

nonreacting flow values of the wall enthalpy gradient<sup>4</sup> (which is defined so as to equal unity far upstream) to assess the influence of arbitrary degrees of finite surface catalytic ranging from fully catalytic ( $\tilde{T}_{iw} \rightarrow \infty$ ) to completely noncatalytic ( $\tilde{T}_{iw} \rightarrow 0$ ). Equation (24) also implies that the diffusive heat flux, like the conductive heating, is proportional to the local interactive wall enthalpy gradient and hence is reduced by the local interactive pressure rise.<sup>4</sup> Theoretical results for the typical shock-impingement effect on the local relative diffusional heating are shown in Fig. 2b as functions of typical values for  $\tilde{T}_{iw}$ . It is seen that the maximum effect, which reduces heating to a minimum at the shock foot, occurs for a fully catalytic wall ( $\tilde{T}_{iw} = \infty$ ), whereas there is no response at all on a completely noncatalytic wall ( $\tilde{T}_{iw} = 0$ ). Intermediate degrees of catalytic effect pertain to the range of values  $0.01 \leq \tilde{T}_{iw} \leq 10.0$ . When assessing effects on the absolute local diffusive flux, one must of course take into account that the upstream value is also influenced by the surface catalytic.

#### IV. Conclusion

Although there appear to be no data on nonequilibrium heat transfer in dissociated-flow interaction zones that could be used to verify the foregoing theory, the prediction of Eq. (24) that the local diffusive heating be proportional to the corresponding conduction heat transfer has been qualitatively checked against the local heat transfer distributions measured by Needham<sup>7</sup> in a Mach 9.7 interacting corner flow.<sup>8</sup>

#### Appendix: Details of the Specie Conservation Equation

The atom specie conservation equation governing the non-equilibrium-dissociated flow in a laminar boundary layer is<sup>9</sup>

$$\rho \left( u \frac{\partial \alpha}{\partial x} + v \frac{\partial \alpha}{\partial y} \right) - \frac{\partial}{\partial y} \left( \mu \frac{\partial \alpha}{\partial y} \right) = -2\rho \kappa'_R T^{\omega-2} \left( \frac{p_e}{R_u} \right)^2 g(\alpha, T) \quad (A1)$$

where  $\kappa'_R$  is the recombination rate constant and  $g(\alpha, T)$  is the net reaction rate function:

$$g(\alpha, T) = \frac{\alpha^2}{1+\alpha} - \frac{\alpha_e^2(1-\alpha)}{(1-\alpha_e^2)} \exp \left[ -\frac{h_D}{R_m T} \left( 1 - \frac{T}{T_e} \right) \right] \quad (A2)$$

When the lengths and the velocities in Eq. (A1) are normalized by  $L$  and  $U_\infty$ , respectively, the resulting nondimensional reaction term on the right-hand side takes the form  $\rho \Gamma_G (T/T_e)^{\omega-2} g(\alpha, T)$ , where

$$\Gamma_G \equiv 2\kappa'_R T_e^{\omega-2} L (p_e/R_u)^2 / U_\infty \quad (A3)$$

is the characteristic convection time to reaction time ratio or homogeneous Damköhler number. The limit  $\Gamma_G \rightarrow 0$  thus pertains to a chemically frozen flow, whereas the opposite limit  $\Gamma_G \rightarrow \infty$  with  $g \rightarrow 0$  pertains to locally chemical equilibrium flow. We note that, for finite nonequilibrium reactions, the variation of  $g$  due to small perturbations in  $\alpha$  and  $T$  about some reference state  $\alpha_0, T_0$  can be expressed by the Taylor series expansion

$$g = g_0(\alpha_0, T_0) + g_{\alpha_0} \cdot (\alpha - \alpha_0) + g_{T_0} \cdot (T - T_0) + \dots \quad (A4)$$

where  $g_{\alpha_0} \equiv (\partial g / \partial \alpha)_0$  and  $g_{T_0} \equiv (\partial g / \partial T)_0$ . This was in fact used in obtaining Eqs. (16), (17), (20), and (21) of the text, in which the modified interactive Damköhler number (proportional to  $\Gamma_G$ ), defined by

$$\hat{\Gamma}_G \equiv \frac{C_{\text{REF}}^{1/4} (T_{\text{REF}}/T_\infty)^{1-\omega}}{\beta^{1/2} \lambda^{3/2}} \cdot \Gamma_G \quad (A5)$$

was introduced. If the reference state is the incoming boundary layer upstream of the shock boundary-layer interaction zone, which is usually locally similar to a good approximation, it can be shown<sup>5</sup> that the solution of Eq. (A1) for the properties at an arbitrarily catalytic surface gives the result cited in Eq. (3), where

$$\Gamma_{c0} = S_c^{2/3} (\kappa_w / U_\infty) \sqrt{2Re_L / C_{\text{REF}} / \lambda} \quad (A6)$$

is the characteristic diffusion time to surface recombination time ratio or heterogeneous Damköhler number, and  $I_R$  in Eq. (3) is a gas-phase reaction rate integral of the function  $g$  across the boundary layer given in Ref. 4.

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## Gas Permeability of Lightweight Ceramic Ablators

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#### Nomenclature

$b$	= permeability slip parameter, Pa
$D$	= sample diameter, m
$K$	= effective permeability, m <sup>2</sup>
$K_0$	= continuum flow permeability, m <sup>2</sup>
$L$	= length, m
$M$	= molar mass, kg-mol <sup>-1</sup>
$\dot{m}$	= mass flow rate, kg-s <sup>-1</sup>
$P$	= pressure, Pa
$P_{\text{av}}$	= average pressure across sample, Pa
$R$	= universal gas constant, J-mol <sup>-1</sup> -K <sup>-1</sup>
$T$	= temperature, K
$\Delta P$	= pressure difference across sample, Pa
$\mu$	= viscosity, Pa-s

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- $\tilde{\rho}_{lca,c}$  = apparent density of charred ablator,  $\text{kg}\cdot\text{m}^{-3}$   
 $\tilde{\rho}_{lca,v}$  = apparent density of virgin ablator,  $\text{kg}\cdot\text{m}^{-3}$   
 $\tilde{\rho}_{r,v}$  = apparent density of resin in virgin ablator,  $\text{kg}\cdot\text{m}^{-3}$   
 $\tilde{\rho}_t$  = apparent density of tile in ablator,  $\text{kg}\cdot\text{m}^{-3}$

### Introduction

MANY lightweight thermal protection system (TPS) materials have a large degree of open porosity, which can make them highly permeable to gas flow. Recently, a permeability measurement apparatus was constructed to test rigid, porous TPS materials, and measurements were reported<sup>1,2</sup> for a variety of TPS tile insulations from the Ames insulation material (AIM), Lockheed insulation (LI), fibrous refractory composite insulation (FRCI), and alumina enhanced thermal barrier (AETB) families, as well as for the commercial product FiberForm<sup>®</sup>. 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)<sup>3</sup> and silicone impregnated reusable ceramic ablator (SIRCA).<sup>4</sup> PICA and SIRCA materials were developed at NASA Ames Research Center as lightweight ablative materials with enhanced structural integrity. LCA materials are composed of fibrous refractory tile substrates partially impregnated with an organic resin to provide additional cooling mechanisms via endothermic decomposition, pyrolysis gas heat transport, and boundary-layer blowing. Permeability data for LCA materials are of particular importance because 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 manufactured by Fiber Materials, Inc., under the name FiberForm, and the phenolic resin Durite<sup>®</sup> SC-1008, manufactured by Borden Packaging and Industrial Products. FiberForm has a nominal density ranging from about 144 to 176  $\text{kg}/\text{m}^3$  (9 to 11  $\text{lb}/\text{ft}^3$ ). Depending on the level of phenolic loading, the nominal density of PICA ranges from about 224 to 248  $\text{kg}/\text{m}^3$  (14 to 15.5  $\text{lb}/\text{ft}^3$ ). SIRCA materials use a variety of ceramic fiber tiles as substrates. The SIRCA samples tested in this work use a nominal 192- $\text{kg}/\text{m}^3$  (12- $\text{lb}/\text{ft}^3$ ) FRCI-12 tile substrate that is impregnated with RTV-655 resin (manufactured by General Electric) to a nominal bulk density of about 240 to 272  $\text{kg}/\text{m}^3$  (15 to 17  $\text{lb}/\text{ft}^3$ ). 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. Eight PICA and six SIRCA samples were tested along the transverse (parallel to the pressing axis) direction, and eight PICA and five SIRCA samples were tested along an in-plane (normal to the pressing axis) direction.

### 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. The effective permeability is expressed in the Klinkenberg form as  $K = K_0(1 + b/P)$ , where  $K_0$  is the gas permeability in the limit of continuum flow, and  $b$  is a permeability slip parameter that accounts for rarified flow effects. Values of  $K_0$  and  $b$  were obtained using the relation<sup>1,2</sup>

$$4\mu\dot{m}RTL/\pi D^2M\Delta P = K_0(P_{av} + b) \quad (1)$$

Equation (1) can be derived by combining the perfect gas law, conservation of mass, Darcy's law, and the Klinkenberg permeability function, presuming a bulk gas flow that is one dimensional, laminar, and isothermal.<sup>1,2</sup>

Both  $K_0$  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 when microstructures remain fixed. 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. Data are reported here for virgin LCA material and for material charred to its pyrolysis endpoint in an inert gas atmosphere. All of the measurements were made with ambient, room-temperature air and at gas pressures ranging from 0.5 to 101 kPa ( $\sim 0.005$  to 1 atm).

The same PICA specimens were tested before and after pyrolysis. Generally, samples are not retested<sup>1,2</sup> to avoid the possibility of gas leakage past abraded specimens. However, retesting of several virgin PICA specimens gave values of  $K_0$  and  $b$  repeatable to within 1 and 4%, respectively. 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 retested. 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 specimens 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 reinserted 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 (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 (mass per sample volume) 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.

### Experimental Results and Uncertainties

A summary of the experimentally derived densities and permeability parameters for the PICA and SIRCA samples tested is given in Table 1. Table 1 lists the average values and standard deviations (in parentheses) obtained for each unique set of samples.

Table 1 Summary of experimental results for PICA and SIRCA specimens

Sample type <sup>a</sup>	Apparent densities, $\text{kg}/\text{m}^3$				Virgin		Charred	
	$\tilde{\rho}_{lca,v}$	$\tilde{\rho}_t$	$\tilde{\rho}_{r,v}$	$\tilde{\rho}_{lca,c}$	$K_0$ , $10^{-12} \text{ m}^2$	$b$ , kPa	$K_0$ , $10^{-12} \text{ m}^2$	$b$ , kPa
PICA- <i>tr</i>	211 (2)	132 (2)	78 (3)	181 (2)	13.3 (1.9)	3.85 (0.46)	38.1 (4.5)	2.50 (0.18)
PICA- <i>ip</i>	223 (4)	147 (7)	75 (6)	194 (6)	34.9 (10.6)	2.09 (0.53)	53.8 (14.6)	1.87 (0.45)
SIRCA- <i>tr</i>	272 (6)	210 (9)	62 (4)	247 (7)	0.00723 (0.00386)	14.7 (3.1)	1.54 (0.11)	5.05 (0.17)
SIRCA- <i>ip</i>	274 (6)	221 (6)	53 (5)	253 (6)	0.00449 (0.00166)	19.1 (3.4)	3.07 (0.25)	3.84 (0.25)

<sup>a</sup>Transverse orientation = *tr*, in-plane orientation = *ip*.

The relative uncertainties in the apparent densities and permeability parameters for an individual sample were estimated from uncertainties in the contributing experimental parameters using conventional methodology.<sup>1,2</sup> For PICA specimens, the uncertainties in the apparent densities are 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, these uncertainties are 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  $K_0$  and  $b$  has been given in Refs. 1 and 2. The estimated uncertainties for rigid tile specimens are +11/−16% for  $K_0$  and +7/−4% for  $b$ . For the LCA materials these uncertainties are raised to +21/−26% for  $K_0$  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<sup>3</sup> for PICA.

## Discussion

The continuum permeabilities for transversely oriented virgin PICA and SIRCA samples are on the order of  $10^{-11}$  m<sup>2</sup> and  $10^{-15}$  m<sup>2</sup>, respectively. Clearly, virgin SIRCA is much less permeable to gas flow than virgin PICA. PICA permeability is comparable with that of unimpregnated fibrous tile insulations such as LI-900 and FRCI-12,<sup>2</sup> whereas SIRCA permeability is four orders of magnitude smaller. The large difference in permeability between PICA and SIRCA can be related to differences in substrate microstructure. FiberForm is less dense than FRCI-12 and is composed of larger-diameter fibers; i.e., ~15- $\mu$ m carbon fibers vs ~2- $\mu$ m silica and ~8- $\mu$ m Nextel<sup>®</sup> fibers. As a result, FiberForm has a much coarser and more open microstructure than FRCI-12. The continuum permeabilities of the transversely oriented FiberForm and FRCI-12 tile substrates are on the order of  $10^{-10}$  and  $10^{-11}$  m<sup>2</sup>, respectively.<sup>2</sup> From the experimental data, it is clear that silicone resin impregnation of FRCI-12 restricts internal gas flow much more than phenolic resin impregnation of FiberForm. There are several possible mechanisms to explain this. First, pressure-driven internal mass flow in a porous material scales to the third power (at least) with the characteristic channel dimension. Thus, comparable resin loadings into substrates with comparable densities are expected to cause greater flow restrictions in the material with the finer microstructure. Secondly, while resin impregnation predominantly coats the fibers, some webbing between fibers is possible and has been observed in scanning electron microscope images. Such webbing would be more likely in the finer microstructure substrate (FRCI-12) and may contribute to the very low continuum permeability of virgin SIRCA.

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.<sup>2</sup> Though FRCI-12 substrates have microstructural anisotropies similar to FiberForm, the transverse permeabilities of the virgin SIRCA specimens are found to be comparable with or greater than the in-plane permeabilities. 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  $K_0$  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. Because 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 on the chemical environment and heating rate to which the material is exposed. For the rapid exposure of SIRCA to high heating rates in an oxidizing environment, evidence exists for the formation of a glassy char layer, which appears to seal the surface.<sup>4</sup> In such an application, the composite permeability of a partially charred SIRCA component would likely be closer to that of virgin SIRCA. For lower heating-rate environments, where such a glassy char layer does not form,<sup>5</sup> SIRCA permeability should tend toward the char values reported here.

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## Effect of Nonspherical Shape on Oscillations of Levitated Droplets

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## Nomenclature

$a, b$	= major and minor axis of the oblate spheroid, cm
$g$	= acceleration of gravity, cm/s <sup>2</sup>
$I_{lm}^{(l)}$	= integral of product of three spherical harmonics
$l, m$	= mode numbers
$p, p_0$	= perturbed and hydrostatic pressure
$p_{\text{ext}}$	= externally applied pressure force
$R$	= equivalent spherical radius, cm
$R_1, R_2$	= local radii of curvature of droplet surface
$r(\theta, \chi, t)$	= shape of oscillating, deformed droplet
$t$	= time, s
$\bar{u}$	= perturbed velocity
$X(\theta, \chi)$	= static and oscillatory deformations
$Z(\theta, \chi, t)$	= of droplet
$Y_{lm}(\theta, \chi)$	= spherical harmonic for mode $l, m$
$\alpha_1, \alpha_2, \alpha_3$	= dimensionless variables
$\beta$	= exponential coefficient of time dependence of $Z$
$\gamma$	= surface tension, dyne/cm

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