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"HIGH PERFORMANCE MATERIALS IN
COAL CONVERSION UTILIZATION"

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1.0 INTRODUCTION

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

2.0 DISCUSSION

2.1 Objective and Scope of Work

The object of this grant is to test, analyze, and improve the heat and coal-slag corrosion resistance of a SiC(p)/Al₂O₃ ceramic composite tubular material. The material will be evaluated for its ability to withstand the pressures, temperatures and corrosion attack which would be encountered within a coal-fired high-temperature, high pressure air heater. The evaluation will include strength testing at elevated temperatures. The feasibility of several joining and coating techniques will also be investigated.

2.2 Task 1- Materials (Lanxide Corporation)

Under Lanxide's cost share portion of the grant, they have provided 21 each of 183 cm (six foot) long, 5 cm (two inch) OD SiC(p)/Al₂O₃ DIMOX™ ceramic composite tubes for testing by UTSI. The first 15 tubes were produced in a horizontal furnace and the final six tubes were produced in a vertical furnace.

Lanxide's progress to date concerning the manufacturing cost reduction goal, has contributed to the redesign of their production process to utilize the vertical furnace. This represents a seven fold higher throughput capacity than obtained with previous production (horizontal) kilns.

An innovative new manufacturing processes is under consideration which could further improve tube quality and reduce costs.

2.3 Task 2- Pre and Post Test Material Characterization

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

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 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.^{1,2} 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.^{1,2}

The two-parameter Weibull distribution is given by:

$$F = 1 - e^{-KA \left(\frac{\sigma_{\max}}{\sigma_o} \right)^m} \quad (1)$$

where F is the probability of failure, $\sigma_{\max}$ is the maximum stress value in a specimen, σ_o is the characteristic strength, and m is the Weibull parameter. In this equation σ_o and m are material properties which are assumed to be independent of geometry and loading conditions. The characteristic strength σ_o 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.³

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 over the surface of a 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

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- 1 D.W. Richerson, "Modern Ceramic Engineering - Properties, Processing, and Use in Design" (Marcel Dekker, Inc., New York, 1982), pp. 82-89, 318.
 - 2 J.D. Sullivan, P.H. Lauzon, Journal of Materials Science Letters 5 (1986) p. 1245.
 - 3 A. De S. Jayatilaka, K. Trustrum, Journal of Materials Science 12 (1977) pp. 1426-1430.

the case in this study. The stress terms such as σ , σ_0 , which represents a distribution of stresses obtained by calculation on the surface area of the specimens, and $\sigma_{\max}$, which are characteristic stress values, 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.

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. For example, 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.¹ 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 systematically 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 ceramics.⁴

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.

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

This equation then provides a way to compute an equivalent load P_s which, if

⁴ O.M. Jadaan, D.L. Shelleman, J.C. Conway, J.J. Mecholsky, and R.E. Tressler, Journal of Testing and Evaluation Vol. 19, No. 3, (May 1991) pp. 181-191.

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

$$I = n\text{Log}(m) - mn\text{Log}(\sigma_o) - \frac{1}{\sigma_o^m} \sum_{i=1}^n \left(\int \sigma_i^m dA \right) + \sum_{i=1}^n \left(\text{Log} \int \sigma_i^{m-1} dA \right) \quad (7)$$

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_o which maximize the value of I are the values which allow the best fit or description of the data set under consideration. To find these values, the partial derivatives of I 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 I . In this case, the maximum point is always located, because for poor values of m and σ_o the likelihood function decreases without bound and has no minimum point.

Setting the derivative of I with respect to σ_o equal to 0, and solving for σ_o gives

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

By substituting this expression for σ_o back into Equation 7 before solving for m , the

value of σ_o need not be computed until after m is found. After such a substitution, setting the derivative of I 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_o 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_o found in Equation 8, becomes

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

A more complete derivation of these expressions will be presented in the final report of this grant (late 1996).

Summary of Solution Sequence

Equations 6, 10, and 11 are then all that is needed to implement the following solution procedure.

- (1) Choose a standard geometry to be used for computation of equivalent loads.
- (2) Determine the stress distribution (σ_{us}) in the standard geometry when a unit load ($P_s = 1$ N) is applied.

- (3) Determine the stress distribution (σ_{ui}) 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 the value of 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 σ_o 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. A more detailed description of the finite element models used will be included in the final report. 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 unit load of one Newton. 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 finite elements on the outer surface. 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 such as ceramics.

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 nonuniform. 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 above. The source code for this program will be submitted in the final report. 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 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_o . In addition to the values of m and σ_o , 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 1 gives a summary of the strength data produced from this analysis while Figure 1 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 1
Summary of Strength Results

<u>Exposure Condition</u>	<u>σ_o Characteristic Strength</u>	<u>m Weibull Parameter</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 1 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 1.

Figure 1 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 $P \left(\int \sigma_{va}^m dA \right)^{\frac{1}{m}}$ where P is the actual load applied to a given specimen, σ_{va} 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 $\frac{1}{1-F}$ 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 $\frac{i-0.5}{N}$ 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 these².

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 ($\text{Log}(\text{Log}(\frac{1}{1-F})) = 0$) 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 in the foregoing, 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 is noticed about many of the fractures is that the slag layer often has 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 nonuniformities 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 1 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 effect 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 2 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.

What this shows is that, 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 1 for the material exposed to this condition is of little value, the Weibull parameter is believed to be reasonably accurate.

Figure 2 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

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.

$$E = \frac{R_e}{R_u} \quad (12)$$

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 2.

Table 2
Modulus of Elasticity Results

Temperature	Elastic Modulus After Slag Exposure	Elastic Modulus Without 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.

Conclusions and Recommendation

This portion of the study has attempted to determine the strength of $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$ ceramic matrix composite tube materials produced by Lanxide Corp. in their horizontal furnace after being exposed to both elevated temperatures and elevated temperature with periodically refreshed coal slag, for temperatures up to 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 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 1 for the Weibull parameter m and characteristic strength σ_0 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.

However, 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. The manufacturer is continuing to make changes to this product, and to the material manufacturing techniques in an attempt to reduce costs and improve dimensional consistency of tubes made with this material. 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.

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

Work continues into the incorporation of kinetic modeling techniques into the numerical analyses routine. Work was delayed somewhat by computer hardware problems.

The acidic nature of the Illinois #6 slag has been shown in prior work to be less corrosive to SiC than other slags. However, the complex nature of the Lanxide material requires more detailed modeling.

Specifically, it seems that global thermodynamic equilibrium calculations are less important than local calculations. That is, the kinetic processes must be evaluated. The three main components of the Lanxide material: SiC, Al₂O₃, and Al-Si residual metal, have very different corrosive/oxidative properties in any environment. Thus, a surface recession rate type of calculation is not very useful - the metal may be entirely gone before the SiC or Al₂O₃ have reacted at all.

The first approach is to apply a linear-parabolic model which was first developed for describing the oxidation behavior of single crystal silicon. This model was developed for oxidation in high purity environments, but as described below, will be useful for this system.

Deal and Grove⁵ described the oxidation of silicon using a mixed control model in which the diffusion of oxygen through the oxide layer and the chemical reaction at the Si/SiO₂ interface act in series. These two processes are coupled by the concentration of the diffusing species (generally assumed to be interstitial O₂ at these temperatures^{6,7} but can be ionic in this case) at the interface. Thus for very thin or very thick oxide layers, either of these mechanisms can limit the oxidation rate, and a broad regime of mixed control is possible. For fast gaseous diffusion, their model is:

$$x^2 + \left(\frac{2D}{k}\right)x = \left(\frac{2DC}{N}\right)(t + \tau) \quad (13)$$

⁵B.E. Deal and A.S. Grove, "General Relationship for the Thermal Oxidation of Silicon," *J. App. Phys.*, 36 [12] (1965)

⁶J.A. Costello and R.E. Tressler, "Isotope Labeling Studies of the Oxidation of Silicon at 1000°C and 1300°C," *J. Electrochem. Soc.*, 131. [8] 1944-1947 (1984)

⁷J.D. Cawley, J.W. Halloran, and A.R. Cooper, "Oxygen-18 Tracer Study of the Passive Thermal Oxidation of Silicon," *Oxid. Met.*, 28, [1] 1-16 (1987)

or more simply:

$$x^2 + Ax = B(t + \tau) \quad (14)$$

where:

x and t are oxide thickness and time, respectively

D is the diffusivity of O_2 interstitials

C is the concentration of dissolved interstitials in equilibrium with the ambient

N is the number of oxygen molecules per unit volume of oxide (22.14 molecules/nm³, assuming the density of the $SiO_2 = 2.2\text{g/cc}$).

τ is the time constant lets the origin ($x=0$) of the model adjust to allow for an initial oxide layer or regime not described by the model (this can be ignored for this purpose, set = 0)

B , or $2DC/N$, is the parabolic rate constant

B/A , or kC/N , is the linear rate constant.

k is the first order reaction rate constant for the chemical reaction at the interface:

A schematic describing the Deal/Grove model is shown in Figure 3. At short times/low temperatures, the chemical reaction can limit the oxidation rate (Figure 3a). The oxygen activity (C_i) at the Si/SiC - SiO_2 interface approaches that at the outer surface (C_o). At long times and higher temperatures, the diffusion limits the reaction rate (Figure 3b). In this case the oxygen activity at the Si/SiC - SiO_2 interface is limited by the thermodynamic equilibrium value.

The reason this model is useful is that it allows the variation of both the parabolic rate constant (B) which describes the diffusion through the oxide/slag layer, and the linear rate constant (B/A) which describes the chemical reaction at the interface. It is important to describe both of these because it is expected that the linear reaction rate constants to be very different for the three materials. Similarly, the viscosity of the slag changes by several orders of magnitude between 1100 and 1400 degrees C (as shown by the pictures in the Oct 94 - Dec 94 quarterly report). Thus, the diffusivity (and parabolic rate constant) will vary greatly over this temperature regime.

Figure 3 Deal/Grove Model

For high purity systems, SiC oxidation is essentially diffusion limited for all times (>1 hour) above 1100°C. However, the diffusivity of oxygen through pure silica is much lower than the diffusivity through various slags. Thus, it is not assumed a priori that the processes are diffusion limited.

Three graphs (Figures 4, 5 & 6) show predicted oxidation rates as the two rate parameters are varied. The lower bound for the parabolic (B) rate constant ($2.4E4 \text{ Ang\AA}^2/\text{min.}$) is the parabolic rate constant for the oxidation of high purity SiC in pure oxygen at 1100°C. The starting point for the linear (B/A) rate constant (Figure 4) is for the same material from the same study.⁸ The parabolic rate constant of the Illinois #6 slag is expected to vary greatly between the component materials.

At low temperatures, the slag viscosity is very high, implying that the diffusivity through the oxide layer is low. Figure 5 shows the projected oxidation rate for materials with varying linear rate constants (our constituent materials) for a given parabolic rate constant. As is shown, the oxidation rate is not unreasonable. We are assuming here that all phases have the same slag/oxide coating on them, which may not be the case. However, it would appear that for a protective slag, oxidation should not be a problem - this is expected.

⁸ C.E. Ramberg, et. al. "Passive Oxidation Kinetics of High Purity Silicon Carbide from 800 to 1100°C," to be published in J. Am. Ceram. Soc.

Figure 4 Oxidation Rates

Figure 5 Oxidation Rates - Varying Linear Rate Constants

The effects of varying the parabolic rate constant for a given linear rate constant are shown in Figure 6. Again, although the oxidation rate is higher, it is not completely unreasonable. A problem occurs when there is a fast linear reaction rate and a fast diffusion process as shown in Figure 6. For this condition, we expect a very rapid oxidation rate.

It is expected that the Al-Si alloy will have a fast linear rate constant. Similarly, we expect the parabolic rate constant (of all materials) to be large at high temperatures. Thus, it appears that at higher temperatures, we may rapidly react the remaining alloy before we significantly corrode the SiC or Al₂O₃. This would create defects that would reduce the strength of the material. This is shown in the final schematic (Figure 6).

Figure 6 Oxidation Rates (Varying Parabolic Rate Constant)

This is all preliminary analysis. The model is still undergoing development and will require input from the experimental observations. Utilization of the thermodynamic modeling has proven difficult but this effort will continue. This is a first cut at incorporating kinetic effects into local equilibrium calculations.

2.4 Task 3 Exposure Testing

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

The remaining bench scale expose tests will involve the tubes produced in the vertical furnace. A determination of how many samples that need to be tested will be conducted by an analysis of the current test results. (The test results will be randomly analyzed to establish the minimum number of data points which yield the same results as the original set.)

2.4.2 Subtask 3B- Field Exposure Tests (UTSI)

The termination of the MHD program has limited field testing to the five tubes exposed during the final MHD test. (At the request of the DOE Contract Monitor, Cliff Smith, one of these tubes was delivered to DOE for additional exposure tests by Dr. Kenith Natasen.) Since these tubes seem to be of less interest due to the potassium seed added to the coal flow, the strength testing of these will be lower in priority than the lab test program. As in the foregoing, a determination of how many samples that need to be tested will be conducted by an analysis of the current test results. (The test results will be randomly analyzed to establish the minimum number of data points which yield the similar results as the original set.)

2.5 Task 4 Project Management

Ms. Nancy Cole, Manager, Fossil Energy Materials, at ORNL, has requested that UTSL give a presentation regarding the laser joining of ceramic composites. This presentation will be scheduled after sufficient experimental data is obtained.

Mr. Bill Boss and Mr. Peter LaRue gave oral presentations at a DOE sponsored Peer Review on February 28, 1995, Knoxville, TN.

Mr. Boss will give a presentation in June in Nashville, TN during the UCRC Contractor's Review Conference.

3.0 SCHEDULE

The exposure and strength testing is the basis for an MS thesis by Pete LaRue. The thesis is on schedule and his anticipated graduation date is May 1995. (Much of the work contained in this report is extracted from this thesis.) A detailed corrosion and microstructural analysis and the effect of coatings will be the basis of a PhD dissertation by Chenge Xiao in 1996. (The progress of the coating work is reported on in Appendix A.)

The work of UTSL, Lanxide Corp and the U of Pa are basically all on schedule.

4.0 CONCLUSION

The overall research continues to go smoothly and all the objectives are being met at this time within budget. The laboratory high temperature exposure tests on the production Lanxide tube samples are now complete and the strength tests of the exposed samples are also complete. The results are published in this report as well as a Master's Degree thesis.

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APPENDIX A
COATING OF LANXIDE SiCp/Al₂O₃
CERAMIC COMPOSITE

LASER INDUCED REACTION COATING TO ENHANCE HIGH TEMPERATURE CORROSION RESISTANT OF SiC/Al₂O₃

In this quarter major efforts were concentrated on improving the laser coating process to enhance the coating quality. In addition, an etching solution was found which reveals the microstructure of the SiC/Al₂O₃ composite sample during SEM observation.

Experiment Procedure

The precursor powder for coating was entrained through a 2-mm diameter copper tube in a carrier medium of air and/or air mixed with pure oxygen, or pure oxygen at a low flow rate (about 4 ~ 8 lit/min) into the irradiation zone of the laser beam over the sample. The carrier gas, in addition to being carrier medium, also provides an interactive medium for chemical conversion of precursor powder into a desired coating. The exit of the copper tube was 10 mm above the sample. The angle of entry of the powder into the irradiation zone was 45° (for the details refer to the Oct. ~ Dec. 1994 quarterly report). Aluminum powder was preheated at 100°C for one hour to remove the moisture and thereby increase the flowability of the powder during the feed process. Powder at the desired feed rate was continuously delivered at the laser/sample interaction zone. The powder was melted, reacted with oxygen and bonded to the substrate. The parameters of the process employed in the investigation are presented in Table I. Microstructure and surface topography were studied by optical and scanning electron microscopy (SEM).

Results and Discussion

LIRC (Laser induced reaction coating) tracks were produced using a range of laser parameters. The investigation was conducted for several features, such as surface, transformation of aluminum, topography, microstructure and phase identification. The observations showed that effective coating could be achieved within a narrow range of laser process parameters. Compared with earlier (the Oct. ~ Dec. 1994 quarterly report) experiments, this time it was noticed that the focal distance above the sample is critical as to sample breaking. The reason is unclear. Figure 1 is the overview of the samples from trial 1 to 31. Figure 2 is a higher magnification view of some samples in Figure 1. Figure 3 is a high magnification view of Figure 2-c.

Good results were achieved by trials 27 ~ 31 compared with the as-received sample and the as-coated sample (coated by Lanxide). The marked difference in their surface is seen in the SEM photographs of Figure 4.

Rippling effects on the surface of the laser coating were observed as illustrated in Figure 3 and Figure 4-c. The main rippling effect is perpendicular to the traverse direction. Similar features have been studied in detail by various researchers^(1,2) for a variety of metallic alloys subjected to laser surface melting. The phenomena involved are complex, and depend on the surface tension driven flow and resonant wave length of the melt pool. This activity is essentially dependent upon

the temperature dependence of the surface tension. This may explain differences between the rippling frequency in metals and the laser ceramic coating. The ripples in metals have a herring bone formation with respect to the traverse direction, whereas in the case of laser ceramics coating they are nearly perpendicular. This may be a consequence of the low thermal conductivity of the ceramics 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 therefore, surface tension differences.

Within the "optimum range " a uniform alumina coating layer was achieved. Outside the optimum range, problems, such as sample breaking during laser processing, or the coating layer being rough and Al or Al alloys, not completely transforming into alumina, appeared (Fig. 1-a, 1-b, 1-c, Fig. 2-a, 2-b, Fig. 5). These experiments indicate that the complete laser induced reaction alumina layer can be obtained only when powder was blown by pure oxygen gas.

The effective nature of the bonding achieved in the optimum range is illustrated in Figure 6. The substrate-coating interface region shows good continuity and no porosity. Although, some micro cracks are observed in the coating (Fig. 4-c), they are shallow and they run neither deep into the coating nor into the substrate (Fig. 6). The coating layer is dense and in general pore free. So far, under this program, mechanical testing has been conducted for only the tubes received as-coated from Lanxide (It is not known exactly how Lanxide coated the tubes). Figure 7 shows that both the coating and the substrate (near the outside surface) are infested with pores. As observed in Fig. 6 and Fig. 7, the quality of the laser coating appears to be much denser and better bonded compared to the coating applied by Lanxide process.

REFERENCE:

1. T. R. Anthony and H. E. Cline, "Surface Ripping Induced by Surface Tension Gradients During Laser Surface Melting," J. Appl. Phys., 48(1977), 3888-3894.
2. I. C. Hawkes, M. Lamb, W. M. Steen and D. R. F. West, "Surface Topography and Fluid Flow in Laser Surface Melting," (proc. 3rd CISFEL Conf., Lyon, France, Sept. 1983), 125-131.

Table 1. Laser Processing and Materials Parameters Used During Laser Induced Reaction Coating of Ceramics with Dynamic Fluidized Bed Powder Feeder (The substrate material is $\text{SiC}_{(P)}/\text{Al}_2\text{O}_3$)

Trial #	Form of Substrate material	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)	Interaction Time (ms)	Specific Energy (J/MM^2)	Remarks
		Air	O ₂									
1	Ti PVD film	40	0	20	500	1800	5	0.75	0.67	22	24.9	no breaks, coarse metal coating.
2	Ti PVD film	30	0	20	500	1800	5	0.5	0.67	22	24.9	broke into two pieces, coarse metal coating.
3	Ti PVD film	30	10 ¹	0	500	1800	5	0.5	0.67	22	24.9	no breaks, coarse metal coating.
4	Ti PVD film	30(0)*	10 ¹ (0)*	0	500(500)*	1800(1800)*	5 (5)*	0.5(0.5)*	0.67	22	24.9	no breaks, broke when remelted. coarse metal coating
5	Ti PVD film	25	20 ¹	0	400	1800	5	0.5	0.67	22	19.9	no breaks, coarse metal coating
6	Ti PVD film	25	20 ¹	0	300	1800	5	0.5	0.67	22	14.5	no breaks, coarse metal coating
7	Ti PVD film	25 (0)*	20 ¹ (0)*	0	300(250)*	1800(1800)*	5 (5)*	0.5 (0.5)*	0.67	22	14.5	no breaks, coarse metal coating
8	Ti PVD film	25 (0)*	20 ¹ (0)*	0	300(200)*	1800(1800)*	5 (5)*	0.5 (0.5)*	0.67	22	14.5	no breaks, coarse metal coating
9	Ti PVD film	25	20 ¹	0	300	1800	5	0.5	0.67	22	14.5	no breaks, coarse metal coating
10	Ti PVD film	25	35 ¹	0	300	1800	5	0.5	0.67	22	14.5	no breaks, coarse metal coating
11	Ti PVD film	25	50 ¹	0	300	1800	5	0.5	0.67	22	14.5	no breaks, coarse metal coating
12	as received	25	50 ¹	0	300	1800	5	0.5	0.67	22	14.5	no breaks, coarse metal coating
13	Ti PVD film	25	35 ¹	0	200	1800	5	0.5	0.67	22	10.0	no breaks, fine metal coating
14	Ti PVD film	15	35 ¹	0	200	1800	5	5	0.67	22	10.0	no breaks, fine metal coating
15	Ti PVD film	7.5	7.5 ²	25	200	1800	5	0.5	0.67	22	10.0	no breaks, fine metal coating
16	Ti PVD film	0	10 ³	25	150	1800	5	0.5	0.67	22	7.46	no breaks, fine metal coating
17	Ti PVD film	0	10 ³	25	250	1800	5	0.5	0.67	22	12.4	no breaks, fine metal coating
18	Ti PVD film	0	10 ³	25	250	1800	10	1.0	1.33	22	6.27	broke into three pieces, smooth alumina coating
19	Ti PVD film	0	20 ³	25	250	1800	10	1.0	1.33	44	6.27	broke into many pieces, smooth alumina coating

20	Ti PVD film	0	20 ³	10	250	1800	10	1.0	1.33	44	6.27	broke into three pieces, smooth alumina coating
21	Ti PVD film	0	15 ³	10	220	1800	10	1.0	1.33	44	5.51	broke into two pieces, smooth alumina coating
22	Ti PVD film	0	15 ³	10	225	1500	10	1.0	1.33	44	5.64	broke into two pieces, smooth alumina coating
23	Ti PVD film	0	15 ³	10	225	1200	10	1.0	1.33	44	5.64	broke into many pieces, smooth alumina coating
24	Ti PVD film	0	15 ³	10	225	2000	10	1.0	1.33	44	5.64	broke into three pieces, smooth alumina coating
25	Ti PVD film	0	15 ³	10	300	1800	10	1	1.33	44	7.52	broke into three pieces, smooth alumina coating
26	Ti PVD film	0	15 ³	10	200	1800	8	1	1.33	44	5.01	broke into two pieces, fine beard coating
27	Ti PVD film	0	15 ³	10	150	1800	8	1	1.07	36	4.67	no breaks, smooth alumina coating
28	Ti PVD film	0	15 ³	10	150	1800	8	0.85	1.07	36	4.67	no breaks, smooth alumina coating
29	Ti PVD film	0	15 ³	10	150	1800	8	0.85	1.07	36	4.67	no breaks, smooth alumina coating
30	Ti PVD film	0	15 ³	10	150	1800	8	0.85	1.07	36	4.67	no breaks, smooth alumina coating
31	as received	0 (0)*	15 (15)*	10 (10)*	150(150)*	1800(1800)*	8 (8)*	0.85(0.85)*	1.07	36	4.67	no breaks, smooth alumina coating

* - subjected to remelting tracks

1 - the outlet of oxygen is the laser nozzle, only using air to flash aluminum powder

2 - the oxygen mixed with air to flash the aluminum powder

3 - only oxygen used to flash the aluminum powder

Figure 1. Overviews of topographical features of a laser induced reaction layers on SiC/Al₂O₃. (a)~(c) samples from trial #1 to trial #17

(d)

(e)

Figure 1 Continued: Overviews of topographical features of a laser induced reaction layers on SiC/Al₂O₃. (d)~(e) sample from trial #18 to trial #31

(a)

(b)

(c)

Figure 2. Magnified view of some samples in Figure 1. (a) trial # 8, (b) trial #17 and (c) trial # 28 .

Figure 3. Higher magnification view of Figure 2-c.

(a)

(b)

Figure 4. SEM microscopy of top view. (a) as received, (b) as coated by manufacturer

(c)

Figure 4. Continued: SEM microscopy of top view. (a) as received, (b) as coated by manufacturer, (c) LIRC (trial 28).

Figure 5. Cross section view of LIRC showing uncompleted reaction layer. Bright region in the coating is untransformed Al and/or Al-alloy.

Figure 6. Cross section view of LIRC (trial # 28).

Figure 7. Cross section view of coating as coated by manufacturer. (b) is the magnified view of (a) at the same location