1997-1998 Annual Report
Thermal Protection Materials Development

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Executive Summary

The main portion of this contract year was spent on the development of materials for high temperature applications. In particular, thermal protection materials were constantly tested and evaluated for thermal shock resistance, high-temperature dimensional stability, and tolerance to hostile environmental effects. The analytical laboratory at the Thermal Protection Materials Branch (TPMB), NASA-Ames played an integral part in the process of materials development of high temperature aerospace applications. The materials development focused mainly on the determination of physical and chemical characteristics of specimens from the various research programs.

Introduction

The Thermal Protection Materials Branch (TPMB) has been involved in various research programs to improve the properties and structural integrity of existing aerospace high temperature materials. Specimens from various research programs were brought into the analytical laboratory for the purpose of materials characterization. The analytical instruments utilized to determine the physical and chemical characteristics of the materials were the Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analyzer (EDX), X-ray Diffraction Spectrometer (XRD), Fourier Transform-Infrared Spectroscope (FTIR), Ultra Violet Spectroscopy/Visible Spectroscope (UV/VIS), and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). In addition to analytical instruments in the analytical laboratory at TPMB, there are several on-going experiments. One particular experiment allows the measurement of permeability of ceramic ablators. From these measurements, the physical characteristics of the ceramic ablators can be derived. Included in this report is a synopsis of the work that has been completed for two different ablators. Currently this work is being reviewed for submission as technical notes to the "Journal of Thermophysics and Heat Transfer."

Scanning Electron Microscopy & Energy Dispersive X-ray analysis

Scanning Electron Microscopy (SEM) is one of the major materials characterization techniques used routinely at TPMB. The materials characterization process of high-temperature aerospace materials was divided into two aspects: physical and chemical. The physical aspect dealt with the corporeal characteristics of the material such as microstructure, relative grain size, grain growth, bonding pattern, and bonding

structure. The chemical aspects of the material dealt with the elemental make-up and chemical behavior of the materials. Chemical analysis included the determination of elements and compounds present and also the chemical properties of a material.

X- Ray Diffraction Spectrometer

X-ray diffraction spectrometer analysis provided useful information in two areas. First, standard diffraction patterns were taken of each specimen prior to testing to check for impurities and unexpected phase transformation that may have been produced due in part to the processing steps. Second, the post test specimens were analyzed to detect the structure of the specimens, which could be crystalline or amorphous.

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)

The ICP-AES is capable of quantitatively analyzing solutions for specified elements with an accuracy of less than one-percent error. Elements often determined are boron, silicon, aluminum, and zirconium in ceramic samples.

In order to prepare a sample the specimen must be put into a solution form. Most often, samples undergo dissolution with mineral acids in order to prepare them for analysis. However, there are samples that are very resistant to dissolving in a mineral acid. These samples contain high amounts of borides and carbides. In order to dissolve these compounds a alkali carbonate or nitrate flux followed by mineral acid treatment is required to be able to analyze these samples.

Gas Permeability of the Lightweight Ceramic Ablators (PICA and SIRCA)

Nomenclature

b	permeability slip parameter, Pa
D	sample diameter, m
F	measurable quantity, see Eq. (2), N
K	effective permeability, m^2
K_o	continuum flow permeability, m^2
L	length, m
M	molar mass, kg/mol
m	mass, kg
$\dot{m}$	mass flow rate, kg/s
P	pressure, Pa
P_{ave}	average pressure $(P_1 + P_2)/2$, Pa
R	universal gas constant, J/mol-K
T	temperature, K
ΔP	pressure difference $P_1 - P_2$, Pa
μ	viscosity, Pa-s
ψ	char yield
ρ	density (mass per solid volume), kg/m^3
$\bar{\rho}$	apparent density (mass per specimen volume), kg/m^3

subscripts

1	upstream
2	downstream
c	charred
lca	lightweight ceramic ablator
t	tile
r	resin
v	virgin

Introduction

Many lightweight thermal protection system (TPS) materials have a large degree of open porosity, which can make them highly permeable to gas flow. In order to model internal gas flows in porous materials, knowledge of the gas permeability is required. Unfortunately this property is not readily available for most TPS materials. Recently, a permeability measurement apparatus was constructed to test rigid, porous TPS materials, and measurements were reported[1,2] for a variety of TPS tile insulations from the AIM, LI, FRCI, and AETB families, as well as for the commercial product FiberForm®. This note presents further gas permeability measurements, made with the same apparatus, on two lightweight ceramic ablator (LCA) materials; viz., Phenolic Impregnated Carbon Ablator (PICA) and Silicone Impregnated Reusable Ceramic Ablator (SIRCA). PICA and SIRCA materials were developed at NASA Ames Research Center as lightweight ablative materials with enhanced structural integrity[3-5]. LCA materials use rigid tile insulations as substrates, which are partially impregnated with an organic resin to provide additional cooling mechanisms via endothermic decomposition, pyrolysis gas heat transport, and boundary layer blowing. Both PICA and SIRCA are actively used in TPS systems. PICA was selected as the fore-body heat shield material for the Stardust sample return capsule[6], is base-lined for Genesis (5th Discovery Mission, Jet Propulsion Laboratory), and is under consideration for the Mars 2005 sample return capsule (Mars Exploration Program, Jet Propulsion Laboratory). SIRCA was used for the aft-plate on Mars Pathfinder[7] and was selected for the leading edges and nose cap of the X-34 vehicle (Orbital Sciences Corporation.) Permeability data for LCA materials are of particular importance since issues such as hot boundary-layer gas penetration and the detailed flow pattern of

decomposition (pyrolysis) products cannot be computationally evaluated until such data are measured.

Materials

PICA and SIRCA are made by partially impregnating fibrous tile substrates with phenolic and silicone resins, respectively. PICA uses a commercially available carbon-fiber tile substrate manufactured by Fiber Materials, Inc. under the name FiberForm® and the phenolic resin Durite® SC-1008 manufactured by Borden Packaging and Industrial Products. FiberForm® has a nominal density ranging from about 144 to 176 kg/m³ (9.0 to 11 lb/ft³). Depending on the level of phenolic loading, the nominal density of PICA ranges from about 224 to 248 kg/m³ (14 to 15.5 lb/ft³.) SIRCA materials use a variety of ceramic fiber tiles as substrates. The SIRCA samples tested in this work are designated as SIRCA-15F and use a nominal 192 kg/m³ (12 lb/ft³) FRCI-12 tile substrate which is impregnated with RTV-655 resin (manufactured by General Electric) to a nominal bulk density of about 240 to 272 kg/m³ (15 to 17 lb/ft³). Both FiberForm® and FRCI-12 have anisotropic material properties due to the manufacturing process, which tends to align fibers preferentially normal to a pressing direction. LCA samples were tested along both "in-plane" (normal to the pressing axis) and "transverse" (parallel to the pressing axis) directions.

Experiment and Data Analysis

The measurement apparatus, and the data analysis procedures used to extract permeability parameters from experimental data, are described in detail in Refs. 1 and 2; a

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brief synopsis is given here. The test rig consists of a two-part, tubular brass test section, which is connected to a mechanical vacuum pump on one side and to a gas inlet line on the other. Cylindrical test specimens are placed into the test section and gases are pulled through the specimens by the vacuum pump. The upstream and downstream gas pressures are measured with capacitance manometer gauges, and the gas flow rates are monitored using calibrated flow meters. Various combinations of pressure and flow rate are obtained by adjusting a leak valve in the gas inlet line and a throttling valve in the vacuum line. Gas leakage along the sides of the sample is mitigated by machining test specimens slightly oversize so that a snug press-fit is achieved. Additionally, the interface between the sample and test section is overlapped on the downstream side by a silicone-rubber gasket which protrudes about 0.02 cm into the bore of the test chamber, and which also serves to seal the bolted flange connection between the two parts of the test section. All the measurements reported here were made with room temperature air and at gas pressures ranging from 0.5 to 101 kPa (~0.005 to 1 atmospheres.)

The experimental data were analyzed using the relationship

$$F = K_o \left[P_{ave} + b \right],$$

(1)

with

$$F = \frac{4 \mu \dot{m} RTL}{\pi D^2 M \Delta P}.$$

(2)

This relationship is derived by combining the perfect gas law, conservation of mass, Darcy's law, and the Klinkenberg permeability function, presuming a bulk gas flow, which is one-dimensional, laminar, and isothermal[1,2]. K_o is the gas permeability in the limit of continuum flow and b is a permeability slip parameter which accounts for rarified flow

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effects. All the quantities in F are known or can be measured, thus K_o and b can be obtained from a linear least-squares fit of a plot of F versus P_{ave}.

Both K_o and b are microstructure dependent and b is additionally a function of temperature and gas composition. A scaling relation to convert values of b, measured with a particular gas at a particular temperature, to values appropriate for other temperatures and gases, is given and validated in Ref. 2. However, this relation holds only for fixed microstructures. The resins in PICA and SIRCA decompose at high temperature, altering the internal microstructure. As a consequence, both permeability parameters are functions of the heating environment, including the chemical composition of the ambient gases and the transient heating history. There are obviously myriad possible heating environments. Measurements are reported here for virgin LCA material and for material charred to its pyrolysis endpoint in an inert gas atmosphere.

For PICA, the same specimens were tested before and after pyrolysis. Generally, samples are not re-tested[1,2], to avoid the possibility of gas leakage past abraded specimens. However, re-testing of several virgin PICA specimens gave values of K_o and b constant to within 1% and 4%, respectively. This repeatability is well below the uncertainties inherent in the measurement[1,2]. Additionally, it was found that charred PICA specimens were slightly expanded (by several thousandths of an inch), which again assured a tight press-fit in the test-rig. On the other hand, SIRCA specimens could not be re-tested. Initial tests on virgin SIRCA samples revealed negligible flow through the test specimens. It was postulated that the end faces of the test specimens were clogged by compaction of the soft silicone resin into the surface layers during machining and/or during insertion of the specimen into the test rig. To alleviate this problem new test specimens were made by

turning longer cylinders and breaking off the ends *in situ* to create fracture surfaces. With these specimens some gas flow was detected and an estimate of the permeability parameters could be obtained. However, these samples could not be removed and re-inserted without damaging (crushing) the fracture surfaces. Therefore sufficiently long cylindrical specimens were machined so that two specimens from the same cylinder could be obtained, one of which was tested in the virgin state and the other in the charred state.

Charring was accomplished by cycling specimens to about 1250 K in a tube furnace under an argon gas flow. Under these conditions, the char yield ψ (percentage of mass remaining after pyrolysis) of the phenolic resin in PICA is about 0.63 and that of the silicone resin in SIRCA is about 0.60. By measuring the sample dimensions and the sample masses before and after permeability testing and pyrolysis, the apparent sample densities in the virgin and charred state, as well as the apparent densities of the substrate and resin loadings in the virgin sample, can be determined. If the subscripts 1, 2, and 3 are used to designate the virgin pre-test state, the virgin pre-char state, and the char pre-test state, respectively, the following equations can be derived:

$$\tilde{\rho}_{lca,v} = \frac{4m_1}{\pi L D_1^2} \tag{3}$$

$$\tilde{\rho}_{lca,c} = \frac{4m_3}{\pi L D_3^2} \tag{4}$$

$$\tilde{\rho}_{r,v} = \frac{4m_1(m_2 - m_3)}{\pi L D_1^2 m_2 (1 - \psi)} \tag{5}$$

$$\tilde{\rho}_t = \frac{4m_1(m_3 - \psi m_2)}{\pi L D_1^2 m_2 (1 - \psi)} \tag{6}$$

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These equations are used to estimate the substrate and resin compositions of the particular LCA specimens tested.

Experimental Results and Uncertainties

The experimentally derived densities and permeability parameters for virgin and charred PICA specimens are listed in Tables 1 and 2, respectively. The same quantities for virgin and charred SIRCA specimens are given in Tables 3 and 4. The last line in each table gives the mean values and standard deviations for the all the samples tested in each group.

The relative uncertainties, $\delta\tilde{\rho}/\tilde{\rho}$, in the apparent densities were computed from the uncertainties of the individual experimental parameters in the usual way[8]. For the PICA specimens $\delta m/m = \delta L_1/L_1 = \delta D_1/D_1 \cong 0.002$, $\delta L_3/L_3 = \delta D_3/D_3 \cong 0.004$, and $\delta\psi/\psi \cong 0.05$, which leads to uncertainty estimates of about 1% for $\tilde{\rho}_{LCA,v}$, and $\tilde{\rho}_{LCA,c}$, 4% for $\tilde{\rho}_t$, and 8% for $\tilde{\rho}_{r,v}$. For SIRCA specimens $\delta m/m = \delta D/D \cong 0.002$, $\delta L/L \cong 0.2$, and $\delta\psi/\psi \cong 0.1$, giving uncertainties of about 10% for $\tilde{\rho}_{LCA,v}$, and $\tilde{\rho}_{LCA,c}$, 14% for $\tilde{\rho}_t$, and 18% for $\tilde{\rho}_{r,v}$. A detailed uncertainty analysis for K_o and b has been given in Refs. 1 and 2. The estimated uncertainties for rigid tile specimens are +11/-16% for K_o and +7/-4% for b. For the LCA materials these uncertainties are raised to +21/-26% for K_o and +17/-14% for b, to account for the uncertain sample length in the case of SIRCA and the possibility of non-Darcian flow contributions[1] for PICA.

Discussion

The continuum permeabilities for transversely oriented, virgin PICA and SIRCA samples are on the order of 10^{-11} m^2 and 10^{-15} m^2, respectively. Clearly virgin SIRCA is much less permeable to gas flow than virgin PICA. PICA permeability is comparable to that of un-impregnated fibrous tile insulations such as LI-900 and FRCI-12[2], whereas SIRCA permeability is four orders of magnitude smaller. The continuum permeabilities of the transversely oriented FiberForm® and FRCI-12 tile substrates are on the order of 10^{-10} m^2 and 10^{-11} m^2, respectively[2]. Comparison of LCA and substrate permeabilities indicates that silicone resin impregnation of FRCI-12 has a much greater affect on internal gas flow than phenolic resin impregnation of FiberForm®. This difference can be traced back to substrate microstructure. FiberForm® is less dense than FRCI-12 and is composed of larger diameter fibers (i.e., ~15 $\square$m carbon fibers versus ~2 $\square$m silica and ~8 $\square$m Nextel® fibers.) As a result FiberForm® has a much coarser, more open microstructure than FRCI-12, which is reflected in its higher permeability. Gas flow is restricted further upon resin impregnation in both cases. However, since internal mass flow driven by an imposed pressure gradient across a porous material scales to the third power (at least) with the characteristic channel dimension, comparable resin impregnation leads to a much greater permeability change in the finer microstructure material.

For PICA specimens, the continuum permeability is larger and the slip parameter is smaller (on average) along in-plane directions than along transverse directions. This result is consistent with the anisotropic microstructure of the FiberForm® substrate, which causes the flow path to be less tortuous and the mean distance between gas-surface collisions to be longer along in-plane directions than transverse directions[2]. Though

FRCI-12 substrates have microstructural anisotropies similar to FiberForm®, the permeabilities of transversely and in-plane oriented virgin SIRCA specimens are found to be comparable. This finding gives further evidence that the internal flow properties of virgin SIRCA are dominated by the microstructural changes produced by resin impregnation.

As expected from the mass loss accompanying pyrolysis, charred specimens of both PICA and SIRCA offer less obstruction to the flow than virgin specimens. For PICA specimens, the relative changes in K_o and b due to the pyrolysis process are larger for the transversely oriented specimens than the in-plane oriented specimens. This result is consonant with the view that resin is likely to agglomerate or "web" at fiber intersections during impregnation. Since fibers are preferentially oriented normal to the transverse direction, agglomerations at fiber intersections would offer more obstruction to transverse flow than in-plane flow, and charring would thus have a greater effect on transverse than in-plane permeability. The continuum permeability changes dramatically for SIRCA specimens upon charring, increasing by three orders of magnitude. Moreover, the underlying anisotropy of the FRCI-12 substrate is recovered; in-plane oriented specimens of charred SIRCA are about twice as permeable as transversely oriented specimens.

It is possible that the permeability of charred PICA in different heating environments (e.g., high temperature, oxidizing atmospheres) could be greater than reported here, however using FiberForm® substrate permeability parameters as approximations for charred PICA would probably still overestimate the true char permeability. As with PICA, SIRCA char formation during a particular application will depend upon the chemical environment and heating rate to which the material is exposed. For the rapid