HIGH-TEMPERATURE BEHAVIOR OF ADVANCED SPACECRAFT TPS

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CONTRACT NAS2—
The objective of this work has been to develop more efficient, lighter weight and higher temperature thermal protection systems (TPS) for future re-entry space vehicles. The research carried out during this funding period involved the design, analysis, testing, fabrication and characterization of thermal protection materials to be used on future hypersonic vehicles. This work is important for the prediction of material performance at high temperature and aids in the design of thermal protection systems for a number of programs including programs such as the National Aerospace Plane (NASP), Pegasus and Pegasus/SWERVE, the Comet Rendezvous and Flyby Vehicle (CRAF) and the Mars mission entry vehicles. Research has been performed in two main areas including development and testing of thermal protection systems (TPS) and computational research.

A variety of TPS materials and coatings have been developed during this funding period. Ceramic coatings were developed for flexible insulations as well as for low density ceramic insulators. Chemical vapor deposition processes were established for the fabrication of ceramic matrix composites. Experimental testing and characterization of these materials has been carried out in the NASA Ames Research Center Thermophysics Facilities and in the Ames time-of-flight mass spectrometer facility. By means of computation, we have been able to better understand the flow structure and properties of the TPS components, estimate the aerothermal heating, stress, ablation rate, thermal response, and shape change on the surfaces of TPS. In addition, work for the computational surface thermochemistry project has included modification of existing computer codes and creating new codes to model material response and shape change on atmospheric entry vehicles in a variety of environments (e.g., Earth and Mars atmospheres).
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Abstract

The objective of this work has been to develop more efficient, lighter weight and higher temperature thermal protection systems (TPS) for future re-entry space vehicles. The research carried out during this funding period involved the design, analysis, testing, fabrication and characterization of thermal protection materials to be used on future hypersonic vehicles. This work is important for the prediction of material performance at high temperature and aids in the design of thermal protection systems for a number of programs including programs such as the National Aerospace Plane (NASP), Pegasus and Pegasus/SWERVE, the Comet Rendezvous and Flyby Vehicle (CRAF) and the Mars mission entry vehicles. Research has been performed in two main areas including development and testing of thermal protection systems (TPS) and computational research.

A variety of TPS materials and coatings have been developed during this funding period. Ceramic coatings were developed for flexible insulations as well as for low density ceramic insulators\textsuperscript{2,3}. Chemical vapor deposition processes were established for the fabrication of ceramic matrix composites\textsuperscript{4-6}. Experimental testing and characterization of these materials has been carried out in the NASA Ames Research Center Thermophysics Facilities\textsuperscript{1,7,8} and in the Ames time-of-flight mass spectrometer facility\textsuperscript{9-13}. By means of computation, we have been able to better understand the flow structure and properties of the TPS components, estimate the aerothermal heating, stress, ablation rate, thermal response, and shape change on the surfaces of TPS\textsuperscript{16-21}. In addition, work for the computational surface thermochemistry project has included modification of existing computer codes and creating new codes to model material response and shape change on atmospheric entry vehicles in a variety of environments (e.g., Earth and Mars atmospheres\textsuperscript{14,15}).
The work described here involves the design, analysis, testing and characterization of thermal protection and/or structural materials to be used on future hypersonic and subsonic vehicles. This work is important for the prediction of material performance at high temperature and aids in the design of thermal protection systems for a number of programs. These include programs such as the National Aerospace Plane (NASP), Pegasus and Pegasus/SWERVE, the Comet Rendezvous and Flyby Vehicle (CRAF) and the Mars mission entry vehicles. Research has been performed in two areas including development and testing of thermal protection systems (TPS) and computational research.

**Development and testing of TPS**

The TPS materials program at NASA Ames has been involved in the development of thermal coatings, ceramic matrix composites and flexible insulations. Testing of specific materials developed at Ames and elsewhere have been conducted using the Ames laser mass spectrometer arc-jet facilities and other supporting equipment. NASA Ames Research Center maintains one of the largest Aerothermodynamic Heating Arc Jet test facilities in the world. These facilities are used for thermal protection systems evaluation, materials characterization, and design validation. Computer models are used in conjunction with data provided by the Arc Jet tests to predict the thermal performance of Thermal Protection Systems concepts in various flight trajectories. Reference 1 gives a general description of two major families of Arc Jets, nozzles used with these devices, a specified description of the facilities available at Ames Research Center, and the procedures through which testing is conducted.

The need for improved coatings on low density reusable surface insulation (RSI) Materials used on the Space Shuttle has stimulated research into developing tougher coatings. The processing of a new porous composite "coating" for RSI called Toughened Unipeice Fibrous Insulation (TUF1) is discussed in reference 2. Characteristics including performance in a simulated high-speed atmospheric entry, morphological structure before and after this exposure, resistance to impact, and thermal response to a typical heat pulse are described. It is shown that this coating has improved impact resistance while maintaining optical and thermal properties comparable to the previously available RCG coating.

Reference 3 describes the effect of ceramic coatings on the thermal performance of ceramic flexible insulations considered for potential use as thermal protection systems of thermal insulation for present and future hypersonic vehicles such as the Shuttle Orbiter and Single Stage to Orbit (SSTO). The thermal response of these materials during and after exposure to aeroconvective heating produced from a plasma arc is described. Materials tested include three different types of ceramic fabrics (silicon carbide and two variations of aluminoborosilicate) which compose the surface of the flexible insulations, and similar fabrics coated with a ceramic coating designated as Protective Ceramic Coating (PCC). The coated and uncoated flexible insulations were exposed to a pair of
similar pressure and power conditions in a plasma arc stream for 150 seconds which simulates aeroconvective heating during entry. These two conditions resulted in surface temperatures of 2100 F and 2500 F. The uncoated insulations exhibited higher surface temperatures than similar coated insulations and failed when exposed to the 2500 F test condition. Coated insulations did not fail under comparable test conditions. The PCC coated insulations also exhibited significantly lower backface temperatures than the uncoated insulations, especially those with the aluminoborosilicate fabric on the top surface. A computer model was utilized to correlate calculated with experimental test values obtained for the backface temperatures of the insulations.

The next generation hypersonic vehicles (NASP, SSTO) that require reusable thermal protection systems will experience acreage surface temperatures in excess of 1100 C. More importantly, they will experience a more severe physical environment than the Space Shuttle due to non-pristine launching and landing conditions. As a result, maintenance, inspection, and replacement factors must be more thoroughly incorporated into the design of the TPS. To meet these requirements, an advanced thermal protection system was conceived, designated "TOPHAT". This system consists of a toughened outer ceramic matrix composite (CMC) attached to a rigid reusable surface insulator (RSI) which is directly bonded to the surface. The objective of this effort was to evaluate this concept in an aeroconvecive environment, to determine the effect of impacts to the CMC material, and to compare the results with existing thermal protection systems.

The RTM Chemical Vapor Infiltration Laboratory (CVIL) has been used for the development of thermal protection system (TPS) for use on advanced hypersonic vehicles. Development of CVD/CVI processes for the deposition of graded and dispersed phases of TiB2 and SiC is currently under investigation in our laboratory. For these deposits it is essential to determine the chemical microscopic structure in order to characterize a successful reactor operating procedure, product, or the product's mechanical and oxidation properties. A study was made to determine which reactor conditions could be used for deposition and which chemical analytical techniques are most compatible to characterize film processing. A brief comparison between established analytical methods is made and the preliminary experimental results of the study are presented.

Reference 6 presents an analysis of high temperature oxidation failures in C/SiC continuous fiber ceramic composites (CFCC). A series of complex shaped C/SiC CFCCs were subjected to multiple cycles in an aeroconvecive heating environment. Testing was conducted in the NASA Ames 20 MW Arc-jet heating facility. The surface heat flux for the test series, which produced failures in 2 cycles or less, was 170 W/cm². This heat flux produced surface temperatures from 1770 to 1810°C. Analysis of the failures was conducted using a stereoscope and an SEM. Surfaces and cross sections of the failed CFCCs were investigated. Results indicate that the oxidation failures occur by matrix oxidation that results in fiber oxidation. This in turn produces cracking, accelerated oxidation of SiC, and in the extreme -- matrix spallation. The oxidation process is attributed to open porosity in the composites that allows for subsurface reactions to occur.
The objective of the study presented in reference 7 was to determine the effect of variations in 2D architecture (orthotropic vs. quasi-isotropic) on material performance and to compare the performance of the composites fabricated by SEP against the composites fabricated by DuPont Inc. (using the licensed SEP process) after exposure to an aeroconvecitive heating environment. The results from the aeroconvecive testing are presented and show that the material manufactured by DuPont perform in the same manner as that previously reported for the SEP fabricated composites.

Hypersonic vehicles experience severe aeroconvecive heating either on ascent insertion or on reentry from low earth orbit. Coated carbon/carbon composites have been used for nose cap and leading edge materials for the Space Shuttle, as the reusable hot structure, to cope with the extreme heating conditions. The major problems encountered with the coated carbon/carbon system have been the result of limitations in the coatings which lead to the subsurface oxidation and coating failure limiting the upper operating temperature. Recent advances in material technology, particularly in ceramic matrix composite development, offers a new materials system that could reduce the problems associated with the state of the art materials. Evaluation of this new class of materials, ceramic matrix composites, as a potential replacement for coated carbon/carbon composites was performed, using the baseline heating of a generic trans-atmospheric Entry research Vehicle (E.R.V.)\textsuperscript{8}. The projected surface temperature for this vehicle are >1500°C for the nose cap and leading edge, and >1000°C for the body surface. Ceramic matrix composite systems comprised of a silicon carbide matrix reinforced with refractory fibers in a 2D architecture were tested in two specific aeroconvecive heating environments which developed surface temperatures of 1500°C to 1100°C. Mass loss, surface recession, and physical dimension changes for the systems were measured. A major concern associated with ceramic matrix composites is the degradation in physical properties of the material due to subsurface oxidation of the interphase material which might occur following prolonged exposure in an oxidizing atmosphere. By comparing the properties before and after exposure to aeroconvecive heating environments, a measure of the subsurface oxidation was attempted. Based on the aeroconvecive and physical property test results, the applicability of ceramic matrix composite materials to transportation systems is given.

Various tests have been performed in the Ames laser/time-of-flight mass spectrometer\textsuperscript{9,10} to identify vapor products produced by the laser desorption of and/or laser vaporization of candidate thermal protection materials. With this instrument it has been possible to identify both ions and neutrals resulting from laser irradiation. The time-of-flight mass spectrometer has been used to monitor time dependent behavior following pulsed laser heating of solids\textsuperscript{11,12}. It was demonstrated by comparing spectra from pure graphitic materials to a carbon phenolic heat shield material that at the onset of laser radiation incident on the carbon phenolic various hydrocarbons were produced followed, subsequently, by the carbon species characteristic of graphite. In experiments on graphite epoxy, the pyrolysis products at various laser power levels have been determined, and it has been possible to discern the time resolved pyrolysis process within the individual laser shots. Similar work with SiC fabric using the time-resolved technique has enabled the detection of CO (due to impurities) among the typical pyrolysis products of Si, SiC\textsubscript{2}, and
Si$_2$C. To a lesser extent other refractory materials, such as, the oxides of aluminum and tungsten have been studied using the laser/time-of-flight-mass spectrometer.

Laser desorption mass spectrometry has also been used to characterize the ash-like substances formed on the surfaces of polymer matrix composites (PMCs) during exposure on LDEF$^{13}$. In an effort to minimize fragmentation, material was removed from the sample surfaces by laser desorption and desorbed neutrals were ionized by electron impact. Ions were detected in a time-of-flight mass analyzer which allows the entire mass spectrum to be collected for each laser shot. The method is ideal for these studies because only a thin layer of ash is available for analysis. Three sets of samples were studied including C/polysulfone, C/polyimide and C/phenolic. Each set contains leading and trailing edge LDEF samples and their respective controls. In each case, the mass spectrum of the ash shows a number of high mass peaks which can be assigned to fragments of the associated polymer. These high mass peaks are not observed in the spectra of the control samples. In general, the results indicate that the ash is formed from decomposition of the polymer matrix.

**Computational Research**

A series of computer codes has been developed to analyze 1-D, 2-D and 3-D near surface fluid/solid response, including surface catalysis, ablation, in-depth pyrolysis, melt flow and shape change. These codes provide a link between pure computational fluid dynamics (CFD) and computational solid mechanics (CSM) models.

Existing codes such as Boundary Layer Integral Matrix Procedure with Kinetics (BLIMPK), GIANTS and GASP2.0 have been used for gap flow field and heating analysis and for arcjet surface catalysis experiments. A BLIMPK and 2-D axis symmetric NS codes have also been used to study the uncertainty in atom recombination coefficients. Coefficients obtained from both arc-jet data and side-arm reactors have been used in these computer codes to investigate the effect of both surface and gas kinetics on the heat transfer rate to advanced TPS materials for future vehicles. The long term goal for this work is to develop full 3-D codes to study the effect of both surface catalysis and non-equilibrium flow chemistry in the shock layer on the heating rate distribution over the surface of the TPS on future space vehicles during entry into Earth or Mars atmospheres.

In references 14 and 15 numerical solutions have been obtained for axisymmetric hypersonic nonequilibrium CO$_2$ flow over a large-angle blunt cone with appropriate surface boundary conditions to account for energy and mass conservation at the body surface. The flow field is described by the Navier-Stokes equations and multicomponent conservation laws that account for both translational and internal vibrational nonequilibrium effects. Complete forebody solutions have been obtained for the peak heating point of the Mars entry trajectory specified in the proposed NASA MESUR (Mars Environmental Survey) project. In these solutions, radiative equilibrium wall temperature and surface heating distributions are determined over the MESUR aeroshell forebody with
varying degree of surface catalysis. The effect of gas kinetics, surface catalysis, and transport properties on the surface heating are examined.

Reference 16 describes flight data obtained from the Catalytic Surface Effects Experiment (CSE) during the space shuttle Columbia flight STS-2 through STS-5. Temperature data were compared using a correlation parameter to define equivalent flight conditions between the trajectories used by the Orbiter during the different flights. In addition, temperature data from CSE were compared with predicted values using the design trajectory 14414.1. Flight data showed that surface catalysis had a direct effect on the heating distribution over both the mid-fuselage and wing areas of the heat shield on the Orbiter.

To support arcjet surface catalysis experiments conducted in NASA-Ames Arc-Jet Facilities, the CFD code, GIANTS (Gauss-Seidel Implicit Aerothermodynamic Navier-Stokes code with Thermochemical Surface Conditions), with appropriate boundary conditions has been developed for the analysis of hypersonic arcjet flows and surface heating over large angle blunt bodies. Because of the low Reynolds number of the arcjet stream, two-dimensional axisymmetric multicomponent full Navier-Stokes equations are solved together with boundary conditions to account for surface slip, surface catalysis, and energy and mass conservation at the body surface. Solutions obtained in this study consider the effects of chemical and thermal nonequilibrium. The predicted solutions for isothermal, noncatalytic, and no-slip surface conditions agree with those of the LAURA code, and the predicted normalized heating distributions over the forebody surface with complete boundary conditions for various cone angles are consistent with the trends of data taken from arcjet experiments. The effects of cone angle, surface catalysis, and surface slip on the surface heat flux and radiative equilibrium surface temperature are examined. The detailed analysis of the flow field may provide information for the experimentalist to design more efficient diagnostic tools for arcjet streams. In conjunction with arcjet data, Navier-Stokes solutions with appropriate surface boundary conditions are important for the prediction of surface catalyzed reaction rates and the subsequent design of Thermal Protection Systems.

Using the three-dimensional non-equilibrium Navier-Stokes code (GASP2.0) and two-dimensional axisymmetric reacting boundary layer code (BLIMPK), respectively, with finite rate surface catalysis, a computational study was conducted to obtain flow field and aerothermal heating distribution over a 140-deg blunt body at various angles of attack and corner radii. Catalytic heat transfer data was obtained for these cases in the NASA-Ames 42-in Shock tunnel. These calculations provide a validation of three-dimensional non-equilibrium full Navier-Stokes calculations, and examine the accuracy of the two-layer (inviscid/boundary layer) method. The latter is a relatively inexpensive alternative for the prediction of aerothermal heating. The comparisons between the surface heat flux data taken from shock tunnel experiments and the surface heating predicted by three-dimensional full Navier-Stokes code, and by the two-layer method were presented and discussed in detail.
The general boundary conditions including mass and energy balances of chemically equilibrated or nonequilibrated gas adjacent to ablating surfaces have been derived\textsuperscript{19}. A computer procedure based on these conditions was developed and interfaced with the Navier-Stokes solver, GASP (General Aerodynamics Simulation Program), for predictions of the flowfield, surface temperature, and surface ablation rates over re-entry space vehicles with ablating Thermal Protection Systems (TPS). The Navier-Stokes solver with general surface thermochemistry boundary conditions can predict more realistic solutions and provide useful information for the design of TPS. A test case with a proposed hypersonic test vehicle configuration and associated freestream conditions was developed. Solutions with various surface boundary conditions were obtained, and the effect of nonequilibrium gas as well as surface chemistry on surface heating and ablation rate were examined. The solutions of the GASP code with complete ablating surface conditions were compared with those of the ASCC (ABRES Shape Change) code.

Based on the geometry of the Project Apollo Lunar/Earth return capsule and an estimated earth trajectory, three dimensional surface heating and ablation rate distributions have been obtained using high Reynolds number, inviscid/boundary layer (two-layer) methods\textsuperscript{20,21}. This application of the two layer method is based on the principles of pseudo-three dimensional, axisymmetric streamline analogy. Inviscid surface streamlines are determined for the forebody portion of the Apollo capsule using the 3-D reacting, inviscid option of a CFD solver. Streamlines are obtained for the 20-deg angle-of-attack flight case, and the associated streamline metrics are determined. Detailed boundary layer heating and ablation calculations are performed using the boundary layer code, BLIMPK. Surface radiative heating estimates were obtained in an uncoupled manner using the engineering level code, QRAD. The general nature of the Apollo trajectory heating results are discussed in detail.
Appendix: Publications not used in previous reports


Publications:


