-FINAL REPORT-

**HIGH PERFORMANCE MATERIALS IN COAL
CONVERSION UTILIZATION**

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-ABSTRACT-

This report describes the research conducted at the University of Tennessee Space Institute on high performance materials for use in corrosive environments. The work was supported by a US Department of Energy University Coal Research grant. Particular attention was given to the silicon carbide particulate reinforced alumina matrix ceramic composite manufactured by Lanxide Corporation as a potential tubular component in a coal-fired recuperative high-temperature air heater. Extensive testing was performed to determine the high temperature corrosion effects on the strength of the material. (A computer modeling of the corrosion process was attempted but the problem proved to be too complex and was not successful. To simplify the situation, a computer model was successfully produced showing the corrosion thermodynamics involved on a monolithic ceramic under the High Performance Power System (HIPPS) conditions (see Appendix A). To seal the material surface and thus protect the silicon carbide particulate from corrosive attack, a dense non porous alumina coating was applied to the material surface. The coating was induced by a defocused carbon dioxide laser beam. High temperature corrosion and strength tests proved the effectiveness of the coating. The carbon dioxide laser was also used to successfully join two pieces of the Lanxide material, however, resources did not allow for the testing of the resulting joint.

-FINAL REPORT-
HIGH PERFORMANCE MATERIALS IN COAL CONVERSION/UTILIZATION

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
1.0 INTRODUCTION	1
2.0 BACKGROUND	1
2.1 UTSI RELATED RESEARCH	1
2.1.1 Materials Screening	1
2.1.2 Heat Transfer Enhancement	2
2.1.3 HTAH Design	2
2.2 Related Research by Others	2
2.3 DOE Joint University/Industry Research Grant	2
3.0 DISCUSSION	3
3.1 DIMOX™ Material	3
3.2 Production Tubes	4
3.2.1 Field Testing & Analysis	4
3.2.2 Laboratory Testing & Analysis	5
3.2.3 Computer Modeling	32
3.3 Development Tubes	35
3.3.1 Preform and Growth	35
3.3.2 Centrifugal Casting	36
3.4 Laser-Induced Processing	40
3.4.1 Coating	40
3.4.2 Joining	79
4.0 CONCLUSIONS	80

TABLE OF CONTENTS

(continued)

	<u>Page</u>
5.0 REFERENCES	82
APPENDIX A MODELING OF HIPPS ENVIRONMENT	A-1
APPENDIX B SUMMARY OF ADDITIONAL WORK ON LOW TEMPERATURE MOLDING	B-1

LIST OF FIGURES

	<u>Page</u>
Figure 1. DIMOX™ Process Composite Formation	3
Figure 2. Characteristic Microstructure of a Particulate Reinforced Ceramic Matrix Composite	4
Figure 3. Laboratory Slag Dispersal System	6
Figure 4. 200 Hours at 1100°C	6
Figure 5. 200 Hours at 1260°C	7
Figure 6. 200 Hours at 1400°C	7
Figure 7. C-ring Section of Tube	8
Figure 8. Material Compression Testing Apparatus	8
Figure 9. C-ring Section Test Position in Furnace	9
Figure 10. Finite Element Calculation of Maximum Principal Normal Stresses in a C-shaped Ring Under Compression.	11
Figure 11. Complete Strength Data	18
Figure 12. Strength Data for the Tube Material Exposed to Slag at 1260°C as a Function of the Ratio of Modulus Elasticity of the Tube and Slag Material.	21
Figure 13. A Microstructure Image of Sample 11# in Middle of Cross Section	24
Figure 14. Aluminum Content vs. Exposure Conditions	26
Figure 15. Alumina Content vs. Exposure Conditions	26
Figure 16. SiC Content vs. Exposure Conditions	27
Figure 17. Porosity Content vs. Exposure Conditions	27
Figure 18. Characteristic Strength vs. Exposure Conditions	28
Figure 19. Cross Section Views of Samples Exposed to Slag at High Temperature	29
Figure 20. Phases Diagram of System CaO - Al ₂ O ₃ (A=Al ₂ O ₃ , C=CaO)	30
Figure 21. Phase Diagram of System CaO - Al ₂ O ₃ - SiO ₂	31
Figure 22. Effect of High Temperature Oxidation on RT DIMOX™ Material Strength (Lanxide)	33
Figure 23. Temperature (°C) Dependence of DIMOX™ Strength	34
Figure 24. Extrusion Preform and DIMOX™ Process	35
Figure 25. A Cross Section View of Tube A, B and C (respectively)	39

LIST OF FIGURES

(continued)

	<u>Page</u>
Figure 26. Scanning Electron Micro-graphs of the As-Received $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$: (a) surface view, (b) cross- section view	45
Figure 27. Scanning Electron Micro-graph of Aluminum Powder	46
Figure 28. Schematic Diagram of the Experimental Set-up for Laser Coating	47
Figure 29. Derivation of 3-Point Flexure Formulas for a Rectangular Bar	50
Figure 30. Derivation of 4-point Flexure Formulas for a Rectangular Bar	50
Figure 31. Sample dimensions	51
Figure 32. Topographical Features of Alumina Coating on $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Samples [(a)~(c) samples from trials #1 to #17; (d)~(e) samples from trials #18 to #31] . . .	55
Figure 33. Magnified Views of Some Samples from Figure 32. [(a) trial #8, (b) trial #17 and (c) trial 28.]	56
Figure 34. SEM Graph of a High Magnification View for the Sample from Trial #28.	57
Figure 35. Cross-sectional View of the Laser-induced Reaction-coated $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$	57
Figure 36. X-ray Diffraction Analysis of Laser-induced Reaction-coated $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$	58
Figure 37. Free energy formation as a function of temperature for SiO_2 , TiO_2 and $(2/3)\text{Al}_2\text{O}_3$	60
Figure 38. Free Energy Formation as a Function of temperature for SiC and $(1/3)\text{Al}_4\text{C}_3$	60
Figure 39. Weight change of $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Specimens after Exposure at 1200°C with a Na_2O_3 Layer	63
Figure 40. Optical Micrograph of Cross-sectional View of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C for 150 Hours (after silicates removed with a HF solution) Showing $\text{Si}/\text{Al}_2\text{O}_3$ Oxidation Product on Surface	64
Figure 41. X-ray Diffraction Pattern of the As-received Composite	65
Figure 42. Phase Diagram of Al-Si Alloy	65
Figure 43. X-ray Diffraction Patterns of the Specimens without the Laser-induced Reaction Alumina Coating (after the corrosion products removed with a HF solution)	67
Figure 44. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C for 50 Hours (after silicates removed with a HF solution)	68

LIST OF FIGURES

(continued)

	<u>Page</u>
Figure 45. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C for 200 Hours (after silicates removed with a HF solution)	69
Figure 46. Optical Micrograph of a Cross-sectional Views of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C (after silicates removed with a HF solution) (a) for 50 hours, (b) for 200 hours	70
Figure 47. SEM Graph of Surface View of Specimen Exposed at 1200°C for 50 Hours Showing Glassy Layer in Center Section (before the corrosion products removed by a HF solution)	71
Figure 48. SEM Graph of Magnified View of the Glassy Area Shown in Figure 47 and its Elementary X-ray Maps	72
Figure 49. X-ray Diffraction Patterns of Specimens without Laser-induced Reaction Alumina Coating (before corrosion products removed by a HF solution)	73
Figure 50. SEM Graph of a Surface View of Structure Underlying Glass Phase (glassy phase removed with a HF solution) and Element X-ray Maps	74
Figure 51. Optical Micrographs of Cross-sectional Views for the Specimens: (a) as-coated with the laser-induced reaction alumina coating, (b) the specimen with the laser-induced reaction alumina coating exposed at 1200°C for 200 hours corrosion (after washing with a HF solution)	75
Figure 52. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite with the Laser-induced Reaction Alumina Coating Corroded at 1200°C for 50 Hours (after washing with a HF solution)	76
Figure 53. X-ray Diffraction Patterns of Specimens with the Laser-induced Reaction Alumina Coating (before the corrosion products removed by HF solution)	77
Figure 54. X-ray Diffraction Patterns of Specimens with the Laser-induced Reaction Alumina Coating (after the corrosion products removed by a HF solution)	78

LIST OF TABLES

	<u>Page</u>
Table 1. Field Test Conditions	4
Table 2. Analysis of Illinois #6 Slag	5
Table 3. Strength Test Matrix_	9
Table 4. Summary of Strength Results	17
Table 5. Modulus of Elasticity Results	22
Table 6. Conditions of Analyzed Samples	23
Table 7. Measurements for Phase Volume Percentage Calculations	24
Table 8. Illinois #6 Slag Composition (%)	30
Table 9. Composition of Illinois #6 Ash by Network	32
Table 10. Tube Dimensions	37
Table 11. The Measurement for Phase Volume Percent (%)	38
Table 12. Summary of Strength Results	40
Table 13. Characteristics of SiC _(p) /Al ₂ O ₃ Composite Substrate	46
Table 14. The parameters used for PVD Coating of Titanium and Aluminum	47
Table 15. Laser Processing Parameters	49
Table 16. Parameters Used for Three-point Bend Testing	51
Table 17. Sample Dimensions (L=22.66 mm)	52
Table 18. Laser Processing Parameters	54
Table 19. Three-Point Bending Test Results for the As-Received Samples	61
Table 20. Summary of Three-Point Bend Testing Results	62

-FINAL REPORT-
HIGH PERFORMANCE MATERIALS IN COAL
CONVERSION/UTILIZATION

1.0 INTRODUCTION

This report describes the research conducted at the University of Tennessee Space Institute (UTSI) on high performance materials for use in corrosive coal fired environments that was supported by a US Department of Energy University Coal Research grant. Particular attention has been given to the ceramic composite manufactured by Lanxide Corporation as a potential tubular component in a recuperative high-temperature air heater. Lanxide served as a subcontractor to UTSI as a source of their material; the University of Pennsylvania was also a subcontractor and provided computer modelling of the effects of the test environment on the Lanxide material. This grant resulted in a M.S. thesis and a Ph.D. dissertation, both written at UTSI.

2.0 BACKGROUND

The UTSI interests in high performance materials relate to the proof-of-concept testing at the US Department of Energy (DOE) Coal Fired Flow Facility (CFFF) magnetohydrodynamic (MHD) installation at UTSI. Achievement of the potentially high efficiency possible through MHD power generation is contingent on the ability to preheat the MHD combustion air to the neighborhood of 1371°C (2500°F)¹. The initial MHD planning called for the development of a cumbersome cluster of *regenerative* high-temperature air heaters (HTAH) to achieve this goal.

Researchers at UTSI performed material evaluations concurrent to the long duration MHD test series to explore the feasibility of a *recuperative* HTAH for the preheating of the MHD combustion air. Such an air heater would be cheaper and much simpler than a *regenerative* HTAH. New advanced ceramics and ceramic composites were screened as candidate materials for components in a high-pressure *recuperative* HTAH. These tests identified a tubular ceramic composite which indicated that it may be feasible to use a *recuperator* to replace the more costly and complicated *regenerator* HTAH concept for the MHD requirement.

More recent interest in a high pressure *recuperative* HTAH has developed since the establishment of the DOE High Performance Power System (HIPPS) Program. This new technology will require a HTAH to achieve the potentially high efficiencies envisioned².

2.1 UTSI RELATED RESEARCH

2.1.1 Materials Screening

From 1989 through 1993, UTSI performed an extensive long duration MHD test series in the US DOE Coal-Fired Flow Facility (CFFF). Concurrent with the MHD tests, a materials screening program was conducted involving over fifteen different types of ceramic and ceramic composites³. These samples were subjected to the exhaust from the combustion of potassium seeded Montana Rosebud or Illinois #6 coal. Several tests lasted up to 300 hours and the materials were exposed in several temperature zones within the CFFF flow train. Of the materials tested, only the Lanxide SiC_p/Al₂O₃ DIMOX™ ceramic composite survived and as a result it was tested extensively. One, two and three inch OD Lanxide tubes with lengths up to six feet long were studied.

One of these tubes survived with minor degradation at a coal exhaust (at a temperature estimated to be about 1400°C (2550°F)) for 247 hours while during the same test a similar tube in only approximately a 55°C higher gas temperature was severely corroded/eroded after only 179 hours.

These two tubes provided an indication of the operating temperatures that should be considered in the MHD environment.

Based on the encouraging results from the materials screening, and a related detailed study at UTSI³, Lanxide, the University of Pennsylvania and UTSI teamed together to submit a proposal to perform additional research on the Lanxide product. This proposal was favorably received and resulted in a grant which is the subject of this report.

2.1.2 Heat Transfer Enhancement

The high cost of ceramic materials dictates the use of heat transfer enhancing devices to reduce the amount of material needed in a HTAH². UTSI, therefore, conducted detailed heat transfer augmentation studies which resulted in three theses presented for Master's of Science degrees^{5,6,7} plus a fourth in progress. These studies all focused on a bayonet style (tube within a closed end tube) counter-flow heat exchanger. Tubulators (to increase convection heat transfer) and larger surfaces areas (to enhance radiation heat transfer) were both considered and deemed essential.

2.1.3 HTAH Design

UTSI designed an innovative pilot HTAH facility for a private firm. This was a proprietary effort that was based on the use of the Lanxide $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ DIMOXTM ceramic composite for the heat exchanger components.

2.2 Related Research by Others

The US DOE has supported research by others similar to that reported herein. The rationale for these somewhat overlapping programs was to compare results from different testing procedures. On going work at the High Temperature Materials Laboratory (HTML) at the Oak Ridge National Laboratory involves the testing of several silicon carbide based ceramics and includes the Lanxide $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ ceramic composite⁸. Similar work was conducted at the Energy & Environment Research Center at the University of North Dakota⁹. The temperatures used in the UTSI study were the same as those used by the HTML and/or North Dakota researchers. The Argonne National Laboratory has also done extensive work in this area².

2.3 DOE Joint University/Industry Research Grant

In October of 1993, UTSI began a three year grant entitled, "High Performance Materials in Coal Conversion Utilization". The grant was for a joint university/industry effort under the Department of Energy (DOE) University Coal Research Program. UTSI was the prime contractor and The University of Pennsylvania and Lanxide Corporation were subcontractors. This report documents the research effort supported by the grant.

The objective of the grant was to test, analyze, and improve the heat and coal slag corrosion resistance of Lanxide's $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ DIMOXTM ceramic composite tubular material. The material was evaluated for its ability to withstand the pressures, temperatures and corrosive environment which would be encountered within a coal-fired high pressure HTAH. The evaluation included strength testing at elevated temperatures. Protective coatings and joining techniques were also investigated.

Cost Sharing

The cost share contributions to this research were as follows:

UTSI upgraded an existing MTS Systems strength testing machine for the mechanical testing of ceramics at elevated temperatures.

3.0 DISCUSSION

3.1 DIMOX™ Material

The DIMOX™ directed metal oxidation process for the manufacture of ceramic composites is shown in Figure 1.

Figure 1. DIMOX™ Process Composite Formation

A preform of the reinforcing material is surrounded by a growth barrier. The preform is placed in contact with a molten metal so that the metal permeates the preform via capillary action into the preform voids. This process occurs in the presence of a reactive gas which turns the metal into a ceramic matrix. Figure 2 is a micro-photograph of the resulting product.

Figure 2. Characteristic Microstructure of a Particulate Reinforced Ceramic Matrix Composite

The DIMOX™ composite material used on in this research incorporated silicon carbide particulate as the reinforcement ceramic. The metal component was aluminum which, in the presence of the reactant gas oxygen, becomes an alumina ceramic matrix. Due to the nature of this growth process, a small amount of residual aluminum remains scattered throughout the resulting composite material.

3.2 Production Tubes

To make tubular products via the DIMOX™ process, tubular SiC preforms were made via slip casting (i.e., the pouring of a SiC slip into plaster molds). The SiC tube preforms were pre-fired to increase their strength prior to the growth process step. The DIMOX™ alumina matrix growth was performed using either an inside-out or outside-in growth direction in a horizontal furnace. Lanxide provided 15 each of these [183 cm (six foot), 5 cm (two inch) OD] SiC_(p)/Al₂O₃ DIMOX™ tubes to UTSI for testing.

3.2.1 Field Testing & Analysis

Although the grant was written to take advantage of the MHD testing series to provide the test environment for the materials, the MHD program was terminated prior to the start of the grant. As a result, four production tubes were exposed in the last MHD test (and shortly before the start of the grant). The tubes were positioned as follows:

Table 1. Field Test Conditions

52 Hours in Potassium Seeded Montana Rosebud Coal Exhaust

Tube	1. 1399°C	(2550°F)	Reducing Zone
Tube	2. 1260°C	(2300°F)	Reducing Zone
Tube	3. 1093°C	(2000°F)	Reducing Zone
Tube	4. 1149°C	(2100°F)	Oxidizing Zone

Since interest in MHD had diminished, a joint meeting between DOE, UTSI, Lanxide, U of Pa and Oak Ridge National Lab (ORNL) personnel was held to redirect the research effort. It was agreed by all that the program could be shifted to the laboratory. The field tests results were no longer as important since the exhaust stream was contaminated by the potassium required for the MHD process. Although all the tubes withstood the 52 hour test, no analysis was attempted by UTSI. (A portion of each tube was sent to Dr. Ken Natesan at Argonne National Laboratory for study).

3.2.2 Laboratory Testing & Analysis

Laboratory Setup

The laboratory testing/analysis of the production tubes was the basis for a UTSI M.S. degree thesis where the details of the following research are more fully described¹⁰. To bracket the envisioned HTAH operating conditions, two each 25 cm (10 inch) sections of two inch OD Lanxide production tubes (93-X3063) were exposed to three different temperatures in a laboratory furnace. This same sequence was again followed but with the addition of exposure to slag.

The slag used was provided by Southern Illinois Power and was produced from Illinois # 6 coal. The slag was pulverized to 250 μm and an ash analysis was performed by UTSI with the following normalized results:

Table 2. Analysis of Illinois #6 Slag

Water	2.25 %
Ash	97.75
Elemental (assumed oxide)	
Al ₂ O ₃	16.57%
CaO	10.37
Fe ₂ O ₃	19.79
K ₂ O	1.48
MgO	2.62
Na ₂ O	0.37
SiO ₂	47.76
TiO ₂	0.85
SO ₃	0.19
Total	100.00%

Two UTSI PerecoTM electric resistance furnaces were equipped with temperature controllers. One was used to heat clean tubes and the other was used for exposing the tubes to pulverized coal slag during the heating process. An automated slag dispersal system, as shown in Figure 3, was added to this furnace so that a fresh layer of the pulverized coal slag could be sprinkled on the tube every hour. The slag dispersal system was designed to refresh the slag deposited at the rate of 1 cm³ of slag per linear cm of tube, once per hour, for 200 hours. (This rate was chosen based on calculated tube slagging rates in the UTSI CFFF based on video tape recordings of the screening tests).

A. System Setup

B. System in Operation

Figure 3. Laboratory Slag Dispersal System

Both furnaces were heated for 200 continuous hours for each condition in the test series matrix at:

1100°C (2012°F) 1260°C (2300°F) 1400°C (2551°F)

Figures 4, 5, and 6 show the results of the tubes that were exposed in the "slagging" furnace. The slag deposited at 1100°C, as shown in Figure 4, was sintered and was easy to remove. It left a clean tube surface which was very similar to the as-received state.

Figure 4. 200 Hours at 1100°C

The slag buildup at 1260°C, as shown in Figure 5, was hard, glassy and full of air bubbles. This covering was much harder and more irregular than the previous sample. It was not possible to remove the slag without damaging the underlying material. [It was partially removed (with a brick saw) in preparation for the subsequent mechanical tests.]

Figure 5. 200 Hours at 1260°C

The slag layer created at 1400°C, as shown in Figure 6, was thin and glassy. (It was not necessary to remove it for the mechanical tests).

Figure 6. 200 Hours at 1400°C

Mechanical Testing

At the completion of the exposure tests, all the heated tubes (plus two that were not) were cut into 10 mm wide C-shaped rings as shown in Figure 7. (Use of the C-ring was based on studies showing that a tube's C-ring compression strength could be equated to the tube's burst strength¹¹.)

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Figure 7. C-ring Section of Tube

Each of these rings was then tested in the UTSI hydraulic universal strength testing machine built by MTS Corporation as shown in Figure 8. The compression force was at the rate of 0.5 mm per minute. Each C-ring was strength tested at the same temperature that it was originally subjected to in the earlier exposure testing phase.

Figure 8. Material Compression Testing Apparatus

A small furnace surrounded the specimens to provide the necessary heating during the tests as shown in Figure 9. The heating elements were covered with a refractory packing to protect them from the high energy broken C-ring fragments.

Figure 9. C-ring Section Test Position in Furnace

The following table describes the strength test matrix:

Table 3. Strength Test Matrix

Temperature	With Slag	No Slag
Room Temperature		40 C-rings
1100°C (2012°F)	40 C-rings	40 C-rings
1260°C (2498°F)	40 C-rings	40 C-rings
1400°C (2696°F)	40 C-rings	40 C-rings

Weibull Analysis of Failure Probability

Deterministic design techniques are usually adequate for metallic materials subject to static loads or under low cycle loads. However, statistical techniques are required for failure estimates of ceramics and (also for metallic materials undergoing highly cyclic stress loadings). For ceramics, the need for a statistical approach to failure estimates is largely due to the brittle nature of ceramics and their sensitivity to flaws. Therefore, while the strength of a metal is typically described by a single yield stress or ultimate tensile stress value, the fracture strength of a ceramic is described by a statistical distribution.

The strength distribution of a ceramic material is usually described by either a two-parameter or a three-parameter Weibull distribution. The three parameter distribution is only used when there is no probability of failure at stresses maintained below some specified level. Since this is not normally the case, the two-parameter Weibull distribution is more commonly used.

The two-parameter Weibull distribution is given by

$$F = 1 - \exp(-KA(\sigma_{\max}/\sigma_0)^m) \quad (1)$$

where:

F is the probability of failure,
 $\sigma_{\max}$ is the maximum stress value in a specimen,
 σ_0 is the characteristic strength, and
 m is the Weibull parameter.

In this equation σ_0 and m are material properties which are assumed to be independent of geometry and loading conditions. The characteristic strength σ_0 represents the stress level which, if present across a unit surface area of material in uniform tension would result in a 63.2% probability of failure. The Weibull parameter m , which was initially considered as a purely empirical constant useful for describing the amount of variation in probability of failure, has been shown to be related to the flaw size distribution in the material to be tested.

In Equation 1, KA is an effective area term defined as

$$KA = \int \left(\frac{\sigma}{\sigma_{\max}} \right)^m dA \quad (2)$$

where σ is the stress distribution in the specimen and dA is a differential element of the surface area of the specimen. It is this term which contains the geometry and load configuration dependent terms. A similar expression for effective volume KV can be substituted for KA throughout this analysis if the critical flaws in the material are volume distributed rather than located at the surface as is the case in this study. The stress terms such as σ , σ_0 , which represents a distribution of stresses obtained by calculation of stresses on the surface of the specimens, and $\sigma_{\max}$, which are characteristic stress values, are all defined as maximum principal normal stresses.

The maximum principal normal stress is the largest tensile stress found at a given point in a stress field, or the smallest compressive stress if no tensile stresses exist, and is used in the prediction of failure of brittle materials. The stress distribution created by the load in these tests (as predicted by a finite element analysis) is shown in Figure 10.

Figure 10. Finite Element Calculation of Maximum Principal Normal Stresses in a C-shaped Ring Under Compression.

Once the Weibull parameter and characteristic strength of a material are known, the probability of failure of a sample of the material subjected to a specified set of loads can be determined. This is done by simply evaluating Equations 1 and 2 to find a value for F . This is then the probability that a given sample will fail because it contains a critical flaw likely to cause the sample to break when the specified loads are applied. (i.e., if a value of 0.01 is found for F , then one out of every hundred samples constructed of the material and subjected to the specified loads is likely to break).

Traditionally, evaluation of the parameters necessary to describe such a probability of failure has required strength testing of professionally prepared samples having uniform, easily described geometries. These samples may be in the form of small beams for three or four point bend tests, circular or C-shaped rings to be tested in tension or compression, or specially designed cylindrical tension specimens. What these samples all have in common is their strict dimensional uniformity and surface preparation requirements. When such samples are used, the data can be fit to Equation 1 in a straight forward manner to determine the values of m and σ_0 which are representative of the material.

However, use of these ideal samples is not always possible. For example, the cost of preparing or obtaining such samples may be prohibitive, the process of producing such samples may alter or destroy a flaw distribution whose effects are to be studied, the dimensions of available stock material may be unsuitable for production of such samples, or sufficient time may not be available to produce such high quality samples. To deal with this problem, a new analysis technique was developed in the present study to allow calculation of the Weibull parameter and characteristic strength of a material, using the results of fast fracture testing of samples of variable geometry.

Equivalent Load Method

The new technique developed, called the equivalent load method, is centered around the computation of an *equivalent load* which, if applied to some standardized geometry, would result in the same probability of failure as the actual specimen when it was subjected to the true applied load. This standard geometry may represent an ideal form of the actual samples being tested or may be entirely different. The theoretical basis for this technique is based on an extension of Jadaan's work with strength of ceramics¹¹.

Jadaan presented Equations 1 and 2 along with a method for equating the probability of failure of two specimens with different geometries or loading configurations once the Weibull parameter (m) is known. That relationship reduces to a statement that if two samples are made of the same material and have equal probabilities of failure, the integral of σ^m over the surface area of each of the samples will be the same. That is, the probability of failure F is the same for two samples when

$$\int \sigma_a^m dA_a = \int \sigma_s^m dA_s \quad (3)$$

If the stress distribution in a sample (σ), expressed in MPa, is proportional to a single load value, then it can be written as $P \cdot \sigma_u$ where P is the magnitude of the load, expressed in Newtons, applied to produce the actual stress distribution and σ_u is a stress distribution produced per unit load, expressed in MPa/N. So,

$$\sigma_u = \frac{\sigma(P)}{P} \quad (4)$$

where $\sigma(P)$ is the distribution of maximum principal normal stresses produced by load P . This substitution should be valid for any linear elastic material subjected to small deflections. Most ceramic materials, including the material evaluated in this study, will satisfy these requirements. Written in this form, two samples with different geometries will have equal probabilities of failure if the following generalization of Jaadan's theory holds true.

$$P_s^m \int \sigma_{u_s}^m dA_s = P_a^m \int \sigma_{u_a}^m dA_a \quad (5)$$

This can then be rearranged into the following form.

$$P_s = P_a \left(\frac{\int \sigma_0^m dA_a}{\int \sigma_0^m dA_s} \right)^{\frac{1}{m}} \quad (6)$$

This equation then provides a way to compute an *equivalent load* P_s which, if applied to some standardized geometry with surface area A_s , would result in the same probability of failure as the actual specimen with surface area A_a had when the true load P_a was applied. However, this expression is a function of m which is initially unknown. Therefore, in practice, an iterative solution technique must be used whereby a value of m is guessed, the *equivalent loads* for each of the specimens are computed using Equation 6, and the resulting data is fit to Equation 1 using traditional iterative techniques. (If the value of m found by fitting the data to Equation 1 is different than the value used to compute the equivalent loads using Equation 6, this is not the true value of m which best matches the experimental data collected. Therefore, the process must be repeated using a different value of m in Equation 6 and again fitting the resulting data to Equation 1. Eventually a value of m will be found which will satisfy both equations. Once this is known, the characteristic strength σ_0 can also be computed).

Maximum Likelihood Criteria

Traditional methods of fitting data to Equation 1 usually involve either a least squares or *maximum likelihood* criteria. Since the *maximum likelihood* method requires an iterative solution, it may easily be combined with the *equivalent load* method described above. A single iteration series can be used which will find a value of m which will satisfy all of the necessary requirements.

The log likelihood function (l) associated with the distribution function (F) given in Equation 1 and applied to a set of n experimental samples can be written as

$$l = n \log(m) - m \cdot n \log(\sigma_0) - \frac{1}{\sigma_0^m} \sum_{i=1}^n \left(\int \sigma_i^m dA \right) + \sum_{i=1}^n \left(\log \int \sigma_i^{m-1} dA \right) \quad (7)$$

where n is the number of samples to be analyzed, and σ_i is the stress distribution in the i th specimen. The values of m and σ_0 which maximize the value of l are the values which allow the best fit or description of the data set under consideration. To find these values, the partial derivatives of l with respect to each of the unknown parameters can be set equal to zero. A solution to the resulting equations results in either a maximum or minimum value of l . In this case, the maximum point is always located, because for poor values of m and σ_0 the likelihood function decreases without bound and has no minimum point.

Setting the derivative of l with respect to σ_0 equal to 0, and solving for σ_0 gives

$$\sigma_0 = \left(\frac{1}{n} \sum_{i=1}^n \int \sigma_i^m dA \right)^{1/m} \quad (8)$$

By substituting this expression for σ_0 back into Equation 7 before solving for m , the value of σ_0 need not be computed until after m is found. After such a substitution, setting the derivative of 1 with respect to m equal to 0 gives

$$m = n \left(n \frac{\sum_{i=1}^n \int \sigma_i^m \text{Log}(\sigma_i) dA}{\sum_{i=1}^n \int \sigma_i^m dA} - \sum_{i=1}^n \left(\frac{\int \sigma_i^{m-1} \text{Log}(\sigma_i) dA}{\int \sigma_i^{m-1} dA} \right) \right)^{-1} \quad (9)$$

Applying the assumption that the stress distribution σ can be written as $P \cdot \sigma_u$, and that the same σ_u can be used for all of the samples allows Equation 9 to be rewritten as

$$m = \frac{n}{\text{Integrals} + \text{Sums}}$$

where

$$\text{Integrals} = n \frac{\int \sigma_u^m \text{Log}(\sigma_u) dA}{\int \sigma_u^m dA} - n \frac{\int \sigma_u^{m-1} \text{Log}(\sigma_u) dA}{\int \sigma_u^{m-1} dA} \quad (10)$$

and

$$\text{Sums} = n \frac{\sum_{i=1}^n P_i^m \text{Log}(P_i)}{\sum_{i=1}^n P_i^m} - \sum_{i=1}^n \text{Log}(P_i)$$

while the expression for σ_0 found in Equation 8, becomes

$$\sigma_0 = \left(\frac{\sum_{i=1}^n P_i^m}{n} \int \sigma_u^m dA \right)^{-1} \quad (11)$$

(A more complete derivation of these expressions can be found in the Appendix.)

Solution Sequence Summary

Equations 6, 10, and 11 used to implement the following solution procedure:

- (1) Choose a standard geometry to be used for computation of equivalent loads.
- (2) Determine stress distribution (σ_u) in the standard geometry when a unit load ($P_s = 1$ N) is applied.
- (3) Determine the stress distribution (σ_u) in each of the actual samples.
- (4) Choose a "First Guess" value for m .
- (5) Use Equation 6 to determine the equivalent load for each of the specimens.
- (6) Use Equation 10 to compute m .

(Note: The $\sum_{i=1}^n \text{Log}(P_i)$ term need only be computed once for each sample set, but the other two sums and the four integrals must be recomputed at each iteration because they are dependent on m).

(7) If the m computed in step (6) is the same as the m used in step (5) then use Equation 11 to find α and the solution is complete. (If the two values of m do not match, choose a new m somewhere between the value used in step (5) and the one computed in step (6) and return to step (5). A value half way between the two will often work, though in some cases a value closer to that used in step (5) resulted in faster convergence in the present study).

Restrictions to the Equivalent Load Method

While the new method of analysis allows the use of samples which would not be suitable for analysis using traditional methods, some restrictions must still be imposed:

The first of these restrictions is that the critical flaws in each of the samples must be members of the same flaw population. (This condition will usually be satisfied if all of the samples come from the same stock material and have been prepared and or treated in a similar fashion).

The second restriction is that the stress distribution within each sample at the time of fracture must be known. (If the geometry and loading of each sample can be accurately described, such a stress distribution can usually be determined. If an exact solution is not available due to irregular geometry or complex loading, a numerical method such as finite element analysis can often be used to find a reasonable approximation of the stress distribution).

It is this second restriction that may be the limiting factor in the accuracy of these calculations. While the load applied to a sample at the time of fracture is usually known, an accurate description of the geometry may be more difficult to obtain. For the ideal specimens used in traditional analysis, the geometry can usually be fully described by a small number of dimensions. However, if the geometry is irregular, a larger number of well placed measurements will be needed. Furthermore, because of the larger number of dimensions which must be determined, it may not be practical to make repeated measurements of each dimension to reduce measurement error. The effects of measurement error may be reduced by applying some sort of "smoothing" to the dimensions. This can be done by fitting a continuous function to the measured data points. In addition to reducing the effects of measurement error, this will convert the coarse discrete data available from the measurements into a continuous description of the geometry which can then be more easily modeled for computation of the stress distribution.

Application of the Equivalent Load Method

The problem for which this solution technique was developed involves the compression testing of C-rings of somewhat irregular geometry. There were two sources of irregularity in the geometry of the specimens. First, the wall thickness of the tubes from which the samples were made was irregular. According to the manufacturer, a variation of up to 15% above or below the nominal value of the wall thickness was unavoidable. This was directly related to the techniques used to manufacture the tubes. The second source of irregularity in the present study was that the equipment needed to cut the tubes into rings of uniform width was not available. Use of the equipment that was available resulted in some variation in the width dimension both from one location to another on a given ring, and from one ring to the next.

The standard geometry chosen for computation of equivalent loads was a C-ring of uniform cross-section. The dimensions used were close to the dimensions of the actual samples. Though it was not necessary to use a standard geometry similar to the actual geometry, doing so provided some verification that the process was working correctly. If the values of the equivalent loads

were much different than the actual loads, while the actual geometry and the standard geometry were very close, that would have provided an indication that something was wrong either with the theory developed or the implementation of that theory.

The stress distributions for the standard geometry, as well as each of the actual geometries, was determined using a finite element model. A variety of mesh densities and element types were tried before deciding to use a mesh consisting of 707 2D 9-node isoparametric elements. Since both the actual and standard geometries produced stress distributions which were proportional to a single load value, all of the finite element models were solved for a one Newton load. Assuming that the material failure can be attributed to a surface distribution of material flaws, the desired output of the finite element model consisted of a maximum principal normal stress value and a corresponding surface area for each of the outer surface finite elements. Maximum principal normal stresses were used because of the tendency of ceramics to fail due to tensile stresses. If the maximum principal normal stress was negative, indicating a compressive stress, then a value of zero was reported since compressive stresses will not generally contribute to the failure of brittle materials.

While the geometry of the standard C-ring was exactly specified, the actual C-ring geometries involved some approximations. For each of the specimens, 10 measurements were taken. These described the width and thickness of the specimen at each of 5 points equally spaced over the portion of the sample experiencing stress during testing. To convert this data into a continuous description of the geometry, the thickness of the material was fit with a cubic polynomial, while the width was fit with a parabola. For most of the samples, the radius of the outer surface of the rings was nearly constant. However, for one of the data sets, specifically those obtained at 1400°C With Slag, the outer radius was also non-uniform. For that data set, 9 diameter measurements were taken for each specimen, and were fit with a sine and cosine series.

A number of fit functions were tried before those were selected. The selection of functions to be used for fitting was based on attempts to match visible patterns in the dimensional irregularity found in the experimental data. Additional measurements of a subset of the full sample were taken and used to verify the ability of these functions to provide a reasonable description of the true sample geometries. As discussed earlier, an additional benefit of this sort of smoothing of the data is that it reduces the effects of measurement error. (The alternative to using a curve fit of some sort would be to take multiple measurements of each of the desired dimensions, and to measure a large number of dimensions. Then, the multiple measurements could be averaged to reduce measurement error, and the large number of known dimensions would provide a nearly continuous description of the geometry. This would have required more time, or more advanced equipment than was available).

A computer program was written to implement the iterative solution sequence described above¹⁰. The integrals found in Equations 6, 10, and 11 were evaluated by summing the appropriate values computed using the outputs of the finite element analysis for each sample. After each loop, the value of m computed from Equation 10 was compared to value of m used to initiate that loop. If these two values were not sufficiently close to each other, a new initial value of m was taken as the average of them and the iteration loop presented in the Solution Sequence Summary was repeated. In a few cases, this resulted in an extremely slow convergence rate. Therefore, if a final value was not found after 50 iterations, new values of m would then be computed as $3/4$ of the previous value plus $1/4$ of the newly computed value.

Once a final value of m was determined, Equation 11 was used to compute σ_0 . In addition to the values of m and σ_0 , the equivalent load values and estimated probability of failure for each of the specimens were provided as outputs.

Limitations to the Equivalent Load Method

Because this technique was recently developed, it has not been fully tested and may contain limitations which have not yet been discovered. One significant problem has been identified. This arises when the data to be fit is such that it does not closely approach a Weibull distribution. This can occur when the critical flaws are not members of a single population or when data sets from different materials are combined and fitted as a single data set. While no attempt to fit such data to a Weibull distribution will produce good results, one does expect the resulting fit parameters to match the data as closely as is possible. (For example, in the case where two different data sets are combined, one would expect the resulting fit parameters to lie between the values associated with the two data sets if evaluated individually. Unfortunately, this is not always what occurs with this analysis method. Therefore, when applying this method, the quality of the fit must be considered. If a poor fit is produced, further analysis, perhaps based on the assumption of a bimodal failure probability distribution, should be considered).

Strength Data

Using the analysis techniques described in the foregoing a characteristic strength and a Weibull parameter was determined for each of the tube material sample sets. Table 4 gives a summary of the strength data produced from this analysis while Figure 11 shows the data from which these results were derived, plotted in the form of the log of minus the log of one minus the probability of failure versus log stress.

Table 4. Summary of Strength Results

<u>Exposure Condition</u>	<u>Characteristic Strength (σ_c)</u>	<u>Weibull Parameter(m)</u>
Room Temp	410 MPa	10.91
1100°C No Slag	282 MPa	9.06
1100°C With Slag	245 MPa	9.73
1260°C No Slag	226 MPa	12.82
1260°C With Slag	328 MPa	6.80
1400°C No Slag	197 MPa	11.18
1400°C With Slag	149 MPa, 142 MPa	5.86, 13.10

While Table 4 gives the necessary values in a form that can easily be applied, it is easier to see the trends in the data by examining Figure 11.

Figure 11. Complete Strength Data

Each point on this graph represents a test specimen. The horizontal axis represents a log stress value. The stress whose log value is displayed is the stress which would have to be applied to a specimen in uniform tension with a unit surface area of one square millimeter to have the same probability of failure as the given specimen had when the actual load was applied. This value is

computed as a numerical approximation of $P \left(\int \sigma_{ua}^m dA \right)^{\frac{1}{m}}$ where P is the actual load applied

to a given specimen, σ_{ua} is the actual stress per unit load for that specimen as computed from the finite element model of the sample, A is the surface area of the specimen, and m is the computed Weibull parameter for the material. So, moving from left to right on the plot represents increasing stress values, and stronger materials.

The vertical axis is related to the probability of failure of a specimen. The actual term plotted is the log of the log of $1/(1-F)$ where F is the estimated probability of failure of the sample. This means that moving upward on the plot represents an increase in the probability of failure of a sample. The value of the probability of failure F is estimated to be equal to $(i-0.5)/N$ where N is the number of samples, and i is the rank of the given specimen within the data set when arranged in order of increasing equivalent fracture load. For example, out of a sample of 40, the specimen which failed at the lowest equivalent load is estimated to have a probability of failure of 1.25% since N would equal 40, while i would equal 1. Because a maximum likelihood criteria was used to compute the values of m and σ_0 , this estimate was not used during computation, as would have to be done if a least squares fit was used. However, this estimator has been shown to provide a reasonable representation of the probability of failure of such specimens and is generally accepted for graphically displaying test results such as these.

When plotted in this way, a data set which fits a Weibull distribution will appear as a straight line. The slope of this line will be the Weibull parameter m , while the stress value corresponding to the point where the line crosses the 63.2% probability of failure ($\text{Log}(\text{Log}(1/(1-F))) = 0$) is the characteristic strength σ_0 . Each of the data sets produced during this test program appears as a reasonable approximation of a straight line. This confirms that a Weibull analysis can be used satisfactorily to estimate failure probability for these materials.

Trends and Irregularities in the Analyzed Data

In general, the trends which can be seen in Figure 1. match the expected results of a test of this type. Moving from left to right across the plot, from weaker materials to stronger materials, the results of exposing the base material to less harsh conditions are seen. The line of data at the far right represents the virgin material tested at room temperature as it was received from the manufacturer. As expected, the material in this sample set is significantly stronger than any of the other material samples.

At the far left edge of the plot are two lines representing the material exposed to slag at 1400°C. This far left location indicates the weakest of the materials, those material samples which were exposed to this harshest set of the exposure conditions. Note that there is a set of points, and a line which has been fit to it, for samples which were cut from each of the two tubes exposed to this condition. This means that significant differences were experimentally observed in the strength of the material from the two sets of material exposed to the harshest condition.

This was the only condition that resulted in a noticeable loss of material. Because of these macroscopic effects, these two tube samples were most sensitive to variations in the exposure conditions. This type of sensitivity is believed to have resulted in the two different slopes (m values) of these lines. Because these two slopes are so different, a single Weibull distribution could not accurately be fit to the combined or full data set. As discussed in earlier, attempts to do so may result in significant error in the calculation of the material parameters. Therefore, the results of fitting these data sets independently are shown. The similarity in the horizontal position of these two lines on the plot indicates that average strength of the material from the two tubes was nearly the same. However, the difference in the slope of the two lines indicates that the failure characteristics when subject to the same loads was significantly different. For all of the other test conditions, this type of variation was not seen. Therefore, each of the other exposure conditions is shown as a single line of points, indicating consistent material failure characteristics.

The next line of data points to the right represents samples which were held at 1400°C for 200 hours in a clean furnace before failure testing. This is followed by data from the results of exposure to 1260°C without slag, 1100°C with slag, and 1100°C without slag. From these data sets, a clear pattern of failure strength behavior can be recognized. As expected, a decrease in exposure temperature results in less loss of strength and better resistance to failure, and material which was not exposed to slag is stronger than material exposed to slag at the same temperature.

However, the one set of data does not follow this pattern. The line of points representing the results of testing the material exposed to slag at 1260°C shows an anomalous behavior. It appears stronger than it should be based on exposure condition. Its position seems to indicate that this material is stronger than any of the three previously mentioned materials all, of which were exposed to less harsh environments. The explanation for these unexpected results is related to the nature of the slag coating on the material test C-rings that was produced at this temperature. As was mentioned earlier, those tubes which were exposed to slag at 1260°C developed a thick, hard, glassy, bubble filled slag layer which was firmly bonded to the tube. Before cutting the mechanical test specimens, most of this slag was removed. However, it was not possible to remove all of the slag without damaging the base material. Therefore, after cutting the C-shaped rings, the slag coat was ground down to a nearly uniform layer approximately 1 mm thick. It was expected that, upon reheating the samples in preparation for fracture, the remaining slag would soften and have little effect on the strength testing. However, this does not seem to have happened.

The high apparent strength of the material suggests that the remaining slag layer provided a significant amount of additional strength to the sample during the mechanical testing. Visual inspection of the slag after fracture confirms that, while it may have softened somewhat, it remained in a stable solid state. At the points of load application, some lasting compression of the

slag layer is often visible, but not to the extent that would be expected for the softened, fluid-like material that was expected to form at this temperature.

Examination of the fractures themselves provide some additional clues as to the properties of the slag layer and its effects on the measured strength of the overall sample. The first thing that was noticed about many of the fractures was that the slag layer often had well defined fracture surfaces with little evidence of plastic deformation. This provides further evidence that the slag coat maintained a well defined solid structure throughout the test. Secondly, the fracture locations are often found to coincide with the location of thin areas that resulted in the slag coat after most of the slag was removed. These thin areas were often the result of a large bubble in the slag. This suggests that non-uniformities in the slag coat may have introduced stress concentrations which influenced the location of the fracture.

As a result of these observations, the stress values computed based on the assumption of a non-load bearing slag layer must be discarded. Therefore, the line of data points labeled "1260°C With Slag" in Figure 11 must be considered as a representation of the effects of a slag layer on the apparent fracture strength of the ceramic material. (One method of extracting useful information from this data is to assume that the slag coat can be modeled as a layer of homogeneous linear elastic material firmly bonded to the ceramic ring. While this is probably not entirely accurate, it may allow a reasonable approximation model for such a structure. By making this assumption, a modified finite element model can be created and solved for each of the specimens exposed to this environment. This then would allow a revised Weibull distribution to be computed).

Even if the linear elastic surface layer model assumption is valid, this still leaves one additional problem that did not exist for the previous finite element models. When a single material is used throughout a finite element model, the value used for the modulus of elasticity for that material will not affect the resulting stress values. However, when two different materials are to be used, such as the base ceramic material and the slag material, the stress values will be dependent on the ratio of the moduli of elasticity used for the two materials. Therefore, without some way of measuring or computing the relative modulus of elasticity of the slag material (at the test temperature), no absolute results can be obtained. However, the revised modeling approach can be exercised by doing a parametric study of the effects of the ratio of elastic moduli on Weibull analysis.

Figure 12 shows the results of an analysis of the strength results of the specimens exposed to this set of conditions (1260°C, slag) based on a finite element stress determination using a number of elasticity ratios.

Figure 12. Strength Data for the Tube Material Exposed to Slag at 1260°C as a Function of the Ratio of Modulus Elasticity of the Tube and Slag Material.

This shows the effect of adding a layer of homogeneous linear elastic material to the outside surface of the test specimens is to adjust the reported characteristic strength of the material while not causing a significant change in the Weibull parameter. This results in the shifting of the line of experimental data from left to right without a noticeable change in the slope of the line. Therefore, while the value of the characteristic strength reported in Table 2 for the material exposed to this condition is of little value, the Weibull parameter is believed to be reasonably accurate.

Rate of Strength Reduction

All of the results presented are based on exposure of the tube samples to the given conditions for a period of 200 hours. Since no variation in the amount of exposure time was used, no conclusive statements can be made about what will happen if these exposure conditions are maintained for longer periods of time. To do so, additional tests are required. However, there are a number of factors which provide clues about what additional testing time may do to the material strength.

The samples exposed to slag at 1400°C showed a significant amount of material loss during this test program. There is no obvious mechanism present which would inhibit removal of additional material. Therefore, it seems reasonable to assume that under these conditions the base material is removed at a constant rate. During these tests a maximum reduction in the tube wall thickness of 1 mm was not uncommon. This suggests that portions of the tube wall would be completely destroyed in as little as 1000 hours of continuous exposure. This would clearly be unsuitable for industrial applications.

For the remainder of the exposure conditions, the lack of visible evidence of corrosion provides little information about the mechanisms responsible for the reduction in strength. This makes estimation of rate information more difficult. However, preliminary theoretical modeling of the reaction mechanisms at work in this system may provide some insight. This work, being conducted by researchers at the University of Pennsylvania under their subcontract to UTSI, has suggested that the different phases in this composite material may be affected at different rates.

Therefore, it is possible that the aluminum alloy phase may be completely destroyed before any significant damage has been done to the SiC and Al₂O₃ ceramic phases. This could cause a slight initial reduction in strength followed by a much longer period of negligible strength change. If this is the case, the strength values found during this test program may be relatively constant for a wide range of time values. Hopefully, additional study of these reaction mechanisms will be able to either refute or support this possibility.

Modulus of Elasticity for Tube Sample Materials

In addition to the strength and reliability data generated from the Weibull analysis, it was possible to estimate the modulus of elasticity of the material under the different exposure conditions. This was done by comparing the slope of the load deflection curves recorded during testing to the load deflection ratio computed using the finite element model, using an assumed 1MPa unit modulus of Elasticity. These terms are related in the following way.

$$E = R_e/R_u \quad (12)$$

where E is the modulus of elasticity in MPa, R_e is the experimentally determined ratio of load to deflection in Newtons per millimeter, and R_u , expressed in millimeters, is the ratio of load to deflection per unit modulus of elasticity. The results of these calculations based on experimental material behavior, averaged for each of the exposure conditions, are shown in Table 5.

Table 5. Modulus of Elasticity Results

Temperature	Elastic Modulus (w slag)	Elastic Modulus (w/o slag)
Room Temp	N/A	276 MPa
1100°C	192 MPa	208 MPa
1260°C	133 MPa	174 MPa
1400°C	95 MPa	133 MPa

As with the strength data, these values follow expected trends. As the temperature is increased, the material becomes more flexible, as indicated by a lower modulus of elasticity. Application of slag simply increases the magnitude of the change. However, the values of elastic modulus computed for the material exposed to slag at 1260°C with slag probably are somewhat in error.

Microstructural Analysis

After the foregoing mechanical testing and analysis work was completed and reported on in the MS thesis noted earlier, a detailed microstructural analysis was conducted on the material remnants from that research (the results of this analysis are not reported on in the thesis). Physical features such as the amount and distribution of porosity have a strong influence on the mechanical properties of ceramics.

A phase image analysis was performed on samples: as-received, exposed without slag and exposed with slag. [The analysis system consisted of an optical microscope and a computer with NIH(National Institute of Health) Image 1.52 software for studying phase distribution and phase quantitative analysis]. Two sample pieces were cut from each exposed condition. (One sample was located on the top side of the tube facing the slag drops and the other was located on the bottom side during the exposure test). Table 6 provides a summary of the analyzed samples. (Each sample was metallurgically prepared by polishing with a series of grit papers. The final polishing was done with a 1 µm diamond paste).

Table 6. Conditions of Analyzed Samples

Sample Number	Exposure Temperature	Exposure condition	Sample Location	Characteristic Strength σ_o
0#	As-received	-----	-----	410 MPa
1#	1100 °C/200 hours	No Slag	Top	282 MPa
2#	1100 °C/200 hours	No Slag	Bottom	282 MPa
3#	1100 °C/200 hours	With Slag	Top	245 MPa
4#	1100 °C/200 hours	With Slag	Bottom	245 MPa
5#	1260 °C/200 hours	No Slag	Top	226 MPa
6#	1260 °C/200 hours	No Slag	Bottom	226 MPa
7#	1260 °C/200 hours	With Slag	Top	328 MPa
8#	1260 °C/200 hours	With Slag	Bottom	328 MPa
9#	1400 °C/200 hours	No Slag	Top	197 MPa
10#	1400 °C/200 hours	No Slag	Bottom	197 MPa
11#	1400 °C/200 hours	With Slag	Top	149 MPa
12#	1400 °C/200 hours	With Slag	Bottom	149 MPa

A video camera was connected to the microscope and interfaced with a computer so that the microstructure image of the sample could be directly transferred to the computer for displaying on the computer screen. The image size on the screen for phase quantitative analysis was 205 mm x 160 mm which represents the real area of 293 μm x 229 μm on the sample. In this study, a 40x objective lens and a 10x eyepiece lens were used. The magnification was approximately 700x. The image analysis was conducted at this high magnification (700x) to reduce or eliminate the poor phase contrast effect due to uneven illumination intensity and the non-flat sample surface. These measurements were done in a two dimensional section and readings for an individual image do not represent volume concentrations of the phases. Therefore, the phase measurements were conducted on eight points from the outside wall of the tube to the inside wall. Such measurements provide an average phase volume percent throughout the tube wall thickness. The distance between the points is about 685 μm .

Microstructure Analysis Results and Discussion

After obtaining the image of the required location on the computer screen, the program NIH Image 1.52 was used to obtain the individual phase volume percent. Figure 13 illustrates one such typical image used to conduct image analysis.

Figure 13. A Microstructure Image of Sample 11# in Middle of Cross Section

Table 7 gives the measurements of all 13 samples. From Table 7, it is obvious that the phase distributions of the as-received samples are almost uniform along the cross section of the tube. After the samples were exposed at high temperature, however, the phase distributions were not uniform within the sample, especially for aluminum and porosity content. The more severe the exposure condition, the more porosity and the less dispersed aluminum near the surface of the tube.

Table 7. Measurements for Phase Volume Percentage Calculations

0# -- As received				
	Aluminum	SiC	Alumina	Pore
Out Wall	4.334961	42.98698	50.24251	2.435547
	3.326823	48.05794	46.85286	1.76237
	3.232096	49.74805	45.73014	1.289714
	3.336914	51.73242	43.82324	1.264648
	3.728841	57.2679	38.0612	0.740234
	3.574219	53.51986	41.86068	1.045247
	3.724284	53.87988	40.57227	1.823568
Inside Wall	3.668294	54.26465	42.44271	0.971354
Average:	3.6158	51.4322	43.6982	1.41659

1# -- Exposed at 1100 °C without slag (top)					2# -- Exposed at 1100 °C without slag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	2.968099	51.83496	41.76563	3.431315	Out Wall	1.707357	46.18424	47.63379	4.474609
	3.426758	49.96094	44.55273	2.05957		2.784505	45.84603	49.0599	2.30957
	3.35319	49.28158	46.22493	1.140299		2.417643	48.97298	46.43848	2.170898
	3.272135	50.22493	44.80013	1.702799		2.55599	49.53125	45.42806	2.484701
	2.653646	49.44987	45.15951	2.736979		3.406576	49.68555	45.2028	1.705078
	4.568359	51.75977	43.23828	0.433594		3.617188	51.19792	43.45475	1.730143
	4.464844	51.97624	41.27995	2.558919		5.964844	50.8431	42.02702	1.165039
Inside Wall	3.950521	50.7819	42.39225	2.875326	Inside Wall	3.030599	47.91016	45.08268	3.976563
Average:	3.58219	50.6588	43.6767	2.11735	Average:	3.18559	48.7714	45.5409	2.50208

Table 7. (continued) Measurements for Phase Volume Percentage Calculations

3# -- Exposed at 1100 °C with slag (top)					4# -- Exposed at 1100 °C with slag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	2.226563	47.09668	48.4554	2.221354	Out Wall	2.708659	46.7347	46.5013	4.055339
	2.979167	51.17383	44.47949	1.367513		3.193034	47.41439	46.32552	3.067057
	2.8125	51.57031	44.28483	1.332357		2.456706	51.38965	43.85059	2.30306
	3.148438	49.22168	43.06771	4.562174		3.422201	51.14616	43.91081	1.520833
	3.084635	50.43066	43.84342	2.641276		4.650065	50.62858	43.64421	0.77181
	3.459961	52.72233	41.95475	1.862956		4.097331	49.56152	44.32194	2.361003
	2.927734	50.39421	42.36751	4.310547		3.597005	51.95378	42.21908	2.230143
Inside Wall	2.838867	52.57324	42.46387	2.124023	Inside Wall	2.587565	47.69434	44.86784	5.366536
Average:	2.93473	50.6479	43.8646	2.55278	Average:	3.33907	49.5654	44.4552	2.70947

5# -- Exposed at 1260 °C without slag (top)					6# -- Exposed at 1260 °C without slag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	1.433268	45.94466	44.45117	8.170898	Out Wall	1.603841	45.68327	46.90234	5.810547
	1.101563	42.61393	47.71582	8.568685		2.359049	47.58431	45.95475	4.101888
	3.238281	45.72591	45.8431	5.192708		4.3125	48.96582	42.65592	4.065755
	3.383789	47.24186	43.92188	5.452474		3.762695	51.61133	40.86719	3.145508
	4.472656	50.80176	42.92448	1.801107		4.547526	49.86686	41.14876	4.436849
	3.719076	51.50521	42.75	2.025716		4.668945	49.1097	42.63281	3.09375
	3.202148	43.87272	45.18945	7.735677		2.683251	49.16081	42.33464	5.821299
Inside Wall	3.378255	46.18555	43.20475	7.848307	Inside Wall	2.798828	49.65853	44.18945	3.35319
average:	2.99113	46.7365	44.5001	5.84945	Average:	3.34208	48.9551	43.3357	4.2286

7# -- Exposed at 1260 °C with slag (top)					8# -- Exposed at 1260 °C with s+G20lag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	2.091797	43.54785	48.25944	6.100911	Out Wall	1.461914	45.73926	45.54818	7.250651
	2.738932	48.89453	46.92676	1.439779		3.873372	46.98763	45.55664	3.582357
	4.203776	48.53288	45.12077	2.142578		3.113281	49.96029	44.26758	2.658854
	2.50944	47.4401	46.52018	3.530273		3.768556	47.97363	45.37728	2.880534
	4.372396	49.24837	44.34831	2.030924		2.347656	49.51888	46.19857	1.934896
	2.735352	46.8265	48.34147	2.09668		2.353841	47.89811	47.5918	2.15625
	2.486328	46.15788	48.42611	1.701497		3.098633	49.46094	44.13216	3.308268
Inside Wall	2.857747	46.68815	47.5179	2.936198	Inside Wall	3.418294	45.16374	47.99219	3.425781
average:	2.99947	47.167	46.9326	2.74736	average:	2.92944	47.8378	45.8331	3.3997

9# -- Exposed at 1400 °C without slag (top)					10# -- Exposed at 1400 °C without slag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	1.802083	45.00749	42.68327	5.366211	Out Wall	3.996094	46.80762	41.0446	8.151693
	2.268229	46.71354	44.34635	6.671875		5.734375	49.45247	41.02116	3.791992
	4.169922	49.09147	39.34115	7.397461		1.742513	48.27116	44.85319	5.133138
	5.451823	48.37663	41.15951	5.012044		3.272461	47.75586	44.50716	4.464518
	6.155924	48.81706	39.93294	5.094076		4.361979	48.86784	39.79492	6.97526
	3.405924	49.23079	44.3112	3.052083		3.02832	51.0638	41.73535	4.172526
	4.173177	49.8763	41.82422	4.126302		2.719727	50.00033	43.06673	4.294271
Inside Wall	2.773763	46.33301	44.21159	6.681641	Inside Wall	2.757813	48.58659	42.9668	5.688802
average:	3.77511	47.9308	42.2263	5.42521	average:	3.45166	48.8507	42.3737	5.33403

11# -- Exposed at 1400 °C with slag (top)					12# -- Exposed at 1400 °C with slag (bottom)				
	Aluminum	SiC	Alumina	Pore		Aluminum	SiC	Alumina	Pore
Out Wall	3.688151	47.81217	40.8151	7.684579	Out Wall	1.887044	43.63509	42.30859	12.16927
	3.829102	47.41927	39.70833	7.876302		2.329427	43.54525	45.40462	8.720703
	5.046224	46.31934	40.89941	7.735026		3.498047	44.50488	43.01986	8.977214
	3.669915	47.50814	39.29688	9.525065		2.286133	43.02767	44.25586	9.231445
	5.51888	48.97396	36.19824	9.308919		3.401367	42.98145	45.47461	8.142578
	5.554036	47.36621	39.6556	7.424154		2.061523	45.67122	43.78906	8.47819
	7.385417	48.7679	36.4821	7.364583		4.575846	46.49121	42.48405	5.863932
Inside Wall	3.652018	46.67025	39.51563	10.16211	Inside Wall	3.603516	45.91895	41.05892	9.41862
average:	4.79297	47.6047	39.0714	8.38509	average:	2.95536	44.472	43.4745	8.87524

Figures 14, 15, and 16 are plots of the average phase volume data in Table 7. Figures 14 and 15 show the change of aluminum and alumina as a function of exposure temperature. The top side of the sample exposed to slag at 1400°C shows a substantial increase (~32%) in aluminum content and a decrease (~11%) in alumina compared to that of the as-received sample at room temperature. It is possible that reduction reaction of alumina occurred and part of alumina reduced to aluminum at the 1400°C-with slag case.

Figure 14. Aluminum Content vs. Exposure Conditions

Figure 15. Alumina Content vs. Exposure Conditions

Average Volume Percent Value of SiC (%)					
	As-received	Top-no slag	Bottom-no slag	Top-slag	Bottom-slag
Room Temperature	51.4322				
1100 oC		50.6588	48.7714	50.6479	49.5654
1260 oC		46.7365	48.9551	47.167	47.8378
1400 oC		47.9308	48.8507	47.6047	44.472

Figure 16. SiC Content vs. Exposure Conditions

The general variation trends in SiC and porosity can be seen from Figures 17 and 18.

Average Volume Percent Value of Pore (%)					
	As-received	Top-no slag	Bottom-no slag	Top-slag	Bottom-slag
Room Temperature	1.41659				
1100 oC		2.11735	2.50208	2.55278	2.70947
1260 oC		5.84945	4.2286	2.74736	3.3997
1400 oC		5.42521	5.33403	8.38509	8.87524

Figure 17. Porosity Content vs. Exposure Conditions

The SiC volume fraction decreases and the porosity increases with the increase of temperature and the addition of slag. The reduction of SiC results in the increase of porosity and the increase of porosity will lead to a decrease in the strength. Figure 18 shows the variation trend in the strength with exposure conditions. As expected, an increase in exposure temperature results in more loss of strength and material. Also, the material not exposed to slag was stronger than material exposed to slag at the same temperature. But the porosity variation trend with the exposure condition is just the reverse of the strength variation. However, there is an exception for the material exposed to slag at 1260°C, showing an anomalous behavior as noted earlier. It appeared stronger than it should be based on its exposure condition; this additional strength was attributed to the slag coating during the analysis of the mechanical tests.

Figure 18. Characteristic Strength vs. Exposure Conditions

There was also an anomalous behavior for porosity content of material exposed at 1260°C with slag. It showed less porosity than expected considering the exposure condition. Figure 19 contains micrographs showing surface appearances of the specimens after exposure to high temperatures with slag. Slag on the tube exposed to 1100°C is still friable and it is easy to remove. Figure 19-(a), shows that there was a layer of alumina coating, produced by the manufacturer, filling pores and no slag remains on the surface. Figure 19-(b) shows a layer of pore free slag firmly bonded onto the layer of alumina coating. The slag also infiltrated into the alumina coating and hence sealed the pores on the alumina layer. This is equivalent to sealing up the micro-cracks on the surface of the tube. In addition, this made it more difficult for oxygen to diffuse into the substrate material so that fewer pores were produced. All of these factors would contribute to the increase of strength.

Figure 19. Cross Section Views of Samples Exposed to Slag at High Temperature

Figure 19(a) and (b) indicate little or no material loss and no reaction with slag at 1100°C and 1260°C with slag. Only noticeable loss of material occurred at 1400°C with slag. Figure 19(c) shows that the alumina coating has totally disappeared. (Apparently a reaction product remained on the substrate material).

After exposure to slag at 1400°C, the thickness of the tube on the top side was 3.24 mm and the bottom side was 4.6 mm. The average thickness of the as-received tube was about 4.7 mm. This indicates that more material loss occurred on the top side which received slag directly than that on the bottom side. Examination of the sample exposed at 1400°C without slag, showed a small amount of material loss. This suggests that there must be some reaction between the substrate material and slag at 1400°C to form a low melting eutectic. The slag used in this study contained more than 10 percent of CaO. Table 8 gives the slag composition (presented earlier) listed by mass.

Table 8. Illinois #6 Slag Composition (%)

Compound	Relative Amount (by mass)
SiO ₂	47.76
Fe ₂ O ₃	19.79
Al ₂ O ₃	16.57
CaO	10.37
MgO	2.62
K ₂ O	1.48
TiO ₂	0.85
Na ₂ O	0.37
	0.19

According to the phase diagram illustrated in Figure 20, Al₂O₃ will react with CaO (at ~50 wt.%) to form a low melting eutectic which melts at or above 1360°C.

Figure 20. Phases Diagram of System CaO - Al₂O₃ (A=Al₂O₃, C=CaO)¹²

In addition, silicon has a stronger affinity towards oxygen, therefore it forms a thin layer of silicon dioxide (SiO₂) on the surface of the silicon carbide. When exposed to high temperatures, such a SiO₂ layer could react with Al₂O₃ and CaO forming a lower melting eutectic (1265°C) according to the phase diagram in Figure 21.

Figure 21. Phase Diagram of System CaO - Al₂O₃ - SiO₂¹³

It is felt that the main reason for material loss at 1400°C with slag was due to the formation of the low melting eutectic. It is predicted that if this material is used below 1260°C with the slag used in this study, there should be no noticeable material loss.

Summary

This study determined the strength of SiC(p)/Al₂O₃ ceramic matrix composite tube materials produced by Lanxide Corporation in their horizontal furnace after being exposed to both elevated temperatures and elevated temperature with (and without) periodically refreshed coal slag, at 1100°C, 1260°C and 1400°C. Unavoidable variations in the as-manufactured geometry of the samples which were used for strength testing, meant that it was not possible to use directly traditional analysis techniques to interpret the strength data obtained. Therefore, new data analysis techniques were developed and used based on the computations of *equivalent loads* for each of the test specimens.

This new *equivalent load* analysis method has shown that the strength of the ceramic composite material continually decreased as the temperature of testing was increased for fixed exposure times. Addition of coal slag to the exposure environment resulted in a further decrease in strength. However, only after exposure to coal slag at 1400°C was a measurable loss of material observed. This suggests that rapid corrosion clearly makes the material unsuitable at and above this temperature level. However, the 30% to 50% reduction in characteristic strength observed at lower temperatures may remain relatively constant over longer periods of time permitting the use of this material at temperatures up to at least 1260°C in heat exchanger tubes and other applications. Values were given in Table 2 for the Weibull parameter *m* and characteristic strength σ of the material under the various test conditions. Using these, along with Equations 1 and 2, it is possible to calculate the probability that a tube made of this material will fail when subjected to a given set of physical loads under the conditions tested.

(Additional work is needed to increase the usefulness of this data. Continued work is needed to better describe the time-dependent nature of the material strength parameters and also to further refine estimates of the maximum temperature at which this material can survive in this highly corrosive environment. If tighter dimensional tolerances can be met, additional strength testing will be greatly simplified, and designs using the resulting tubes will become much more reliable. As material produced by these new techniques becomes available, additional testing will also be needed to evaluate any resulting changes in strength and high-temperature corrosion resistance of the material.)

A microstructural analysis indicated that the material loss at 1400°C with slag was due to the formation of a low melting eutectic. This analysis verified the prediction from the strength analysis that if this material is used below 1260°C exposed to the slag used in this study, there should be no noticeable material loss.

3.2.3 Computer Modeling

The goal of the University of Pennsylvania in this research was to investigate the applicability of equilibrium thermodynamic modeling calculations to high temperature oxidation and corrosion in coal combustion environments. Using the nominal composition of the Lanxide $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3/\text{Al-Si}$ DIMOXTM ceramic composite, and the composition of the Illinois #6 slag as shown in Table 9, the initial object was the prediction of stable phase formation in these multicomponent systems, through the minimization of the system's Gibbs Free Energy. This requires (i) an accurate description of the Gibbs Free Energy of all the potential substances and interactions over the desired temperature range, and (ii) a robust technique for numerically minimizing the system's free energy.

The thermodynamic modeling program MTDData was purchased for this purpose. This software utilizes a database of assessed thermodynamic data for the Gibbs Free Energies, along with a numerical code module to minimize the free energy of the system.

Table 9: Composition of Illinois #6 Ash by Network

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

With respect to the requirement (i), the components in the system of study ($\text{SiC}_{(p)}/\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Na}$ -etc.) have a broad range of information quality. For example, the thermodynamic data for Na and S are relatively well known (known is defined here as critically assessed by SGTE and are included in the MTDData package). The energies of various Na-S phases are known to varying extents, while the interaction energy between (for example) Na and SiC is essentially unknown. As a result, the calculated free energy information for the system, which critically depends on the thorough knowledge of all potential phases, compounds, and their interaction energies, can vary significantly depending on whether or not all of this information is present.

It was found that requirements (i) and (ii) were nominally satisfied by the MTDData software. The fundamental problem with this modeling was the application of global equilibrium thermodynamics to a system in which reaction kinetics play a major role, and localized effects are important. For reaction kinetics, the equilibrium thermodynamics of the system do not change significantly

between 1100°C and 1400°C, the temperature range of the study. The thermodynamic modeling predicted extensive reaction between the SiC and the slag/gas phase, as well as the Al-Si residual metal and the slag/gas phase, over all temperatures studied. However, the kinetics of the reactions must be considered in order to predict experimental behavior. UTSI's experimental studies showed a broad range of slag viscosities between 1100°C and 1400°C. The very high viscosity of the slag at 1100°C, which appeared to have only resulted in preliminary sintering of the slag powder, is in sharp contrast to the very low viscosity of the molten slag at 1400°C. Although the relevant thermodynamics change little between 1100°C and 1400°C, the expected kinetic processes - reaction rates between the slag and ceramic and diffusion of oxygen through the slag, were extremely different. Thus, the different corrosion rates at various temperatures were dominated by kinetic effects (diffusion through the slag phase) rather than thermodynamic issues.

Additionally, the microstructure of the DIMOX™ composite proved to be too complex for global thermodynamic modeling. Localized corrosion/oxidation of the residual Al-Si alloy pockets had a more pronounced effect on strength than the global oxidation predictions. These pockets, which can be as large as 30 microns, lose their load bearing capability at temperatures above the melting point of aluminum. As shown in Figure 22, the room temperature strength of the DIMOX™ material is significantly reduced after high temperature oxidation, presumably due to the localized oxidation of the residual metal phase.

Figure 22. Effect of High Temperature Oxidation on RT DIMOX™ Material Strength (Lanxide)

Figure 23 summarizes the characteristic strength behavior from the present study. While Figure 22 shows the room temperature strength after high temperature exposure, Figure 23 shows the strength at temperature of the samples after high temperature exposure in slagged and no-slag experiments. As shown, it is difficult to separate the effects of high temperature oxidation (of the residual alloy) from the effects of the Illinois #6 slag additions.

Figure 23. Temperature (°C) Dependence of DIMOX™ Strength¹⁰

As described previously, the samples exposed to slag at 1100°C barely reacted with the slag. Similarly, the slag viscosity was so high that the slag powder only slightly sintered during the exposure. At 1260°C, the slag powder formed a thick, viscous liquid that reacted with the tube during oxidation. At 1400°C, the very low viscosity slag essentially poured off the tube walls; these samples reacted significantly with the liquid slag phase.

Based on the lack of reactivity between the slag and the coated DIMOX™ tube at 1100°C, it seemed 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 supports this conclusion. Different samples of the DIMOX™ material had variations in phase content that may have led to the differences in characteristic strengths.

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 for high strain rate 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 was analyzed at UTSI. Although the scatter in the data was 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. Thus, in both slagging and no-slag experiments, it appeared that oxidation of the residual metal phase was responsible for the decreased strength of the DIMOX™ material.

In summary, it was found that global equilibrium thermodynamic modeling techniques were not effective in describing the behavior of the DIMOX™ composite material during high temperature oxidation and corrosion. The complexity of the system led to localized corrosion effects that dominated the high temperature strength behavior. Additionally, the variation in kinetic properties, specifically the viscosity of the oxide slag, had a much more pronounced effect on corrosion rates than the small variations in thermodynamic values over the temperature range studied.

3.3 Development Tubes

3.3.1 Preform and Growth

Slip Casting Improvements

Lower cost SiC powders were obtained in an attempt to reduce tubes costs potentially up to 40%. A new slip cast system for producing preforms was evaluated. The resulting preforms created under this study, however, were weaker than those used in the production tubes and thus this idea was not successful.

Extrusion Preform

Extrusion, as shown in Figure 24, was evaluated as a low cost alternative to slip casting for preforming tubes. More work is needed, however, before this process can be considered an improvement.

Figure 24. Extrusion Preform and DIMOX™ Process

High Density Furnace

A demonstration of production size runs of 5 cm OD, 183 cm long slip-cast preforms in vertically oriented kilns for matrix growth was successful. This represents a seven fold higher throughput capacity than obtained with previous production (horizontal) kilns. Although six of these tubes were delivered to UTSI and appeared to be the same as those produced in the horizontal furnace, there was not sufficient resources to allow the evaluation of this product.

3.3.2 Centrifugal Casting

Advantages

The slip cast method (described earlier) for the manufacture of production tubes has several potential disadvantages. They are:

- the limited life of the preforming plaster mold,
- the cycle time,
- the need for using small particles in the slip in order to keep the larger particles suspended, *(small SiC particles oxidize readily during prefiring and matrix growth, thus effectively reducing the SiC volume loading. However, a high loading is desired in many cases to assure high thermal conductivity, a low coefficient of thermal expansion (CTE), and high thermal shock resistance of the composite tubes).*
- the limitation in making uniformly round tubes with very thin walls.

An attempt was made to develop an alternate preforming technique that could potentially overcome the listed limitations of slip casting. The new approach utilized the principles of centrifugal casting. The potential advantages of centrifugal preforming are manifold:

- The need for using very small particles (used in slip casting) no longer exists,
- The preform fabrication times are potentially shorter and mold lifetime is expected to be considerably longer than for plaster molds,
- It should be possible to produce uniformly round preforms with very thin walls, and
- The strength of these preforms should be quite high.

CERASET™ Preceramic Polymer

A cylindrical mold cavity was filled with a mixture of SiC particles and Lanxide's novel preceramic polymer, CERASET™ SN. (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). During the spinning of the mold the SiC particles were forced radially outward and the spaces between the particles were filled with the preceramic polymer. Upon heating of the spinning mold, the preceramic polymer cured to form a rigid material. Cooling of the mold resulted in a hard and strong preform which could be taken from the mold. Further heating of the preform converted the cured preceramic polymer into a ceramic.

Several development issues were observed in conjunction with the centrifugal casting of preforms using a slurry of SiC particles in the CERASET™ preceramic polymer. The polymer stuck to the mold and also a polymer layer formed on the inner tube diameter during centrifugal casting as the SiC particles move radially outward. Even though the cost of CERASET™ as a preceramic polymer is low in comparison to competitive products, its cost would not be negligible in a centrifugal tube manufacturing process.

Slurry

In consideration of development needs and cost restraints, a potentially simpler approach was taken. In essence, the methods of low temperature molding and centrifugal casting were

successfully combined. 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 form 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. The experimental centrifugal set-up was modified 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 were submitted for infiltration with an alumina matrix by directed metal oxidation. Surprisingly, it was observed that there was a lack of alumina matrix growth into the preforms. Several different lay-up schemes were tried, however, without success. The lack of matrix growth was completely unexpected, because preforms fabricated by low temperature molding had been successfully infiltrated routinely in the past. An extensive analysis of the preform material and the aluminum alloy used for the matrix growth attempts was conducted. The extensive characterization paid off in that it showed the presence of an unexpected contamination of the silicon carbide powder. A new lot of powder was procured and analyzed to be free of contamination. Growth experiments with the new lot of powder were also successful.

Testing and Analysis of the Development Material

Three development $\text{SiC}_{\text{p}}/\text{Al}_2\text{O}_3$ composite tubes were tested and analyzed to evaluate the influence of centrifugal preform casting. One was a production tube which could be compared to both the "CERASETTM" and the "slurry" development tubes.

Tube A -- Production (93-X-3063), tubular SiC preforms were fabricated by slip casting.

Tube B -- Development, tubular SiC preforms were fabricated by centrifugal casting using a mixture of 500 grit SiC particles and CERASETTM preceramic polymer.

Tube C -- Development, tubular SiC preforms were fabricated by centrifugal low temperature molding of an aqueous 500 grit SiC slurry.

The measured tube dimensions are listed in table 10.

Table 10. Tube Dimensions

Tube	Outside Diameter (mm)	Wall Thickness (mm)
A	51 ± 0.5	5.0 ± 1.0
B	37.80 ± 0.2	2.55 ± 0.4
C	37.57 ± 0.5	3.85 ± 0.4

Microstructural Analysis

A phase image analysis was conducted with a system consisting of an optical microscope connected to a video camera and a computer. Phase (chemical and physical) distribution and the corresponding quantitative analysis were performed using optical images and NIH (National Institute of Health) Image 1.52 software. Table 11 summarizes the analysis results. Figure 25 shows the microstructures within the tubes.

Table 11. The Measurement for Phase Volume Percent (%)

Tube	SiC	Al ₂ O ₃	Pore	Al
A	61.4	34.7	1.4	2.5
B	62.5	32.1	2.7	2.7
C	59.2	32.2	5.4	3.2

a)

b)

c)

Figure 25. A Cross Section View of Tube A, B and C (respectively)

Mechanical Testing

The experiment procedures used in this study were the same as used in the production tube testing and analysis. This test, however, was conducted only at ambient temperature. Forty C-shaped test specimen rings were made from Tubes A, B, and C. Table 12 is a summary of the strength data obtained from this testing.

Table 12. Summary of Strength Results

Tube	σ_0 Characteristic Strength	m Weibull Parameter	E Elastic Modulus
A	410 MPa	10.91	276 GPa
B	352 MPa	8.81	274 GPa
C	385 MPa	7.47	246 GPa

Summary

The new slip casting and extrusion processes for preform manufacture were unsuccessful in improving the product. The use of the high density (vertical) furnace for matrix growth appeared to be a significant process improvement but UTSI was unable to evaluate the new product due a lack of resources.

The new centrifugal processing methods used for the preform creation appeared to provide marginally higher precision for the wall thickness compared with the production tubes. Tests preformed by UTSI, however, showed that these new techniques resulted in higher material porosity and decreased strength for both the "CERASET™" and the "slurry" preforming processes. (After the foregoing tests, Lanxide refined the process and the results are in Appendix B).

3.4 Laser-Induced Processing

3.4.1 Coating

Corrosion Mechanisms

As discuss earlier, the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite can be unstable under condensed hot alkali environments. Some of the corrosion mechanisms are as follows:

Oxidation

At elevated temperature, oxygen interacts with any exposed surface of SiC. If the oxygen partial pressure is roughly 1 mm Hg or higher, SiO_2 will form a protective layer at the surface. This is referred to as passive oxidation. The chemical reaction to form silica on silicon carbide is:

The formation of SiO_2 is initially be rapid, but will decrease as the thickness of the layer increases. Under these conditions, oxidation will be controlled by oxygen diffusion through the SiO_2 layer and will be parabolic. The oxidation rate increases as temperature increases. At low partial pressure (1 mm Hg or below) of oxygen, inadequate oxygen is present to form a protective SiO_2 layer. Instead, SiO (silicon monoxide) gas forms:

This is called active oxidation. It is roughly linear and continuous and the component can be completely consumed. Active oxidation conditions are not common but must be kept in mind.

Depending on the ceramic, the temperature, and the initial surface condition, oxidation can increase, decrease, or not affect the strength. For example, a study was performed in which specimens with grinding grooves parallel to the length (longitudinal) and thus parallel to the stressing direction were shown to be much stronger than those with grinding grooves perpendicular to both the length (transverse) and stressing direction. Low-temperature oxidation (1000°C) significantly increased the strength for the transverse machined specimens by blunting or reducing the severity of the surface flaws associated with the grinding damage. High-temperature oxidation completely removed the grinding grooves, but resulted in formation of surface pits, which had an equivalent or worse effect on the strength.

Gaseous Corrosion

Most high temperature corrosion of ceramics can be attributed to gaseous corrosion and hot corrosion. The corrosion processes are ultimately controlled by the nature of the products that are formed as a result of the reaction between the gas and the ceramic.

Since the cations of the ceramics are in the oxidized state and the following corrosion processes can be proposed:

First, the cations may be oxidized to higher states, which in the case of oxygen as oxidant, would result in oxygen being incorporated into the ceramics. Such a process could result in the formation of new phases or merely a change in stoichiometry of the phase being oxidized.

Second, the atoms or molecules of the gas may form more stable compounds with the cations of the ceramics. This type of reaction will depend on the properties of the products formed upon the surface of the ceramic but the effects produced by the elements displaced by the oxygen can also be very important.

A third possibility involves the formation of volatile species such as the reduction of SiO_2 (s) to SiO (g). Such reactions probably would involve diffusion through gaseous boundary layers and could proceed rapidly compared to those of processes involving the formation of condensed phases on the surface of the ceramics.

Finally, molecules in the gas such as SO_3 , CO_2 or H_2O may possess a significant affinity for the cationic component or its oxide and react to form compounds such as sulfates, carbonates or hydrates. The rates of such processes will be dependent upon transport through corrosion products and rather complicated mechanisms may prevail.

The possible reactions are:

The kinetics of gaseous corrosion of ceramics involves the transport of reactions and products which often determine the overall rate of the corrosion process. The corrosion reaction rate depends on: the relative corrosion rate of the various phases, the viscosity of the liquid, the density gradient in the liquid, the concentration gradient in the liquid, the porosity of the solid, the wettability of solid phases by the liquid, the boundary layer at the interface, and the geometry of the system.

The grain size and the pore structure are major factors in controlling the rate of dissolution. Fine grain materials dissolve faster than coarse grain materials. The liquid may penetrate into the grain boundaries resulting in engulfment of the solid grains by the liquid. As a result, the influence of the microstructure on the corrosion complicates the interpretation of corrosion experiments more, so that for fundamental studies simple systems with simple geometries and microstructures must be used. This is valid also for gaseous corrosion studies since, except for the wetting effect, the grain size, the pore structure and the grain boundaries should play a role similar to liquid corrosion. Although there is great deal of literature regarding the oxidation of silicon carbide, however, the only literature on gaseous corrosion of simple oxides appears to be on their reduction and volatilization, particularly for silica. Silica at high temperature under low oxygen pressures volatilizes forming SiO (g) by thermal decomposition and/or by reaction with hydrogen or CO. For instance, significant weight losses were observed in wet hydrogen at 1400°C. Alumina is much more resistant to conditions of this type and tends to lose impurities such as sodium at high temperatures. Significant losses of alumina are only observed at very high temperatures, of the order of 1900°C.

Hot Corrosion

In combustion systems, various compounds such as Na₂CO₃, Na₂SO₄ may be generated in addition to combustion gases. Below some temperatures these compounds condense in the engine and often enhance the gaseous corrosion in a complex process named hot corrosion. At their melting points, both Na₂CO₃ and Na₂SO₄ dissociate easily to Na₂O:

These alkali oxides, such as Na₂O, in turn react with silicon-based ceramics to form low melting glass phases with a resultant loss of structural integrity. When normally protective SiO₂ films are contaminated with Na₂O, a lower viscosity and higher oxygen diffusivity result. This allows active oxidation to occur at the SiO₂/SiC interface as the following reaction, causing surface recession of SiC.

Little hot corrosion has been observed in Na₂SO₄/SO₃ environments for high purity SiC at 1000°C since Na₂SO₄ environment tends to cause impurity effects in ceramics to become a problem at lower temperature than does simple oxidation. However, other studies have revealed that thin films of Na₂CO₃ lead to thick glassy products on SiC at 1000°C. This result is consistent with the removal of the normally protective SiO₂ film to form a non-protective silicate melt. The SiO₂ layer is unstable in the presence of Na₂SO₄ at 1000°C for high oxygen ion activities. Additionally, the penetration of contamination ions (Na, S) down grain boundaries has been postulated to lead to altered mechanical properties.

Exposed to a steel soaking pit environment for 800 hr. at ~1250°C, sintered α-SiC forms a silicate-based slag on its surface, but with no measurable loss of α-SiC material; a slight increase in fracture strength following the exposure has been observed. Corrosion of α-SiC by a basic coal slag at 1200°C proceeds by SiO₂ dissolution and formation of low melting silicates, leading to large corrosion pits. The pits are responsible for a time-dependent strength degradation of the α-SiC material. Exposure of SiC to a coal-fired gas turbine environment for from 100 to 1000 hours at 1200 to 1425°C results in corrosion/oxidation pits and loss of strength.

Three specific cases for molten salts reacting with SiC are:

For an acidic salt film, such as Na_2SO_4 , little or no reaction occurs. This is due to the presence of a stable SiO_2 layer between the salt melt and SiC .

For a basic salt film such as Na_2CO_3 , the protective SiO_2 layer is dissolved and accelerated corrosion occurs.

The third case is an oxygen-depleted (carbon-containing) melt. In this case SiO (g) forms at the SiC surface and reacts to form Na_2SiO_4 , resulting in rapid corrosion.

Corrosive Environments

Corrosion in Heat Engines

SiC and Si_3N_4 are being evaluated in gas turbine engines for combustor liners, stator vanes (nonmoving airfoil shapes that guide the hot-gas flow in the optimum direction into the rotor), rotors, and a variety of liners for hot-gas flow through the turbine. Although under operating conditions, these components are exposed to oxidizing atmospheres flowing at moderate to high velocity, oxidation does not appear to be a problem due to the formation of a passive SiO_2 surface layer. However, corrosion can occur as a result of the combined effects of the oxygen plus gaseous, condensed, or particulate impurities introduced via the gas stream. These impurities can either increase the rate of passive oxidation (i.e., modify the transport rate of oxygen through the protective scale), cause active oxidation, or produce compositions which chemically attack the ceramics.

The following mechanisms are of particular concern:

1. Change in the chemistry of the SiO_2 layer, increasing the O_2 diffusion rate;
2. Bubble formation, disrupting protective SiO_2 layer and allowing increased O_2 access;
3. Decreased viscosity of the protective surface layer, which is then swept off the surface by the high velocity gas flow;
4. Formation of a molten composition at the ceramic surface that is a ceramic solvent;
5. Localized reducing conditions, decreasing the oxygen partial pressure at the ceramic surface to a level at which active oxidation can occur;
6. Formation of new surface flaws, such as pits or degraded microstructure, which decrease the load-bearing capability of the component.

High Temperature Heat Exchanger

The prevailing conditions in a coal fired heat exchanger are known to cause structural material wastage via corrosion, sulfidation, and oxidation, as well as degradation of mechanical properties and heat transfer effectiveness as surface deposits build up and/or spall off.

Another application of heat exchangers is found in the energy intensive glass industry. In an effort to increase efficiency, recuperative heat exchangers are being studied. In a series of preliminary tests in a simulated Advanced Glass Melter flue environment, the DIMOXTM $\text{SiC(p)}/\text{Al}_2\text{O}_3$ composites indicated promise as a material for the heat exchangers. In these tests, sintered α - SiC had adequate thermal and mechanical properties, but was severely attacked by the molten sodium silicate deposited from the combustion gases.

Laser-Induced Coating Process

Researchers at the ORNL suggest that alumina is one of the best candidates for protecting silicon based ceramics from alkali attack. If a $\text{SiC(p)}/\text{Al}_2\text{O}_3$ tube surface was continuously covered by an alumina coating, the corrosion rate of the tube should totally be limited by the alumina. Alumina ceramics are particularly resistant to corrosion because the transport of aluminum and oxygen through alumina is extremely slow compared to transport through most other oxides.

Few research efforts related to ceramic coatings on ceramics have been reported in the available open literature, partly due to the inherent problems associated with the process. The conventional methods used are:

chemical vapor deposition (CVD);
physical vapor deposition (PVD);
sol-gel; air spraying; and
plasma spraying electron beam-physical vapor deposition (EBPVD).

None of these processes are fully satisfactory because the coatings produced have: excessive porosity; inclusions; microcracks; coating segmentation; and poor adhesion. At high temperature this leads to premature cracking, degradation, and failure by internal sulfidation, spallation, reduced mechanical strain, pitting corrosion, condensed salt penetration, and oxygen penetration. Poor adhesion appears to be the major problem because all of these coatings produced by conventional methods are mechanical bonding with the substrate.

A laser-induced cladding provided an improved method for the deposition of high-quality coatings, and offers the following advantages:

- ability to control dilution and produce ultrafine and/or metastable microstructures;
- ability to deposit a wide range of materials of high and low melting points;
- minimal distortion and damage of the underlying substrate;
- possibility of selectively coating inaccessible and localized areas;
- rapid deposition rate;
- readily automated;
- metallurgical bonding between the coating and the substrate (the most important aspect).

Based on the foregoing considerations, UTSI initiated an extensive program to develop a laser-induced alumina coating technique. (This research was supported by the DOE grant and is discussed in detail in the resulting PhD dissertation¹⁴.) In this research *aluminum* powder was used instead of *alumina* powder. Aluminum transforms to alumina by laser-induced reaction in the presence of oxygen and avoids the adhesion problems. The direct cladding used in this investigation was accomplished by melting a limited layer of the underlying $\text{SiC}_p/\text{Al}_2\text{O}_3$ substrate (see Figure 26) in a defocused laser beam and blowing a stream of fine aluminum particles (see Figure 27) to produce a very strong metallurgically bonded coating on the substrate. Table 13 shows the characteristics of $\text{SiC}_p/\text{Al}_2\text{O}_3$ composites substrate

Figure 26. Scanning Electron Micro-graphs of the As-Received SiC_p/Al₂O₃.
(a) surface view, (b) cross- section view

Table 13. Characteristics of SiC_(P)/Al₂O₃ Composite Substrate

Material Characteristics	
SiC content, volume %	45
Al ₂ O ₃ content, volume %	52
Residual aluminum alloy content, volume %	1.6
Porosity content, volume %	1.4
Density, g/cm ³	3.4
Tube Dimensions, mm	
Outside diameter	50
Inside diameter	40
Wall thickness	5
Specimen Dimension, mm	
Length	30
Width	10
Thickness	5

In this study, *aluminum* powder (from ALCOA)was used instead of a high melting point *alumina* powder as a precursor to the alumina coating so that it was possible to use a less intense beam to lessen or avoid causing cracking of the ceramic substrate during processing. The particle size was from 1 μm to 5 μm , and the average size was 2.5 μm . Figure 27 shows the particle features.

Figure 27. Scanning Electron Micro-graph of Aluminum Powder

PVD Precoating

In order to create a sound bond and higher wettability between the substrate and the coating material, a bond coat was first deposited on the ceramic substrate prior to the laser coating process. A bond layer about 5 μm thick of either titanium or aluminum was deposited on the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ substrate using physical vapor deposition (PVD) prior to the laser coating process. PVD was applied with a commercially available Dayton Vacuum unit. Multiple samples were produced simultaneously. The sample stage was inclined at 45° and was continuously rotated at 30 rpm around the vertical axis. This arrangement provided the condition for deposition a uniformly thick bond coat on the substrate surface. The parameters employed for PVD are given in Table 14.

Table 14. The parameters used for PVD Coating of Titanium and Aluminum

Coating Material	Current (amp)	Voltage (volt)	Vacuum (torr)	Time (min)
Titanium	25-30	80-95	2×10^{-5}	5
Aluminum	15-20	25-40	2×10^{-5}	5

Laser Processing

The experimental arrangement for laser coating is shown diagrammatically in Figure 28.

Figure 28. Schematic Diagram of the Experimental Set-up for Laser Coating

The experimental set up consists of two units: the laser and powder feeder system. The laser system, a Rofin-Sinar RS3000 CO₂ laser, was employed for this experiment. (The RS3000 laser is a fast axial-flow, radio-frequency (27.12 MHz) excited CO₂ laser with an operating power range from 200 to 3700 Watts. It may be configured to produce TEM₀₀, TEM₁₀, TEM₂₀, or TEM₀₁* spatial modes in a linearly polarized beam which is circularly polarized with external optics. An optical beam delivery system with a 150 mm focal length copper off-axis parabolic provides focusing of the beam to a 300 μ m diameter spot size). The laser may be operated in one of four modes:

full CW
5 kHz modulated power
pulse (25 kHz Max.) or
superpulse (25 kHz, Max.)

A computer numeric controlled (CNC) five-axis Aerotech workstation is used to translate the work-table during laser processing while also providing control of the laser and associated equipment such as flow valves for the cover gas. For the experiments carried out in this study, the laser was operated in 5 kHz modulated power, a quasi-continuous wave (Q-CW) mode. Argon was blown through the nozzle to shroud the work area and also to protect the lens.

As depicted in Figure 28, a dynamic fluidized-bed powder feeder (designed and fabricated at UTSI) delivered the precursor aluminum powder at the laser-substrate interaction region. A pneumatic vibrator in conjunction with high-pressure air/gas separates the powder clusters into individual particles by breaking the weak electrostatic forces between them. The high-pressure air/gas also fluidizes the powder particles and entrains to the laser-material interaction region via a delivery tube. An air filter at the top of the powder container avoids excessive pressure build-up while ensuring a continuous and smooth powder flow. The air/gas flow rate controls the powder delivery rate. A efficient powder delivery can be achieved by selecting a proper combination of the inlet air/gas flow rate and the frequency of the pneumatic vibrator. In addition, as the inlet gas is a carrier for the powder, it provides a reactive environment at the laser-material interaction region for conversion of aluminum into an Al₂O₃ ceramics.

Laser in-situ reaction coating of Al₂O₃ with an aluminum powder was initially conducted on as-received, a bond-coated (titanium or aluminum) SiC_(p)/Al₂O₃ substrate. The best pre-existing surface condition was then chosen according to the coating quality. The laser beam, defocused on the sample surface, was scanned continuously with some overlap between consecutive passes to cover the entire surface. The laser processing was carried out with a slight overpressure of oxygen. The main parameters in this coating process are beam power, beam diameter, traverse (or scanning) speed, powder flow rate, and overlap rate. These parameters were varied to identify the optimum conditions for obtaining complete coverage, and a smooth and adherent coating. Large areas of the substrate were covered by making a series of parallel overlapping tracks. The laser processing parameters used are tabulated in Table 15.

Table 15. Laser Processing Parameters

Laser Power (watt)	150 ~ 1500
Beam Mode	TEM ₁₀
Traverse Speed (mm/s)	20 ~ 30
Focal Position (mm)	5 ~ 25 above substrate surface
Shielding Gas (l/min)	Argon (coaxial), 2
Reaction Assistant Gas (l/min)	Oxygen, 2
Overlap (%)	30~60
Powder Feeder (mg/s)	50 ~ 250
Powder Outlet Nozzle Angle	30 ~ 60° to the horizontal

Post Processing of the Samples Treated by Laser Coating Processing

The initial laser-coated samples were cross-sectioned and mounted in epoxy. Each sample was metallographically prepared by polishing with a series of grit papers for microstructural evaluation. The final polishing was done with a 1 μ m diamond paste.

Microstructures and surface topography were studied by optical and scanning electron microscopy (SEM). Chemical composition and phases were determined by energy dispersive spectroscopy (EDS) and x-ray diffractometry (XRD). Through out these analytical techniques, the optimum conditions (parameters) of laser processing were determined for obtaining a high conversion rate of reaction, complete coverage, and a smooth and adherent coating. All the rest of the samples were laser processed with these optimum parameters and then mechanically and corrosion tested.

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 modulus 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 $I = bd^3/12$ and, where $c = d/2$ is the thickness of the specimen and b is the width. Figures 29 and 30 illustrate the derivation of 3-point

and 4-point flexure formulas for rectangular bars.

Figure 29. Derivation of 3-Point Flexure Formulas for a Rectangular Bar

Figure 30. Derivation of 4-point Flexure Formulas for a Rectangular Bar

The mechanical testing performed in this study was not designed to produce an absolute 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) due to high thermal shock to the material during laser processing. Due to the limitation of small dimensions testing material available, the three-point bend was used.

Two sets of samples for strength testing were produced from the as-received and laser-induced reaction coated samples. Each set included ten coupons: each coupon approximately 30 mm long and 10 mm wide on the outside surface. (The inside surface width was not as wide as the outside surface due to the curvature of the samples). Figure 31 gives sample coupon dimensions. The coupon was roughly considered as rectangular and $B = (a + b)/2$ as its width.

The bend strength is given by:

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

Figure 31. Sample dimensions

Ten of these coupons from each of the as-received and laser-induced reaction coated samples were selected for bend testing using an Instron testing machine. Table 16 gives the parameters used in the three point bend tests. Table 17 gives the sample dimensions and the measurement results.

Table 16. Parameters Used for Three-point Bend Testing

Load Speed	Normal Load	Record Chart Speed
0.5 mm/min	250 kg.	130 mm/min

Table 17. Sample Dimensions (L=22.66 mm)

Sample	Sample #	a (mm)	b (mm)	c (mm)	B (mm)
As Received Samples	1	9.94	8.26	4.96	9.10
	2	9.88	7.52	5.08	8.70
	3	9.72	8.84	5.30	9.28
	4	9.52	7.68	4.62	8.60
	5	10.54	8.72	4.96	9.63
	6	9.26	7.62	4.76	8.44
	7	9.34	7.90	5.40	8.62
	8	12.30	9.58	5.04	10.94
	9	9.22	7.26	5.04	8.24
	10	10.80	8.26	5.42	9.53
	Average	10.05	8.16	5.06	9.11
Laser Induced Reaction Coated Samples	1	9.70	8.42	4.80	9.06
	2	10.34	8.48	5.04	9.41
	3	9.70	8.16	4.82	8.93
	4	10.30	8.24	5.40	9.27
	5	10.58	8.64	5.44	9.61
	6	9.80	8.46	5.24	9.13
	7	10.52	8.44	4.94	9.48
	8	10.50	9.26	4.96	9.88
	9	9.80	8.76	5.14	9.28
	10	10.70	9.26	4.80	9.98
	Average	10.19	8.61	5.06	9.40

Hot Corrosion Testing

To evaluate the effectiveness of the coating, hot corrosion tests were conducted on the coated sample and, for comparison, as-received samples. There are two common approaches for hot corrosion testing: (1) Burner studies with a salt solution aspirated in the burner and (2) Laboratory furnace studies with thin salt films.

A burner system (1) comes closer to duplicating actual environments than a laboratory furnace, but burner experiments are expensive and it is difficult to precisely control all operating parameters.

The laboratory corrosion study was employed in this investigation. In a laboratory corrosion study, a thin salt film is sprayed on a ceramic coupon. The coupon is then placed in a laboratory controlled-atmosphere furnace. Such experiments are inexpensive and allow precise control of temperature, pressure, and salt chemistry. The kinetics of reaction can be followed by continuous weight change measurements or by taking samples for chemical analysis after various time intervals. The major drawback to these experiments is that they involve a one-time deposition of salt and not a continuous deposition as would occur in an actual condition.

Eight coupons for hot corrosion testing were produced from both as-received samples and laser-induced reaction coated samples. The sample dimensions were approximately 5 by 10 by 30 mm. All the specimens were sprayed with 2-3 mg/mm² coatings of Na₂CO₃ from a saturated aqueous salt solution. The specimens were then exposed to 1200 °C in air for 50, 100, 150 and 200 hours

respectively. The exposure temperature was achieved and maintained inside a Pereco™ electric resistance furnace. The furnace was brought up to the 1200°C at a rate of approximately 100°C per hour. Once that temperature was reached, it was held constant ($1200 \pm 10^\circ\text{C}$) for the designated period. The hot corrosion testing performed in this study was designed to determine if there was any difference in the corrosion resistance in a basic environment between the as-received material and the laser-induced reaction coated material.

Post-exposure evaluation of the specimens included measurement of weight change, x-ray diffraction (XRD), and scanning electron microscopy (SEM) equipped with energy dispersive spectrum (EDS) analysis. Initially, the corrosion product layer surface was examined. Next, the product layer surface was removed with 10% HF of H₂O solution for six hours at 90°C, then the etched substrate was examined. Control samples of the uncorroded as-received SiC_{py}/Al₂O₃ composite were also subjected to this HF dissolution treatment. Very little dissolution for the uncorroded samples was observed from weighing the sample before and after the HF dissolution treatment on an analytical balance with a sensitivity of 0.01 mg.

Some of the laser-induced reaction ceramics coating runs were initially conducted on the samples with different pre-existing surface conditions, such as the as-received, Al, and Ti PVD surface coated. These runs were conducted with some of the laser processing parameters given in the Table 15 at different nozzle angles (30~60°) of powder feeder. The initial experiments showed that the samples with Ti PVD pre-coating appeared to have highest wettability for the laser-induced alumina coating. The nozzle angle variation had a great influence on the reaction coating quality. Under the same conditions, the best coating results were achieved when the nozzle angle was at 55°. Therefore, Ti PVD pre-coating and 55° nozzle angle were chosen for all the later laser-induced reaction alumina coating experiments.

In order to obtain a set of optimum process parameters, laser-induced reaction alumina coating tracks were produced using a range of laser processing parameters. The process parameters employed in the investigation are presented in Table 18. The investigation was conducted for several features such as surface quality, transformation of aluminum, topography, microstructure and phase identification.

Table 18. Laser Processing Parameters

Trial #	Powder Feeder Flow Meter Reading (mm)		Argon Flow Meter Reading (shield gas) (mm)	Laser Power (watts)	Traverse Speed (mm/min)	Focal Position above the Sample Surface (mm)	Overlap (mm) (%)	Laser Beam Diameter (mm)	Remarks
	Air	O ₂							
1	40	0	20	500	1800	5	56	0.67	no breaks, coarse metal coating.
2	30	0	20	500	1800	5	37	0.67	broke into two pieces, coarse metal coating.
3	30	10	0	500	1800	5	37	0.67	no breaks, coarse metal coating.
4	30	10	0	500	1800	5	37	0.67	no breaks, broke when remelted. coarse metal coating
5	25	20	0	400	1800	5	37	0.67	no breaks, coarse metal coating
6	25	20	0	300	1800	5	37	0.67	no breaks, coarse metal coating
7	25	20	0	300	1800	5	37	0.67	no breaks, coarse metal coating
8	25	20	0	300	1800	5	37	0.67	no breaks, coarse metal coating
9	25	20	0	300	1800	5	37	0.67	no breaks, coarse metal coating
10	25	35	0	300	1800	5	37	0.67	no breaks, coarse metal coating
11	25	50	0	300	1800	5	37	0.67	no breaks, coarse metal coating
12	25	50	0	300	1800	5	37	0.67	no breaks, coarse metal coating
13	25	35	0	200	1800	5	37	0.67	no breaks, fine metal coating
14	15	35	0	200	1800	5	37	0.67	no breaks, fine metal coating
15	7.5	7.5	25	200	1800	5	37	0.67	no breaks, fine metal coating
16	0	10	25	150	1800	5	37	0.67	no breaks, fine metal coating
17	0	10	25	250	1800	5	37	0.67	no breaks, fine metal coating
18	0	10	25	250	1800	10	38	1.33	broke into three pieces, smooth alumina coating
19	0	20	25	250	1800	10	38	1.33	broke into many pieces, smooth alumina coating
20	0	20	10	250	1800	10	38	1.33	broke into three pieces, smooth alumina coating
21									
22	0	15	10	225	1500	10	38	1.33	broke into two pieces, smooth alumina coating
23	0	15	10	225	1200	10	38	1.33	broke into many pieces, smooth alumina coating
24	0	15	10	225	2000	10	38	1.33	broke into three pieces, smooth alumina coating
25	0	15	10	300	1800	10	38	1.33	broke into three pieces, smooth alumina coating
26	0	15	10	200	1800	8	38	1.33	broke into two pieces, fine beard coating
27	0	15	10	150	1800	8	47	1.07	no breaks, smooth alumina coating
28	0	15	10	150	1800	8	40	1.07	no breaks, smooth alumina coating
29	0	15	10	150	1800	8	40	1.07	no breaks, smooth alumina coating
30	0	15	10	150	1800	8	40	1.07	no breaks, smooth alumina coating
31	0	15	10	150	1800	8	40	1.07	no breaks, smooth alumina coating

The observations showed that effective coating could be achieved within a narrow range of the laser process parameters. It indicated that the complete laser-induced reaction alumina coating could be obtained only when aluminum powder was delivered by pure oxygen gas. This results in very low laser power needed for the reaction coating.

Figure 32 shows an overview of the samples from trial 1 to 31. Figure 33 is a higher magnification view of some samples in the Figure 32. Figure 34 is a high magnification view of Figure 32(c). The best coating results in this study were achieved by trials 27-31 and their process parameters were considered as the optimum. It appeared that trials 27-31 produced a adherent, relatively smooth and crack-free coating of Al_2O_3 on the $\text{SiC}_p/\text{Al}_2\text{O}_3$ substrate surface. The marked difference in the surface roughness of the as-received and the laser-induced alumina coating may be seen from comparing Figure 26(a) and Figure 34.

Figure 32. Topographical Features of Alumina Coating on $\text{SiC}_p/\text{Al}_2\text{O}_3$ Samples
[(a)~(c) samples from trials #1 to #17; (d)~(e) samples from trials #18 to #31]

Outside the optimum range, problems appeared such as: samples breaking during laser processing, a rough surfaced coating layer, metal beads forming on the surface, and incomplete aluminum transformation into alumina.

Although there were some microcracks within the coating as seen in Figure 34, these cracks are very shallow. Few of them penetrate further into the coatings or substrate as illustrated in Figure 35. Cross-sectional view indicates a defect free interface and the coating appeared uniform with a limited amount porosity. The laser induced transformation of the aluminum into the ceramic coating was confirmed by using x-ray diffraction. Figure 36 shows the x-ray diffraction analysis of the laser-induced reaction transformed alumina coating on the $\text{SiC}_p/\text{Al}_2\text{O}_3$ substrate.

Figure 33. Magnified Views of Some Samples from Figure 32.

[(a) trial #8, (b) trial #17 and (c) trial 28.]

Figure 34. SEM Graph of a High Magnification View for the Sample from Trial #28.

Figure 35. Cross-sectional View of the Laser-induced Reaction-coated $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$

Figure 36. X-ray Diffraction Analysis of Laser-induced Reaction-coated $\text{SiC}_{(\text{p})}/\text{Al}_2\text{O}_3$

The x-ray pattern indicates the existence of Al_2O_3 peaks and the absence of any other phase within the sensitivity of the instrument.

Rippling effects on the surface of the laser coating were observed as illustrated in Figure 34. The main rippling effect is perpendicular to the traverse direction. Similar features have been studied in detail by various researchers for a variety of metallic alloys subjected laser surface melting. The phenomena involved are complex, and depend on the surface tension driven flow and the resonant wave length of the melt pool. This activity is essentially a function of the temperature dependence of the surface tension. This may explain differences between the rippling in laser melted metals and the laser coated ceramics. The ripples in metals have a herring bone formation with respect to the traverse direction, whereas, in the case of the laser ceramics coating, they are nearly perpendicular. This may be a consequence of the low thermal conductivity of the ceramic and the fact that, unlike most metals, the conductivity of alumina is effectively invariant with temperature. These characteristics of the conductivity will affect the temperature gradient, and hence surface tension differences.

Initially the aluminum and titanium bond layer was deposited using the PVD (physical vapor deposition) technique because this nanoscale particle layer provides a strong interface via formation of reaction products (phases) with the base ceramic. It also provides a resilient metallic buffer zone to very high thermal stresses developed between the ceramic substrate and the ceramic coating during the laser-induced reaction treatment. The absence of surface cracks and the strong adherence of the coating indicate that both bond coatings have served their purpose in the present case. In practice, wetting may be improved by adding other reactive elements, especially titanium. The beneficial effects of reactive additives on wettability have been mainly addressed as due to a reduction of interface energy. It was observed in this study that the titanium bond coat provided better wettability than the aluminum bond coat. The formation of Al_2O_3 during laser treatment in oxygen atmosphere primarily occurs according to the following reaction:

The Gibbs free energy of the above reaction is:

$$\Delta G^\circ = 1,676,000 + 320T \text{ (J) for } 973\text{-}1800\text{K}^{(85)}$$

where T is the temperature in K

The formation of Al_2O_3 in the above reaction can occur by either of possible two mechanisms: 1) self-diffusion of aluminum through a thin surface layer of alumina with oxidation occurring at the alumina-oxygen interface, or 2) diffusion of oxygen through a thin surface layer of alumina with the oxidation occurring at the alumina-aluminum interface. However, the diffusivity D_{Al} , for aluminum diffusion in alumina ($9.48 \times 10^{-15} \text{ cm}^2/\text{sec}$) is higher than the diffusivity for oxygen (D_{oxygen}) in alumina ($4.4 \times 10^{-18} \text{ cm}^2/\text{sec}$), indicating that the aluminum transport dominates. The initial supply of oxygen is such that other oxides in addition to Al_2O_3 also are formed via reactions of the type:

where M indicates other metallic elements. In order for the Al_2O_3 to form, the following additional reaction must be favorable:

The amount of oxidation depends upon the composition of the alloy, the stability of the oxides formed, the growth rate of the oxide, and the diffusion of aluminum to the alloy-oxide interface. For the Equation 35 to proceed forward, the standard free energy of formation of Al_2O_3 must be more negative than that of MO, and the activity of aluminum at the alloy-oxide interface should be large compared to the activity of M. In the present case, although the oxide of silicon or titanium is quite stable, Al_2O_3 is more stable than these oxides because it has lower standard free energy of formation than SiO_2 and TiO_2 . This warrants the formation of Al_2O_3 through precise control over processing parameters such as laser power and powder feeder rate.

The formation of other possible undesirable products such as SiO_2 , TiO_2 and Al_4C_3 , due to the reaction between oxygen, aluminum, titanium, and $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$, is ruled out. The phase Al_2O_3 has a substantially lower free energy of formation than SiO_2 and TiO_2 over a full range of temperatures up to 1800°C , which reduces the chances of the formation of SiO_2 and TiO_2 over Al_2O_3 (Figure 37). The possibility of the reaction

between aluminum and SiC to form Al_4C_3 is ruled out, especially at high temperatures ($>650^\circ\text{C}$), because SiC has a lower free energy of formation over the full range of temperatures up to 1600°C . These arguments are substantiated by the x-ray diffraction analysis of the laser-induced reaction coated ceramic substrates (Figure 38), which showed the existence of only Al_2O_3 peaks.

Figure 37. Free energy formation as a function of temperature for SiO₂, TiO₂ and (2/3)Al₂O₃.

Figure 38. Free Energy Formation as a Function of temperature for SiC and (1/3)Al₄C₃

Mechanical Testing of As-received vs. Coated Samples

Table 18 is the mechanical testing results and Table 19 is the summary. As seen in Table 19, the reduction of about 14% in the strength of the laser coated sample compared to the as-received sample is realized. Such a reduction may be due to a single or combination of factors such as: 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 a combination of materials and processing parameters at optimum levels for the production of sound and strong coatings.

Table 19. Three-Point Bending Test Results for the As-Received Samples

As-Received Samples			
Sample #	Fracture load P (lbs)	s (Kpsi)	s (MPa)
1	322	31.49	217.13
2	366	35.75	246.48
3	360	30.28	208.81
4	338	40.35	278.25
5	408	37.76	260.39
6	291	33.37	230.09
7	496	43.23	298.06
8	400	31.56	217.58
9	324	33.94	234.05
10	474	37.13	256.00
AVG.	378	35.49	244.68

Table 19. continued

Laser Induced Reaction Coated Samples			
Sample #	Fracture load P (lbs)	s (Kpsi)	s (MPa)
1	275	28.84	198.83
2	315	28.90	199.26
3	381	40.27	277.67
4	468	37.97	261.78
5	422	32.50	224.09
6	294	25.72	177.32
7	288	27.30	188.23
8	288	25.98	179.15
9	323	28.85	198.89
10	286	27.23	187.74
AVG.	334	30.35	209.30

Table 20. Summary of Three-Point Bend Testing Results

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

When a $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite is heated to 1000~1500°C, its strength will reduce about 36% (compared to the strength at room temperature). The study by Jon Winkler⁴ indicated that the strength of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite was degraded by 24% after the composite was exposed at MHD furnace at 1150°C for 107 hours. The research by Peter LaRue¹⁰ showed that the strength of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite was degraded by 30~65% after the composite was exposed at 1100, 1260 and 1400°C with slag for 200 hours (the mechanical strength was measured at 1100, 1260 and 1400°C). Research conducted by Breder and Parten⁸ indicated that the strength of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ was degraded by 25% after the composite was exposed at 1260°C with slag for 500 hours (the mechanical strength was measured at 1260°C). In this study, the bending tests showed a 14% reduction of strength after laser-induced reaction alumina coating. If the coating will provide corrosion protection for the composite, the 14% reduction of strength is acceptable compared to the strength loss due to corrosion

Corrosion of $\text{SiC}_{(\text{P})}/\text{Al}_2\text{O}_3$ Composite

A. Corrosion of $\text{SiC}_{(\text{P})}/\text{Al}_2\text{O}_3$ composite without laser-induced reaction alumina coating

Figure 39 shows the changes in weight for composite specimens with and without a laser-induced reaction alumina coating after 50, 100, 150, and 200 hours of exposure at 1200°C following application of a Na_2O_3 layer. Each data point represents mean values of two test specimens. The samples were soaked in a HF water solution to remove corrosion products. All of the specimens exhibited an increase in weight. The samples without the laser-induced reaction alumina coating gained $30\sim 32\text{ mg/cm}^2$, while the laser-induced reaction alumina coated samples experienced much a small increase in weight, of only $7.8\sim 9.3\text{ mg/cm}^2$. There was no significant effect of time of exposure between 50 and 200 hours on the weight change.

The increase in weight of the specimens was due to the growth of a $\text{Si}/\text{Al}_2\text{O}_3$ oxidation product which had a morphology very similar to that of the matrix of the composite itself. Figure 40 is an optical micrograph of the surface region of a specimen which had been exposed at 1200°C with a Na_2O_3 layer for 150 hours. It appears that the oxidation product in the upper portion of the Figure differs from the original $\text{SiC}_{(\text{P})}/\text{Al}_2\text{O}_3$ composite only because it does not contain SiC particulate.

Figure 39. Weight change of $\text{SiC}_{(\text{P})}/\text{Al}_2\text{O}_3$ Composite Specimens after Exposure at 1200°C with a Na_2O_3 Layer

Figure 40. Optical Micrograph of Cross-sectional View of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C for 150 Hours (after silicates removed with a HF solution) Showing $\text{Si}/\text{Al}_2\text{O}_3$ Oxidation Product on Surface

There are more white-bright particles on the top of the oxidation product layer and more pores on the bottom of the oxidation region. The source of metal Al for the oxidation process was apparently residual metal contained in the composite, and this oxidation can be thought of as an uncontrolled resumption of the liquid metal oxidation process by which the composites were originally fabricated.

The $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite material was made by the directed oxidation of a molten aluminum alloy through a porous SiC preform. The microstructure of this material consists of SiC particles surround by a matrix of continuously interconnected Al_2O_3 and residual metal formed by the oxidation process. The composite is approximately 45% SiC, 52% Al_2O_3 and 1.6% residual metal Al by volume. While the exact composition of the starting alloy is proprietary, it is a hypereutectic aluminum-silicon alloy (to minimize reactions with SiC during fabrication) doped with magnesium and zinc to promote the direction metal oxidation. It is expected that the SiC in the composite along with the residual metal give the material a high thermal conductivity, strength and toughness, while the interpenetrating Al_2O_3 skeleton provides corrosion resistance at high temperature. In this study, it was found that the composite consists of four phases. Except for SiC, Al_2O_3 , and residual Al mentioned above, there exists another phase, Si. (Figure 41 shows the x-ray diffraction data for the as-received composite; it indicates the presence of silicon phase).

Figure 41. X-ray Diffraction Pattern of the As-received Composite

Figure 42. Phase Diagram of Al-Si Alloy

Figure 42 is a phase diagram of Al-Si alloy. There are only two phases, α phase and β phase, at room temperature. The α phase is a solid solution at which silicon solves in aluminum. At the eutectic temperature, 577°C, the maximum solubility of silicon in aluminum is 1.65%, and only

0.05% at room temperature. Since the solubility of silicon in the α phase is very low and the properties of the α phase are very similar to those of pure aluminum, it may be considered same as the Al phase. The β phase is a solid solution of aluminum solving in silicon. Because the solubility of aluminum in the β phase is extremely low, the β phase may be considered as pure silicon. When the amount of silicon in Al-Si alloy exceed 12.6%, it becomes the hypereutectic composition. During the solidification of the Al-Si alloy with a hypereutectic composition, the first solidification phase is β , called initial Si; at 577°C, eutectic ($\alpha+\beta$) appears and usually the β in eutectic ($\alpha+\beta$) is called eutectic Si. Because the residual metal Al in $\text{SiC}_p/\text{Al}_2\text{O}_3$ composite possesses hypereutectic composition, there should be some silicon or β phase exiting in the composite at the room temperature

When the composite was exposed at high temperature, initially, some of the molten residual Al-Si alloy was drawn to the surface of the composite by capillary forces, but was not able to spread over the surface due to the relative low surface energy. As the composite was further heated, the exposed SiC particles were oxidized to form a thin layer of SiO_2 causing an increase in the surface energy. Molten Al-Si alloy from the interior of the composite was then most likely drawn to the SiO_2 , where it was able to spread over the surface and undergo rapid oxidation to form a solid Al_2O_3 thin film on the liquid metal surface.

With an increase in exposure time, the oxidation film will become thicker to form an oxidation layer and the silicon content in the residual liquid metal will become richer. The growth direction of the oxidation product is from the inside surface to the outside surface of the composite. This caused that the outer the oxidation layer, the more Si there is (refer to the Figure 40). The growth rate of the oxidation layer on the outside of the composite surface should depend on the extrusion rate of the Al molten liquid to the outer surface.

At the same time, in the wetting of the liquid Al on the SiO_2 , the following chemical reaction occurred at their interface:

The volume of the ceramic substrate was reduced by 38% from 3SiO_2 to $2\text{Al}_2\text{O}_3$. If it is considered that Si formed from reaction (Eq 37) will be melted in aluminum liquid (because the solubility of Si in Aluminum is 67% at 1200°C) and this liquid will be drawn to the surface of the composite during exposure, the volume of the substrate will be reduced by 58% from $(3\text{SiO}_2 + 4\text{Al})$ to $2\text{Al}_2\text{O}_3$. Even if all of the silicon stays at the original location, the volume is still reduced by 28% from $(3\text{SiO}_2 + 4\text{Al})$ to $(2\text{Al}_2\text{O}_3 + 3\text{Si})$. As a consequence, the Al_2O_3 grains formed in the substrate were separated by cavities along the boundaries due to the volume shrinkage. Some of the liquid metal would diffuse easily into these cavities. In front of the wetting triple line, surface cavities may be induced due to the shrinkage of the ceramics substrate during the reaction. This may hamper a further spreading of the liquid drop over the surface. Meanwhile, Al and Si liquid alloy may diffuse to the surface cavities through the boundary cavities of the Al_2O_3 grains. A further reaction will then occur in front of the triple line. In this way, the chemical reaction takes place on the surface of SiO_2 before the spreading of liquid metal and leaves the cavities on the surface of the SiC particles. Under this condition, the growth direction of the corrosion product, Si/ Al_2O_3 , is from the original surface of the composite to inside of the composite. This indicates that the protective SiO_2 layer on the SiC is also removed by aluminum (Eq 37). The unprotected SiC is then attacked by the oxidizing atmosphere and molten salt. The growth rate of the oxidation layer inside the composite might depend on at least the rates of two reactions: First is the oxidation

of SiC particles to become SiO_2 . Second is the dissolution of SiO_2 through the reaction (Eq37). It is obvious that the growth rate of the oxidation layer on the outside surface of the composite is faster than in the inside of composite.

The chemical reaction (Eq 37) also explains why there was a much higher increase in porosity within composite after it was exposed at high temperature because the reaction (Eq 33) may occur at the inside of the composite. Jon Winkler⁽⁴⁾ observed that the porosity increased from 1.95% in the as-received $\text{SiC}_p/\text{Al}_2\text{O}_3$ composite to 23.24% after the composite was exposed to high a temperature with coal slag. The residual aluminum in the as-received composite was only about 7.16%. If all the residual aluminum was drawn out from the composite, the porosity should not have been more than 10% for his experiment. In this study, the beginning residual aluminum was about 1.6. The porosity increased from 1.4% for the as-received composite to 4.78% after exposure at 1200°C with a layer of Na_2CO_3 for 200 hours.

Part of the silicon produced through reaction (Eq 37) will be melted in the aluminum liquid until the liquid saturates with silicon. At 1200°C , the maximum solubility of silicon in aluminum is about 67%. The surplus silicon will precipitate out just like the initial Si. Figure 43 shows x-ray diffraction patterns of the $\text{SiC}_p/\text{Al}_2\text{O}_3$ composite after exposure at 1200°C for different time increments.

Figure 43. X-ray Diffraction Patterns of the Specimens without the Laser-induced Reaction Alumina Coating (after the corrosion products removed with a HF solution)

The specimens were washed with HF solution prior to x-ray analysis. The diffraction patterns indicate that there is no residual aluminum in the surface layer and all aluminum extruded from substrate to surface had been oxidized into Al_2O_3 . There are minor amounts of Si and SiC existing in the oxidation layer. The presence of Si in the oxidation layer is consistent with above the discussion. Figures 44 and 45 are SEM cross-section views of some corroded samples and their element x-ray maps. These pictures provide further proof concerning the existence of silicon and its distribution within the oxidation layer. Both Figure 44(SI) and Figure 45(SI) indicate that there is more silicon in both the top and the bottom of the oxidation layer than in the center of the layer.

Figure 44. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the SiC_p/Al₂O₃ Composite Corroded at 1200°C for 50 Hours (after silicates removed with a HF solution)

The elementary x-ray maps of Si in Figure 44 and Figure 45 also show that some of SiC was attacked in the interface of the oxidation layer and the substrate composite because the interface is rather rough compared to the Si x-ray map in Figure 52 for the sample coated with laser-induced reaction alumina coating.

Figure 45. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C for 200 Hours (after silicates removed with a HF solution)

The growth of the oxidation layer was not uniform. There were regions on the surfaces where it was absent or very thin, and other regions where it was up to $300\ \mu\text{m}$ thick. The areas where no or a thin $\text{Si}/\text{Al}_2\text{O}_3$ oxidation product formed were subject to corrosion by the sodium salt. Figure 46 is a cross-sectional micrograph of the $\text{SiC}_{\text{py}}/\text{Al}_2\text{O}_3$ composite after 50 and 200 hours corrosion at 1200°C respectively. Corrosion is indicated by surface roughening and recession.

Figure 46. Optical Micrograph of a Cross-sectional Views of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ Composite Corroded at 1200°C (after silicates removed with a HF solution)

(a) for 50 hours, (b) for 200 hours

Selective oxidation could result in selective corrosion. It is well known that SiC is resistant to oxidation because it forms a protective SiO₂ film. However, silica is soluble in basic salt melts according to reaction :

The corrosion begins with selective oxidation of the SiC particles on or near the surface (to form SiO₂) and the aluminum metal (to form Al₂O₃) in the composite followed by dissolution of the oxides in the molten salt. Because Al₂O₃ is generally regarded as much more corrosion resistant than SiC, the corrosion rate appears to be controlled by the corrosion resistance of the Al₂O₃ matrix. There are some areas on the surface containing more SiC particles and less Al₂O₃ than other areas since the distribution of SiC particles is not uniform from a microscopic view. Consequently, there was more SiO₂ formed in these local areas. In the presence of Na₂CO₃, SiO₂ can react directly with Na₂CO₃ melt to form the low melting compound:

where $x = 1$ or 2

For $x=2$, the reaction product is Na₂Si₂O₅ whose melting point is 837°C. Na₂Si₂O₅ can further react with Al₂O₃ to form a still lower melting eutectic NaAlSiO₄ whose melting point is 760°C. Repeated oxidation and dissolution reactions at these local areas probably occur until all the Na₂CO₃ is depleted. A characteristic feature of SiC corroded by alkali compounds is the presence of a previously molten silicate glass layer containing alkali oxides. Figure 47 shows some localized regions of the silicate glass layer which form on the specimens.

Figure 47. SEM Graph of Surface View of Specimen Exposed at 1200°C for 50 Hours Showing Glassy Layer in Center Section (before the corrosion products removed by a HF solution)

Figure 48 is a magnified view of the glassy area in Figure 47 and its elementary x-ray maps. It shows that the major constitute element is silicon. EDS analysis provide the composition of the glassy phase: 68.27 Si, 26.05 Al and 5.68 Na (by wt%). X-ray diffraction phase analysis also indicates that corrosion products contain some $\text{Na}_2\text{Si}_2\text{O}_5$, NaAlSiO_4 , and $\text{Na}_2\text{Al}_{22}\text{O}_{34}$. The melting point of $\text{Na}_2\text{Al}_{22}\text{O}_{34}$ is rather high, more than 1900°C .

Figure 48. SEM Graph of Magnified View of the Glassy Area Shown in Figure 47 and its Elementary X-ray Maps

[illegible]

Figure 50 is a surface view of the structures underlying the glassy phase (glassy phase removed with HF solution) and elementary x-ray maps. It also shows a localized pattern of attack on the surface. Some SiC particles were missing, leaving voids and some SiC particles were incompletely attacked due to the depleted Na_2CO_3 layer.

Figure 50. SEM Graph of a Surface View of Structure Underlying Glass Phase (glassy phase removed with a HF solution) and Element X-ray Maps

This result is consistent with Figure 43 which indicated there was still some of the SiC phase existing on the surface of the specimens after the corrosion test.

B. Corrosion of $\text{SiC}_{(P)}/\text{Al}_2\text{O}_3$ composite with laser-induced reaction alumina coating

The weight change for the composite with the laser-induced reaction alumina coating after exposure

at 1200°C for 50, 100, 150 and 200 hours was shown in Figure 39. Each data point for the coated samples is based on the mean values of two test specimens (same as uncoated samples). Compared with the uncoated samples, the alumina coated samples experienced a much smaller weight increase. The edge areas of the specimens were not processed during the laser coating processing, thus these areas should experience same corrosion as the specimens without the laser-induced reaction alumina coating. This edge effect would attribute some weight increase for laser coated specimens. If the surface of specimens was totally covered by the laser-induced reaction alumina coating, the weight change would be even less.

Figure 51 shows optical graphs of cross-sectional views of the specimen as-coated with the laser-induced reaction alumina coating and the specimen with the laser-induced reaction alumina coating exposed at 1200°C for 200 hours corrosion after washing with a HF solution.

Figure 51. Optical Micrographs of Cross-sectional Views for the Specimens: (a) as-coated with the laser-induced reaction alumina coating, (b) the specimen with the laser-induced reaction alumina coating exposed at 1200°C for 200 hours corrosion (after washing with a HF solution)

Figure 52. SEM Graph of a Cross-sectional View and Elementary X-ray Maps of the $\text{SiC}_{(\text{py})}/\text{Al}_2\text{O}_3$ Composite with the Laser-induced Reaction Alumina Coating Corroded at 1200°C for 50 Hours (after washing with a HF solution)

Figure 52 is a SEM graph of the cross-sectional view and elementary x-ray maps of the $\text{SiC}_{(\text{py})}/\text{Al}_2\text{O}_3$ composite with laser-induced reaction alumina coating corroded at 1200°C for 50 hours after washing with a HF solution. Both Figure 51 and 52 show the laser coated samples experienced very little attack on the outside surface of the coating, no defects appeared in the joint interface between the substrate and the coating after corrosion test, and none of the composite

under the coating was attacked. This indicates the laser-induced reaction alumina coating provided an effective protection to the composite. The bonding between the composite and the laser-induced reaction alumina coating was excellent. It also prevented aluminum from extruding to the composite surface as there was no $\text{Si}/\text{Al}_2\text{O}_3$ oxidation product formed on the surface of the coating. This might be the reason that the weight change of the coated specimens was much less than the uncoated specimens

Figure 53 pictures x-ray diffraction patterns of specimens with the laser-induced reaction alumina coating before corrosion products were removed by a HF solution. It shows $\text{Na}_2\text{OAl}_2\text{O}_3\text{SiO}_2$ and $\text{Na}_2\text{Al}_{22}\text{O}_{34}$ formed on the surface of the composite during corrosion testing. Both $\text{Na}_2\text{OAl}_2\text{O}_3\text{SiO}_2$ and $\text{Na}_2\text{Al}_{22}\text{O}_{34}$ are highly refractory. The melting points are approximately 1500°C and 2000°C , respectively. Therefore, the laser-induced reaction alumina coating protects the $\text{SiC}_p/\text{Al}_2\text{O}_3$ composite from corrosion by at least two aspects: First the coating is almost an impenetrable layer to corrodents such as salt and oxygen. Second, the coating lessens the effect of reaction by becoming part of the corrosion product. By introducing one or more refractory compounds into the corrosion product, the refractoriness of the SiO_2 -rich layer is increased. For example, all compositions in the Na_2O - SiO_2 binary system are partially or totally liquid at temperatures above approximately 1200°C , whereas certain compositions in the Na_2O - SiO_2 - Al_2O_3 ternary system are solids at the same temperature.

Figure 53. X-ray Diffraction Patterns of Specimens with the Laser-induced Reaction Alumina Coating (before the corrosion products removed by HF solution)

A coating containing a high Al_2O_3 content might equalize beneficially with the chemically altered SiO_2 layer. Figure 54 shows x-ray diffraction patterns of the specimens with the laser-induced reaction alumina coating after the corrosion products were removed by a HF solution. It indicates silicon and silicon carbide was detected by the x-ray diffraction analysis. The trace amount of Si and SiC detected are attributed to the edge effect (no coating) of the alumina coated specimens.

Figure 54 X-ray Diffraction Patterns of Specimens with the Laser-induced Reaction Alumina Coating (after the corrosion products removed by a HF solution)

Laser Induced Coating Conclusions

The un-coated $\text{SiC}_p/\text{Al}_2\text{O}_3$ composite experienced an increase in weight during the exposure to Na_2CO_3 at 1200°C due to the oxidation of residual aluminum metal in the composite. (There was no significant weight change difference experienced during exposure times between 50 and 200 hours). The oxidation layer formed on the composite surface consisted of Si and Al_2O_3 (after washing a HF solution). The oxidation layer grew inward and inside outward from the original surface of the composite. (The growth rate in the outside direction was faster than in the inside direction). The formation of the $\text{Si}/\text{Al}_2\text{O}_3$ oxidation layer on the composite was nonuniform, and localized corrosion was observed as a result. The porosity within the composite increased after exposure is due to the reaction:

An alumina coating of about 50 micron thickness was successfully deposited on the $\text{SiC}_p/\text{Al}_2\text{O}_3$ ceramic composite substrate using a laser-induced reaction technique. The coating appeared to be adherent to the substrate and free of cracks and porosity, although a few surface microcracks were observed. X-ray diffraction analysis indicated that the entire coating was alumina. The evaluation of the coated samples (in comparison with the as-received samples) based on three-point bending test results indicated a strength reduction of about 14%. The laser-induced reaction alumina

coating effectively provided protection for the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ composite, however, by separating corrodents and forming some refractory compounds. After exposure to Na_2CO_3 at 1200°C for 200 hours, the bonding between the alumina coating and the composite appeared to be unchanged.¹⁴

3.4.2 Joining

There is a great deal of interest in developing techniques to join ceramics and ceramic composites. Progress has been made in this area at the Idaho National Engineering Laboratory¹⁵. One drawback to the procedures is due to the requirement that both pieces to be joined, regardless of size, must be placed in a furnace.

Preliminary attempts at UTISI to develop a concept and establish a general procedure for laser-induced reaction joining (LIRJ) of monolithic SiC ceramics, $\text{SiC}_{(f)}/\text{SiC}$, $\text{C}_{(f)}/\text{SiC}$ and $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ ceramic composites have been conducted with reasonable success. The ceramic materials were joined with a titanium-base interface reactant material. The joints thus created were believed to possess properties compatible to those of the base ceramic materials.

The joining was conducted in air with high traverse speeds ranging from 1500 mm/min to 3500 mm/min using a pulse width modulated (PWM) CO_2 laser ($10.6\text{ }\mu\text{m}$) beam at suitable power levels (350-700 watts). The LIRJ technique minimizes the residual thermal stresses and improves both expansion matching and strength characteristics through the evolution of appropriate phase structure in and around the joint region. Based on these initial trials, it appears that the laser joining techniques for ceramics holds great promise and can be developed further for a variety of ceramic materials. Time and financial constraints limited the effort that could be devoted to this research, however, these efforts have already contributed to winning US patent # 5,503,703; April 1996, entitled, "Laser Bonding Patent."²⁷

4.0 CONCLUSIONS

Mechanical Testing and Analysis

Part of the study attempted to determine the strength of production SiC(p)/Al₂O₃ ceramic matrix composite tube materials produced by Lanxide Corporation in their horizontal furnace. Specimens were evaluated after being exposed to both elevated temperatures (1100°C, 1260°C, and 1400°C) and elevated temperature with periodically refreshed coal slag. Unavoidable variations in the as-manufactured geometry of the samples which were used for strength testing, made impossible it to directly use traditional analysis techniques to interpret the strength data obtained. Therefore, a new data analysis technique was developed and used based on the computations of *equivalent loads* for each of the test specimens.

(The *equivalent load* is defined as that load which, when applied to a standard (perfect) test specimen, would result in the same fracture probability as the actual that was applied to the actual (non-perfect) test specimen when it failed. The method is based on equating equivalent integrals of stresses over the areas on which they act, for both the perfect and the actual sample. This requires the unit maximum principal stress distributions in the inconsistent sample geometries when subjected to both a unit load and the actual load. This led to the development of a finite element model of the C-ring to calculate the theoretic stress distributions in C-ring geometries due to both a unit load and the actual applied load and, from these distributions, carry out integration theoretically of the stress over areas upon which they act. This procedure and the experimental fracture data made it possible to determine the two parameters of Weibull fit function for the ceramic composite under all the test conditions).

This new analysis method has shown that the strength of the ceramic composite material continually decreased as the temperature of testing was increased for fixed exposure times. Addition of coal slag to the exposure environment resulted in a further decrease in strength. However, only after exposure to coal slag at 1400°C was a measurable loss of material observed. This suggests that rapid corrosion clearly makes the material unsuitable at and above this temperature level. However, the 30% to 50% reduction in characteristic strength observed at lower temperatures may remain relatively constant over longer periods of time permitting the use of this material at temperatures up to at least 1260°C in heat exchanger tubes and other applications. Values were obtained for the Weibull parameter m and characteristic strength σ_0 of the material make it possible to calculate the probability that a tube made of this material will fail when subjected to a given set of physical loads under the conditions tested.

Additional work is needed to increase the usefulness of this data. Continued work is needed to better describe the time-dependent nature of the material strength parameters and also to further refine estimates of the maximum temperature at which this material can survive in this highly corrosive environment.

This portion of the research resulted in a MS thesis and additional details are reported therein¹⁰.

Computer Modeling

An attempt was made to model the thermodynamics and kinetics of the corrosion mechanism involving coal slag and the SiC(p)/Al₂O₃ DIMOX™ material at elevated temperatures. The complexity and large number of variables made this task impossible. Small changes in the assumptions made large differences in the modeling results which were deemed to be meaningless.

To reduce the parameters involved in the modeling process, Dr. Kristin Breder of ORNL suggested the modeling of the proposed DOE High Performance Power System (HIPPS) ceramic heat exchanger. This modeling involved a monolithic ceramic and carbon dioxide, water, nitrogen and oxygen at elevated temperatures. Although this work deviated from the initial objective of the grant, it produced useful information that may be of value to the HIPPS program. This research is presented in Appendix A.

Development Tubes

Although several attempts were made to improve and reduce the costs of the DIMOX™ tubes, only the switch from a horizontal to a vertical furnace to increase the furnace loading six-fold was fruitful. The results from this new procedure were not tested by UTSI, however. After UTSI evaluated one of the innovative preform processes and discovered some deficiencies, Lanxide refined the procedure and this is documented in Appendix B.

Laser Induced Coating

A technique was developed to apply a metallurgical bonding of alumina to the surface of the $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ DIMOX™ ceramic composite via a laser induced reaction. This cladding was extremely dense and was basically non-porous. Although there was some strength degradation to the underlying material associated with the coating process, this was offset by a large improvement in its corrosion resistance.

A patent has been applied for regarding the laser induced coating procedure²⁶. This portion of the research contributed toward a PhD dissertation and additional details can be found therein⁽¹⁴⁾. Over the three years period of the grant, six papers relating to the coating were presented/published¹⁶⁻²¹.

Laser Induced Reaction Joining

Several trials were conducted to investigate the feasibility of joining DIMOX™ materials (as well as other ceramics) via a carbon dioxide pulsed laser induced reaction. The results were very promising, however, the mechanical strengths of the joints were not tested due to limited resources. This is a very promising technology that warrants further research and UTSI has received a patent²⁷ for this process.

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APPENDIX A
MODELING OF HIPPS ENVIRONMENT

Appendix A: Modeling of HIPPS Environment

As described in a previous report, an equilibrium thermodynamic modeling study of the expected reactions between the DIMOX SiC/Al₂O₃/Al composite and the Foster Wheeler HIPPS environment was begun. Table 1 shows the gas compositions on the "air" and "gas" sides of the heat exchangers, while Table 2 shows the nominal composition of the DIMOX composite system used for the study:

Table 1.

	"Air"	"Gas"
CO ₂	2.0	18.6
H ₂ O	2.4	7.6
N ₂	75.5	71.3
O ₂	20.1	2.5

Table 2:

Substance	Mole Fraction	Component	Mole Fraction
SiC	0.62	Si	0.625
Al ₂ O ₃	0.35	C	0.62
Al	0.025	Al	0.725
Si	0.005		

The potential reactions between the two gas environments and the model composite were examined by minimizing the Gibbs Free Energy of the system subject to various constraints.

Although there are thermodynamic data for over 200 substances in the {C,H,O,N,Al,Si} system, free energy minimization of a 200 parameter system is impossible. Thus, smaller systems (C,H,O,N and Al,O,Si) were first examined to determine the expected predominant substances.

Figures 1.a and 1.b show the calculated compositions vs. temperature for the air side C,H,O,N composition on linear and log scales, respectively. Figures 2.a and 2.b show similar data for the gas side. Figures 3.a and 3.b show similar data for a sample Al-O-Si system.

These preliminary calculations were used to determine the final subset of potential phases and substances for the global calculations. Table 3 shows the components, potential phases (gas, liquid, or various crystallographic structures) and substances (species that can exist) for this model system.

Table 3:
Elements, Phases, and Substances used for Equilibrium Calculations

SYSTEM ELEMENTS : AlCHNOSi

NUMBER REF.P	COMPONENT	STATUS	AMOUNT	DELTA
1	C	NORMAL	1.00000	
2	H	NORMAL	1.00000	
3	O	NORMAL	1.00000	
4	N	NORMAL	1.00000	
5	Al	NORMAL	1.00000	
6	Si	NORMAL	1.00000	

NUMBER	PHASE	STATUS	MODEL
1	Al	NORMAL	PURE SUBSTANCE
2	GAS	NORMAL	IDEAL GAS
3	Al2O3	NORMAL	PURE SUBSTANCE
4	ANDALUSITE	NORMAL	PURE SUBSTANCE
5	MULLITE	NORMAL	PURE SUBSTANCE
6	BETA CSI	NORMAL	PURE SUBSTANCE
7	N4Si3	NORMAL	PURE SUBSTANCE
8	CRISTOBALITE	NORMAL	PURE SUBSTANCE
9	Si	NORMAL	PURE SUBSTANCE

NUMBER	SUBSTANCE	STATUS/CONSTRAINT	SOURCE
1	Al	NORMAL	sub_sgte
2	AlHO2<g>	NORMAL	sub_sgte
3	AlO<g>	NORMAL	sub_sgte
4	AlO2<g>	NORMAL	sub_sgte
5	CH4<g>	NORMAL	sub_sgte
6	C2H2<g>	NORMAL	sub_sgte
7	CO<g>	NORMAL	sub_sgte
8	CO2<g>	NORMAL	sub_sgte
9	H2<g>	NORMAL	sub_sgte
10	H3N<g>	NORMAL	sub_sgte
11	H2O<g>	NORMAL	sub_sgte
12	N2<g>	NORMAL	sub_sgte
13	O2<g>	NORMAL	sub_sgte
14	OSi<g>	NORMAL	sub_sgte
15	O2Si<g>	NORMAL	sub_sgte
16	Al2O3	NORMAL	sub_sgte
17	Al2O5Si<ANDALUSITE>	NORMAL	sub_sgte
18	Al6O13Si2<MULLITE>	NORMAL	sub_sgte
19	CSi<BETA_CSI>	NORMAL	sub_sgte
20	N4Si3	NORMAL	sub_sgte
21	O2Si<CRISTOBALITE>	NORMAL	sub_sgte
22	Si	NORMAL	sub_sgte

Figure 4 shows the expected predominant equilibrium phases formed when the DIMOX composite is equilibrated with the "air" side. At the temperatures of interest (1300-1500 Kelvin) Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and Cristobalite (SiO_2) are the predicted solid phases formed. Figure 5 shows similar results for the "gas" side. Thus, the change in gas chemistry does not appear to significantly alter the predicted oxidation products. For a relatively "clean" system, cristobalite is an excellent diffusion barrier. Thus retention of a significant cristobalite phase content is important. For a contaminated system, Al_2O_3 is often a better diffusion barrier. These calculations imply that the UTSI laser coating process, which effectively increases the aluminum concentration for these calculations, should push the equilibrium phase assemblage toward Mullite - Al_2O_3 . This should enhance the corrosion resistance in these contaminated environments.

Figures 6 and 7 show the gaseous species expected for the "air" and "gas" sides, respectively. As described in a previous report, SiC can actively oxidize, through the formation of volatile $\text{SiO}_{(\text{g})}$ rather than protective SiO_2 . This can occur in reducing environments, such as that on the "gas" side. Figure 8 shows the effect of varying equilibrium oxygen pressure at a fixed temperature of 1500 K. Equilibrium predictions show that the $\text{SiO}_{(\text{g})}$ partial pressure is low for the target gas compositions. However, active oxidation is a kinetically controlled process that is largely affected by the gaseous boundary layer adjacent to the SiC surface. It is expected that the Al_2O_3 phase in the DIMOX composite will enhance the resistance of the material to active oxidation by inhibiting the outflux of $\text{SiO}_{(\text{g})}$ through the boundary layer. The laser coated Al_2O_3 coatings are expected to make these materials even more resistant to active oxidation.

Air side gas eq. vs. T, CHON=2/4.8/46.6/151

Figure 1.a.

Air side gas phase equilibrium vs. T, log scale, CHON=2/4.8/46.6/151

Figure 1.b.

Gas side, gas equilibrium vs. T, CHON = 18.6/15.2/49.8/142.6

Figure 2.a.

Gas side, gas equilibrium vs. T, CHON = 18.6/15.2/49.8/142.6

Figure 2.b.

Al,O,Si, linear plot n(*) =1,1,2 moles

Figure 3.a.

Al, Si, O, log plot, note component amounts

Figure 3.b.

air side calculation, CHONAlSi

Figure 4

Gas side, CHONAlSi

Figure 5

air side, log scale

Figure 6

Gas side, log scale

Figure 7

Figure 8

APPENDIX B
SUMMARY OF ADDITIONAL WORK ON
LOW TEMPERATURE MOLDING

APPENDIX B

SUMMARY OF ADDITIONAL WORK ON LOW TEMPERATURE MOLDING

UTSI's final report describes the manufacture of silicon carbide particulate reinforced alumina tubes by infiltrating preform tubes made via freeze casting an aqueous silicon carbide slurry. The freeze casting process allows for the production of a ceramic preform by irreversibly setting the colloidal silica in the system and then prefiring the part. The composites manufactured using the freeze cast preforms were found to be inferior to other production techniques, primarily due to the presence of porosity within the tubes. In an effort to alleviate the reported porosity in tubes made with 500 grit freeze cast silicon carbide preforms, two different powder systems were investigated. The systems studied were a binary blend of 500 plus 600 grit silicon carbide and a three component blend of 320 plus 500 plus 600 grit. The two different systems improved the particle loading and packing of the powders in the slurry. The better packing led to better flow properties of these systems. These two factors, loading and flow, should lead to a reduction in both the amount and size of the porosity within the preforms, and therefore, potentially to a reduction in porosity within the grown composite tubes.

The formulations of the two systems were: 60% 500RG and 40% 600RG silicon carbide in the 500/600RG system, and 83% 320 grit, 10% 500RG and 7% 600RG silicon carbide for the 320/500/600RG blend. The solids loading of these two systems were set at 2.34 and 2.35 g/cm³ for the 500/600RG and 320/500/600RG blends, respectively.

The slips were mixed, poured and freeze cast in a manner very similar to the process used to produce the original 500RG tubes. The disc shaped preforms were frozen at -75°C and prefired at 825°C. All the preforms produced were dense and easily handleable. No large scale porosity was found within the samples. Green densities for the 500/600RG systems were approximately 66% of theoretical. The 320/500/600RG system was denser, at 73% of theoretical density. The relatively high density is primarily due to the improved particle packing of this ternary blend.

In conclusion, this work centered on altering the particle packing of the SiC slurry system, leading to better flow properties of the slip and lower porosity within the cast preforms. High density disc shaped preforms were produced without any large scale porosity within the microstructure. The uniformity of the pore channel microstructure should lead to a uniform infiltration front when infiltrated via the DIMOX™ directed metal oxidation process, yielding a resultant composite material that should be free from local porosity. Tubular preforms were not produced due to the fiscal and time constraints of the project.

In an effort to alleviate the previously reported problems with freeze cast silicon carbide tubes, different powder systems were investigated. The systems studied were a 500/600RG silicon carbide system and a 320 - 500/600RG system.