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13. ABSTRACT (Maximum 200 words) Three technical areas were pursued during this three year project: 1. oxidation resistant beta-alumina fiber-matrix interface coatings, 2. prediction and experimental verification of the microstructure of CVD/CVI carbon, and 3. a new class of laminated matrix composite. Magnetoplumbite and beta-alumina fiber coatings were synthesized by powder feeding of metalorganic reagents into a hot wall reactor. Annealing temperature was found to control both the phase assemblage and the extent of preferred orientation. For the second area, combination of thermodynamic-microstructure and densification models permitted prediction of the microstructure of the carbon matrix deposited during forced flow-thermal gradient chemical vapor infiltration (FCVI). The model also showed that it should be possible to deposit, by the FCVI process, either isotropic or highly anisotropic carbon. The former might be desirable for structural applications while the later is best when high thermal conductivity is of most interest. Finally, a new class of composite material possessing a laminated matrix was conceived. The new material was experimentally demonstrated with alternate layers of carbon and SiC having layer thicknesses in the range 0.01 to 0.5 μm. It is anticipated that the laminated matrix will enhance fracture toughness and may provide improved resistance to oxidation compared to carbo-carbon composites.				
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**Final Report
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BETA-ALUMINA FIBER-MATRIX INTERFACIAL COATINGS

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Beta-Alumina Fiber-Matrix Interfacial Coatings

Introduction

The initial objective of this three-year AASERT project was to develop an oxidation resistant beta-alumina or magnetoplumbite fiber-matrix interface coating that was resistant to oxidation. After about 18 months the goal, with the Program Manager's concurrence, was broadened to include other research still in the area of high temperature composites. As a result, a total of three technical areas were pursued. These were:

1. Beta-alumina and magnetoplumbite fiber-matrix interface coatings applied by CVD.
2. Development and experimental verification of a model for prediction of the anisotropy in the carbon matrix of carbon-carbon composites prepared by forced flow-thermal gradient chemical vapor infiltration, and
3. Conception and demonstration of a new class of composites consisting of a reinforcement phase such as fiber or particulate and a matrix comprised of alternate thin layers of two or more materials. The remainder of this report is divided into those three areas.

Beta-Alumina Fiber-Matrix Interfacial Coatings

Excellent progress was made on this task. The majority of the work was performed by Ms. Regina Richards and co-op students Elliot Pickering, Harry King, and Michael Miller. Ms Richards' work culminated in her receiving an M.S. degree in Materials Science and Engineering. Her thesis "The Chemical Vapor Deposition of Hexagonal Aluminates As a Fiber-Matrix Interface Coating For Oxide-Oxide Composites", provides the details of her research and is available through the Georgia Tech library¹. A brief summary follows:

Layered hexagonal aluminates with the beta-alumina and magnetoplumbite structure offer promise as oxidation resistant interface coatings for oxide-oxide composites. These structures consist of spinel-like blocks of Al^{3+} and O^{2-} ions with stabilizing cations in interstices between these layers. These blocks are bridged along the c-axis by Al-O-Al bonds that define weak basal planes that easily cleave. Possible extensive ion substitution produces the ideal formulae for β alumina and magnetoplumbite as $\text{MAI}_{11}\text{O}_{17}$ and $\text{MAI}_{11}\text{O}_{19}$, respectively, where M is a large cation.

Magnetoplumbite, $\text{LaAl}_{11}\text{O}_{18}$, and other aluminates were deposited by chemical vapor deposition (CVD) in hopes of achieving an oriented coating that would encourage debonding. The CVD process should favor the growth of hexagonal aluminates in the desired orientation, i.e., c-axis perpendicular to the substrate. The coatings were grown

on polycrystalline Al_2O_3 flat substrates and single-crystal Al_2O_3 fibers. A statistical study was conducted to optimize the coatings by varying the experimental CVD parameters. A four factor factorial with a central composite design (CCD) allowed for variation of deposition temperature, reagent powder input ratio, annealing temperature, and gas flow rates. The coatings were characterized with x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). Two software packages, Minitab 7.2 and Statgraphics 5.0, were used to perform statistical analyses on the characterization results of the study.

XRD patterns showed that all the coatings were amorphous in the as-deposited state. Regression determined that the annealed coating phase assemblage was dependent on annealing temperature. A sharp phase transformation was seen from LaAlO_3 to $\text{LaAl}_{11}\text{O}_{18}$ at 1400°C . The higher the annealing temperature, the more likely the phase had completely transformed to $\text{LaAl}_{11}\text{O}_{18}$.

Stoichiometries produced by EDS did not correspond to phases present in the coatings. However, EDS analysis was used to model the compositional variation of the Al to La ratios in the coatings. Regression revealed that the Al to La ratio in the as-deposited coatings increased with increasing deposition temperature, indicating that the aluminum reagent deposited more efficiently than the lanthanum reagent at higher temperatures. The Al to La powder input ration also appeared to have a slight influence on the Al to La ratio in the as-deposited coatings. However, the regression equation generated for the Al to La ratio in the annealed coatings was a complex, empirical model that was difficult to physically describe. This seven factor surface response did reveal effects from annealing temperature and the interaction of deposition temperature and the Al to La powder input ratio.

SEM micrographs of surface morphology and fracture surface interfaces revealed that the desired c-axis orientation increased with annealing temperature. This was further verified on XRD patterns by the increase in basal plane peak intensities with increasing annealing temperature. There was concern that high temperature annealing would be detrimental to the strength of the substrates. However, cracks that propagated parallel to the substrate were observed in several coatings. Also, annealing did not appear to cause significant interaction between the substrate and coating. This lack of substrate-coating interaction led to the theory that an extra Al_2O_3 phase was being deposited initially. This experimental work did offer a promising result in that a $\text{LaAl}_{11}\text{O}_{18}$ interface coating could have the ability to debond, thus possible toughening an oxide-oxide composite. However, the effectiveness of a $\text{LaAl}_{11}\text{O}_{18}$ interface coating seemed to depend more on the morphology and phase assemblage, which was controlled by annealing temperature, than on the compositional models produced by regression. The results of the statistical study proved that annealing temperature was the most important experimental parameter in the deposition of optimum $\text{LaAl}_{11}\text{O}_{18}$ coatings.

Model for Prediction of Carbon Matrix Microstructure

It is well known that the microstructure, that is, the degree of preferred orientation of the crystallites, of pyrolytic carbon is strongly dependent on the processing conditions and can vary from highly isotropic to highly anisotropic. Also, it is clear that the extent of the preferred orientation has a very large influence on mechanical, thermal, electrical, and other properties of CVD/CVI carbon. While the influence of processing conditions on the structure of CVD carbon is understood, the CVI of carbon is more complex and is not as thoroughly understood. That is, a model for prediction of the degree of anisotropy of CVI carbon is not available, primarily due to the complexities of knowing the gas phase chemistry as a function of position within the preform. In other words, the diffusional phenomena present in the conventional/diffusional types of CVI are difficult to analyze. The forced flow-thermal gradient CVI process (FCVI) is somewhat easier to analyze due to less reliance on diffusion, and a model for predicting the degree of anisotropy for a carbon matrix deposited via FCVI was developed and experimentally validated. The students participating in this effort were J.S. Lewis and S. Vaidyaraman. Mr. Lewis's work resulted in a B.S. thesis in the School of Materials Science and Engineering two open literature publications and a presentation.^{2,3} A condensed version of the paper won a Best Paper Award in the undergraduate student category. The model combined thermodynamics and the kinetics of densification of preforms with carbon via FCVI. The kinetic portion of the model is described in detail in Dr. Vaidyaraman's Ph.D. theses⁴ and open literature publication⁵. Dr. Vaidyaraman's thesis placed second in the Carbon Journals international competition for Ph.D. theses in the area of carbon research. A brief summary of this work follows.

A model has been developed to predict the microstructure of the carbon matrix deposited during forced flow-thermal gradient chemical vapor infiltration (FCVI). This method employs previous thermodynamic-microstructure and densification models to determine conditions throughout the preform as a function of time. The model was verified by comparison with samples prepared over a range of deposition temperatures, reagent concentrations and flow rates. The model also showed that should be possible to deposit a matrix of uniformly high thermal conductivity onto conventional size carbon fibers, as well as small diameter, low cost, high thermal conductivity carbon whiskers.

Laminated Matrix Composites

A new class of composite materials referred to as "laminated matrix composites" was conceived and experimentally demonstrated. A patent application was filed with the U.S. Patent Office. The new material consists of fiber, particulate, or platelet reinforcement plus a laminated matrix. That is, the matrix consists of alternate thin layers of two or more materials. It is anticipated that both the reinforcement and the matrix will contribute to mechanical toughness. The research was performed by the following students from the School of Materials Science and Engineering here at Georgia Tech: John S. Lewis III, Harry C. King, Michael A. Miller, Giancardo Giannetti and Bruce N. Beckloff. Each of these students were able to perform their co-op work sessions with Dr. Lackey as a result of this AASERT project.

Three publications and two presentations, one of which was invited, have resulted from this research.⁶⁻⁸

A brief summary of this research follows.

A new type of composite, which consists of a reinforcement phase plus a matrix composed of many alternate thin layers of two different materials, has been prepared. CVI appears to be an appropriate process for the fabrication of this class of materials. We have successfully fabricated such a composite using the forced flow-thermal gradient CVI process. A carbon fibrous preform was infiltrated with alternate layers of C and SiC having thicknesses of 0.01 to 0.5 μ m. For a fixed cycle time, layer thicknesses increased with distance from the fiber surface. Crack deflection patterns indicate that the laminated matrix may contribute to mechanical toughness. More recently, we have replaced the fiber with SiC particulate and SiC platelets. Both were infiltrated with alternate layers of carbon and SiC. These reinforcements are considerably less expensive than fiber.

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