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

**FOR THE PERIOD  
JANUARY 1, 1996 THROUGH MARCH 31, 1996**

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## 1.0 INTRODUCTION

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

UTSI has completed all the initially planned laboratory exposure tests involving pulverized coal slag on the production Lanxide DIMOX™ ceramic composite material. In addition, the strength testing (at temperature) and analysis of C-ring sections of the exposed production composite is complete. The evaluation of a laser-induced coating to laser coat the material has been the major activity this quarter while awaiting an innovatively produced new DIMOX™ test sample.

## 2.0 DISCUSSION

### 2.1 Objective and Scope of Work

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

### 2.2 Task 1-Materials (Lanxide Corporation)

In the previous report, several development issues observed in conjunction with the centrifugal casting of preforms using a slurry of SiC particles in CERASET™ preceramic polymer were described. 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.

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.,  $-15^\circ\text{C}$ ) 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 have been 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.

Additional tubular preforms by the centrifugal low temperature molding process for subsequent densification via alumina matrix growth are currently being fabricated. The microstructures of the grown tubes will be characterized. If the microstructures are satisfactory, several tubes will be fabricated for testing at UTSI.

## 2.3 Task 2-Pre and Post Test Material Characterization

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

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

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

Work this quarter has focused on three major areas - continuation of the viscosity/diffusion modeling, preliminary modeling of the laser heat treating process being developed at UTSI, and the expansion of the modeling effort into the Foster Wheeler HIPPS ceramic heat exchanger system.

The time dependent strength behavior described in previous reports is being combined with the corrosion modeling to examine the effects of the residual metal pockets on long time mechanical stability. While the thermodynamic properties of the coal ash slag do not vary significantly with temperature, the kinetic properties - viscosity and diffusivity - have very large temperature dependencies. Current work focuses on first modeling a system with 50% SiO<sub>2</sub>, 20% Al<sub>2</sub>O<sub>3</sub>, and 30% network modifiers. This model system was previously found to represent the DIMOX/slurry coated sample combined with Illinois#6 ash slag. Final results of this stage are pending.

In an attempt to complement UTSI's supplemental work on Laser Coating, corrosion modeling has also focused on the effects of laser coating on long term

performance. While the laser coated DIMOX samples exhibited a 14% decrease in bend strength, preliminary results imply that the long term behavior of the laser coated samples should be at least as good as the uncoated samples. Modeling results will be compared with UTSI's experimental work and the model will be refined.

The MTDData thermodynamic software license was renewed. The software is being used to model the Foster Wheeler HIPPS system. This system is cleaner, with fewer impurities in both the solid and gas phases. Thus, equilibrium thermodynamic modeling may be fruitful. While the oxygen rich side is predicted to yield a dense, protective  $\text{SiO}_2$  layer, the gas side may result in active oxidation. Because active oxidation involves both thermodynamic and kinetic processes, this new thrust is in line with the efforts to date.

## 2.4 Task 3-Exposure Testing

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

The remaining bench scale exposure test will involve the tube produced by the polymer preform discussed in Task 1. This tube will be exposed to coal slag for 200 hours at 1260°C. The tube will then be cut into 10 mm wide C Sections for strength tests at 1260°C.

### 2.4.2 Subtask 3B-Field Exposure Tests (UTSI)

This subtask is complete.

## 2.5 Task 4-Project Management

Dr. Narendra Dahotre presented a paper in Anaheim, California during the High Temperature Coatings-II '96 conference. The paper is entitled "Evolution of Microstructure and Mechanical Properties in Laser Induced Reaction Coating of  $\text{Al}_2\text{O}_3$  on  $\text{SiC}/\text{Al}_2\text{O}_3$  Composite" and was published as part of the proceedings. (A copy is attached to this report as Appendix B).

## 3.0 SCHEDULE

The next major event will be the testing of the polymer preformed composite ceramic tube. Due to problems discussed under Task 1, the testing of this tube was delayed and it is anticipated that the testing will be completed during the April - June 1996 quarter.

The coating research will be completed in the July - September 1996 quarter and will result in a Ph.D. Dissertation.

## 4.0 CONCLUSION

The overall research continues to go smoothly and most of the objectives are being met at this time. The laboratory high temperature exposure tests on the production Lanxide tube samples, the strength tests of the exposed samples, and their analysis are all complete.

The computer modeling of the corrosion process has not been successful as of yet due to the complexity of the problem. An effort to simplify the model is underway.

As reported in Appendix A, the coating work is making steady progress. High-temperature corrosion tests and strength tests of the coated vs. uncoated samples are currently being analyzed.

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

APPENDIX A

HOT CORROSION OF UNCOATED AND COATED  $\text{SiC}_{(p)} / \text{Al}_2\text{O}_3$

## QUARTERLY REPORT

JANUARY 1--MARCH 31, 1996

### Hot Corrosion of Uncoated and Coated $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$

#### Experimental Procedure

The material used in this study was Lanxide's  $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$  DIMOX<sup>TX</sup> tubular ceramic composite with a 50 mm outside diameter and a wall thickness of 5.0 mm. Lanxide's material designation for this material is 93-X-3015. Test specimen coupons of approximately 5x10x30 mm were cut from the tube.

Eight coupons for hot corrosion testing were produced from both as-received samples and laser-induced reaction coated samples. All the specimens were sprayed with 2-3 mg/mm<sup>2</sup> coatings of  $\text{Na}_2\text{CO}_3$  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<sup>TM</sup> electric resistance furnace. 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.

The specimens were prepared for initial analysis by removing all the corrosion products by a six hour 10% HF-H<sub>2</sub>O dissolution at 90 °C. Control samples of the uncorroded as-received  $\text{SiC}_{(p)}/\text{Al}_2\text{O}_3$  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.

#### Results and Discussions

An initial analysis was conducted on the as-received samples corroded with a  $\text{Na}_2\text{CO}_3$  film resulting from a 50 hours exposure at 1200 °C. Figure 1 is the surface view of a scanning electron micrograph. It shows that corrosion products had a smooth, glassy appearance with some micro-cracks. Figure 2 is the EDS plot of the corrosion products in the surface. The plot indicates the present of Na, Al and Si only. These products should be primarily  $\text{SiO}_2$  and  $\text{NaO}\cdot\text{x}(\text{SiO}_2)$  with a small amount of  $\text{Al}_2\text{O}_3$  and some residual Al.

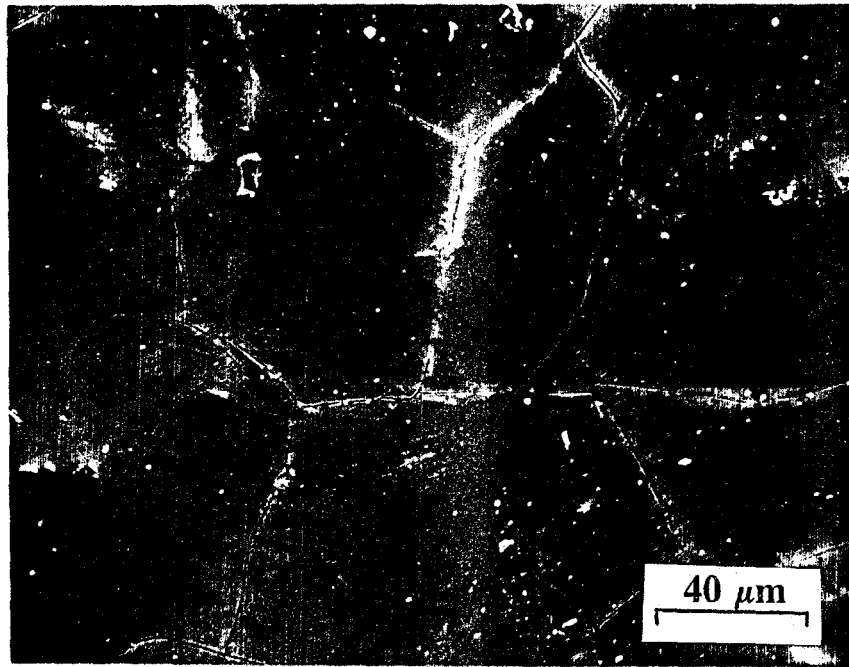


Figure 1 Scanning electron micrograph of reaction product surface formed by  $\text{Na}_2\text{CO}_3/\text{air}$  melt

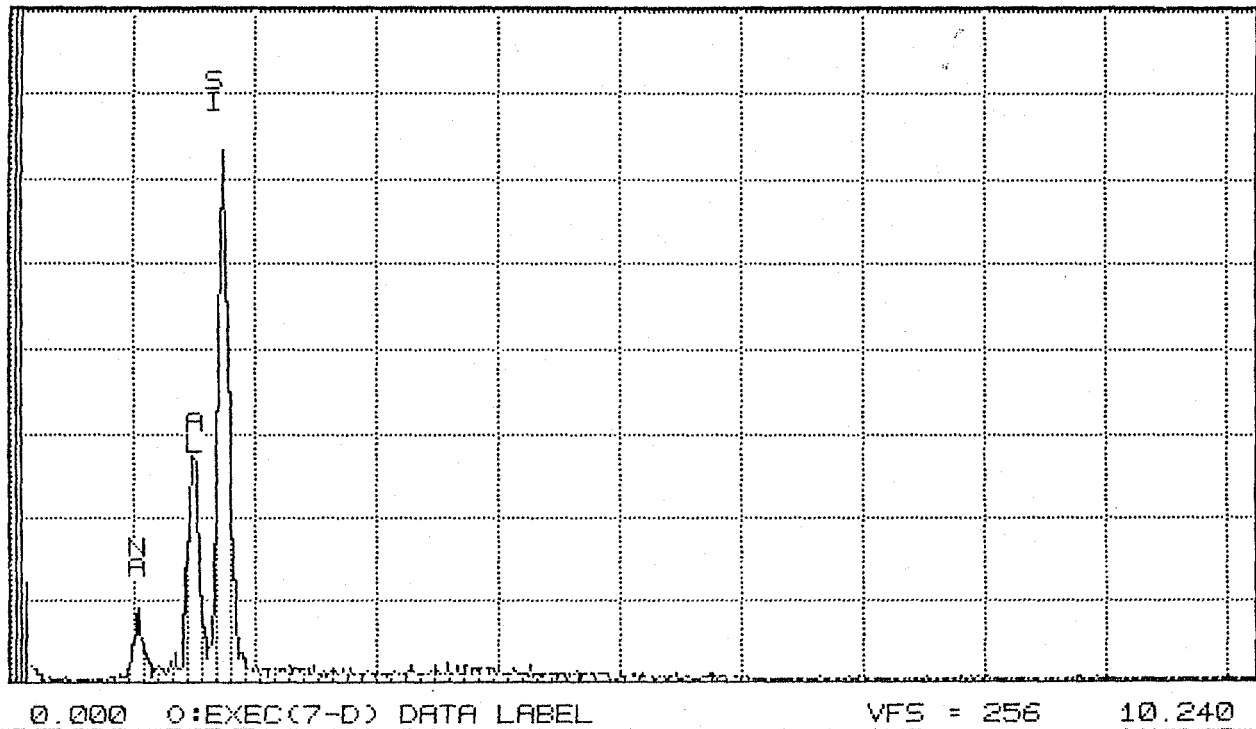


Figure 2 EDS plot of the corrosion products in the surface

After the entire corrosion product layer was removed with a HF solution, the etched substrate surface showed a localized pattern of attack. All of the SiC particles were missing, leaving voids. The HF attack on the  $\text{Al}_2\text{O}_3$  was much less severe than that on the SiC. This effect is shown in Figures 3 and 4. Figures 5 and 6 are the micrographs of uncorroded sample washed by HF from next page.

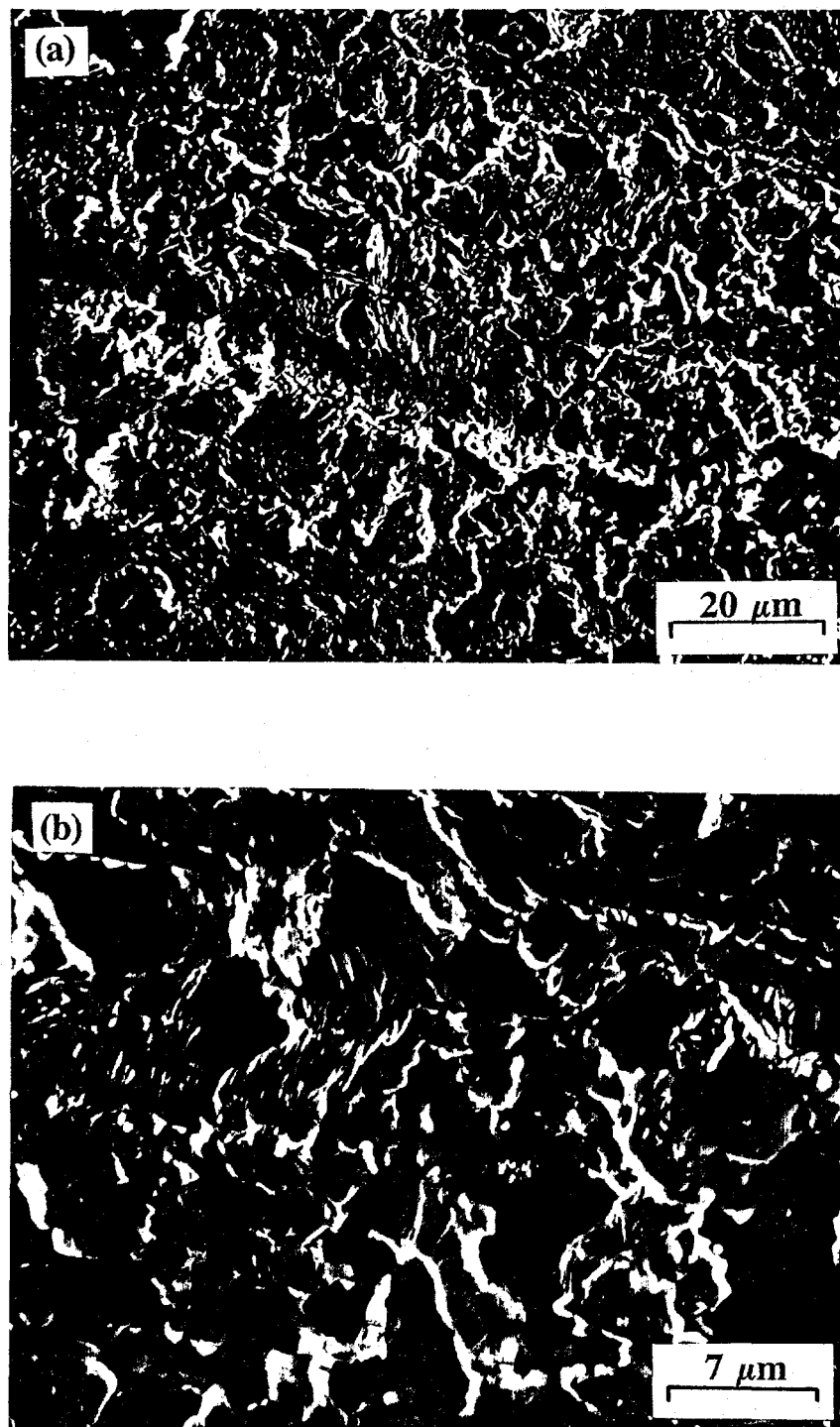


Figure 3 Scanning electron micrographs of  $\text{Na}_2\text{CO}_3$ /air-corroded surface (the corrosion products in the surface removed with HF) (a) overview; (b) detail of (a)

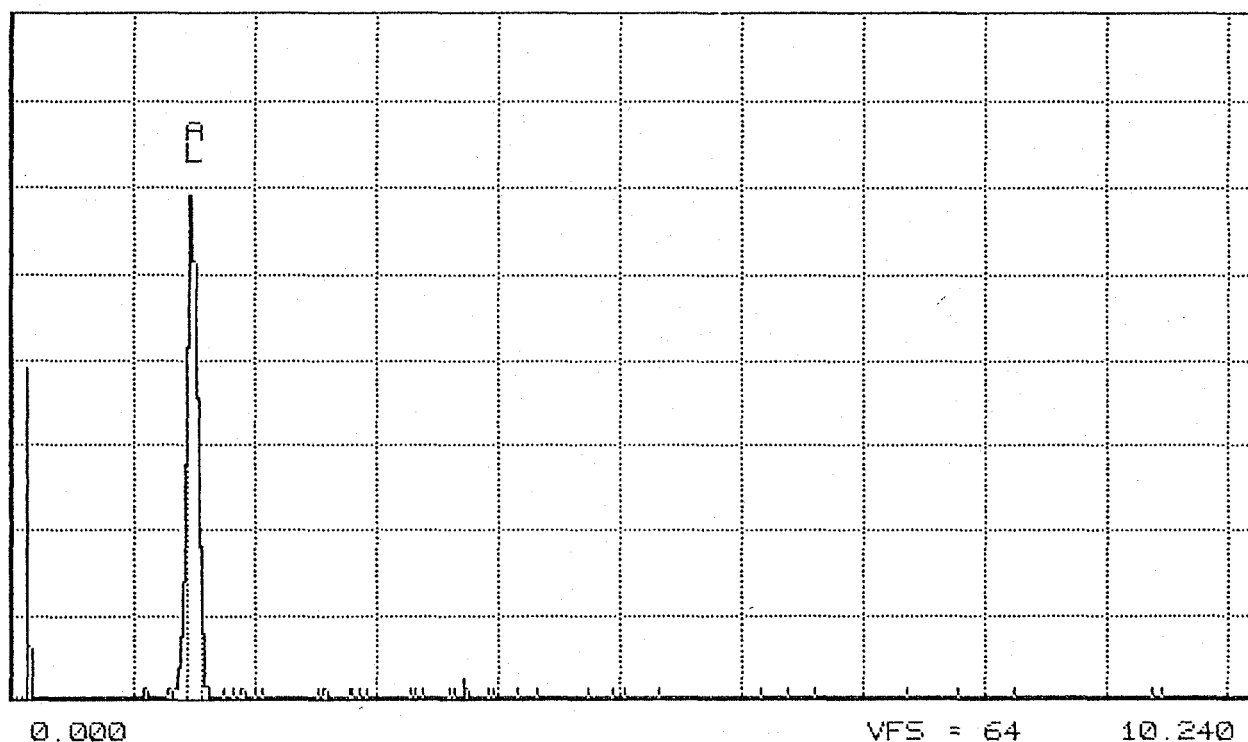
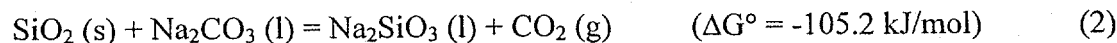


Figure 4 EDS plot of the sample shown in Figure 3

solution. Compared to the uncorroded material, the corroded substrate has an extremely porous honeycomblike structure. It appears that large chunks of material had either spalled or dissolved out of the substrate (Figure 3). The HF solution, however, did not seem to dissolve the SiC (Figure 5).

The main reactions that can occur at 1200 °C are:



Considering the foregoing probable sequence of the reactions is that SiO<sub>2</sub> forms on the SiC, which is further dissolved by the Na<sub>2</sub>CO<sub>3</sub> melt. Repeated oxidation and dissolution occur until all the available Na<sub>2</sub>CO<sub>3</sub> is depleted. SiO<sub>2</sub> must then continue to form. Because the presence of salt can dramatically enhance the oxidation of SiC,<sup>1</sup> all SiC particles at or near the surface are oxidized into SiO<sub>2</sub>. The SiC particles below the surface were protected by the Al<sub>2</sub>O<sub>3</sub> layer.

As seen in Figure 7, for a certain composition (~33% Na<sub>2</sub>O + 67% SiO<sub>2</sub>) the compound Na<sub>2</sub>O•2SiO<sub>2</sub> melts at a much lower temperature (~820 °C). Also, it is possible that there is a formation of complex low melting eutectic compounds of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Na<sub>2</sub>O which have even lower melting points (732 °C, 740 °C and 760 °C in Figure 8) than the test temperature (1200 °C). Such situations would contribute to a loss of SiC particles from the matrix thereby leaving voids (Figure 3) during the high temperature attack of Na<sub>2</sub>CO<sub>3</sub> on the composite.

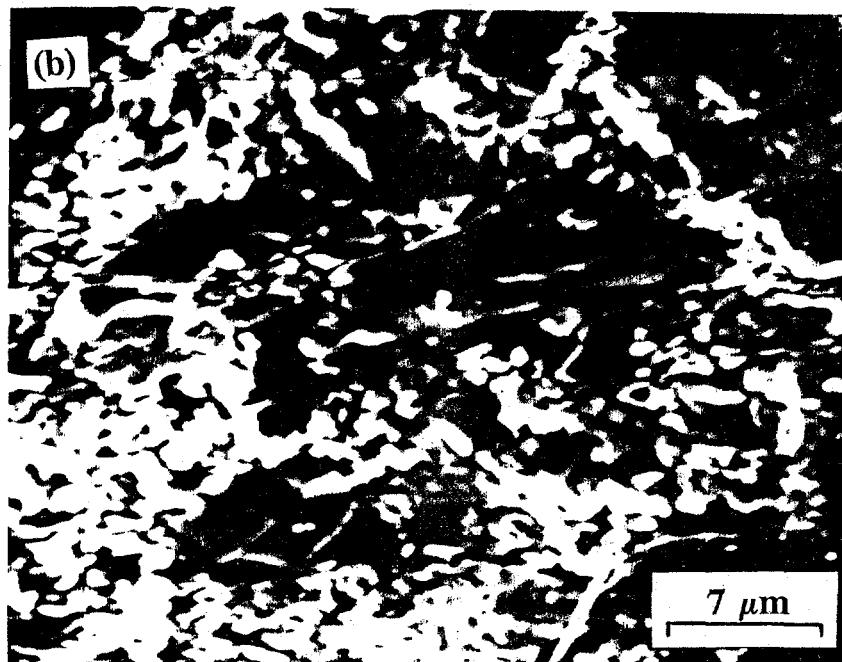
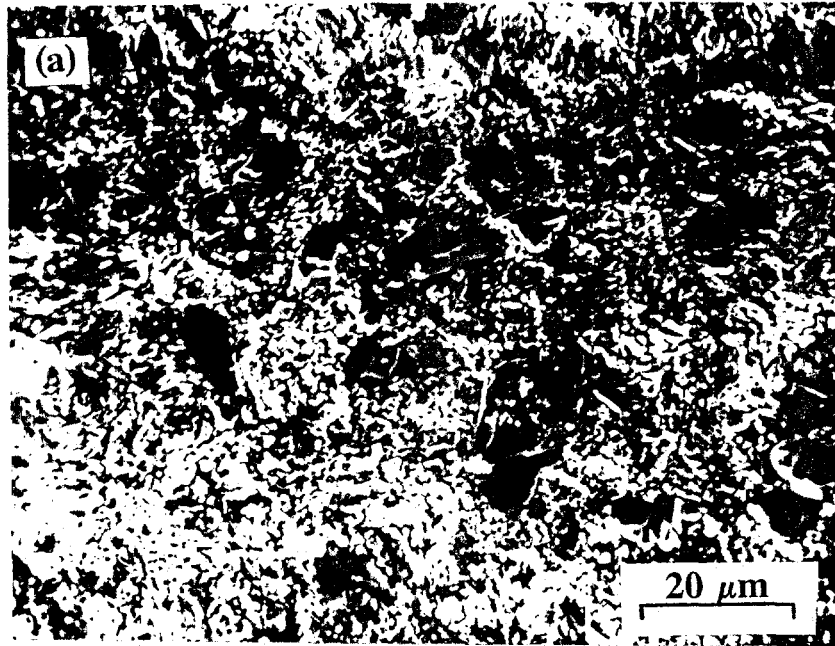


Figure 5 Scanning electron micrographs of as-received material surface treated by HF solution; (a) overview, (b) detail of (a).

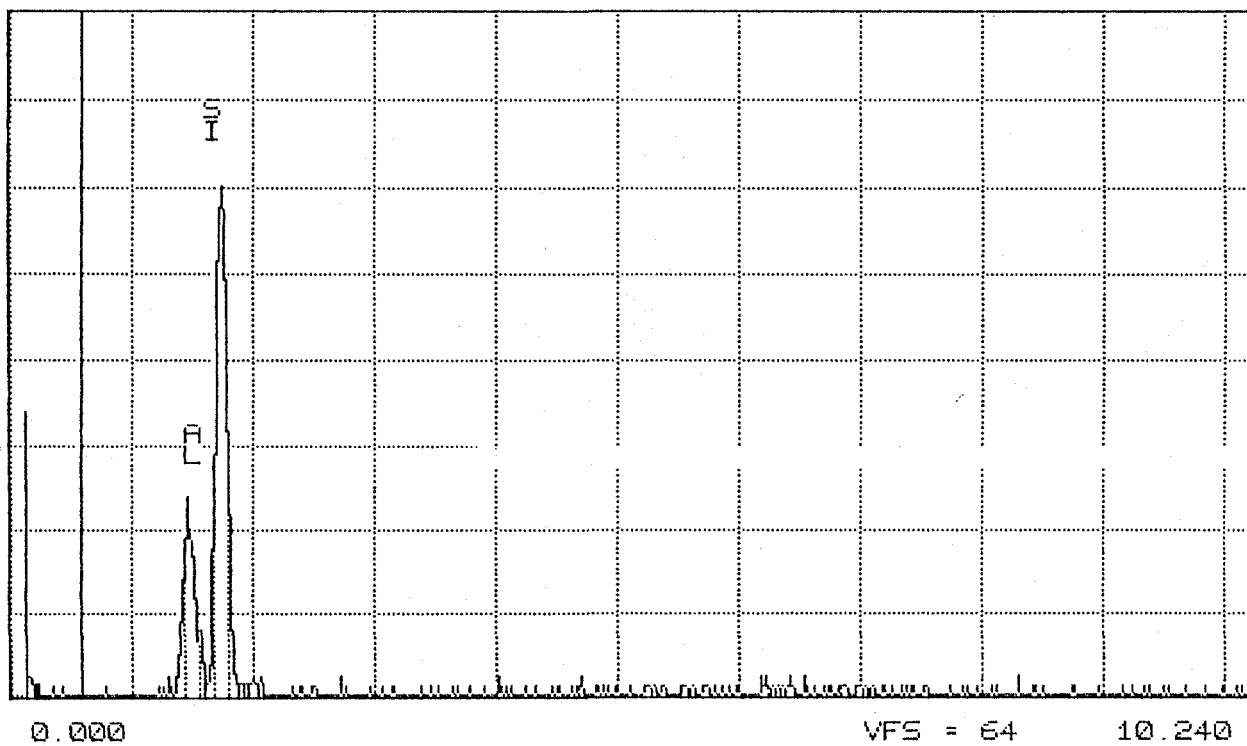


Figure 6 EDS plot of the sample shown in Figure 5

$\text{Na}_2\text{O}-\text{SiO}_2$

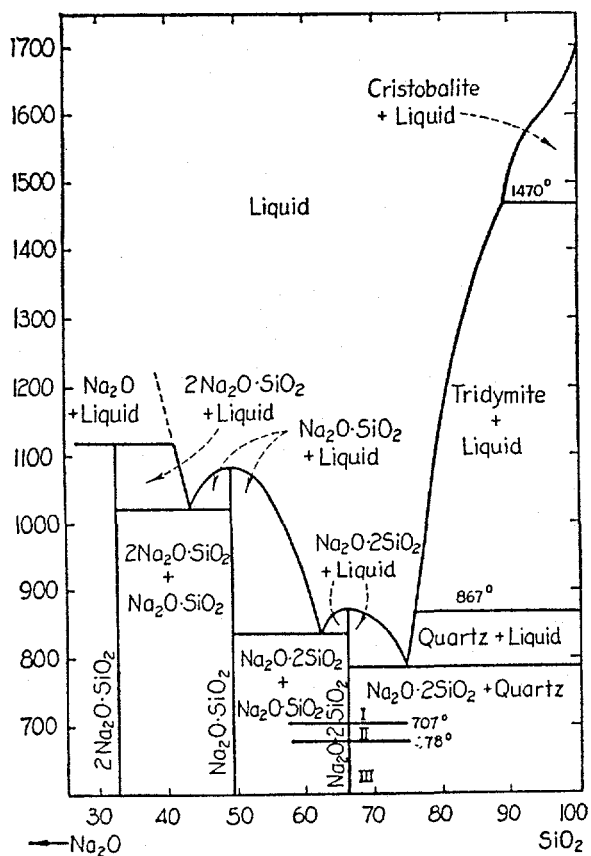


Figure 7 The phase diagram of a  $\text{Na}_2\text{O}-\text{SiO}_2$  system<sup>2</sup>

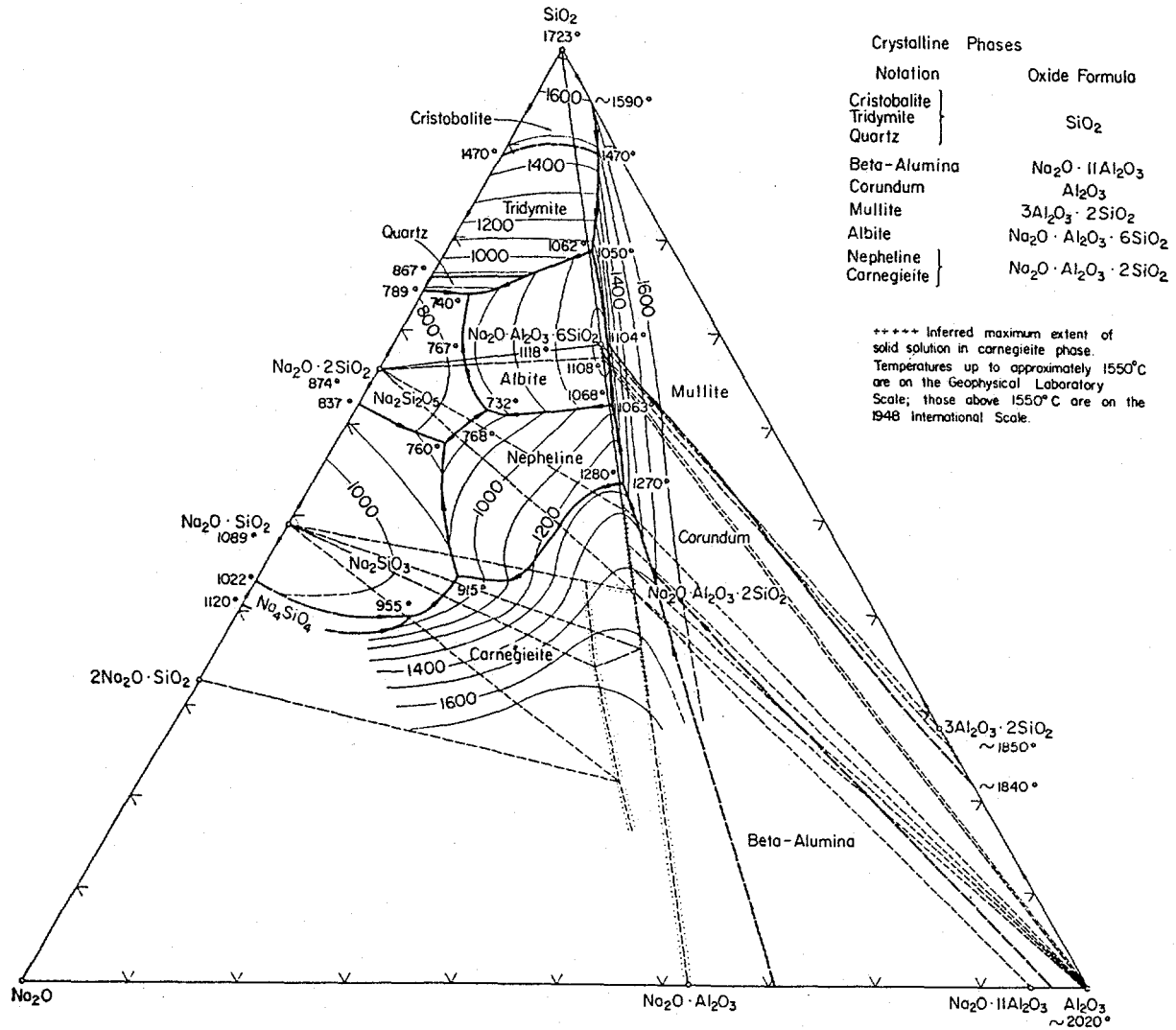


Figure 8 Phase diagram of a Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system<sup>3</sup>

Further detailed analysis of these samples and laser induced reaction coated samples will continue into next quarter. Such analysis includes the techniques such as WDS, x-ray diffractometry and microprobe for identification of corrosion products (phases), distribution of chemical species and morphological features. The information derived from these efforts will be reported in the next quarterly report.

Reference

1. N. S. Jacobson and J. L. Smialek, "Hot Corrosion of Sintered  $\alpha$ -SiC at 1000 °C"; *J. Am. Ceram. Soc.*, 68 [8] 432-439 (1985).
2. Margie K. Reser, *Phase Diagram For Ceramists*, Volume 1, P. 84, the American Ceramic Society, fifth printing 1985.
3. Margie K. Reser, *Phase Diagram For Ceramists*, Volume 1, P. 181, the American Ceramic Society, fifth printing 1985.

**APPENDIX B**

**COPY OF PAPER PRESENTED AT HIGH TEMPERATURE COATINGS-II, IN  
ANAHEIM, CALIFORNIA, FEB 4-8, 1996**