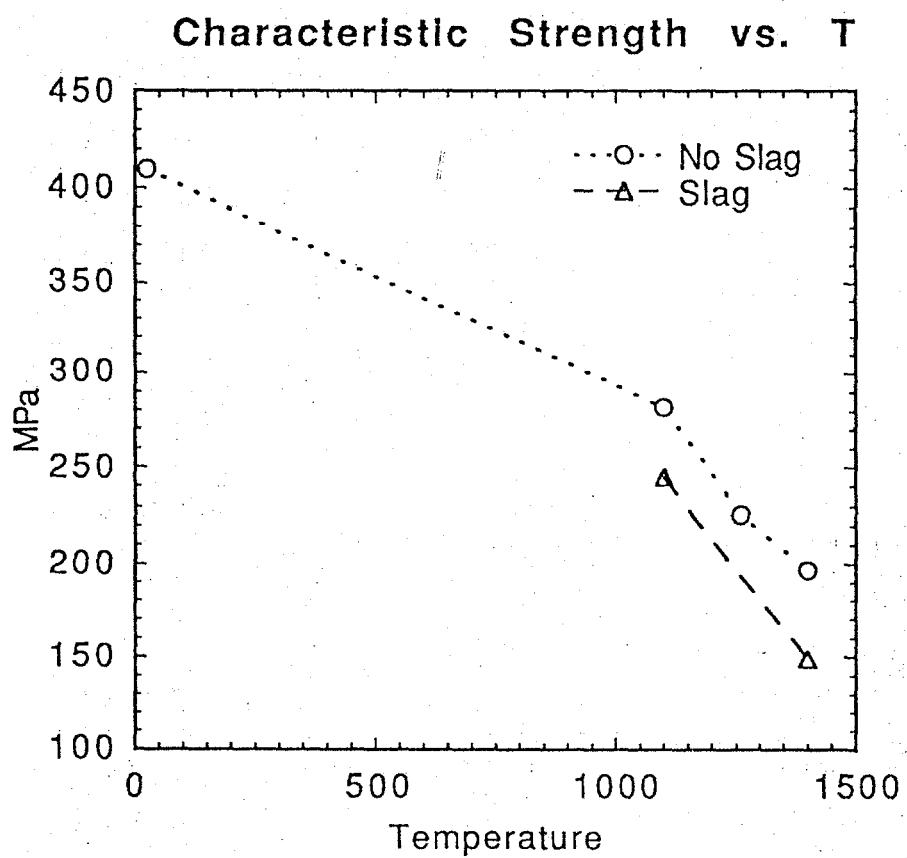


Figure 2. Temperature dependence of DIMOX strength (P. LaRue M.S. Thesis, UTSI)

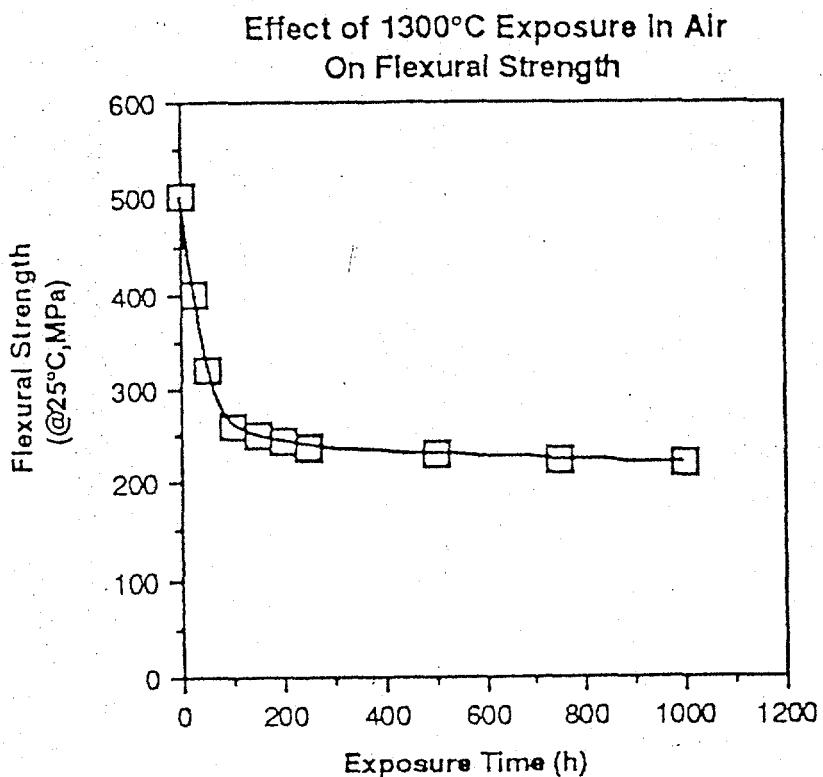


Figure 3. Effect of High Temperature Oxidation on Room Temperature Strength of the DIMOX material.

2.4 Task 3 Exposure Testing

2.4.1 Subtask 3A-Bench Scale Lab Tests (UTSI)

The remaining bench scale expose test will involve a 30.5 cm tube produced by the polymer preform. This tube will be exposed to coal slag for 200 hours at 1260°C. The tube will then be cut into 10 mm wide C ring sections for strength tests at 1260°C.

2.4.2 Subtask 3B-Field Exposure Tests (UTSI)

The termination of the MHD program has limited field testing to the five tubes exposed during the final MHD test. Since these tubes seem to be of less interest due to the potassium seed added to the coal flow, UTSI is devoting most of their effort to bench scale tests. Dr. Ken Natesan of the Energy Technology Division at Argonne National Laboratory has offered to perform a corrosion analysis on the field-tested tubes as his time permits. The results of Dr Natesan analysis will be included in a future quarterly report.

2.5 Task 4-Project Management

A paper has been submitted for publication in the October 1995 issue of the Journal of Minerals, Metals and Materials entitled, "Coating Ceramic Composites by a Laser In-Situ Reaction Technique."

A heat exchanger manufacturer has indicated great interest in using the Coal-Fired Flow Facility at UTSI for testing and analysis of their high-temperature, high-pressure heat exchanger based on DIMOX™ Lanxide tubes. Results from this grant would be invaluable to their program.

3.0 SCHEDULE

The next major event will be the testing of the polymer preformed tube. The test should be completed during the Jan-Mar 1996 quarter.

The coating research will be completed in the July-September 1996 quarter.

4.0 CONCLUSION

The overall research continues to go smoothly and most of the objectives are being met at this time. The laboratory high temperature exposure tests on the production Lanxide tube samples are now complete and the strength tests of the exposed samples, and their analysis is also complete. The coating work is making steady progress and there has been interest shown by a commercial firm in having some Lanxide tubes coated.

The financial position of the program is on target and no funding problems are anticipated.

5.0 REFERENCES

1. P. F. LaRue, "An Evaluation of the Strength of a $\text{SiC}_{(p)}$ /Al₂O₃ Ceramic Matrix Composite Exposed to Coal Slag at Elevated Temperatures," MS Thesis, University of Tennessee Space Institute (1996).
2. "High Performance Materials in Coal Conversion Utilization," Technical Progress Report for the Period April 1995 - June 1995, prepared for The United States Department of Energy, prepared by The University of Tennessee Space Institute, Tullahoma, TN 37388, No. DOE/PC/93225-7, July 1995.

APPENDIX A

**LASER INDUCED SURFACE MODIFICATION OF CERAMICS COATED CERAMIC
COMPOSITE FOR HIGH TEMPERATURE CORROSION PROTECTION**

APPENDIX A

Laser Induced Surface Modification of Ceramics Coated Ceramic Composite for High Temperature Corrosion Protection

In this quarter, work concentrated on preparing samples for laser coating and conducting laser coating experiments. All laser coating runs should be finished by the end of October 1995. This will be followed by microstructure analysis, phase analysis using SEM, EDS and x-ray analytical techniques of the coatings.

Sample Preparation

In order to systematically study the laser induced ceramic reaction coating, approximately 200 sample coupons were cut from a Lanxide $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite tube, (labeled 92-x-3105) which is the material in the as-fabricated state, of 5 cm OD x 30.5 cm length. The coupon dimensions are roughly 5mm x 10mm x 30mm.

Five coupons were coated with a 5 μm thick aluminum layer and 120 coupons were coated with a 5 μm thick titanium layer. All coatings were applied using the Physical Vapor Deposition (PVD) technique. The parameters employed for PVD are given in Table 1.

Table 1. Parameters used in Al and Ti PVD Coating

Material coated by PVD	Current (amp)	Voltage (volts)	Vacuum (torr)	Coat Time (min)
Aluminum	15-20	25-40	2×10^{-5}	5
Titanium	25-30	80-95	2×10^{-5}	5

Laser coating processing

Several laser induced ceramic reaction coating runs were conducted for the samples with different pre-existing surface conditions such as as-received, Al and Ti PVD surface coated. These runs were conducted with processing parameters given in Table 2 at different nozzle angle of the powder feeder.

Table 2. Laser Processing Parameter

Delivered power	150 watts
Mode of laser operation	Quesi continuous wave
Beam mode	TEM ₁₀
Beam polarization	Circular
Traverse speed	30 mm/sec
Focal position	8 mm above surface of sample
Beam diameter	1.1 mm
Beam overlap	22% (about 0.25 mm)
Powder feeder nozzle angle	30°, 40°, 45°, 50°, 55°
Assist gas	oxygen, 1-2 l/min

The experiments showed that the sample with a Ti PVD pre-coating had highest wettability. The nozzle angle variation has great influence on the reaction of 2Al + 3O₂ → 2Al₂O₃. (The higher the nozzle angle, the more complete the reaction appears to be; the more complete the reaction, the smoother the coating).

After an initial analytical analysis of these coated samples, a set of processing parameters will be chosen to conduct the remaining coating experiments.