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NASA-CR-199401

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DEVELOPMENT OF PROCESSING TECHNIQUES FOR ADVANCED THERMAL PROTECTION MATERIALS

(NASA-Ames Grant No. NAG2-848)

Annual Progress Report

June 1, 1994-May 31, 1995

N96-12977
Unclas
G3/27 0067506

(NASA-CR-199401) DEVELOPMENT OF PROCESSING TECHNIQUES FOR ADVANCED THERMAL PROTECTION MATERIALS Annual Progress Report, 1 Jun. 1994 - 31 May 1995 (San Jose State Univ.) 9 p

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June 15, 1995

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Introduction

The main effort for the period June 1, 1994 through May 31, 1995 has been in the development and characterization of materials for high temperature applications. Thermal Protection Systems (TPS) are constantly being tested, and evaluated for increased thermal shock resistance, high temperature dimensional stability, and tolerance to environmental effects. Materials development was carried out through the use of many different instruments and methods, ranging from extensive elemental analysis to physical attributes testing. The six main focus areas include: (1) protective coatings for carbon/carbon composites, (2) TPS material characterization, (3) improved waterproofing for TPS, (4) modified ceramic insulation for bone implants, (5) improved durability ceramic insulation blankets and (6) ultra-high temperature ceramics. This report describes the progress made in these research areas during this contract period.

(1) Protective Coatings for Carbon/Carbon Composites

The thermal and structural properties of Carbon/Carbon (C/C) composites are ideal for many thermal protection applications. However, carbon is highly reactive in an oxidizing environment and must have a protective coating to ensure survival in an oxygen containing reentry environment. One potentially useful method of protecting these tiles involves coating the surface with a polymer which is pyrolyzed to form an inert inorganic surface layer. Several polymers have been tested in an effort to produce the inorganic layer i.e., pure SiC. For SiC polymer precursors, it has been found that, under the pyrolysis conditions used so far, the surface layer contains a large amount of SiCO. Correlating these analyses with the coating preparation procedures used will result in the development of more effective protective layers.

(2) TPS Material Characterization

Several experimental methods have been used to study TPS materials and particularly changes in their composition under different thermal conditions. These include IR spectroscopy, ThermoGravimetric Analysis (TGA) and Inductively Coupled Plasma (ICP) emission spectroscopy. Materials containing significant amounts of boron, silicon, aluminum, and zirconium are of most interest and the ICP provides the most quantitative compositional data. However, samples to be analyzed with ICP must be introduced into a solution. Research has therefore been initiated to produce an appropriate analytical technique, including determining how to dissolve refractory materials . Materials containing carbides (above) and borides are particularly resistant to traditional methods of dissolution, so new approaches, such as alkali carbonate flux dissolutions, were examined.

Carbonate Flux Dissolution of Carbides

By experimenting with different fluxes and conditions, several techniques for dissolving samples containing carbides, with minimal error, are being investigated. The original flux used was a 1:1 molar mixture of potassium carbonate and sodium carbonate. It was thought that the lower melting point of this flux, 710°C, as compared to each of the carbonates alone, 901°C and 854°C respectively, would lessen any error due to volatilization. This method produced errors between ten and twenty percent, which was unacceptable. Fusion attempts using only sodium carbonate produced more promising results. Although a higher temperature was required to achieve fusion, error ranges were cut in half, to less than ten percent. Due to instrument down time, this research is not complete and will continue into next year. It is projected that the error produced, by this technique or a modification of it, will be lowered to between one and two percent.

Results of Oxidation Resistance Tests

The Scanning Electron Microscope (SEM) has been utilized extensively to support research of high temperature carbon materials. The objective of the research is to develop a carbon material that can withstand a high temperature oxidizing environment without changes in chemistry or morphology. Both carbon felts and carbon tiles are being modified and tested in different environments (i.e.,chemical vapor deposition) at different temperatures for controlled periods of time. SEM micrographs show that the surface characteristics differ from specimen to specimen (Figure 1). Some show a rough, porous

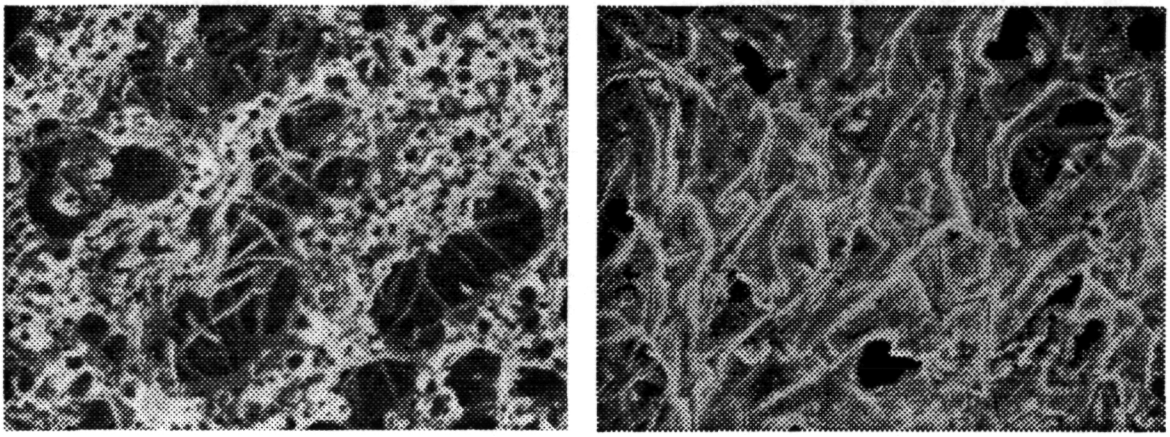

Figure 1: Rough surfaced specimen (left) vs smooth surfaced specimen (right). Magnified 38x.

surface and others show a relatively smooth, dense surface. Surface chemical analyses have not been done due to limitations in the capability of energy dispersive x-ray analyses unit attached to the SEM. This will be resolved during the next year. SEM micrographs

taken in cross section show that many of the surface coatings fail to protect the carbon fibers from oxidizing even though the coatings were thick around the fibers. Examining carefully at a higher magnifications (5000X +), cracks in the coating at the intersections of fibers were detected. Some coatings looked dried and cracked up, which may have allowed the carbon fibers to be exposed to the atmosphere, thus allowing oxidation to occur. This research is continuing. Making a low density carbon/carbon composite TPS survive in a high temperature oxidizing environment would be very advantageous due to the high temperature mechanical strength of carbon.

(3) Improved Waterproofing for TPS

Currently, the Space Shuttle will be exposed to water (rain) and humidity both at the launch and landing sites and as it is transported between them. As a result, the blanket insulation located on the top of the shuttle may gain as much as 500 wt% due to water absorption. This increase in weight is not acceptable given the high cost per pound for a launch. The current system is also laborious, unhealthy and slow. Therefore, research was initiated in order to find an easily applicable substance that will waterproof the Space Shuttle.

Silicon carbide is very effective in many thermal protection systems as a coating, but still allows the passage of water to the underlying TPS. Developmental work is underway in which waterproofing coatings are applied to SiC by flowing the vapors of the waterproofing agent over the surface in a Chemical Vapor Deposition (CVD) reactor. Surface analytical techniques will be used to examine fluorinated SiC as well as surfaces exposed to silanes. This will help to correlate surface composition with reactor conditions (i.e. gas pressure and composition and temperature). Gas composition is currently being determined through Gas Chromatography Mass Spectrometry (GCMS).

X-ray Photoelectron Spectroscopy (XPS) will be used extensively in this research to determine the surface composition of specimens and also provide information on atomic bonding. It will be important to examine the surface composition of the SiC before and after exposure in the CVD reactor to optimize the deposition procedures. Much of the XPS work to date has involved preparation of the instrumentation for improved and more reliable data acquisition. An argon ion gun was installed in order to increase this instrument's usefulness by allowing for composition determination below the surface of a sample and cleaning off surface carbon. The ion gun is currently being tested in order to maximize its etching capabilities.

CVD experiments have been performed on approximately 160 blanket insulation specimens. The experiments were performed in an attempt to deposit a hydrophobic coating on the silica blanket insulation. Various chemicals, including the current waterproofing agent, have been tested at different concentrations, run times, temperatures, and mixture ratios in order to find the most

effective coating and coating conditions. Coating effectiveness is determined through a 15 minute water immersion test. Specimens that gained less than 5 wt% water are considered to be waterproof.

Chemical concentrations are monitored by taking before and after weight measurements on the bubbles. Also, a GCMS is used in some experiments to verify reactant and product species. CVD testing is still being conducted and results will be presented at a later date.

(4) Modified Ceramic Insulation for Bone Implants

The Bone Implant Study has been involved with modifying the charactistics of Alumina Enhanced Thermal Barrier (AETB) and Fibrous Refractory Composite Insulation (FRCI), which represent two families of TPS materials, to make them acceptable as a bone implant. At the beginning of the project, the objective was to make tiles with pores of 150 μ in size, so that bone tissue would grow into them. The SEM was utilized to determine the size and distribution of the pores. However, it is difficult to control the size and distribution of the pores within these materials. In attempting to create this more open pore structure, many approaches were taken, including varying the temperature, adding different forms of fluxes to remove small fibers in firing, adding carbonaceous ("fugitive") components, and manually drilling holes. The two approaches with the highest prospect of achieving uniformity as determined by SEM, are the addition of a "fugitive" component and manually drilling holes. SEM micrographs show that the amount of "fugitive" component controls the pore size within the specimen although lack of homogeneity represents a significant problem. Modifications to the processing procedures are therefore being evaluated by examination in the SEM, to determine a process to improve the homogeneity of the resultant material. Similarly, SEM micrographs taken at very low magnification (e.g., 9x) demonstrate the structure created by manually drilling holes as uniform and rows and columns can be observed. This procedure is not advantageous as it represents an additional step and does not allow bone growth throughout the materials.

(5) Improved Durability Ceramic Insulation Blankets

Pursuit of the development of multi-mission spacecraft requires improvement of the durability of current ceramic TPS. Current systems, especially the flexible blanket concepts, are subject to surface degradation from on-ground vehicle service, airborne particle impacts, and aerodynamic forces.

Efforts to minimize these deleterious effects have resulted in a concept that involves the attachment of a metal foil to the outer surface of existing flexible ceramic blanket TPS. These "enhanced" TPS fall into two general categories known as DurAFRSI

(Figure 2) and DuraTABI; the main difference between the two being the underlying ceramic blanket TPS. The general concept, including most of the foil attachment techniques, can be applied to either the Advanced Flexible Re-usable Surface Insulation (AFRSI) or the Tailorable Advanced Blanket Insulation (TABI) (Fiqure 3) architecture; therefore, the concept is being developed using the AFRSI TPS as a basis due to material availability and manufacturing cost factors.

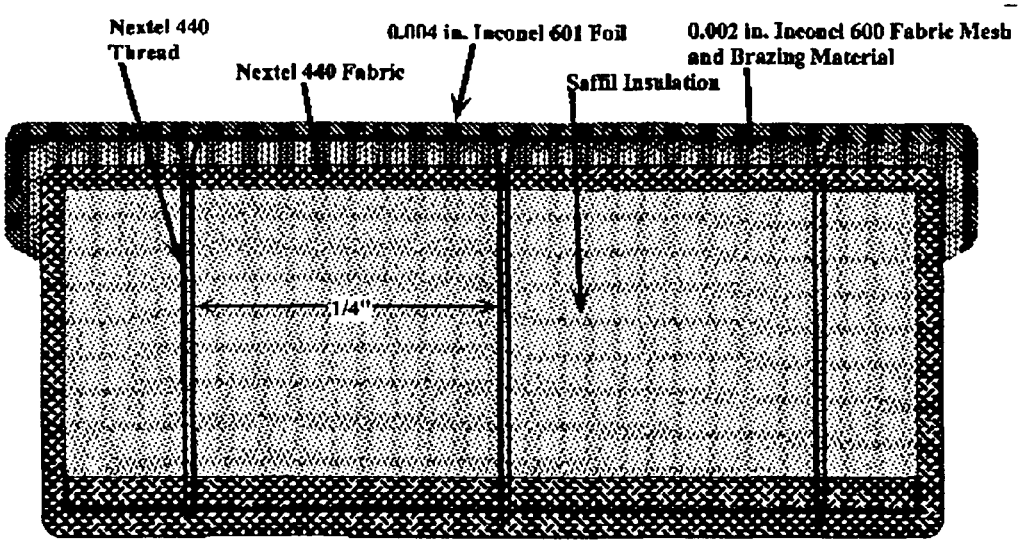

Figure 2: DurAFRSI blanket cross-section. Note the two top layers of extra material

Development of the DurAFRSI/DuraTABI concept has thus far included conceptual design, establishment and maintenance of specifications and sub-contracts for manufacture of the TPS and its sub-components, determination of test criteria and parameters, design and fabrication of test fixtures, supervision of testing, interpretation of test data, selection of an optimal material combination based on test results, and establishing a plan for future testing and development of the concept.

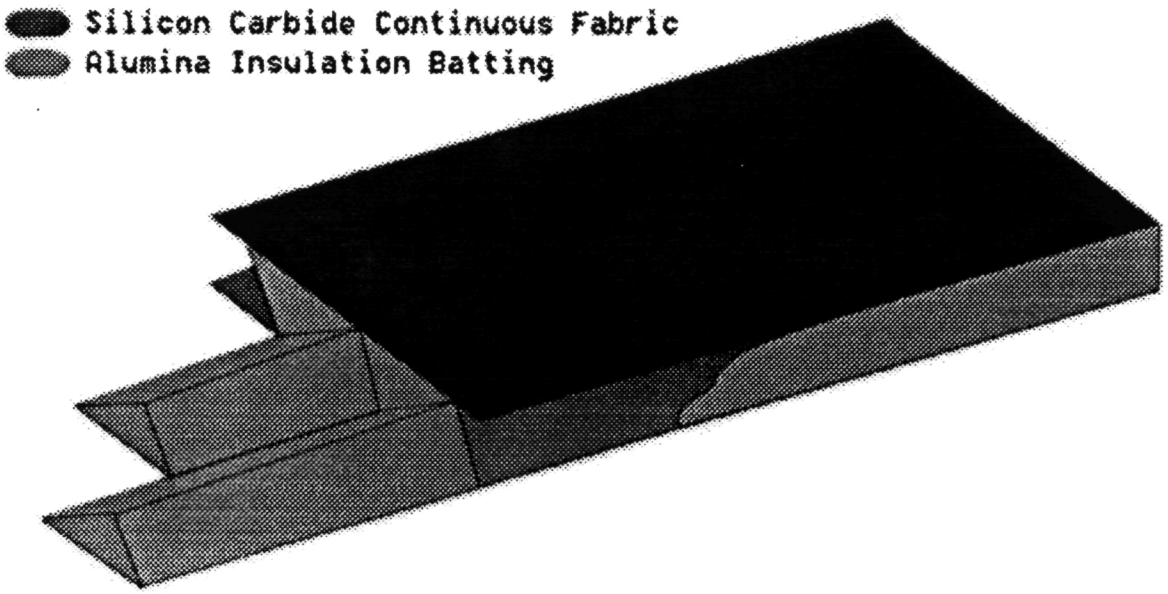

Figure 3: TABI construction. Note that the same extra layers shown in Figure 2 can be applied to this system.

Testing completed to this point has mainly addressed the oxidation of the metal foil when exposed to dissociated species at maximum operating temperatures. The 60MW Panel Test Facility Arc Jet was used to expose multiple sets of specimens of various candidate alloys to transitional flow of dissociated species which heated the specimens to the maximum extended period operating temperature range. While the extent of oxidation as determined by this testing is the primary issue of concern in selecting an individual alloy from the candidate list, the results of other testing will be considered also. Mechanical testing to evaluate a portion of the foil attachment system is well underway, and spectrophotometric measurements of the optical properties of the oxidized alloy specimens is beginning.

The potential of this type of TPS has been acknowledged by both NASA and outside aerospace companies who are currently involved in the design and development of a reusable launch vehicle. The tolerance to foreign object impact and resistance to water intrusion is superior to that of existing flexible ceramic TPS. A US Patent is currently being pursued for the DurAFRSI/DuraTABI technology.

(6) Ultra-High Temperature Ceramics (UHTC)

The materials development effort has focused on advanced UHTC materials that are borides and carbides of the group IV metals, capable of withstanding temperatures up to 3000°C in an aeroheating environment. These UHTC materials will allow development of new types of leading edges for hyper-sonic vehicles to increase aerodynamic performance.

Arc Jet testing of several combinations of materials was recently completed in the Aero Heating Facility (AHF) at Ames. The goal was to evaluate materials that have an oxidation layer that is thin, dense, and adherent. In order to accomplish this, samples

need to be analyzed before and after Arc Jet testing in order to investigate material performance in aeroheating environments. The samples involved in this series of testing were 0.75" in diameter and 0.25" thick. Some of the specimens had a small hole bored in the back-face that came to within 1/32 of an inch from the front surface. A fiber optic sensor, mounted inside the model assembly, protruded into this hole and was used to measure an in-depth temperature. Other sensors were used to make temperature measurements on the front surface of the specimen. With these two measurement schemes, the temperature differential across the thin oxide layer could be measured. The fiber optic sensor was also used to measure the back-face temperatures of specimens without in-depth holes. Typically, the oxide layers measured about 400 mm thick and had as much as a 300° C differential in temperature. The measurements of the back-face temperature showed a 500-700° C temperature drop across the full 0.25" thick sample. Samples were analyzed using petrography, X-Ray Diffraction (XRD) analysis, SEM, Energy Dispersive X-ray analysis (EDX), InfraRed (IR), as well as other techniques. During testing, unknown coatings formed on the model holders. ICP analysis showed that these coatings were formed by out-gassing of one of the constituents of the sample. Petrographic techniques had to be developed to analyze the microstructure of the pre- and post-test samples. An optical microscope was used to analyze the steps in developing petrographic techniques. Upon completion of sample preparation, the microscope was used to obtain a photographic image which could be reviewed and studied. Analysis of the microstructure shows that during processing agglomerations form between fine grained particles. These agglomerations cause highly porous regions that initiate failure and cause poor ablation response. Therefore, more work needs to be concentrated on the processing of these materials.

XRD analysis provided useful information in two areas. First, standard diffraction patterns were taken of each sample prior to testing to check for impurities and unexpected phase transformations that may have been produced in the processing stage. It was found that no new phases formed during processing and that impurities were negligible. Second, back-surface stress analysis of post-test samples was accomplished. To do this test, a Cr X-Ray tube had to be installed in the XRD. This required full readjustment and calibration of the machine. A powder sample containing the same material combination as the Arc Jet samples was analyzed to achieve a baseline stress (powder samples should have surfaces that are relatively stress free). After this analysis was completed, pre- and post-test samples were placed in the XRD to measure the back-surface stress due to Arc Jet testing. It was found that the post-test samples had unexpected back-faces in compression. XRD diffraction patterns were also taken on selected post-test samples to analyze the change in surface chemistry due to the formation of an oxidation layer. In the future, all test surfaces will be analyzed for determination of materials present before and after testing.

Flexure testing and analysis of UHTC materials, using four-point bending in accordance with MIL Standard 1942, was completed. The relative strengths pertaining to different combinations of ZrB_2, ZrC, and SiC was evaluated. The relative strength of HfB_2/SiC was also examined. Pre-test analysis performed on each sample consisted of bulk density and weight measurements, along with sonic modulus testing. Sonic modulus testing is a non-destructive technique that is used to determine Young's Modulus. It involves measuring the natural frequency of a material when elasticity tapped, and converting to modulus. Flexure testing was performed using a computer controlled Instron 1122 testing machine. Data received from the Instron's computer is in a form that is not easily transferable to other computer platforms, so macros were written in an EXCEL spreadsheet to help analyze the data. These macros are adaptable to future testing programs. Post-test analysis involved doing petrography on specimens after fracture. A correlation between strength, SiC agglomerations and density was developed. From comparing micrographs to average strength, average density and SiC agglomeration formations, it was concluded that while additions of SiC helped to increase the average density and strength, porous agglomerations of SiC limited the strengths possible. It is known that a properly processed ZrB_2/SiC material can exhibit strengths on the order of 140 ksi. In this group of specimens the highest individual strength recorded was 108 ksi, but a high deviation in strengths brought the average down to 45 ksi. This is attributed to a high quantity of SiC agglomerations that formed during processing. However, these flexure bars were machined out of a scrap section of the pressing billet and are presumed to be a worst case scenario. The conclusion from flexure and Arc-Jet testing is that further work needs to be concentrated on the processing of these materials to improve the uniformity of the specimens and reduce SiC agglomerations.

A new all graphite model holder, coated with SiC for reusability, has been designed for the next series of Arc-Jet testing. The purpose of the upcoming experiment is to measure the catalyticity of UHTC materials. The specimens have been changed to 3" in dia and 0.125" thick. Holes that come within 1/64 of an inch from the front-face of the sample will bwe bored into the sample. With the increase in diameter of the specimen, more locations for fiber optic sensors have been added. A total of five sensors can be installed at one time as opposed to only one in previous testing. This additional capability will allow in-depth and back-face temperatures to be determined simultaneously.