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

FOR THE PERIOD
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Table of Contents

Page

List of Figures

1.0 INTRODUCTION

This is the ninth 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 U. S. 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 is complete. The development of a technique to laser coat the material has been the major activity while awaiting an innovatively produced new test sample. This sample will be tested and compared to the production tubes tested at UTSI.

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 $SiC_{(p)}/Al_2O_3$ 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 will also be investigated.

2.2 Task 1-Materials (Lanxide Corporation)

In the previous 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 installation of a centrifugal tube casting machine was completed and casting trials commenced. The machine exists 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. Several preforms were successfully cast. Several preforms measuring 2 in. OD by 12 in. long have been prepared. An alumina matrix was grown into several preforms using the DIMOX™ directed metal oxidation process. The tubes were cut and metallographic cross sections were prepared and characterized. The microstructures of the tubes were typical for a 500 grit SiC containing alumina matrix composite prepared by directed metal oxidation. Hence, the fabrication of SiC/alumina tubes using centrifugally cast, CERASET™ polymer bound preforms was successful. Two limitations of this novel fabrication approach were noted. First, the strong affinity of the CERASET™ polymer to metal surfaces requires that the mold be coated before it is charged with material. Second, after centrifugal molding, a CERASET™ polymer layer stays behind on the inner diameter of each preform tube. This layer gets voided of particles as they move radially outward during spinning of the mold. We were able to remove this polymer layer through controlled heating of the preform tube.

In consideration of the issues of the polymer sticking to the mold, formation of a polymer layer on the inner tube diameter, and also polymer cost, we came up with a potentially simpler approach. In essence, we successfully combined the methods of low temperature molding and centrifugal casting. In low temperature molding, an aqueous slurry of particles containing a small amount of colloidal silica is injected into a cold (e.g., -15°C) cavity. At these low temperatures, the water freezes to ice and the colloidal silica binder sets permanently. Upon heating, the ice melts and the resulting water evaporates. The colloidal silica stays behind and provides the preform with green strength. We modified our experimental centrifugal set-up by replacing the set of heat guns with an arrangement of liquid nitrogen evaporator nozzles. Upon charging the mold with aqueous 500 grit SiC slip, the mold was spun and the nitrogen nozzles were turned on. Following cooling, the mold was removed from the set-up and opened to remove the frozen preform. This preform was then heated to remove any water, and further heated to about 850°C to increase preform green strength. Several preforms were made in this manner. Two preforms have been submitted for infiltration with an alumina matrix by directed metal oxidation. The microstructures of the grown tubes will be characterized. If the microstructures are satisfactory, several tubes will be fabricated for testing at UTSI.

2.3 Task 2-Pre and Post Test Material Characterization

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

Activity under this subtask is inactive while awaiting the last sample tube delivery and its exposure under Subtask 3A below.

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

Work this quarter has expanded to include assessment of the UTSI experimental data and support for the continued UTSI goals. The strength vs. oxidation time behavior reported in previous quarterly reports refocused the corrosion investigation toward the reaction of the residual metal alloy during exposure. The largest of the residual metal pockets (>30 microns) may become critical flaws at high temperatures after oxidation. Thus, these pockets are expected to significantly influence the high temperature strength.

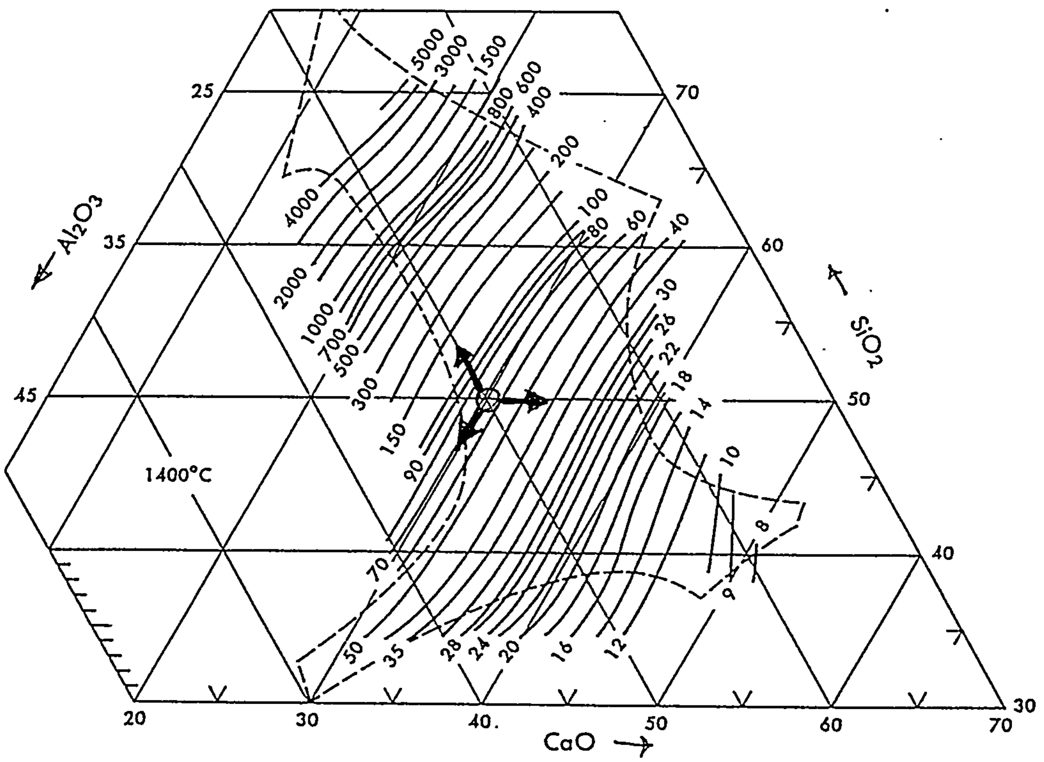
Literature information on the viscosity of steelmaking slags has been used to examine the behavior of the DIMOX™ material during oxidation. Because diffusion through the scale varies inversely with viscosity of the scale, viscosity information can yield useful insight about diffusion and oxidation.

The composition of the Illinois #6 slag is shown below:

network formers	Al_2O_3	16.6%
	SiO_2	47.8
	TiO_2	0.85
network modifiers	CaO	10.37
	Fe_2O_3	19.9
	K_2O	1.5
	MgO	2.62
	Na_2O	0.37

The network forming oxides tend to increase viscosity, and thus limit diffusion. Network modifiers tend to decrease viscosity and enhance diffusion. Thus, slag composition is roughly 17% Al_2O_3, 48% SiO_2 and 35% network modifiers. To account for the aluminosilicate slurry coating applied to the tube during processing, the model slag composition was enriched in Al_2O_3 and SiO_2. Thus, the literature search is focusing on slags with the composition ~50% SiO_2, 20% Al_2O_3 and 30% network modifiers.

Figure 1 shows isoviscosity lines for the SiO_2-Al_2O_3-CaO ternary system at 1400°C. Although the behavior of various cations as network modifiers is variable, the assumption of 30% CaO as the complete network modifier composition is reasonable for this first estimation.



Compositions, w/o.

J. S. Machin and T. B. Yee, *J. Am. Ceram. Soc.*, 31, 200 (1948).

Figure 1. Isoviscosity lines (poise) in the CaO-Al2O3-SiO2 system at 1400°C.

Future work will attempt to determine the reaction direction during oxidation. As shown in Figure 1, composition changes in the slag can have a large effect on viscosity. Examination of the UTSI experimental results and discussion with the UTSI group should yield information about the reaction process.

2.4 Task 3-Exposure Testing

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

The remaining bench scale exposure test will involve the tube produced by the polymer preform discussed in Task1. 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 Sections for strength tests at 1260°C). During this quarter, the slag powder feeder system used in previous exposure tests was refurbished in preparation for the final test.

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 has devoted most of the effort to bench scale tests and coating research..

2.5 Task 4-Project Management

Preparations are underway for the presentation of a "laser coating" paper next quarter that will be partially funded by this grant.

3.0 SCHEDULE

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

The coating research will be completed in July-September 1996 quarter and will result in a PhD dissertation.

4.0 CONCLUSION

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

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

APPENDIX A

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

APPENDIX A

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

During this quarter, a laser coating was applied to test coupons which were mechanically strength tested. The strength test results were compared to similar tests on as-received coupons.

MECHANICAL TESTING

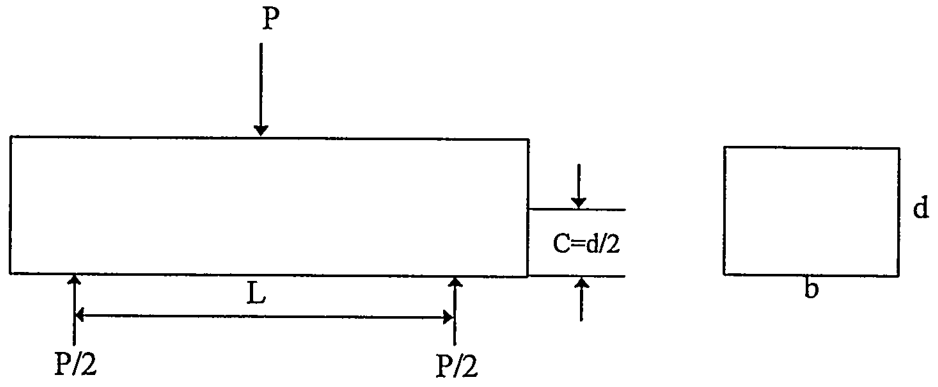
The strength of ceramic materials is generally characterized by bend testing (also referred as flexure testing). The test specimen can have a circular, square, or rectangular cross section and is uniform along the complete length. Such a specimen is much less expensive to fabricate than a tensile specimen.

Bend testing is conducted with the same kind of universal test machine used for tensile and compressive strength measurements. The test specimen is supported at the end and the load is applied either at the center (3-point loading) or at two positions (4-point loading). The bend strength is defined as the maximum tensile stress at failure and is often referred to as the modules of rupture, or MOR. The bend strength for a rectangular test specimen can be calculated using the general flexure stress formula:

$$\sigma = \frac{Mc}{I}$$

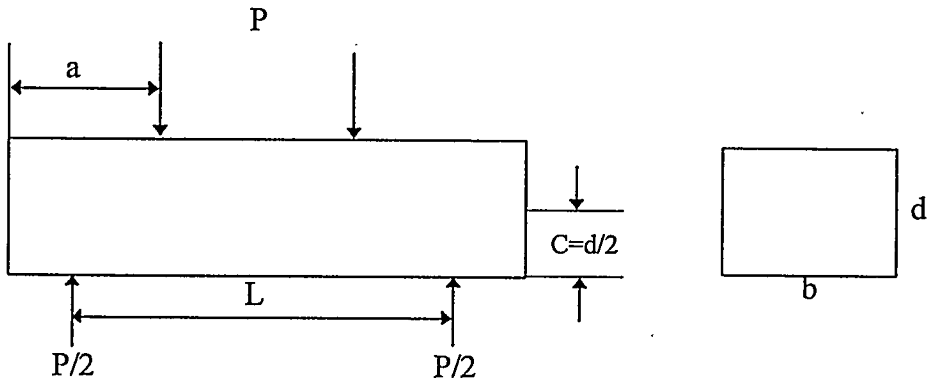
where M is the moment, c the distance from the neutral axis to the tensile surface, and I the moment of inertia. For a rectangular test specimen $I = \frac{b\,d^3}{12}$ and $c = \frac{d}{2}$, where d is the thickness of the specimen and b is the width. Figure 1 illustrates the derivation of 3-point and 4-point flexure formulas for rectangular bars.

The mechanical testing performed in this study was not designed to produce an absolutely measured value but, rather, to detect any difference in the mechanical properties between the as-received material and laser-treated material (laser induced reaction coated). Because of high thermal shock to the material during laser



$$M=\frac{L}{2}\frac{P}{2} \qquad I=\frac{b\,d^3}{12} \qquad \sigma_{3-PT}=MOR=\frac{Mc}{I}=\frac{3PL}{2b\,d^2}$$

(a) 3-POINT



$$M=\frac{p}{2}a \qquad I=\frac{b\,d^3}{12} \qquad \sigma_{4-PT}=MOR=\frac{Mc}{I}=\frac{3Pa}{b\,d^2}$$

(b) 4-POINT

Figure 1 Derivation of 3- and 4-point flexure formulas for a rectangular bar processing, the purpose of the mechanical testing was to determine any change in the mechanical properties due to the laser surface processing. Due to the limitation of the small dimensions of the testing material available, the three-point bend test was used.

The material supplied for this test was cut from a DIMOX™ tube with a 51 mm outside diameter and a wall thickness of approximately 5.0 mm. Lanxide's material designation for this material was 93-x-3015. The sample coupons were cut from the tube, each coupon approximately 30 mm long and 10 mm wide in outside surface. (The inside surface width was less than that of the outside surface). Figure 2 gives the sample coupon dimensions. The coupon was roughly considered as rectangular and B ($B = \frac{a+b}{2}$) as its width. The bending strength is:

$$\sigma = \frac{3PL}{2B_c^2}$$

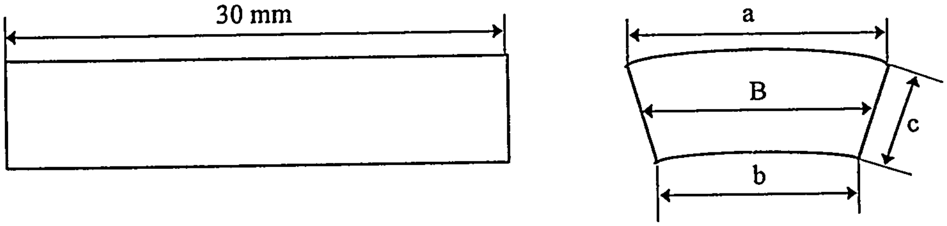


Figure 2. Sample dimensions

Ten of these coupons from each of the as-received and laser-induced reaction coated samples were selected for bend testing. An Instron testing machine was used. Table 1 gives the parameters used in three bend testing. Table 2 gives the sample dimensions and the measurement results.

Table 1. Parameters used for bend testing

Load Speed	Normal Load	Record Chart Speed
0.02 in/min	500 lbs	50 in/min

Table 2. Measure Results (L = 22.66 mm)

Sample #	a (mm)	b (mm)	c (mm)	B (mm)	Fracture load P (lbs)	σ (Kpsi)	σ (MPa)
As-Received Samples							
1	9.94	8.26	4.96	9.10	322	31.49	217.13
2	9.88	7.52	5.08	8.70	366	35.75	246.48
3	9.72	8.84	5.30	9.28	360	30.28	208.81
4	9.52	7.68	4.62	8.60	338	40.35	278.25
5	10.54	8.72	4.96	9.63	408	37.76	260.39
6	9.26	7.62	4.76	8.44	291	33.37	230.09
7	9.34	7.90	5.40	8.62	496	43.23	298.06
8	12.30	9.58	5.04	10.94	400	31.56	217.58
9	9.22	7.26	5.04	8.24	324	33.94	234.05
10	10.80	8.26	5.42	9.53	474	37.13	256.00
AVG.	10.05	8.16	5.06	9.11	378	35.49	244.68
Laser Induced Reaction Coated Samples							
1	9.70	8.42	4.80	9.06	275	28.84	198.83
2	10.34	8.48	5.04	9.41	315	28.90	199.26
3	9.70	8.16	4.82	8.93	381	40.27	277.67
4	10.30	8.24	5.40	9.27	468	37.97	261.78
5	10.58	8.64	5.44	9.61	422	32.50	224.09
6	9.80	8.46	5.24	9.13	294	25.72	177.32
7	10.52	8.44	4.94	9.48	288	27.30	188.23
8	10.50	9.26	4.96	9.88	288	25.98	179.15
9	9.80	8.76	5.14	9.28	323	28.85	198.89
10	10.70	9.26	4.80	9.98	286	27.23	187.74
AVG.	10.19	8.61	5.06	9.40	334	30.35	209.30

A summary of the test data obtained may be seen in Table 3.

Table 3. Summary of three-point bend testing results

Average Value	σ (MPa)	Relative Value
As-received Samples	244.68	1
Laser Induced Reaction Coating Samples	209.30	0.86

As seen in Table 3, the reduction of about 14% in the strength of the laser coated sample compared to the as-received sample is realized. Such reduction may be due to a single or combination of factors, i.e., thickness of the coating, physical characteristics (porosity and cracks) of interface between the coating and the substrate, soundness of the coating (pores, cracks and inclusions), surface topography of the coating (roughness cracks and pores) and chemical phases at the interface between the coating and the substrate. The evaluation of the relative strength provides a tool to choose an optimum combination of materials and processing parameters for production of sound and strong coatings with minimum strength loss.