

EFFECT OF INTERFACIAL THERMAL CONDUCTANCE AND FIBER  
ORIENTATION ON THE THERMAL DIFFUSIVITY/CONDUCTIVITY OF  
UNIDIRECTIONAL FIBER-REINFORCED CERAMIC MATRIX COMPOSITES

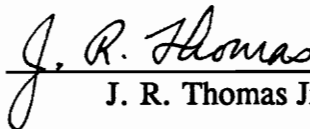
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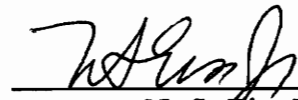
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## ABSTRACT

The role of an interfacial barrier at the fiber-matrix interface in the heat conduction behavior of an uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride and the effect of fiber orientation on the heat conduction characteristics of carbon fiber-reinforced borosilicate glass was investigated.

In the study of the effect of an interfacial thermal barrier, a composite with fibers having a carbon-rich coating of about 3  $\mu\text{m}$  was chosen as the reference material. The fiber-matrix interface was then modified by preferential oxidation of the carbon coating on the fibers, using fibers with no carbon coating and using hot-isostatic-pressing (HIP) after nitridation. The formation of an interfacial gap at the interface due to thermal expansion mismatch between the fiber and the matrix in reference and HIP'd composites, and removal of carbon coating for oxidized composites, resulted in the dependence of thermal diffusivity/conductivity on the surrounding atmosphere. This effect was attributed to gaseous heat transfer at the interface. However, no atmospheric effects were observed for composites with fibers without the carbon coating due to very strong bonding between the fiber and the matrix. HIP'ing increased the thermal diffusivity/conductivity of the composites due to densification of the matrix, crystallization of the fibers and increased physical contact at the interface. Removal of the interfacial carbon layer by preferential oxidation lowered the interfacial conductance considerably, due to decrease in the direct thermal contact between the fibers and the matrix. Interfacial contact conductance determined from measurements made in vacuum for reference and HIP'd composites increased rapidly

with increasing temperature in accordance with interfacial gap closure. These observations indicate that the heat conduction behavior of all the composites investigated was strongly affected by the existence of an interfacial thermal barrier, for heat transfer transverse to the fiber direction.

An analysis was conducted to determine the expression for the effective thermal conductivity of a uniaxially reinforced finite composite strip with insulated edges as a function of the angle between the fiber direction and the temperature gradient. Carbon fiber-reinforced aluminoborosilicate glass composite specimens were used to carry out experimental verification of this analysis. Three types of specimens were used for this study: thin, angled and thick rectangular. The thin specimens and the angled specimens with geometry such that the net direction of heat flow was parallel to the fiber direction represented the case of a composite infinite in extent. The thick rectangular specimens were expected to behave like a finite composite strip. For thin and angled specimens, the thermal conductivity dependence on fiber orientation showed excellent agreement with theoretical behavior predicted from the analysis of a semi-infinite plate. However, for thick specimens the thermal conductivity turned out to be much lower than for thin and angled specimens, especially for small fiber angles below  $45^{\circ}$ . Thermal conductivity values calculated from the analytical model developed for a finite composite strip with insulated sides agreed very well with experimental values for the thick rectangular specimens for high fiber angles greater than  $45^{\circ}$ .

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# 1.0

## INTRODUCTION

Ceramics are superior to metals and other materials for high temperature structural applications because of their high melting points, lower density, thermodynamic stability, refractoriness, and resistance to corrosion and abrasion. However, in the case of single-phase ceramics, the factors which result in these favorable properties also induce a high degree of brittleness, high susceptibility to mechanical surface damage, statistical variation in strength values and catastrophic failure.

Ceramic matrix composites have the potential to overcome the shortcomings associated with single-phase ceramics. Composites based on silicon nitride, silicon carbide, alumina, zirconia, glass ceramics and transformation toughened ceramics, ceramics with particulate reinforcement and whisker and fiber reinforced ceramics have been the focus of a majority of investigations for potential structural applications. These composites can exhibit greatly improved mechanical properties including fracture toughness, tolerance to surface damage, non-catastrophic failure and better reliability. Potential applications of these composites are heat shields for space vehicles, components of heat engines, rocket nozzles, heat exchangers, turbine blades, and others. Almost all these applications involve high temperatures and high levels of transient and/or steady state heat flow. Under these conditions, the performance of the ceramic matrix composites depends critically on their thermophysical properties such as

thermal diffusivity, thermal conductivity and specific heat. A thorough knowledge of the parameters governing the thermophysical properties of these ceramic composites is critical for the prediction of their performance in engineering design.

The main purpose of the investigation described in this dissertation is to study the effect of two parameters, namely the thermal contact resistance at the fiber-matrix interface and the fiber orientation on the effective thermal properties of unidirectional fiber reinforced ceramic matrix composites.

## 1.1 *Basic Theory*

The thermal behavior of a material for steady-state conduction is dependent on three independent parameters: the thermal conductivity ( $K$ ), the specific heat ( $c_p$ ), and the density ( $\rho$ ). Thermal conductivity is a material property, which relates the applied heat flux to the temperature gradients in the specimen.

The heat conduction equation for transient heat flow is

$$\nabla(K\nabla T) + q''' = c_p \rho \frac{\partial T}{\partial t} \quad (1)$$

where  $K$  is the thermal conductivity,  $c_p$  is the specific heat,  $q'''$  is the heat generated per unit volume in the sample,  $\rho$  is the density,  $T$  is the temperature and  $t$  is the time.

For the case where the material is homogeneous and isotropic and there is no heat generation within the sample, the thermal conductivity can be assumed to be independent of position and the heat conduction equation reduces to the form:

$$\nabla^2 T = \frac{c_p \rho}{K} \frac{\partial T}{\partial t} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (2)$$

Therefore, in the case of transient heat conduction, thermal diffusivity ( $\alpha$ ) is the transport property, which describes the rate of temperature propagation in the material.

The above two equations are sufficient to describe macroscopically the heat conduction behavior of any solid provided the assumptions inherent in the derivation of the equations hold true. From a microscopic perspective, heat is conducted in any solid by various carriers: electrons, phonons, photons and in some cases magnetic excitations [1-5]. Therefore, total conductivity is comprised of the relative contributions from each of these carriers. The thermal conductivity can then be given by,

$$K = \frac{1}{3} \sum c_i v_i l_i \quad (3)$$

where  $c$  is the volumetric specific heat of each carrier,  $v$  is the velocity of the carrier,  $l$  is the mean free path and the subscript  $i$  denotes the type of the carrier.

In metals and alloys, the electrons are the most important carriers of heat. In insulating and dielectric solids the phonons are the major carriers of heat. The other two types of carriers, magnetic spin waves or magnons and photons contribute to the heat conduction for magnetically insulating solids and solids partially transparent to radiation, respectively.

For heterogeneous materials, such as composites, the thermal conductivity is a function of position. Therefore,  $K$  cannot be removed outside the del operator in equation (2). Hence, strictly speaking, it is not possible to define thermal diffusivity as a characteristic property of composite materials. However in recent years the concept of an effective thermal diffusivity and conductivity has been extended to composites and other heterogeneous materials by considering them to be homogeneous at the macroscopic level, with the implicit assumption that the relationships of the thermophysical properties of the homogeneous media are also valid for composite materials [6-16].

## ***1.2 Effective conductivity of composites***

A large number of studies have been carried out in the area of theoretical prediction and experimental verification of the effective thermal conductivity of composites. These studies can be divided into two basic categories: models based on Ohm's Law and models based on Fourier's Law. For the models based on Ohm's Law, a unit cell representative of the composite is isolated and the effective thermal conductivity is derived based on the electrical analogy of effective resistance of a system of resistances in series and/or parallel. The most important assumptions made in the analysis are one-dimensional heat transfer, parallel isotherms in the composite or uniform heat transfer in the direction of heat flux [17-23]. In the case of Fourier's law models, a unit cell of idealized geometry representative of the composite is determined and the temperature distribution in each of the components is determined. The effective thermal conductivity is then determined by applying the Fourier-Biot law to the composite [24-39]. Both the dilute case in which due to the low volume fraction of the

second phase, the temperature fields of the second phase do not interact with each other and the non-dilute case where due to the high volume fraction of the second phase their temperature fields interact have been investigated. Using the above two approaches the effective thermal conductivity of composites for a number of simple morphologies of the second phase has been determined.

The results of these studies can be used to identify the various parameters that govern the effective thermal conductivity of composites. The various parameters governing the thermal conductivity of composites are the thermal conductivity of the various components, the size and distribution of these components, and their volume fraction. Recently, theoretical work done by Hasselman and Johnson [40] has shown that the existence of a thermal barrier at the interface of the matrix and the second phase can considerably influence the effective thermal conductivity of the composite. Using the approach similar to Maxwell [24] and Rayleigh [25] and by modifying the boundary conditions to incorporate the thermal barrier resistance at the interface between the second phase and the matrix, the effective thermal conductivity of composites containing dilute volume fractions of spherical, cylindrical and flat plate type dispersions was determined.

For a composite uniaxially reinforced with cylindrical fibers, having a thermal barrier at the fiber-matrix interface, the effective thermal conductivity in the direction perpendicular to the fibers in terms of the interfacial conductance,  $h_i$ , was shown to be [40]:

$$K_c = K_m \frac{\left[ \left( \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]}{\left[ \left( 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]} \quad (4)$$

where  $K$  and  $V$  are the thermal conductivity and volume fraction of the fibers, respectively; subscripts  $c$ ,  $m$  and  $f$  refer to composite, matrix and fiber respectively;  $a$  and  $h_i$  are the fiber radius and the interfacial conductance.

Subsequently, Benveniste [41] determined the effective thermal conductivity of particulate composites with spherical inclusions having a thermal barrier at the interface for non-dilute volume fractions of the second phase in the composite.

### 1.3 Interfacial Heat Transfer

Heat transfer across two surfaces in contact has been extensively investigated, both theoretically and experimentally, over the last forty years. Heat transfer across an interface can occur by solid conduction through areas of direct contact, by gaseous conduction due to the presence of the gas phase at the interface and by radiation. Therefore, the total interfacial conductance ( $h_i$ ) is then given by:

$$h_i = h_c + h_g + h_r \quad (5)$$

The contact conductance depends on the real area of contact between the two surfaces. Therefore, the contact conductance is a function of the surface roughness of the two surfaces, their microhardness characteristics, and the applied mechanical load [42-45].

In normal heat transfer applications, gaseous conduction often is the predominant mode of heat transfer as compared to the conduction due to the solid-solid contacts at the interface. The gaseous conductance is a function of the Knudsen number ( $K_n$ ), which is defined as the ratio of the mean free path ( $\lambda$ ) of the gaseous species to the mean gap separation ( $d$ ). Based on the Knudsen number the gaseous conduction can be classified into three heat flow regimes; continuum, transition, and free-molecular [46-48].

In the continuum regime ( $K_n \ll 1$ ) the interfacial heat transfer is controlled by the collisions between the gas molecules. However, for conditions of very low gas pressure or for very small interfacial gap, the interatomic or intermolecular collisions in the gas are rare and the mechanism of heat transfer is the exchange of energy due to the collisions between the gas atoms/molecules and the gap surfaces. This heat flow regime is called the free-molecular regime and is typical for  $K_n > 10$ . For this regime the contact conductance is a function of the thermal accommodation coefficient (TAC), which represents the efficiency of energy exchange between the gap surfaces and the gas atoms/molecules. In between the continuum regime and the free-molecular regime is the transition regime corresponding to the  $K_n$  range of  $0.1 < K_n < 10$ . In this region both the intermolecular collisions and the energy exchange between the gap surfaces and the gas molecules are important.

The mechanical properties and the fracture toughness of ceramic matrix composites are strongly influenced by the nature of the fiber-matrix interface [49-58]. It has been observed that composites having a 'weak' interface; i.e., an interface having low interfacial shear strength exhibits the best mechanical behavior due to increased fiber pullout and interfacial sliding. Interfaces in ceramic matrix composites

are tailored by applying coatings to the fibers to minimize fiber-matrix interactions or by selecting appropriate fiber-matrix combinations. This can usually result in incomplete thermal contact at the interface resulting in a significant interfacial thermal barrier at the fiber-matrix interface. Therefore, interfacial heat transfer is expected to play a very important role in the determination of the effective thermophysical properties of these composites.

## 1.4 *Effect of Fiber Orientation*

Another important parameter which can significantly influence the effective thermal conductivity of fiber reinforced composites is the fiber orientation with respect to the direction of heat flow. Previous studies in this area have concentrated on the determination of the effective thermal conductivity of uniaxial fiber reinforced composite in a direction relative to the fibers from the principal thermal conductivities, parallel and perpendicular to the fiber direction [59,60]. These analyses are only valid for a composite infinite in extent, where the heat flow is not constrained by conditions at the boundaries. For an infinite composite plate, the effective thermal conductivity as a function of fiber orientation, unaffected by the presence of insulated edges is [61],

$$K_{zz} = K_p \cos^2 \theta + K_n \sin^2 \theta \quad (6a)$$

$$K_{xx} = K_p \sin^2 \theta + K_n \cos^2 \theta \quad (6b)$$

$$K_{xz} = (K_p - K_n) \sin \theta \cos \theta \quad (6c)$$

where  $K$  and  $\theta$  are thermal conductivity and angle between the fiber direction and the temperature gradient and the subscripts  $p$  and  $n$  refer to the directions parallel and

perpendicular to the fiber, respectively. The two subscripts of  $K$  on the L. H. S. represent the direction of the heat flux and the temperature gradient, respectively.

The composite thermal conductivity parallel to the fibers can be determined from the simple rule of mixtures formula, which is given by:

$$K_p = K_m V_m + K_f V_f \quad (7)$$

where  $K$  and  $V$  are the thermal conductivity and the volume fraction, respectively, and the subscripts  $m$  and  $f$  represent the matrix and the fiber, respectively.

The composite thermal conductivity,  $K_n$ , perpendicular to the fiber direction, including the effect of an interfacial thermal barrier can be determined using eqn. (4).

The effective thermal conductivity relative to the fibers of the uniaxial fiber reinforced composite of finite size is expected to differ significantly from the values determined by using the previous analyses, especially for composites with highly anisotropic principal conductivities [61-63].

## **1.5 Objectives**

The principal objectives of this study were to :

(1) Experimentally investigate the existence of an interfacial thermal barrier at the fiber-matrix interface and its effect on the effective thermal diffusivity/conductivity of unidirectional fiber reinforced ceramic composites having different types of interfaces.

(2) Develop an analytical expression for the effective thermal conductivity of uniaxial fiber reinforced composite in a direction relative to the fibers, having insulating boundary conditions on their sides. In addition, experimentally verify the analysis by measuring the effective thermal conductivity of various composites for different fiber orientations and compare to the calculated values.

## ***1.6 Materials and Experimental Techniques***

The composite used to study the effect of an interfacial thermal barrier on the effective thermal conductivity was silicon carbide (SCS-6) fiber reinforced reaction-bonded silicon nitride composite obtained from NASA Lewis Research Center, Cleveland, OH. Details of the manufacturing process for these composites are reported in the subsequent chapters. The fiber-matrix interface in these composites was modified by the preferential oxidation of the carbon coating on the fibers, using fibers without the carbon coating and HIP'ing the composites.

The composites used for studying the effect of fiber orientation were carbon fiber (P-55)-reinforced borosilicate glass composites obtained from Corning, Inc.

The thermal diffusivity of the composite and matrix samples was measured using the laser-flash technique [64,65]. The specific heat of these samples was determined using differential-scanning-calorimetry. Detailed descriptions are given in the subsequent chapters.

## ***1.7 Presentation of results***

The results of this study are presented in the form of journal and conference publications, which appear as separate chapters (chapter 2 to 6) following the introduction. It should be noted that each chapter is complete within itself, i.e. it has its own introduction, theory, results, discussions, conclusions and references. The overall summary and conclusions of the entire study are given in chapter 7. The references used in the introduction chapter are listed separately as chapter 8.

This paper titled

**EFFECT OF FINITE INTERFACIAL CONDUCTANCE ON THE  
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REINFORCED REACTION BONDED SILICON NITRIDE  
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## 2.0

### **EFFECT OF FINITE INTERFACIAL CONDUCTANCE ON THE EFFECTIVE THERMAL DIFFUSIVITY/CONDUCTIVITY OF SiC FIBER REINFORCED REACTION BONDED SILICON NITRIDE COMPOSITES**

#### **2.1 ABSTRACT**

Experimental data are presented which show that the thermal diffusivity/conductivity of uniaxial silicon carbide fiber reinforced reaction bonded silicon nitride, for heat flow transverse to the fiber direction, is strongly affected by the existence of an interfacial thermal barrier. Measurements made in vacuum, nitrogen and helium indicate that the gas phase within the interface contributes strongly to the total interfacial thermal conductance. Removal of the interfacial carbon layer by preferential oxidation lowers the conductance appreciably. Measurements in vacuum, in which the contribution of the gaseous conductance is suppressed, indicate that the contact conductance increases rapidly with temperature, as the result of gap closure due to thermal expansion or other effects.

## 2.2 INTRODUCTION

Fiber or whisker reinforced ceramic matrix composites offer considerable advantages in applications involving elevated temperatures. The thermal conduction characteristics of ceramic matrix composites become critical information when designing for these service conditions, involving transient or steady-state heat flow and the possibility of failure by thermal shock and fatigue.

Analytical studies have shown that the effective thermal conductivity of a composite depends on the thermal conductivity values, the volume fraction and the distribution of individual components within the composite [1-6]. A number of more recent studies have identified the role an interfacial thermal barrier plays in the effective thermal conductivity of composites [7-10].

For a composite uniaxially reinforced with fibers of circular cross section and an interfacial barrier to heat flow expressed in terms of an interfacial conductance, the effective thermal conductivity for heat flow perpendicular to the fiber axes is [8]:

$$K_c = K_m \frac{\left[ \left\{ \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right\} V_f + \left\{ 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} \right]}{\left[ \left\{ 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} V_f + \left\{ 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} \right]} \quad (1)$$

where K and V represent the thermal conductivity and volume fraction, resp., the subscripts c, m, and f refer to the composite, matrix and fiber phases, resp., a is the radius of the fiber and  $h_i$  is the interfacial conductance.

The effect of the interfacial conductance on the composite thermal conductivity is governed by its influence on the magnitude of the nondimensional parameter,  $K_f/ah_i$ . For  $h_i = \infty$  (i.e., perfect interfacial thermal contact), the expression for  $K_c$  reverts to the equation derived by Rayleigh [1]. For  $h_i = 0$ ,  $K_c$  corresponds to that of a porous composite, independent of the value of  $K_f$ .

For heat flow parallel to the fibers in a uniaxially reinforced composite, the effective thermal conductivity is unaffected by the existence of an interfacial thermal barrier and is given by:

$$K_c = K_m \left[ 1 - V_f \left\{ 1 - \frac{K_f}{K_m} \right\} \right] \quad (2)$$

The assumption that thermal conductivity parallel to the fiber direction is independent of the existence of an interfacial thermal barrier is strictly valid only for steady-state heat flow. However, for transient heat flow, transverse heat flow between the fibers and matrix is expected to occur, especially for components with significantly different thermal diffusivities. This effect is the subject of a separate study currently underway. In the meantime, the validity of Eq. (2) for both steady-state and transient heat flow will be assumed.

Incomplete thermal contact at the fiber-matrix interface can arise from poor chemical or mechanical adhesion between the fiber and matrix and mismatches in the coefficients of thermal expansion of the fiber and matrix. In particular this latter effect will occur for composites in which the coefficient of thermal expansion of the fiber phase exceeds the corresponding value for the matrix. On cooling this results in

an interfacial gap, especially in those composites with poor or no adherence between the fibers and matrix.

Interfacial heat transfer across the fiber-matrix interface can occur by solid conduction through points or areas of direct contact, by gaseous conduction through the gas phase present within the interface and by radiation. As a result, the net interfacial conductance becomes [11]:

$$h_i = h_c + h_g + h_r \quad (3)$$

where  $h_c$ ,  $h_g$  and  $h_r$  are the contact, gaseous and radiative conductances, resp.

The contact conductance is a strong function of the roughness of the two surfaces in contact and is expected to vary from one situation to another. Since the degree of direct contact between fibers and matrix in a composite is not easily established, a quantitative estimate of the interfacial contact conductance in a composite cannot be made at this time [12].

The gaseous interfacial conductance is a function of the ratio of the mean-free-path of the gaseous species ( $\lambda$ ) and the gap thickness ( $d$ ) defined by the Knudsen number:

$$K_n = \frac{\lambda}{d} \quad (4)$$

For  $K_n \ll 1$ , the interfacial heat transfer is controlled by the collisions between the molecules. In this case, referred to as the continuum regime, the gaseous conductance is:

$$h_g = \frac{K}{d} \quad (5)$$

where  $K$  is the thermal conductivity of the gas. In this regime,  $h_g$  is independent of pressure and inversely proportional to the gap thickness.

For  $K_n > 10$ , inter-atomic or -molecular collisions are rare and heat transfer at the surface of the interfacial gap is controlled by the energy exchange due to collisions between the gaseous species and the gap surfaces. In this regime, referred to as the "free-molecular" regime, the conductance can be described by [12]:

$$h_g = \left[ \frac{c_p \mu}{\lambda} \right] \left[ \frac{(\gamma + 1)}{2\gamma} \right] \left[ \frac{(2 - C_1)}{C_1} + \frac{(2 - C_2)}{C_2} \right]^{-1} \quad (6)$$

where  $c_p$  and  $\mu$  are the specific heat and viscosity of the gas phase,  $C_1$  and  $C_2$  are the thermal accommodation coefficients for each surface,  $\gamma$  is the ratio of the specific heats at constant pressure and constant volume and  $\lambda$  is the mean-free-path of the gas. The thermal accommodation coefficient represents the efficiency of energy exchange between the gap surfaces and the colliding gaseous atoms or molecules [13].

In the "free-molecular" regime the conductance,  $h_g$ , is independent of the gap thickness and directly proportional to the density, i.e., the pressure, of the gas in the interfacial gap. Examination of Eqs. (5) and (6) indicates that the gaseous conductance is expected to be a function of the gas phase within the interfacial gap.

The radiative conductance ( $h_r$ ) can be derived from the effective radiative thermal conductivity [14] to be:

$$h_r = \left[ \frac{4\epsilon}{(2-\epsilon)} \right] \sigma n^2 T^3 \quad (7)$$

where  $\epsilon$  is the emissivity of the two surfaces (assumed to be equal),  $\sigma$  is the Stefan-Boltzmann constant,  $n$  is the refractive index of the medium within the interfacial gap and  $T$  is the absolute temperature.

In a recent study, the present authors compared experimental data for the effective thermal diffusivity of a reaction-bonded silicon nitride uniaxially reinforced with silicon carbide fibers in atmospheric pressure nitrogen and in vacuum [15]. The data suggested the existence of a significant interfacial thermal barrier at the fiber-matrix interface. Of interest was the observation that such a thermal barrier existed in both the as-received composite and in a composite from which the interfacial carbon layer had been removed by selective oxidation.

The purpose of the present study was to extend the previous study to include helium as a gaseous environment in addition to vacuum and nitrogen.

## 2.3 EXPERIMENTAL

### 2.3.1 *Description of Composite*

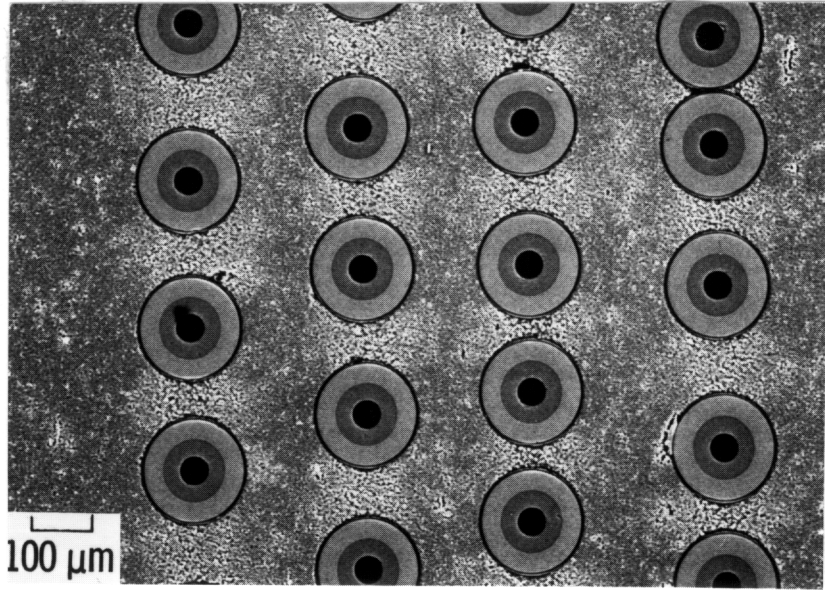
The composite samples consisted of reaction-bonded silicon nitride uniaxially reinforced with SiC mono-filaments. Details of the manufacturing process can be obtained from earlier reports [16-18]. The fibers had a diameter of 142  $\mu\text{m}$  and contained a central carbon core with diameter of approximately 37  $\mu\text{m}$ . At a diameter of approximately 80  $\mu\text{m}$ , the fibers exhibited a change in grain structure.

The surface of the fibers was coated with an  $3.0 \mu\text{m}$  thick carbon rich layer. The volume fraction of the fibers was approximately 32%. Their coefficient of thermal expansion was measured to be  $4.6 \times 10^{-6}/\text{C}$ . The silicon nitride matrix, with density of  $1.983 \text{ gm/cc}$ , contained approximately 38 % porosity with a mean pore size of approximately  $0.02 \mu\text{m}$ . The composite density was  $2.17 \text{ gm/cc}$  with a total pore content of 31%. Figures 1 and 2 are optical micrographs of polished sections of the composite showing the microstructure and details of the fiber-matrix interface. The oxidation treatment subjected the matrix and composite samples to flowing oxygen at  $600 \text{ C}$  for 100 hours. Because of relatively free oxygen access throughout the surrounding matrix, this treatment resulted in the preferential oxidation of the carbon coating on the fibers and some oxidation of the carbon core of the fibers.

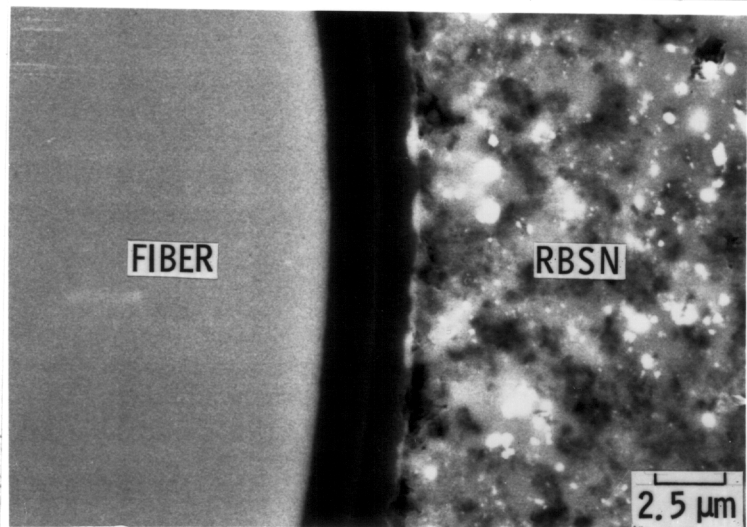
The coefficients of thermal expansion for the matrix and composite perpendicular to the fiber direction were measured to be  $3.6 \times 10^{-6}/\text{C}$ . For the composite parallel to the fiber direction the coefficient of thermal expansion was  $4.1 \times 10^{-6}/\text{C}$ .

### **2.3.2 *Determination of Thermophysical Properties***

The effective thermal diffusivity was measured by the flash-diffusivity technique [19]. A glass-Nd laser was used as the flash source. The specimens were lightly coated with colloidal carbon to promote absorption and prevent direct transmission of the laser pulse. An InSb IR-detector was used to monitor the transient temperature of the specimen up to temperatures of  $700 \text{ C}$  and a Si-photodiode detector was used for temperatures above  $700 \text{ C}$ . The detectors viewed a circular area of the specimen with a diameter of about  $5 \text{ mm}$ . The thermal diffusivity up to  $1000 \text{ C}$  was measured over



**Fig. 1:** Optical micrograph of cross section of uniaxial SiC fiber reinforced reaction-bonded silicon nitride transverse to the fiber direction.



**Fig. 2:** Optical micrograph of interface in uniaxial SiC fiber reinforced reaction-bonded silicon nitride showing interfacial carbon layer.

intervals of approximately 100 C in helium and nitrogen at atmospheric pressure and in vacuum at a pressure of about 0.13 Pa. The experimental accuracy of the laser-flash technique was about 5%.

The specific heat was measured by differential scanning calorimetry from room temperature to 600 C. Data for specific heat from 600 C to 1000 C were established by extrapolation.

The thermal conductivity was calculated from the experimental thermal diffusivity data and the product of density and specific heat. In this manner, data were established for the matrix phase without fibers and for the composites with heat flow parallel and perpendicular to the fiber direction, prior to and following oxidation.

### **2.3.3 *Analysis of Interfacial Conductance***

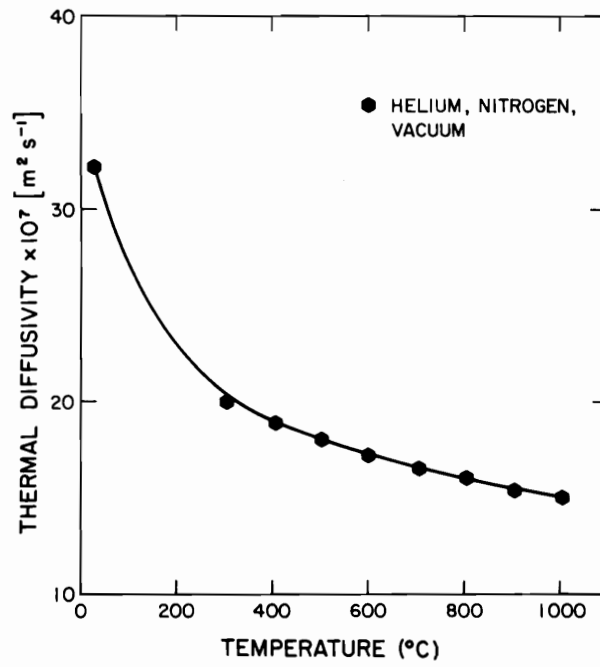
The estimate of the interfacial conductance was based on a number of simplifying assumptions. The matrix and silicon carbide phase within the fibers were assumed to exhibit isotropic thermal conductivity. The fibers themselves can be regarded as a composite material. The carbon core within the fibers, in view of its highly preferred crystallographic orientation, is expected to exhibit highly anisotropic thermal conductivity [20-26]. Parallel to the fiber direction, the thermal conductivity of the carbon core is expected to be comparable to that of the silicon carbide. Transverse to the fiber direction, the thermal conductivity is expected to be quite low compared to the silicon carbide and for simplicity was assumed to be zero. This latter assumption is not expected to introduce a major error, as the core represents only 6.8 volume percent of the fiber, or only 2-3 volume percent for the composite as a whole. It is also assumed that the oxidation treatment removes the carbon core completely. The

effective thermal conductivity of the fibers can then be estimated using the appropriate porosity correction obtained from using Eq. (1). In turn, Eq. (1) will be used to analyze the role of the thermal barrier resistance in terms of the effective composite thermal conductivity.

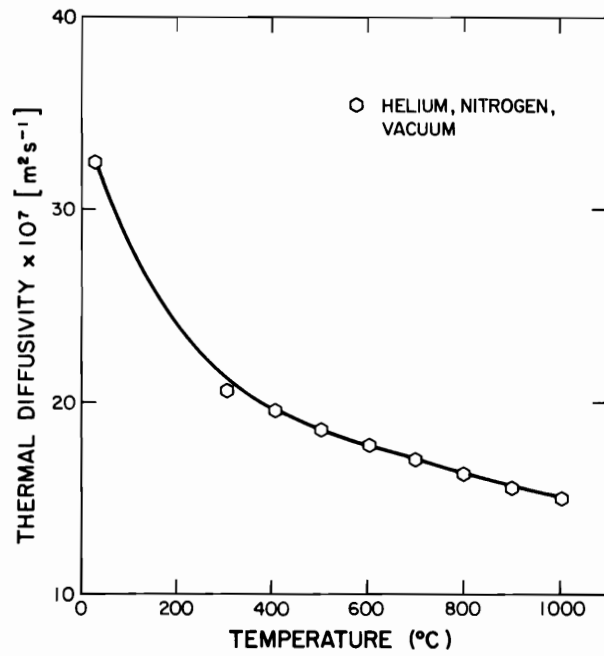
## **2.4 EXPERIMENTAL RESULTS**

Figures 3a and 3b show the experimental data for the thermal diffusivity in helium, nitrogen and vacuum for the as-received and oxidized matrix phase, resp. These data indicate that within the expected experimental scatter and possible specimen-to-specimen variation, the oxidation treatment had no effect on the thermal diffusivity. Also, heat conduction through the matrix phase appears to be unaffected by the nature of the gaseous environment. In fact, the data for the helium, nitrogen and vacuum atmospheres were too close to be plotted separately.

Figures 4a and 4b present the thermal diffusivity data for the as-received and oxidized composite samples with heat flow parallel to the fiber direction. General comparison with Figs. 3a and 3b show that the presence of the fibers increased the thermal diffusivity by a factor somewhat greater than two. Assuming the validity of the rule of mixtures, this increase implies that for a fiber volume fraction of approximately 32%, the thermal diffusivity of the fibers must be some five times that of the matrix phase. For the as-received sample, the data for helium and nitrogen were too close to be plotted separately. The data for vacuum, however, were consistently lower, indicating the existence of an effect due to the presence or absence of the gaseous environment. Qualitatively this is expected, considering the large differences between the thermal diffusivity of the matrix and fibers, which will lead to transverse heat flow from the fiber into the matrix and vice-versa

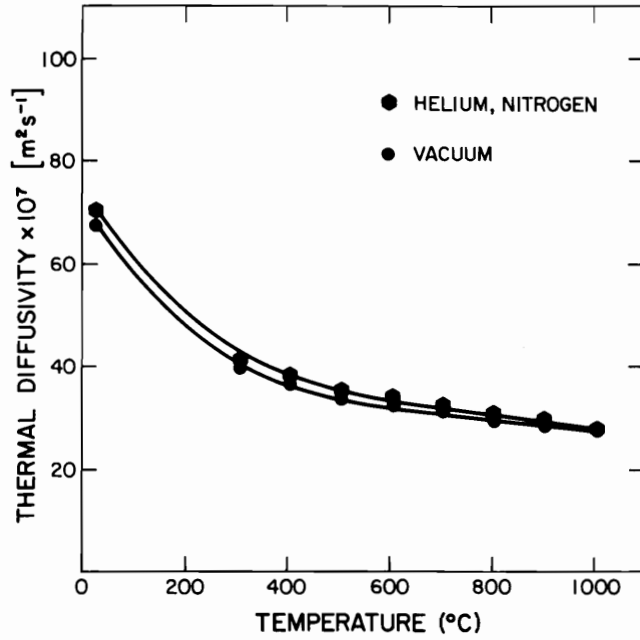


(a)

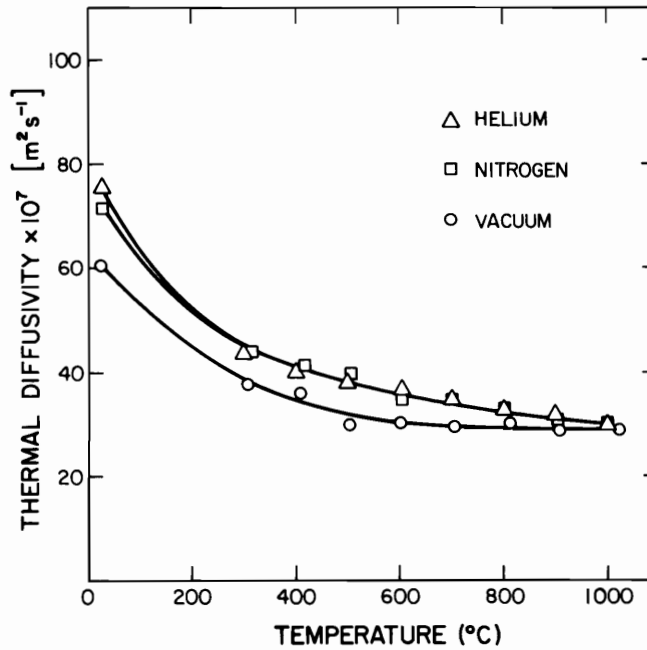


(b)

**Fig. 3:** Thermal diffusivity of reaction-bonded silicon nitride in vacuum, nitrogen and helium: (a) as-received and (b) oxidized at 600 C.



(a)



(b)

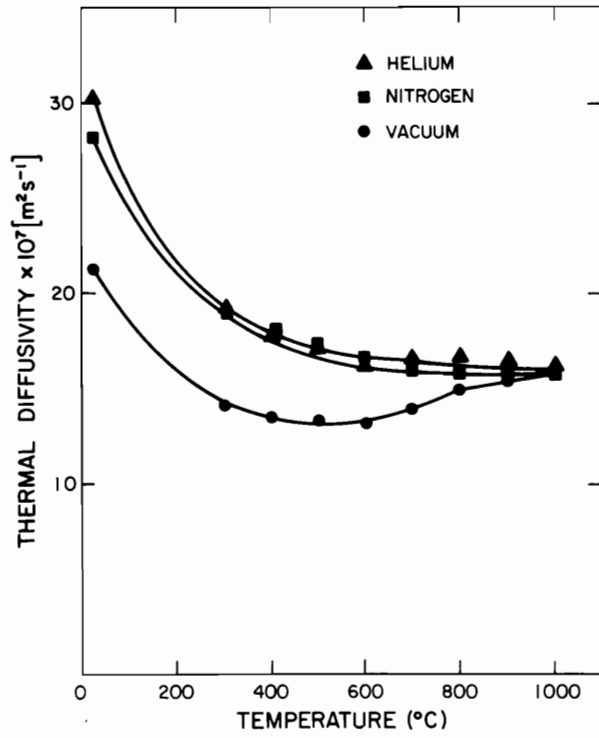
**Fig. 4:** Thermal diffusivity of uniaxial silicon carbide fiber reinforced reaction-bonded silicon nitride in vacuum, nitrogen and helium for heat flow parallel to the fiber direction; (a) as-received and (b) oxidized at 600 C to remove interfacial carbon layer.

Such transverse heat flow will be affected by the existence of an interfacial thermal barrier.

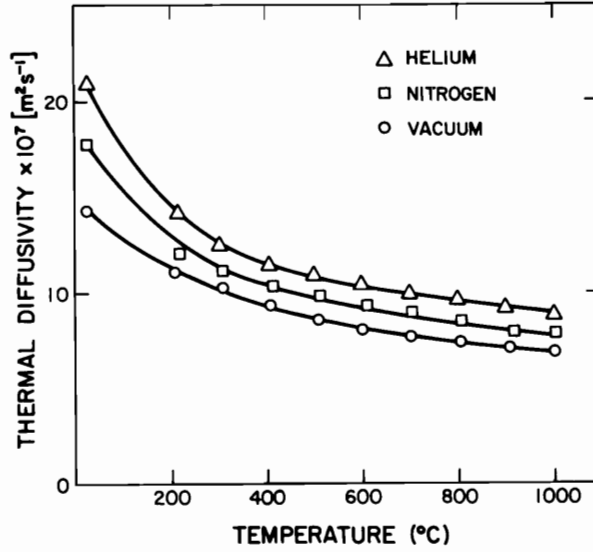
For the oxidized sample, Fig. 4b indicates that the thermal diffusivity in nitrogen and helium are almost identical, with the possible exception of the values at room temperature. The thermal diffusivity in vacuum, however, is well below the corresponding values for the helium and nitrogen atmospheres. Again, the effect of an interfacial thermal barrier is indicated.

Comparison of Figs. 4a and 4b show that the thermal diffusivity of the oxidized sample in helium and nitrogen appear to be somewhat higher than the corresponding values for the as-received sample. Possibly, these differences can be attributed in part to the combined effects of experimental accuracy of the laser-flash technique and to specimen-to-specimen variation. However, it is speculated that these differences may also result from differences in the effect of the interfacial thermal barrier on the transverse transient heat flow, which is expected to be affected in turn by the presence or absence of the interfacial carbon coating on the fibers.

Figures 5a and 5b show the data for the thermal diffusivity perpendicular to the fiber direction, for the as-received and oxidized composite samples. The effect of atmosphere is quite pronounced, much more so than for heat flow parallel to the fiber direction. Especially for vacuum, the data for the as-received sample lie well below those for helium and nitrogen over most of the temperature range. However, as the temperature approaches 1000 C, the data for vacuum, nitrogen and helium are nearly equal. This effect will be discussed in more detail later.



(a)



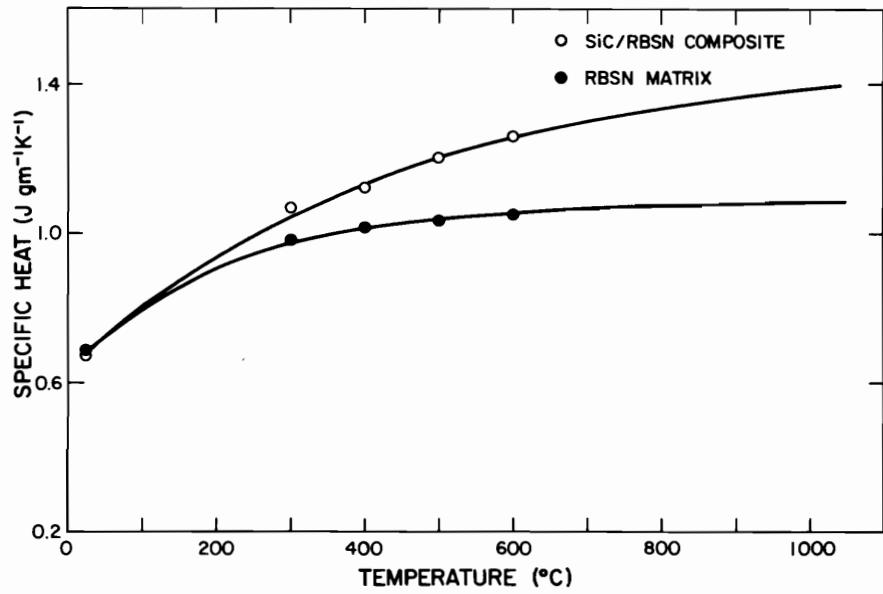
(b)

**Fig. 5:** Thermal diffusivity of uniaxial silicon carbide reinforced reaction-bonded silicon nitride in vacuum, nitrogen and helium for heat flow transverse to the fiber direction: (a) as-received composite and (b) composite oxidized at 600 C to remove interfacial carbon layer.

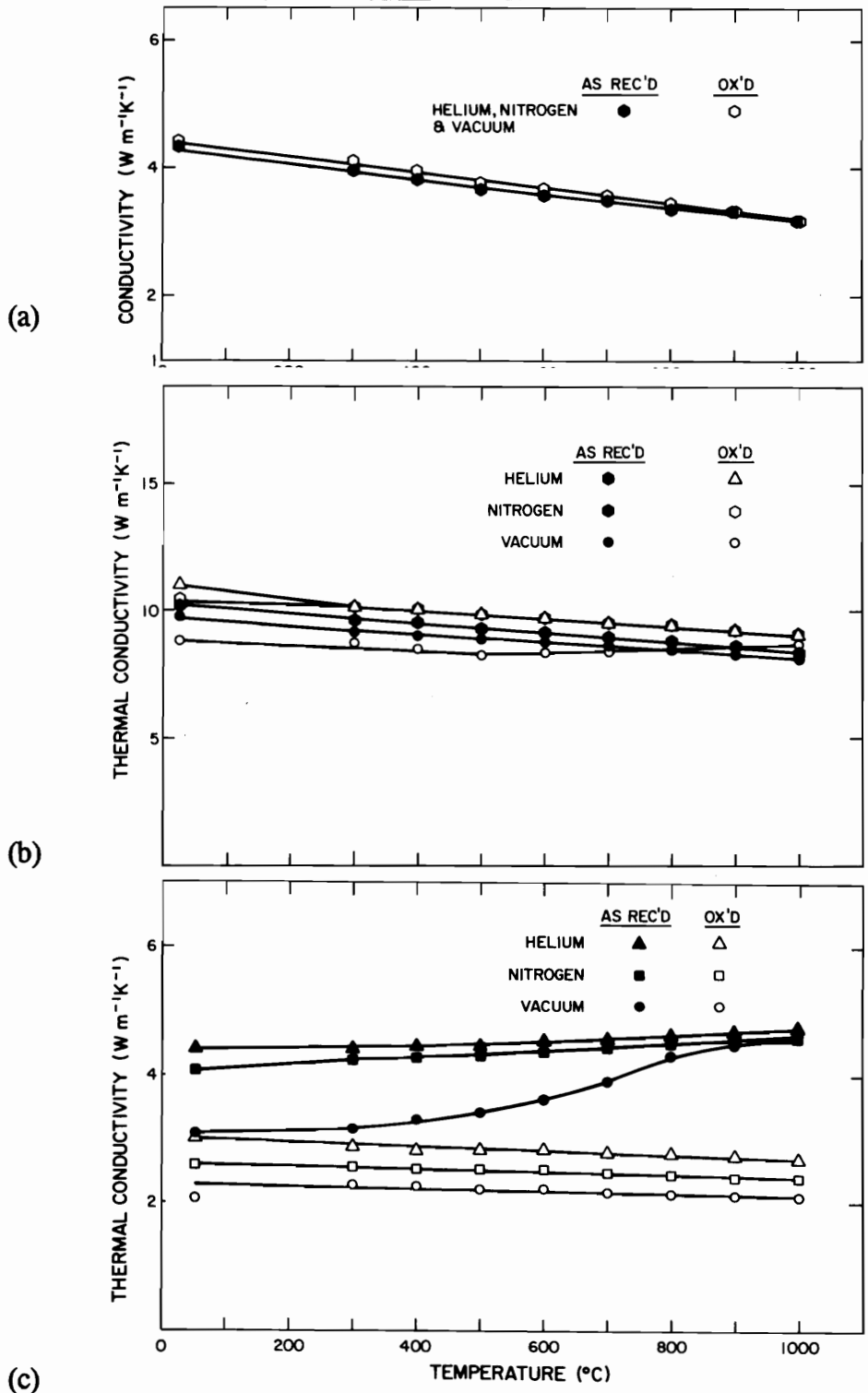
Fig. 6 shows the data for the specific heat of the matrix and composite. The data above 600 C were obtained by extrapolation of the experimental data below 600 C.

Figures 7a, b, and c show the thermal conductivity values calculated from the density, specific heat and thermal diffusivity values obtained at 100 C intervals from the smooth curves drawn through the experimental data shown in Figs. 3, 4 and 5. The dependence of the thermal conductivity on oxidation treatment and gaseous environment is relatively similar to the corresponding dependence for the thermal diffusivity as indicated in Figs. 3, 4, and 5. In view of the positive temperature dependence of the specific heat, the relative temperature dependence for the thermal conductivity is less pronounced than for the thermal diffusivity. Using Eq. (2), the thermal conductivity of the fibers parallel to the fiber direction was calculated from the data for the composite sample for heat flow parallel to the fiber direction and the data for the matrix as shown in Figs. 3a and 7b. At 25 C the thermal conductivity of the fibers parallel to their axis was found to be approximately 20 W/m.K decreasing to about 10 w/m.K at 1000 C. As discussed earlier, the thermal conductivity of the fibers perpendicular to the fiber direction was obtained by the appropriate porosity correction [Eq. (1)] with  $h_i = \infty$  and  $K_f = 0$  in order to account for the presence of the carbon core or longitudinal pore in the as-received or oxidized samples, resp.

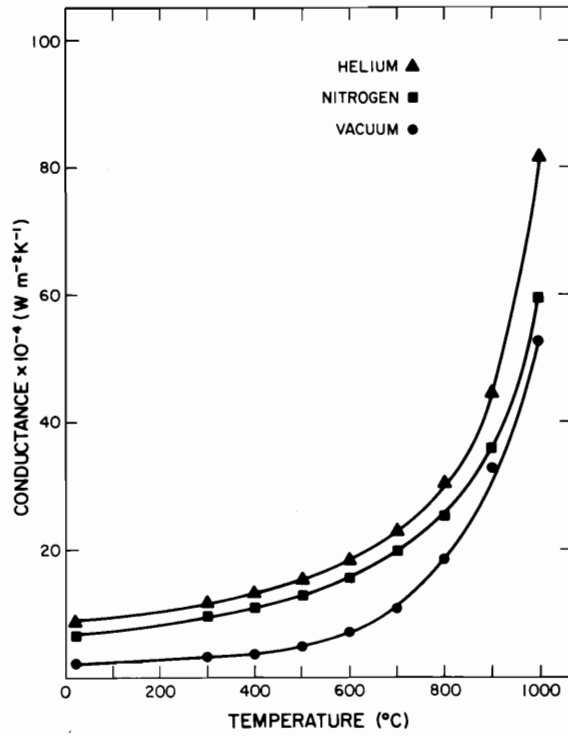
Figures 8a and 8b show the values for the interfacial conductance for the as-received and oxidized composite samples for heat flow perpendicular to the fiber direction. These values were calculated from Eq. (1) and the thermal conductivity values obtained from the smooth lines drawn throughout the data points of Fig. 7, the fiber radius and the volume fraction.



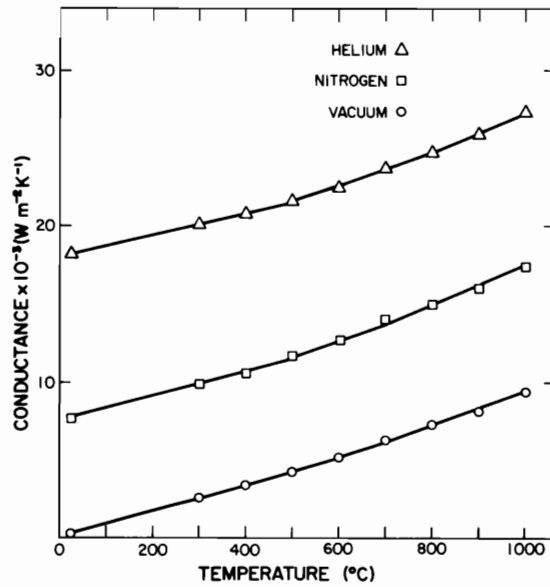
**Fig. 6:** Specific heat of reaction-bonded silicon nitride with and without silicon carbide fiber reinforcing phase.



**Fig. 7:** Thermal conductivity of as-received and oxidized uniaxial silicon carbide fiber reinforced reaction-bonded silicon nitride in vacuum, nitrogen and helium: (a) matrix phase only, (b) heat flow parallel to fibers and (c) heat flow transverse to the fibers.



(a)



(b)

**Fig. 8:** Interfacial thermal conductances for uniaxial silicon carbide reinforced reaction bonded silicon nitride in vacuum, nitrogen and helium for heat flow transverse to the fiber direction: (a) as-received composite and (b) composite oxidized to remove interfacial carbon layer.

## 2.5 DISCUSSION AND CONCLUSIONS

A general comparison of the data for the as-received and oxidized composite samples shows that for heat flow perpendicular to the fiber direction, the removal of the interfacial carbon layer had a profound effect on the thermal diffusivity/conductivity and the interfacial conductances. The relative values of these quantities are consistent with the relative heat conduction behavior for vacuum, nitrogen and helium.

Most surprising, at least to these authors, was the observation that even for the as-received samples, with the interfacial carbon layer intact, a significant effect of atmosphere was found, especially for heat flow perpendicular to the fiber direction. The effect of atmosphere was found to be non-existent for the matrix phase and is not expected to be significant for heat flow in the SiC fibers. This leads to the inescapable conclusion that in the as-received samples heat flow is also affected by an interfacial thermal barrier accessible by the surrounding gas phase. This barrier most likely originates from the difference in thermal expansion behavior of the fibers and matrix. Because the coefficient of thermal expansion of the SiC exceeds that of the matrix, on cooling from the processing temperature the fibers will tend to shrink away from the matrix resulting in internal stresses. For insufficient bond strength this will lead to the formation of an interfacial crack. The near equality of the coefficients of thermal expansion of the matrix and composite transverse to the fiber direction provides indirect evidence that an interfacial gap exists. From the difference in coefficients of thermal expansion of the fibers and matrix, the width of the interfacial crack can be calculated to be of the order of  $0.1 \mu\text{m}$ . It should be noted that the coefficient of thermal expansion of the composite parallel to the fiber direction is in

between the values for the matrix and the fibers. This indicates that the fibers and matrix have not de-bonded completely. Direct thermal contact is therefore expected to still contribute to the total heat transfer between the fiber and the matrix.

An increase in temperature of the composite sample should lead to a closure of the interfacial gap and an increase in the contact conductance. It is thought that this effect is responsible for the positive temperature dependence of the thermal diffusivity and conductivity for the composite sample in vacuum as shown in Figs. 5a and 7c and, in particular, for the strongly positive dependence of the conductance in vacuum, as shown in Fig. 8a.

Due to the near absence of the gas phase, the conductance in vacuum is thought to closely represent the contact conductance. The presence of a gas phase gives rise to an additional contribution to the interfacial conductance in the form of gaseous conductance. The radiative conductance, calculated by using Eq. (7), was found to be negligible compared to the measured conductances over the total temperature range used in this study. Therefore the numerical difference between the conductance values in vacuum and in nitrogen and helium represents the gaseous conductances. A quantitative analysis of the values for the gaseous conductances required an estimate of the Knudsen number, as defined by Eq. (4). For simplicity, this estimate will be limited to a single temperature, for convenience chosen to be 300 C. Using the kinetic theory of gases and data for the thermal conductivity or viscosity [27,28], the mean-free-path of nitrogen can be calculated to be  $1.47 \times 10^{-7}$  m and 0.115 m at 1 atm and 0.13 Pa, resp. The corresponding values for He are  $4.3 \times 10^{-7}$  m and 0.24 m, resp. For an interfacial gap width of  $0.1 \mu\text{m}$  in the as-received composite, the Knudsen number ranges from about 1 to  $10^6$ . This places the mode of gaseous heat

transfer in the "free molecular" regime, for which the conductance is controlled by the thermal accommodation coefficients. For the present material, no information on these coefficients is available and no quantitative analysis of the interfacial gaseous conductances and their temperature dependencies for the as-received composites can be given. Such an analysis is handicapped further by noting that the gaseous and contact conductances are expected to be competitive processes. As the interfacial gap closes, thereby increasing the fractional contact area of the interface, the fractional area available for gaseous conduction decreases correspondingly. All that can be stated at this stage is that, in view of the mean atomic and molecular velocity, the gaseous conductances for helium will exceed that for nitrogen, in qualitative agreement with the observations.

A brief comment is in order in regard to the experimental data for the thermal diffusivity for heat flow parallel to the fiber direction as shown by Figs. 4a and 4b. Ideally, under steady-state conditions, an interfacial thermal barrier should not affect the heat flow, as the temperature distribution is uniaxial. However, under transient conditions for composites with components having different thermal diffusivities, a transverse component of the temperature distribution is introduced in the immediate vicinity of the fiber matrix interface. In this case, heat conduction will be affected by an interfacial thermal barrier as the heat flows from the fiber into the matrix and vice-versa, as the transient temperature propagates throughout the specimen. It is this latter effect which is thought to be responsible for the effect of atmosphere on the thermal diffusivity shown in Fig. 4. Nevertheless, Eq. (2) was assumed to be valid for the calculation of the thermal conductivity of the fibers. Clearly, the validity of this assumption needs to be checked. With the development of the appropriate theory for transient heat conduction in uniaxial composites with heat flow parallel to the fiber

direction, the calculated values for the thermal conductivity and conductances can be refined further.

Removal of the carbon interfacial layer causes a significant decrease in the interfacial conductances as easily ascertained by comparison of Figs. 8a and 8b. This result would be expected due to the anticipated decrease in direct thermal contact between the fibers and the matrix. As for the as-received samples, as discussed earlier, the conductance values for the oxidized composite in vacuum represent the contact conductances. Puzzling, at least to these authors, is its strong positive temperature dependence. It appears difficult to explain on the basis of closure of the interfacial gap by thermal expansion. An answer possibly may be found by future research, such as the measurement of the temperature dependence of the frictional forces between the fibers and the matrix. Regardless of the details, the values for the solid conductances (in vacuum) are quite low, indicative of the lack of direct contact between the fibers and matrix.

For the oxidized samples, with the carbon interfacial layer removed, the differences between the conductances in helium and nitrogen and the conductance in vacuum represent the contribution by gaseous conductance. As indicated by Fig. 8b, this difference appears to be more or less independent of temperature. The width of the interfacial gap can be assumed to be equal to the original carbon layer thickness of  $3 \mu\text{m}$ . The mean free paths of nitrogen and helium at 300 C and 1 atm are approximately  $1.5 \times 10^{-7}$  m and  $4.3 \times 10^{-7}$  m resp., which yield corresponding values for the Knudsen number of 0.05 and 0.14. These values are between the Knudsen number of  $\ll 1$  and  $> 10$  for the continuum and molecular regimes. It is anticipated therefore that the observed values for the gaseous conductances will be

below the values calculated from the gaseous thermal conductivities and gap thickness. Again, at 300 C the gaseous conductivities for the nitrogen and helium are approximately 0.0422 and 0.246 W/m.K [28]. For a gap thickness of  $3 \times 10^{-6}$ m, these values for thermal conductivity yield values for the gaseous conductances of  $1.4 \times 10^4$  and  $8.2 \times 10^4$  W/m<sup>2</sup>K for nitrogen and helium, resp., which are higher than the observed values, as expected. Considering also that the conductance values can range from 0 to  $\infty$ , even an order of magnitude difference between calculated values and those inferred from the thermal conductivity data of composites is not unexpected.

In general, the results of this study indicate that in addition to the well known variables such as the volume fraction, distribution and values of the thermal conductivity of the components, the heat conduction behavior of composites also can be significantly affected by the existence of an interfacial thermal barrier. From a practical perspective this could have implications for the development and selection of composite materials which in service may be exposed to pressures other than atmospheric. This, in turn, implies that the heat conduction behavior of composites should be determined over the total range of pressure to which they may be subjected.

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This paper titled

**EFFECT OF FIBER ORIENTATION ON THE THERMAL  
CONDUCTIVITY OF A UNIAXIAL FIBER-REINFORCED  
COMPOSITE STRIP WITH INSULATED SIDES**

has been accepted for publication in  
**JOURNAL OF COMPOSITE MATERIALS**

This paper titled

**EFFECT OF HOT-ISOSTATIC-PRESSING ON THE EFFECTIVE  
THERMAL CONDUCTIVITY/DIFFUSIVITY AND INTERFACIAL  
THERMAL CONDUCTANCE OF UNIAXIAL SILICON CARBIDE  
FIBER-REINFORCED REACTION BONDED SILICON NITRIDE.**

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## **3.0**

### **EFFECT OF HOT-ISOSTATIC-PRESSING ON THE EFFECTIVE THERMAL CONDUCTIVITY/DIFFUSIVITY AND INTERFACIAL THERMAL CONDUCTANCE OF UNIAXIAL SILICON CARBIDE FIBER-REINFORCED REACTION BONDED SILICON NITRIDE.**

#### **3.1 ABSTRACT**

Hot-isostatic-pressing was found to increase the thermal diffusivity/conductivity of uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride matrix composites, as the result of the densification of the matrix, the increase in the grain size of the silicon carbide and the improved thermal contact between the fibers and the matrix. Transverse to the fiber direction the thermal diffusivity/conductivity was found to be a function of the surrounding gaseous atmosphere, as the accessibility of the gas phase to the fiber-matrix interface, which was facilitated by the existence of an interfacial gap due to the thermal expansion mismatch between the fibers and the matrix. The interfacial conductance was found to exhibit a strong positive temperature dependence as the result of the closure of the interfacial gap with increasing temperature.

## 3.2 INTRODUCTION

Fiber- or whisker-reinforced ceramic matrix composites offer considerable advantages over single phase ceramics in applications involving elevated temperatures in view of their improved fracture toughness, non-catastrophic failure mode and lower sensitivity to surface damage. The thermal conduction characteristics of ceramic matrix composites are critical when designing for service conditions involving transient or steady-state heat flow and the possibility of failure by thermal shock and fatigue.

Theoretical studies have shown that the effective thermal conductivity of a composite depends on the thermal conductivity values, the volume fraction and the distribution of the individual components within the composite [1-6]. Recently, a number of other studies have identified the role an interfacial thermal barrier can play in establishing the effective thermal conductivity of composites [7-10].

For a composite uniaxially reinforced with fibers of circular cross section, the effective thermal conductivity perpendicular to the fiber axes is [8]:

$$K_c = K_m \frac{\left[ \left\{ \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right\} V_f + \left\{ 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} \right]}{\left[ \left\{ 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} V_f + \left\{ 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right\} \right]} \quad (1)$$

where K and V represent the thermal conductivity and volume fraction, respectively, the subscripts c, m, and f refer to the composite, matrix and fiber phases, respectively, a is the fiber radius and  $h_i$  is the interfacial thermal conductance.

The effect of the magnitude of the interfacial conductance on the composite thermal conductivity is governed by its influence on the magnitude of the non-dimensional parameter  $K_f/ah_i$ . For  $h_i = \infty$  (i. e., perfect thermal contact) the expression for  $K_c$  reverts to the equation derived by Rayleigh [1]. For  $h_i = 0$ ,  $K_c$  corresponds to that of a porous composite, and is independent of the value of  $K_f$ . Note that for imperfect thermal contact ( $h_i$  is finite), the effective thermal conductivity is also a function of the size of the fibers.

Less than perfect thermal contact at the fiber-matrix interface in composites can arise from poor chemical or mechanical adhesion between the fiber and the matrix and from mismatches in their coefficients of thermal expansion. In particular, this latter effect can occur for composites in which the coefficient of thermal expansion of the fiber is greater than that of the matrix. On cooling from the fabrication temperature internal stresses and interfacial de-bonding are generated, especially for those composites with poor interfacial adherence. Even with perfect mechanical contact, an interfacial thermal barrier can arise from less than perfect thermal coupling between the dominant mechanism of heat transfer in the individual components of the composite.

For steady-state heat flow parallel to the fiber direction in a uniaxially reinforced composite the effective thermal conductivity is not affected by the existence of an interfacial thermal barrier and from the rule of mixtures is given by:

$$K_c = K_m \left[ 1 - V_f \left\{ 1 - \frac{K_f}{K_m} \right\} \right] \quad (2)$$

Earlier studies on the effect of an interfacial barrier on the effective thermal conductivity concentrated on a silicon carbide fiber-reinforced reaction-bonded silicon

nitride matrix composite [11,12]. The presence of an interfacial gap, which resulted from the thermal expansion mismatch between the fiber and the matrix, was found to play a major role. The presence of such a gap was inferred from the observation that transverse to the fiber direction the effective thermal diffusivity/conductivity was a function of the atmosphere, i.e., it was lower in vacuum than in nitrogen or helium. It was also noted that by the selective oxidation of the interfacial carbon layer, the thermal diffusivity/conductivity of the composite transverse to the fiber direction was lowered even further, with major differences in the values occurring in vacuum, nitrogen or helium.

From the perspective of the present study, it should be noted that the reaction-bonded silicon nitride matrix phase of these earlier studies was relatively porous with a mean value of porosity of about 38 %, but with localized regions, especially in the immediate vicinity of the fibers, with pore contents much higher than the average value. Such porosity levels are expected to govern the direct physical contact between the matrix phase and the fiber and thereby affect the value of the interfacial thermal conductance. Removal of the pore phase from the matrix by hot-isostatic-pressing would modify the thermal contact between the fiber and matrix and thereby affect the overall effective thermal conductivity of the composite. The purpose of the present paper is to report the results of such a study.

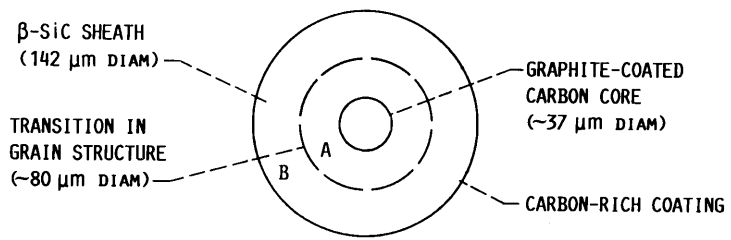
## 3.3 EXPERIMENTAL

### 3.3.1 *Material*

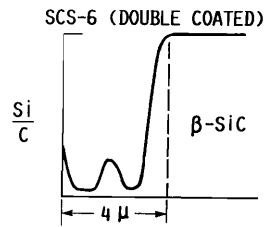
The starting materials for the composites of this study were double-coated SCS-6 SiC monofilaments made by the Textron Specialty Materials Division, Lowell, Massachusetts, USA, and high-purity silicon powder having an average particle size of  $0.3 \mu\text{m}$ , made by the Union Carbide Corporation of New York, New York, USA.

The SiC fibers, produced by chemical vapor deposition of methyl-trichlorosilane onto a heated carbon substrate, have a complex microstructure and can be regarded as microcomposites in themselves. A schematic diagram of the cross section of the fiber is shown in Figure 1a. The fiber consists essentially of a SiC sheath with an outer diameter of  $142 \mu\text{m}$  surrounding a pyrolytic graphite coated carbon core with diameter of  $37 \mu\text{m}$ . The sheath consists entirely of columnar  $\beta$ -SiC grains and contains two zones; the inner zone, referred to as A in Figure 1a, contains carbon-rich SiC and the outer zone, referred to as B, is essentially stoichiometric SiC. The outer surface of the SiC sheath contains two layers of a carbon-rich coating, for which the chemical composition as a function of thickness is shown schematically in Figure 1b.

The composites were fabricated by a three-step process. In the first step, SiC fiber mats and silicon cloth were consolidated using two different polymer fugitive binders - one polymer for maintaining proper spacing between the fibers in the fiber mat and the other polymer for preparing pliable silicon cloth. The volume fraction of fibers in the final composite was controlled by either varying the thickness of the silicon cloth or by changing the spacing between fibers in the mat. In the second step, alternate layers of



COATING COMPOSITION



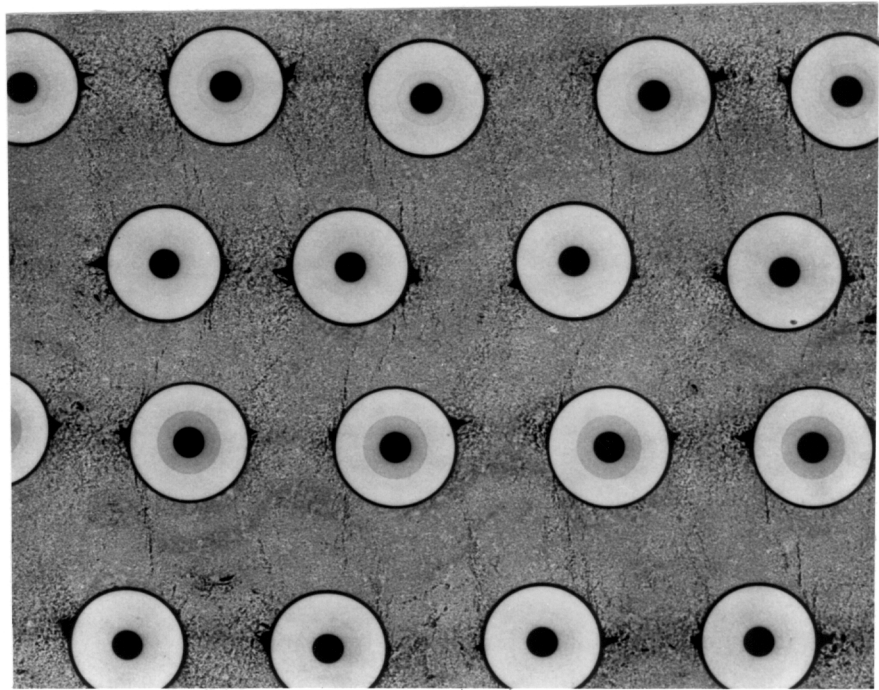
**Fig. 1:** Schematic of SiC fiber showing the cross section and composition profile of carbon coating.

SiC fiber mats and silicon cloth were stacked in a metal die and pressed in a vacuum hot press under an applied stress ranging from 27 to 2000 MPa for up to 1 hour in the temperature range from 600 to 1000 C. In the third step, the consolidated SiC/Si preforms were heat-treated in a high-purity (99.99%) nitrogen environment at temperatures ranging from 1000 to 1400 C for up to 100 hours to convert them to their final form. The typical dimensions of the as-nitrided composite panels were 150 by 50 by 2.2 mm. Hot-isostatic-pressing of the as-nitrided composites was carried out in an Argon atmosphere at a pressure of 138 MPa and a temperature of 1850 C for a period of 1 hour. The density of the as-nitrided composite was found to be 2.17 g/cc, whereas the density of the HIP'd composite was measured to be 3.05 g/cc.

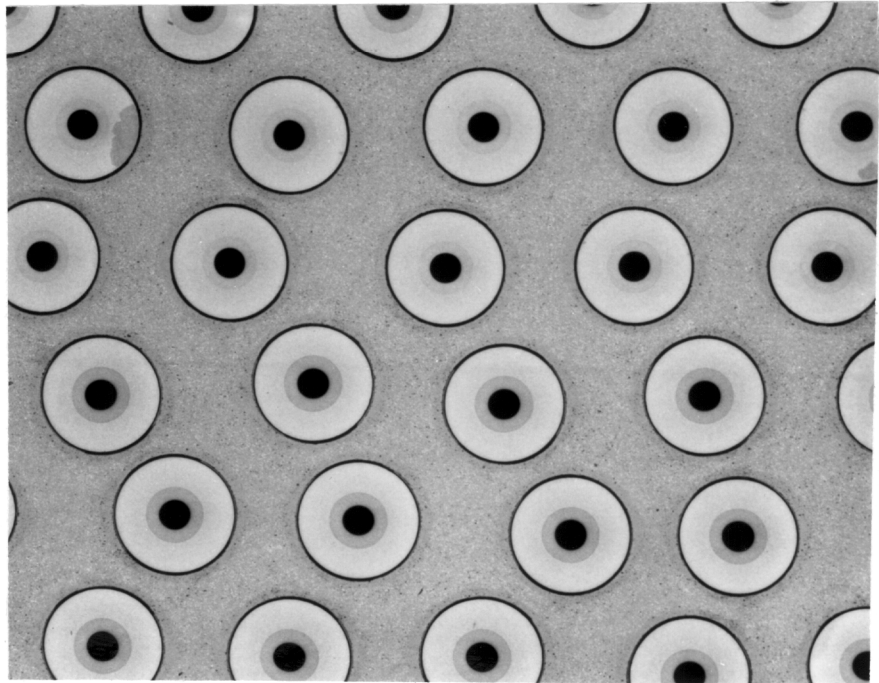
Figures 2a and b show representative photomicrographs of polished cross sections of as-nitrided and HIP'd composite specimens, respectively. The fiber volume fraction was approximately 32 % in the as-nitrided composite and 42 vol. % in the HIP'd composite. The matrix phase of the as-nitrided composite contained about 38 % porosity, whereas in the HIP'd composite the matrix phase was essentially pore-free. The carbon core, the surface coating and the two silicon carbide zones in the fibers are clearly evident.

Figures 3a and 3b show SEM-micrographs of the regions in the immediate vicinity of a fiber in an as-nitrided and HIP'd composite, respectively. In the as-nitrided composite the highly porous regions in the matrix phase immediately adjacent to the fiber is clearly evident. In the HIP'd composite this region is absent.

For purposes of comparison, samples were also made of the as-nitrided and HIP'd matrix without fibers, following identical fabrication techniques used for preparation of the composite samples.

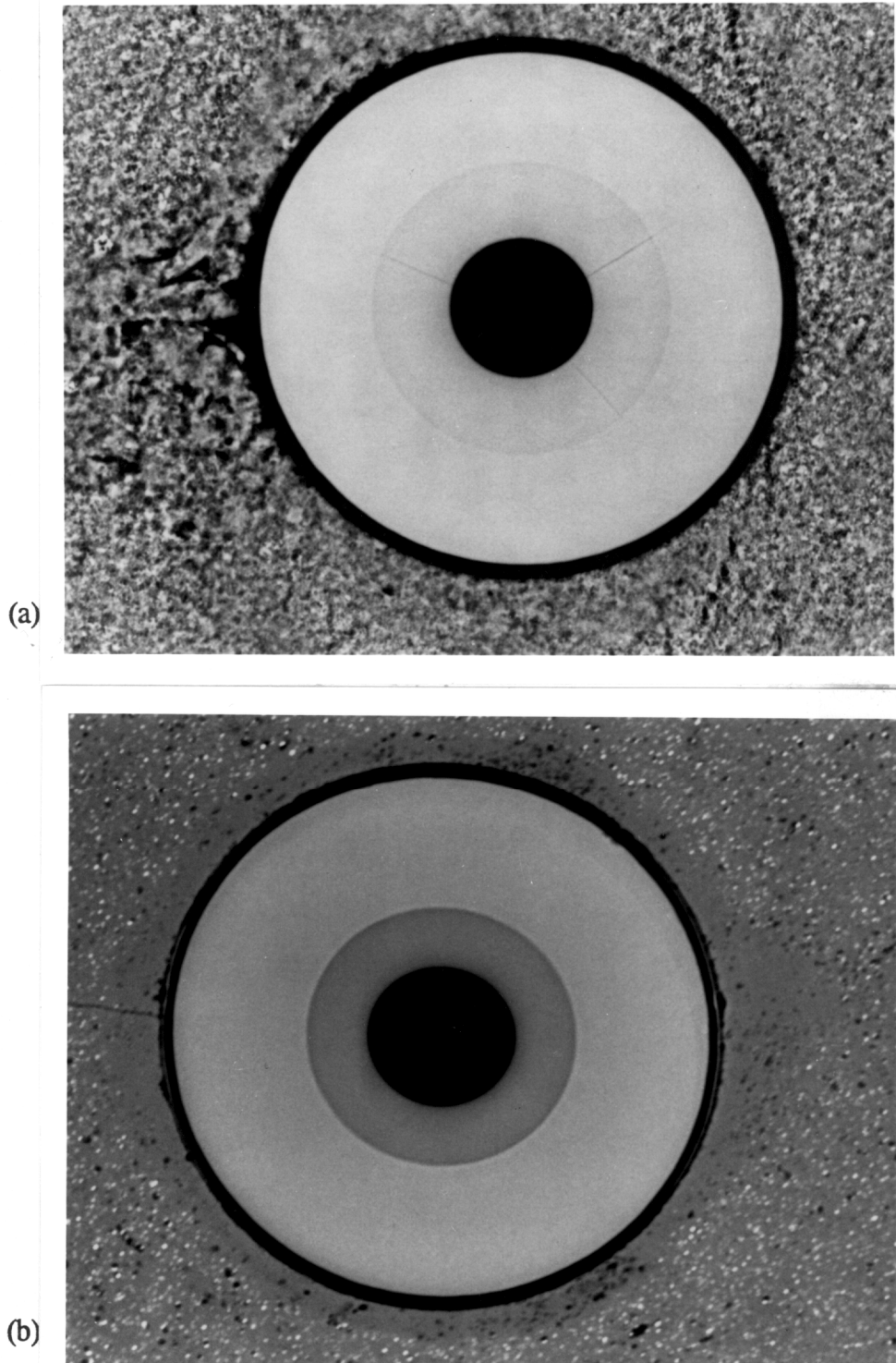


(a)



(b)

**Fig. 2:** Optical micrograph of a cross section of uniaxially SiC fiber-reinforced reaction-bonded silicon nitride transverse to the fiber direction; (a) as-nitrided and (b) HIP'd.



**Fig. 3:** Scanning electron micrograph of polished section in immediate vicinity of fiber: (a) as-nitrided and (b) HIP'd.

### **3.3.2 *Determination of thermophysical properties.***

The effective thermal diffusivity was measured by the laser-flash technique [13,14]. The specimens, in the form of square platelets with dimensions of approx. 8 by 8 by 2 mm, were cut from the larger as-nitrided and HIP'd blocks. A glass-Nd laser was used as the flash source. The specimens were lightly coated with colloidal carbon to promote absorption and prevent direct transmission of the laser pulse. An InSb IR-detector was used to monitor the transient temperature rise of the specimen up to temperatures of 700 C and a Si-photodiode detector was used for temperatures above 700 C. The detectors viewed a circular area having a diameter of approximately 5 mm. The thermal diffusivity up to 1000 C was measured at intervals of about 100 C in helium and nitrogen at atmospheric pressure and in vacuum at a pressure of about 0.13 Pa.

The specific heat was measured by differential scanning calorimetry from room temperature to 600 C using sapphire as the standard. Data from 600 to 1000 C were obtained by extrapolation guided by general trends presented in the literature.

The values for the thermal conductivity were calculated by multiplying the data for the thermal diffusivity with the product of the density and the specific heat. In this manner, values for the thermal conductivity were established from room temperature to 1000 C for the as-nitrided and HIP'd matrix phase and for the composites parallel and perpendicular to the fiber direction.

The coefficients of linear thermal expansion for the matrix and composites perpendicular to the fiber direction were found to be equal, with a mean value of  $3.4 \times 10^{-6}/\text{C}$  over the range from room temperature to 1200 C. For the composite parallel to the fiber direction the corresponding value for the coefficient of thermal

expansion was  $4.1 \times 10^{-6}/\text{C}$ . These values were used during the calculation of the thermal diffusivity to adjust for the increase in sample dimension with increasing temperature. These values were also used in the calculation of the thermal conductivity to adjust for the decrease in density with increasing temperature. The coefficient of thermal expansion of the fibers was measured to be  $4.58 \times 10^{-6}/\text{C}$ .

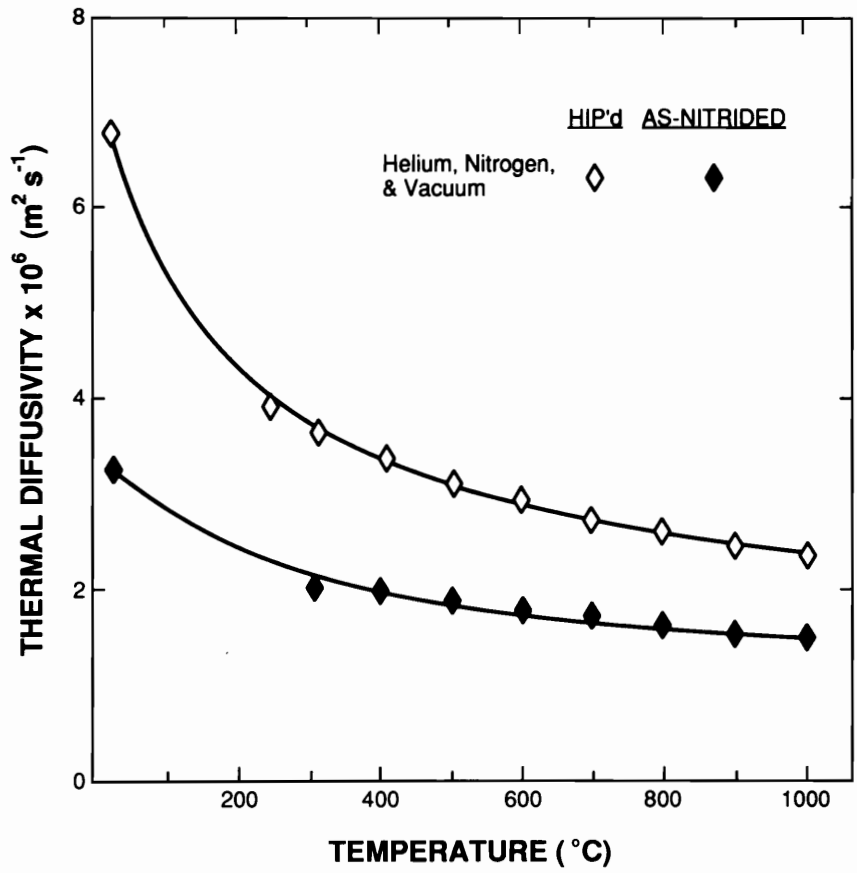
### **3.3.3 *Calculation of the interfacial conductance.***

The value for the interfacial conductance was calculated based on a number of simplifying assumptions. The silicon nitride matrix and the silicon carbide of the fibers were assumed to exhibit isotropic thermal conductivity. The fibers themselves were considered to be a composite consisting of an outer silicon carbide sheath and a carbon inner core. This carbon core, in view of its preferred crystallographic orientation, was assumed to exhibit anisotropic thermal conductivity. The thermal conductivity of the silicon carbide phase in the fibers parallel to the fiber direction was calculated from the thermal conductivity of the matrix, the thermal conductivity of the composite for heat flow parallel to the fiber direction and the thermal conductivity of the core using the rule of mixtures for a three-phase composite. The thermal conductivity of the carbon core was inferred from the correlation between Young's modulus and the thermal conductivity established by Nysten et al [15]. For a value of Young's modulus for the carbon core of 41 GPa, this led to a value of the thermal conductivity of the carbon core of 29 W/m.K. This low value for the thermal conductivity, which is well below the value for many other carbon fibers, indicates that the crystal structure of the fiber core is highly defective. For this reason, the thermal conductivity of the core was assumed to be independent of temperature as the phonon mean-free-path was thought to be primarily

governed by the defect structure. It should be noted that this assumption introduces little error in the final results of the thermal conductivity of the fibers as the core represents only 6.8 % volume fraction of the fiber and an even smaller value of the composite as a whole. The transverse thermal conductivity of the silicon carbide in the fibers was assumed equal to the thermal conductivity of the fibers parallel to their axis. The carbon core within the fibers, in view of its highly preferred crystallographic orientation, is expected to exhibit highly anisotropic thermal conductivity [16-18]. For this reason, transverse to the core the thermal conductivity is expected to be quite low compared to the value parallel to the core and for simplicity was assumed to be zero. Again, as pointed out earlier, this assumption is not expected to introduce a major error, as the core represents a small volume fraction of the fibers or composite as a whole. The effective thermal conductivity of the fibers transverse to their axis was then obtained from equation 1 by using the appropriate porosity correction. From the resulting thermal conductivity data for the matrix, fibers and the composite sample with heat flow transverse to the fiber direction, the interfacial thermal conductance was then calculated by means of equation 1.

### **3.4 RESULTS, DISCUSSION AND CONCLUSIONS**

Figure 4 shows the experimental data for the thermal diffusivity of the as-nitrided and HIP'd matrix phases in atmospheres of helium, nitrogen and vacuum. Clearly, HIP'ing caused a significant increase in the thermal diffusivity due to the elimination of the pore phase. Within the experimental scatter and possible specimen-to-specimen variation, the differences in gaseous environments appeared to have no significant effect on the thermal diffusivity of either matrix. In fact, the experimental data in the three gaseous



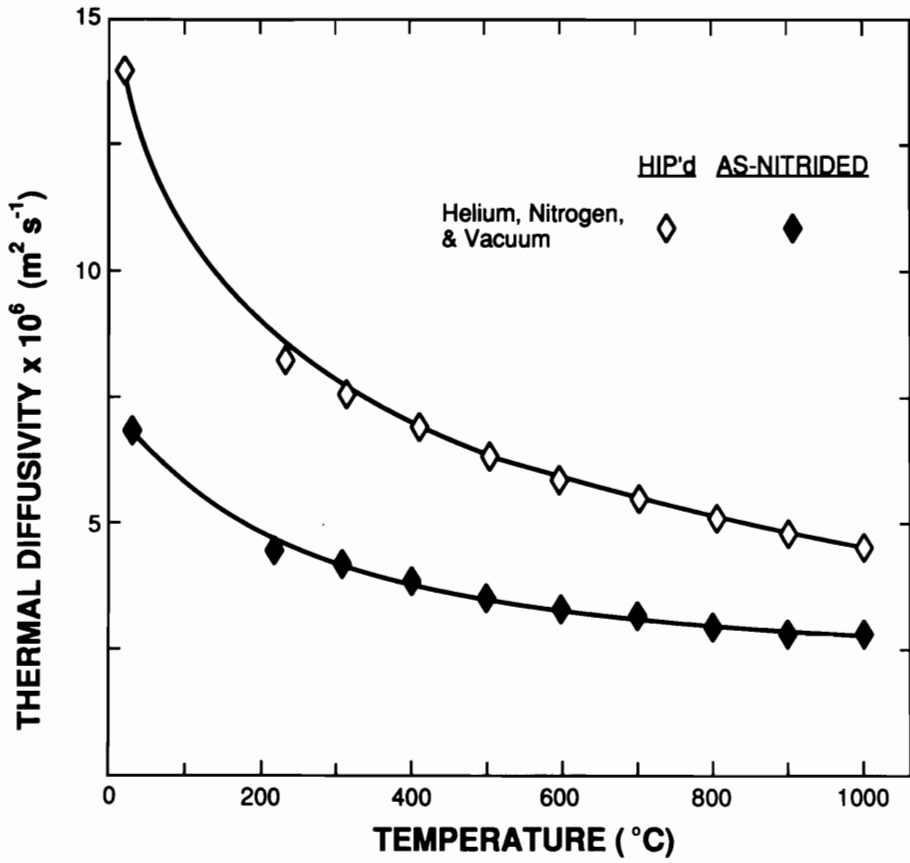
**Fig. 4:** Thermal diffusivity of as-nitrided and HIP'd reaction-bonded silicon nitride matrix phases in helium, nitrogen and vacuum.

atmospheres were so close, they could not be plotted separately. The relative temperature dependence of the data, shown in figure 4, is typical for dielectric materials in which phonon heat transfer is the primary mechanism of heat conduction.

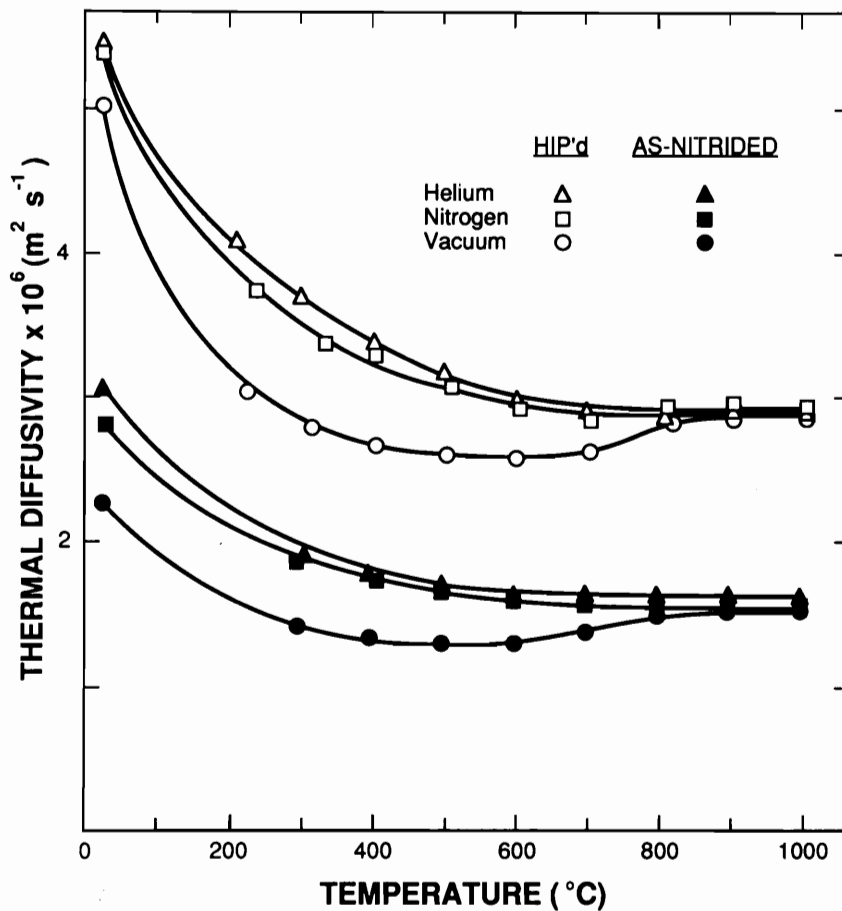
Figure 5 shows the data for the thermal diffusivity of as-nitrided and HIP'd composite samples for heat flow parallel to the fiber direction in the presence of helium, nitrogen and vacuum atmospheres. Again, HIP'ing caused a significant increase in the thermal diffusivity, attributable to the densification of the matrix and, as to be discussed, an increase in the thermal conductivity of the fibers.

Comparison of figures 4 and 5 shows that the presence of the fibers increases the effective thermal diffusivity by about a factor of two over the corresponding value for the matrix. This implies that the thermal conductivity of the fibers significantly exceeds the value for the matrix. These values will be presented shortly.

Figure 6 shows the data for the effective thermal diffusivity of as-nitrided and HIP'd composite samples transverse to the fiber direction in helium, nitrogen and vacuum. As expected, HIP'ing increased the thermal diffusivity for all environmental conditions. Also note that the thermal diffusivity for the as-nitrided and HIP'd samples in the different atmospheres exhibits significant differences. This observation came as quite a surprise, at least to these authors. In order to find a plausible explanation for this effect it should be noted that the coefficient of thermal expansion of the silicon carbide fiber is higher than that for the matrix. This implies that on cooling from the nitriding temperature tensile internal stresses are generated across the interface, which, for weakly bonded interfaces, can lead to interfacial cracking. Assuming that such cracks are uniform around the interface, their width at room temperature is of the order of  $0.1 \mu\text{m}$ ,



**Fig. 5:** Thermal diffusivity of as-nitrided and HIP'd SiC fiber reinforced reaction-bonded silicon nitride parallel to fiber direction in helium, nitrogen and vacuum.



**Fig. 6:** Thermal diffusivity of as-nitrided and HIP'd SiC fiber reinforced reaction bonded silicon nitride transverse to the fiber direction in helium, nitrogen and vacuum.

as calculated from the differences in the coefficients of thermal expansion of the fiber and the matrix, the fiber size and the range of temperature over which the composite is cooled. Such a crack width is sufficient for the environmental atmosphere to enter the interface and contribute to the conduction of heat across the interface. Raising the temperature of the sample will result in a decrease in the width of the interfacial crack. This, in turn, will result in improved direct physical contact and expulsion of the gas phase from the interface as the temperature approaches the composite's processing temperature. This is in agreement with the observation that the thermal diffusivity data in vacuum are well below the corresponding values in helium and nitrogen at the low temperatures, but are almost equal at temperatures from about 800 to 1000 C. Direct evidence for the existence of such a crack by scanning-electron-microscopy of fracture surfaces could not be obtained. However, parallel studies of mechanical behavior showed that interfacial fracture usually occurred within the carbon coating on the SiC fibers and occasionally at the interface between the SiC and the carbon layer, but not at the interface between the carbon coating and the silicon nitride. Of course, the effect of the gas phase on the thermal diffusivity represents indirect evidence for the existence of an interfacial gap.

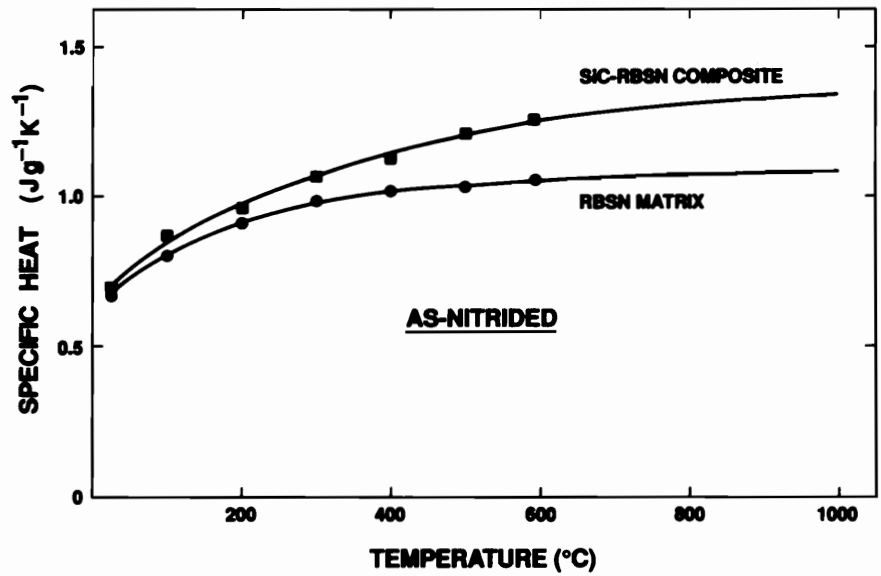
The above unexpected finding suggests that for the as-nitrided and/or HIP'd composites the thermal expansion crack is expected to play a major role in establishing the effective thermal conductivity transverse to the fiber direction. Figure 6 also indicates that for any given processing history, the values of the thermal diffusivity are highest in a helium atmosphere, followed by nitrogen and are the lowest in vacuum. This ranking is in accordance with the ranking of the thermal conductivity of helium, nitrogen and vacuum, providing indirect evidence for the hypothesis that the gaseous atmosphere can enter the interfacial gap and thereby contribute to the heat transfer between the fiber

and matrix. A more detailed discussion of the nature of the heat transfer across gaps will be presented as part of the discussion of the values for the interfacial thermal conductance.

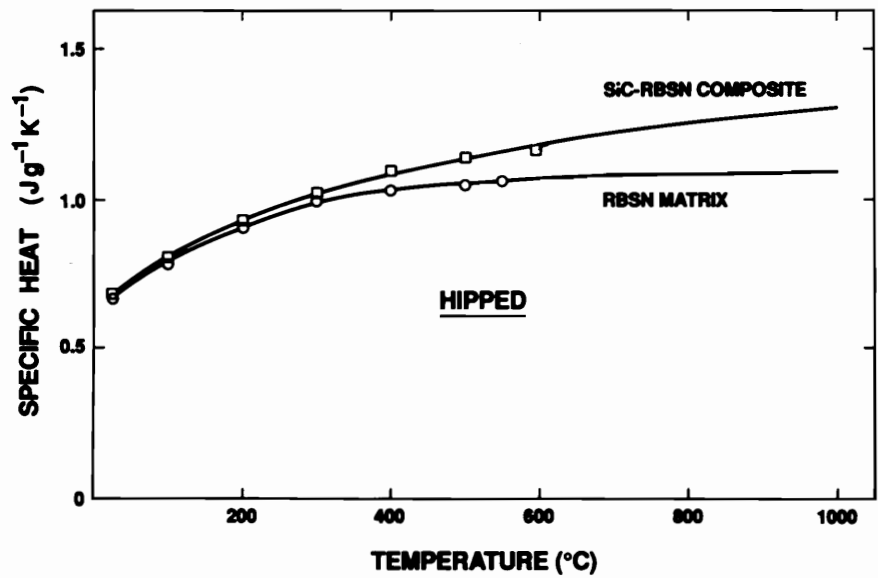
Figures 7a and 7b show the experimental and extrapolated values for the specific heat of the as-nitrided and HIP'd silicon nitride matrix and the silicon carbide-silicon nitride composite, respectively. The magnitude of the specific heat for the matrix phase appears to be unaffected within the accuracy of the experimental method, estimated to be about 3 %. The HIP'ing, however, appears to have decreased the specific heat of the composite samples. No information is available to explain this effect.

Figure 8 shows the calculated values for the thermal conductivity of the as-nitrided and HIP'd matrix samples in helium, nitrogen and vacuum. These data reflect the same relative differences as those found for the thermal diffusivity, with the exception that because of the positive temperature dependence of the specific heat, the temperature dependence of the thermal conductivity is less negative than for the thermal diffusivity.

Figure 9 shows the calculated values for the thermal conductivity of the composite samples for heat flow parallel to the fiber direction. Again, these data show the same relative values as found for the thermal diffusivity, with the same exception, that the relative temperature dependence of the thermal diffusivity is more negative than the corresponding dependence of the thermal conductivity. The data of figure 9 also indicate that HIP'ing appears to have increased the relative negative temperature dependence of the thermal conductivity compared to the as-nitrided composite. Calculation of the fiber thermal conductivity from the thermal conductivity data of the matrix and the composite for heat flow parallel to the fiber direction, using equation 2,

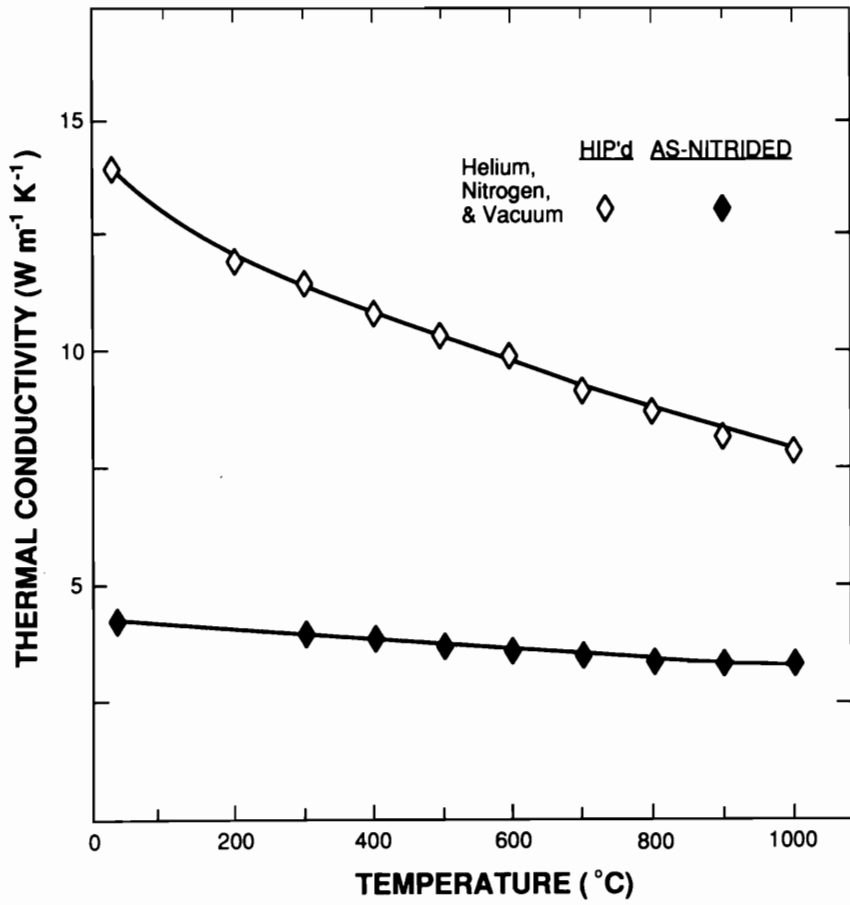


(a)

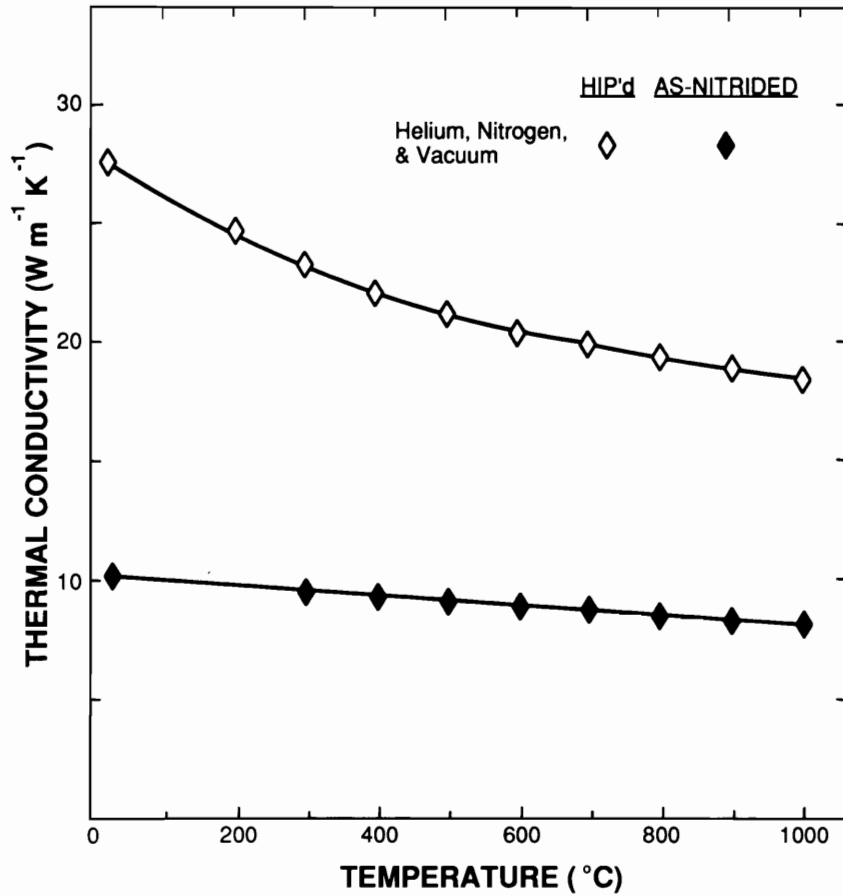


(b)

**Fig. 7:** Experimental and extrapolated data for the specific heat: (a) as-nitrided and HIP'd silicon nitride matrix and (b) SiC fiber reinforced silicon nitride.



**Fig. 8:** Calculated values for the thermal conductivity of the as-nitrided and HIP'd silicon nitride matrix in helium, nitrogen and vacuum.

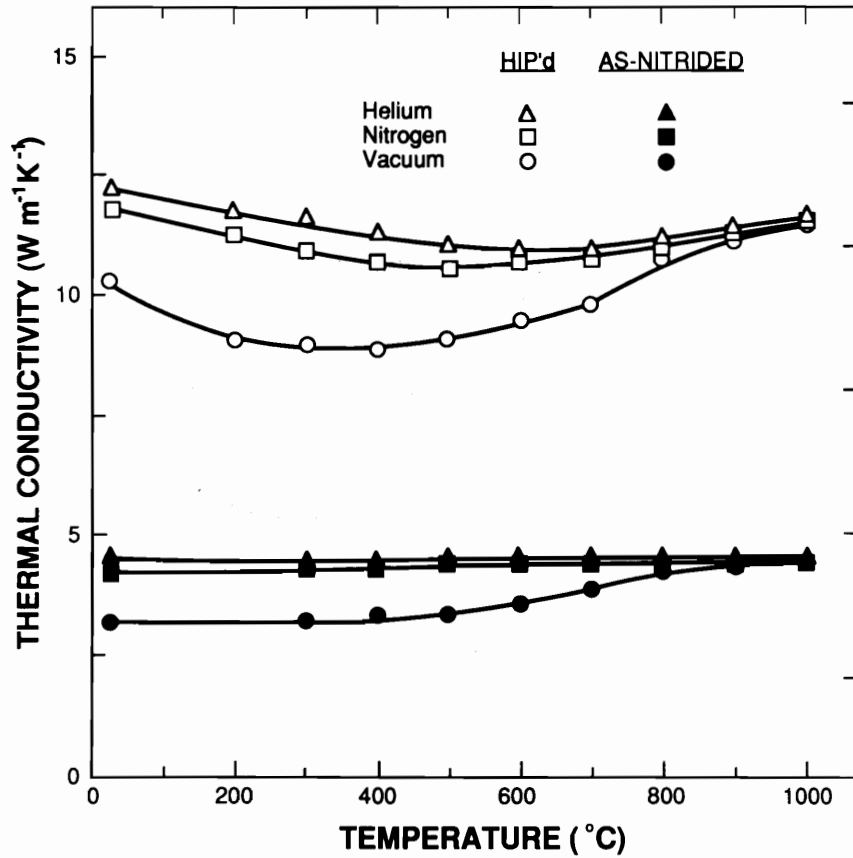


**Fig. 9:** Calculated values for the thermal conductivity of SiC fiber reinforced reaction-bonded silicon nitride parallel to the fiber direction in helium, nitrogen and vacuum.

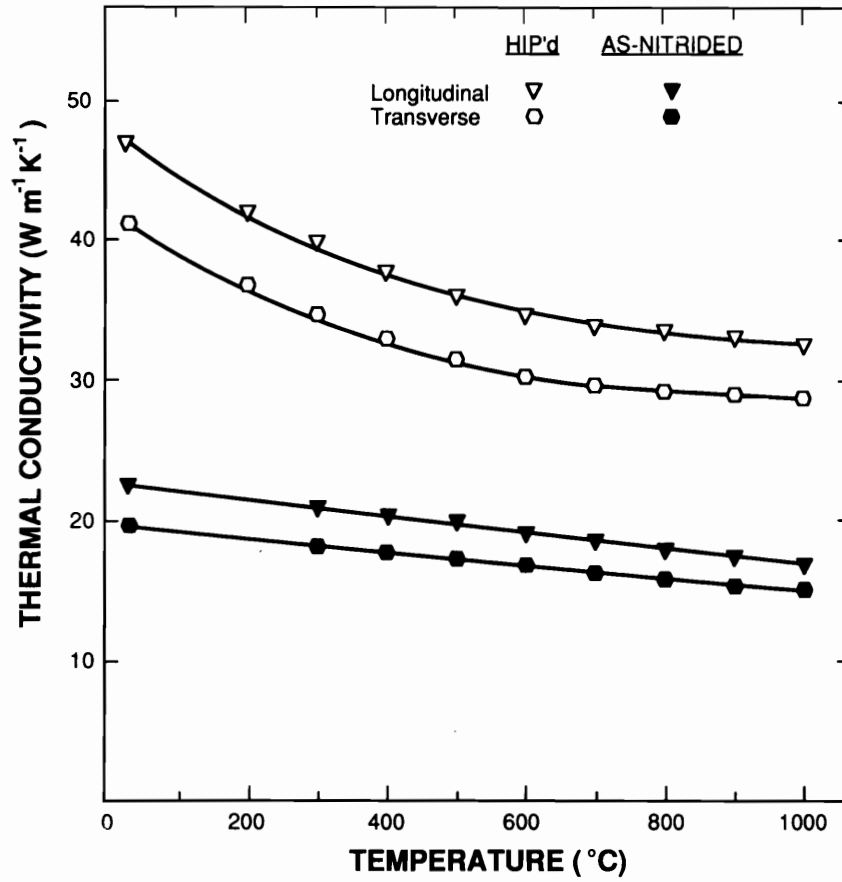
showed that HIP'ing also increased the thermal conductivity of the fibers significantly. Such an increase most likely is the result of the annealing of structural defects, introduced in the silicon carbide during chemical-vapor-deposition, at the much higher temperature of the HIP'ing process. As a result the temperature dependence of the thermal conductivity of the HIP'd silicon carbide fibers is expected to be more controlled by the negative temperature dependence due to phonon-phonon interactions, rather than the athermal effects associated with phonon-defect interactions. In turn, this is reflected in the relative temperature dependence of the composite samples.

Figure 10 shows the calculated values for the thermal conductivity of the composite samples in the as-nitrided and HIP'd composite samples for heat transfer transverse to the fiber direction in helium, nitrogen and vacuum. These data reflect the relative differences in the data for the thermal diffusivity shown in fig. 6, with the exception that the relative temperature dependence of the thermal conductivity is less negative than the corresponding dependence for the thermal diffusivity for the same reason stated earlier.

Figure 11 show the values for the thermal conductivity of the fibers parallel and transverse to the fiber direction, calculated in the manner described earlier. The thermal conductivity transverse to the fiber direction is lower than the corresponding value parallel to the fiber direction, because the contribution of the carbon core (with thermal conductivity assumed to be equal to zero) will be relatively greater transverse to the fiber direction than in the parallel direction. This is easily ascertained by a comparison of equation 1 ( with  $h_i = 0$  ) and equation 2. The transverse conductivity is lower than the parallel conductivity by about 13 %. The data of figure 11 also indicate that the HIP'ing operation has led to a significant increase of the thermal conductivity of the fibers, of as much as a factor of two at room temperature. Transmission electron



**Fig. 10:** Calculated values for the thermal conductivity of SiC fiber reinforced reaction-bonded silicon nitride transverse to the fiber direction in helium, nitrogen and vacuum.

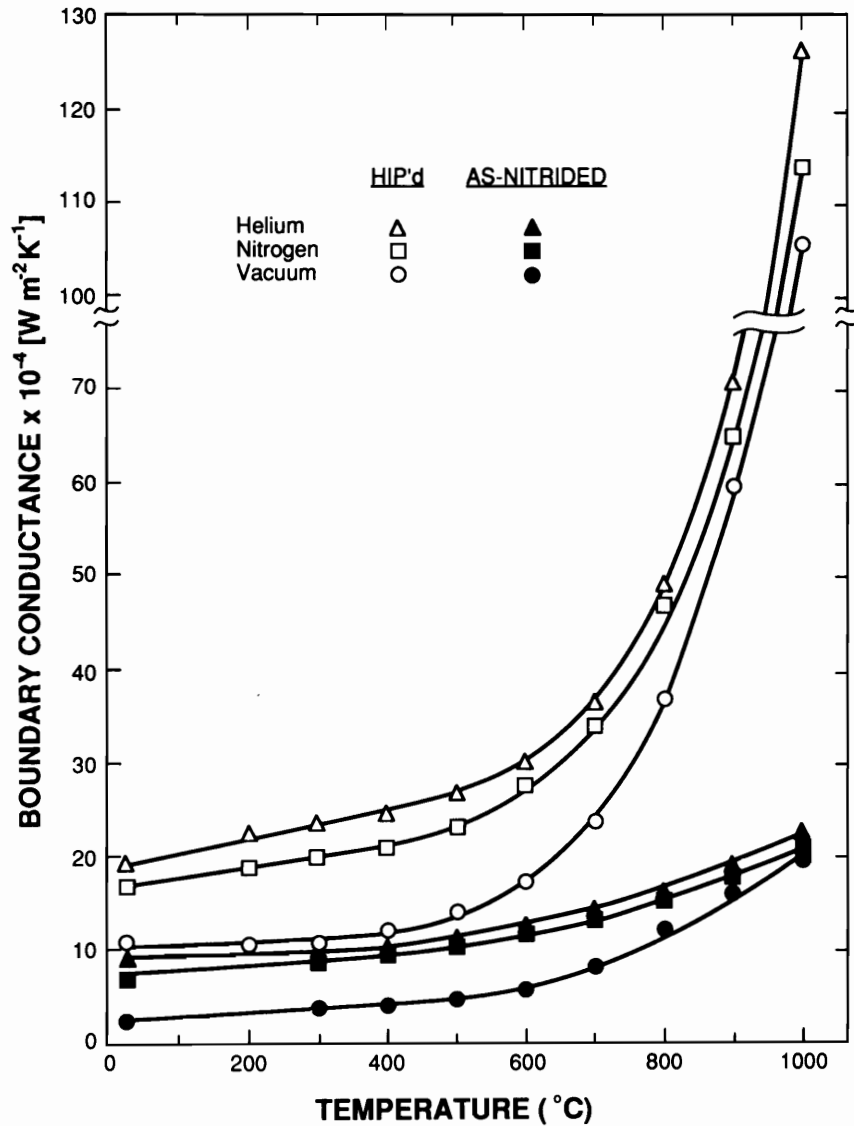


**Fig. 11:** Calculated values for the longitudinal and transverse thermal conductivity of SiC fibers prior to and following HIP,ing in helium, nitrogen and vacuum.

microscopy showed that this increase can be attributed to the extensive growth of crystallites, rather than to a decrease in density of the stacking faults. The data also confirm the earlier speculation that the relative negative temperature dependence of the thermal conductivity of the SiC fibers in the HIP'd composite is greater than in the as-nitrided composite, which represents evidence for a decrease in the density of lattice defects, such as vacancies. Nevertheless, whether in the as-nitrided or HIP'd composites, the magnitude of the thermal conductivity of the SiC fibers is still relatively low, compared to sintered SiC with values at room temperature near 100 W/m.K, BeO-doped SiC with a value near 200 W/m.K or a high-purity single crystal with a value approaching 500 W/m.K [19,20]. Some of the differences in the data shown in figure 11 also reflect the differences in the experimental thermal diffusivity values, possibly related to transverse transient heat flow, as discussed earlier.

Figure 12 shows the values for the interfacial thermal conductance, calculated using equation 1 from the data for the thermal conductivity of the matrix, fibers and the composite for heat flow transverse to the fiber direction. For simplicity, the pore phase in the intermediate vicinity of the fiber was assumed to be part of the interfacial conductance, so that the calculation of the conductance could be based on the value of the conductivity of the homogeneous matrix.

In comparing the data of figure 12, it should be noted that the interfacial conductance is the sum of the conductances due to heat transfer as the result of direct physical contact across the interface, heat transfer by gaseous conduction and heat transfer by radiation at those positions where no direct contact across the interface exists, expressed by [21]:



**Fig. 12:** Calculated values for the interfacial conductances in as-nitrided and HIP'd SiC fiber reinforced silicon nitride composites for heat flow transverse to the fiber direction in helium, nitrogen and vacuum.

$$h_i = h_c + h_g + h_r \quad (3)$$

where  $h_c$ ,  $h_g$  and  $h_r$  are the contact, gaseous and radiative conductances, respectively.

The radiative conductance can be derived to be[11]:

$$h_r = \left[ \frac{4 \epsilon}{(2 - \epsilon)} \right] \sigma n^2 T^3 \quad (4)$$

where  $\epsilon$  is the emissivity of the two surfaces (assumed to be equal),  $\sigma$  is the Stefan-Boltzmann constant,  $n$  is the refractive index of the medium within the gap and  $T$  is the absolute temperature. Substitution of reasonable values for  $\epsilon$  and  $n$  into equation 4 indicates that over the temperature range of this study the radiative conductance is negligible compared to the magnitude of the values shown in figure 12.

The contact conductance,  $h_c$ , is a strong function of the roughness of the two surfaces in contact and is expected to vary from one situation to another [22]. Since the degree of contact between the fibers and matrix of the composites of this study is not easily established, no independent estimate of the contact conductance can be made. Furthermore, as gaseous conduction will occur only at those interfacial regions with no direct physical contact, the processes of contact and gaseous interfacial conduction are expected to be competitive.

The gaseous conductance,  $h_g$ , is a function of the ratio of the mean-free path ( $\lambda$ ) of the gaseous species and the width ( $d$ ) of the interfacial gap, defined by the Knudsen number:

$$N_{Kn} = \frac{\lambda}{d} \quad (5)$$

For  $N_{Kn} \ll 1$ , referred to as the "continuum regime", the gaseous heat transfer is controlled by the collisions between the gaseous species. In this regime, the gaseous conductance is:

$$h_g = \frac{K}{d} \quad (6)$$

where  $K$  is the thermal conductivity of the gas. In the continuum regime,  $h_g$  is independent of pressure and inversely proportional to the gap thickness.

For  $N_{Kn} > 10$ , inter-atomic or -molecular collisions are rare and the conductance is controlled by the energy exchange during the collisions of the gaseous species with the surfaces of the gap. In this regime, referred to as the "free molecular regime", the conductance is given by [22]:

$$h_g = \left[ \frac{c_p \mu}{\lambda} \right] \left[ \frac{(\gamma + 1)}{\gamma} \right] \left[ \frac{(2 - c_1)}{c_1} + \frac{(2 - c_2)}{c_2} \right]^{-1} \quad (7)$$

where  $c$  and  $\mu$  are the specific heat and viscosity of the gas phase,  $C_1$  and  $C_2$  are the thermal accommodation coefficients for each surface,  $\gamma$  is the ratio of the specific heats at constant pressure and constant volume and  $\lambda$  is the mean-free-path of the gas. The thermal accommodation coefficient represents the efficiency of energy exchange during the collision between the gap surfaces and the gaseous atomic or molecular species.

In the free molecular regime, the gaseous conductance,  $h_g$ , as expressed by equation 6, is independent of the gap thickness and is directly proportional to pressure. For the mean gap thickness for the present samples of the order of  $0.1 \mu\text{m}$ , and values for the mean-free-path at the pressures of this study [23,24], the gaseous conductance is expected to be governed by criteria for the free molecular regime.

Because no quantitative information is available on any measure of direct physical contact across the interface or on the magnitude of the thermal accommodation coefficients, independent quantitative estimates of the contact and gaseous conductances cannot be given at this time. For this reason, when discussing the data shown in figure 12, emphasis will be placed on a comparison of the data. It is of interest to note, however, that the conductance values shown in figure 12, compare favorably with those found in experimental studies of surfaces in contact [25,26].

The data of figure 12 indicate that the nature of the gaseous phase has a significant effect on the magnitude of the interfacial conductance. Because of the almost complete absence of a gaseous phase under vacuum conditions, it appears reasonable to conclude that the conductance in vacuum represents the contact conductance due to direct physical contact across the interface. The difference between the conductance values in vacuum and the total conductance in helium or nitrogen must be attributed to the contribution of the gaseous conductance. The relative values of the conductances in helium and nitrogen are in accordance with the differences in the mean velocity of the helium atoms and the nitrogen atoms, inferred from the kinetic theory of gases. It should be noted that the actual values for the accommodation coefficients for the helium and nitrogen could well differ significantly, so that no quantitative measure of the relative differences in the gaseous conductances for helium and nitrogen can be made at this time.

Of particular interest is the finding, as seen in figure 12, that the conductance values for the as-nitrided and HIP'd samples increase with temperature. As discussed earlier, most likely this effect can be attributed to the closure of the thermal expansion crack, due to the thermal expansion mismatch between the fiber and matrix, as the composite is heated again towards the temperature at which it was fabricated. Related to this effect is the finding that the relative difference between the conductances in vacuum and helium or nitrogen decreases with increasing temperature. This is expected, as with increasing temperature and associated tendency for crack closure, increased physical contact will occur between the fiber and matrix with a corresponding decrease in the opportunity for gaseous heat transfer. The conclusion that the strong positive temperature dependence of the conductance is the result of increased physical contact across the interfacial thermal expansion crack is supported by the findings, to be published elsewhere, that the interfacial shear stress required to cause sliding between the fiber and matrix also increases with temperature.

The HIP'ing operation caused a significant increase in the magnitude as well as the temperature dependence of the conductance. A number of reasons, necessarily qualitative, can be given for this effect. The primary effect of the HIP'ing operation was the densification of the matrix. As a result, for the as-made composites following HIP'ing, the fiber is in far greater degree of direct physical contact with the matrix than was the case for the highly porous matrix in the as-nitrided material. For the porous matrix much of the heat transfer between the fiber and matrix would require gaseous conduction through the pores at the fiber-matrix interface. This contribution, however, is expected to be minor, as, in general, the effective thermal conductivity of a gas phase in a pore, whether in the free molecular or continuum regime, is much less than the net thermal conductivity of the direct solid- to-solid contact. As a very first approximation, a

pore phase will reduce the relative area of direct physical contact at the fiber-matrix interface by an amount equal to the volume fraction porosity. With a pore phase content of approximately 37 % for the matrix phase of the as-nitrided composite, elimination of the pore phase would cause an increase in the area of direct interfacial contact by about 50%. This estimate, however, assumes that for the porous matrix, perfect contact exists between the solid fraction of the matrix and the fibers. In other words, it assumes that the morphology of the solid part of the matrix conforms exactly to the morphology of the fiber surface. The nitriding reaction, however, was not carried out at a pressure at which the matrix could be compacted against the fiber. Therefore, any direct physical contact between the fiber and matrix most likely occurs at the outer points or edges of the individual grains of the matrix. If so, the fractional area of direct interfacial contact is expected to be a great deal less than the volume fraction of solid within the matrix phase. HIP'ing, however, will deform the grains to greatly increase the direct contact between the fiber and matrix with a corresponding large increase in the interfacial conductance. It was hoped that evidence in the form of fractographs could be presented which would support this hypothesis. Unfortunately, for the as-nitrided and HIP'd composite samples fracture always occurred at the interface between the silicon carbide and the carbon coating or within the carbon coating rather than at the carbon-silicon nitride interface. Looking at this from another angle, the overall interfacial thermal conductances represent the sum effects of the silicon carbide-carbon interface, the carbon-matrix interface and possible effects within the carbon coating itself. The HIP'ing operation is expected to have primarily affected the conductance of the matrix-carbon coating interface.

In general, the observations of this study indicate the very powerful role interfaces can play in the effective thermal conductivity of composites. Especially seen in the light of the current technical development of tailoring interfaces with fiber coatings in order to

optimize interfacial mechanical properties and corresponding fracture toughness of composites, significant interfacial thermal effects should be expected and accounted for. The results of this paper also clearly indicate that the measurement of the thermal diffusivity or conductivity can be used as a qualitative non-destructive tool to determine the integrity of the fiber/matrix interface and to monitor microstructural changes occurring in the fibers, matrix and interface during fabrication or during service.

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**This paper titled**

**ROLE OF INTERFACIAL CARBON LAYER IN THE THERMAL  
DIFFUSIVITY OF SILICON CARBIDE FIBER REINFORCED  
REACTION BONDED SILICON NITRIDE MATRIX COMPOSITES**

**has been accepted for publication in  
JOURNAL OF AMERICAN CERAMIC SOCIETY**

## 4.0

### **ROLE OF INTERFACIAL CARBON LAYER IN THE THERMAL DIFFUSIVITY OF SILICON CARBIDE FIBER REINFORCED REACTION BONDED SILICON NITRIDE MATRIX COMPOSITES**

#### **4.1 ABSTRACT**

The role of an interfacial carbon coating in the heat conduction behavior of a uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride was investigated. For such a composite without an interfacial carbon coating the values for the thermal conductivity transverse to the fiber direction agreed very well with the values calculated from composite theory using experimental data parallel to the fiber direction, regardless of the ambient atmosphere. However, for a composite made with carbon-coated fibers the experimental values for the thermal conductivity transverse to the fiber direction in vacuum at room temperature were about a factor of two lower than those calculated from composite theory assuming perfect interfacial thermal contact. This discrepancy was attributed to the formation of an interfacial gap, resulting from the thermal expansion mismatch between the fibers and the matrix in combination with the low adhesive strength of the carbon coating. In nitrogen or helium the thermal conductivity was found to be higher due to the contribution of gaseous conduction across the interfacial gap. On switching from vacuum to nitrogen a transient effect in the thermal diffusivity was observed, attributed to the diffusion-limited entry of the gas

phase into the interfacial gap. These effects decreased with increasing temperature, due to gap closure, to be virtually absent at 1000 C. Key words: Composites, silicon nitride, thermal conductivity, thermal diffusivity, interfacial conductance.

## 4.2 INTRODUCTION

The heat conduction behavior of fiber-reinforced composites, as shown theoretically, is governed by the values for the thermal conductivity of the individual components, as well as by the volume fraction, orientation and anisotropy of the fiber phase [1-11]. The existence of a thermal barrier at the fiber-matrix interface has been identified and found to also play a critical role [12-14]. Earlier experimental research by the present authors on the effect of the interface on effective thermal properties focussed on uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride(RBSN) composites [15]. The fibers in these composites were made by the chemical-vapor deposition of SiC onto a carbon fiber substrate, with a final carbon coating approximately 3  $\mu\text{m}$  thick. It was found that the preferential in-situ oxidation of this carbon coating significantly lowered the effective thermal diffusivity and conductivity of these composites transverse to the fiber direction. Furthermore, it was found that in vacuum the thermal diffusivity and conductivity were significantly lower than in nitrogen under atmospheric pressure, an effect not observed for the matrix phase alone or for the composite with heat flow parallel to the fiber direction. These observations indicated the significant role of gaseous heat transfer across the interface in establishing the effective thermal conductivity of such composites.

Most surprising to these authors was the observation that such a significant atmospheric effect was also found for the control specimen of these composites in which the carbon coating at the interface was not oxidized, but kept intact [15]. This effect was attributed to the existence of an interfacial gap resulting from the thermal expansion mismatch between the SiC fibers and the RBSN matrix. Independent fracture studies of these composites indicated that this interfacial gap most likely formed either within the carbon coating itself or at the SiC-carbon interface. The observed effects of atmospheric differences on the effective thermal diffusivity or conductivity suggested that this gap was sufficiently wide and continuous to permit access of the surrounding atmosphere to the interface. Measurement of the differences in the thermal diffusivity in various atmospheres and after removal of the carbon coating provided information on the corresponding changes in the heat transfer characteristics of the interface. A quantitative measure of the total effect of the presence of the carbon coating on the interfacial thermal conductances can be obtained only by direct comparison with the behavior of the same composites without an interfacial carbon coating. Making such a comparison was the subject of this study.

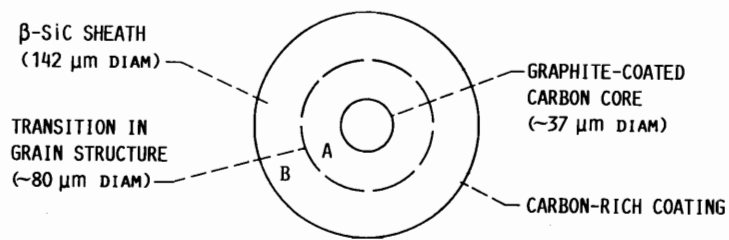
## **4.3 EXPERIMENTAL DETAILS**

### **4.3.1 *Materials***

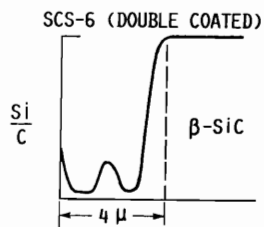
The composite samples consisted of RBSN uniaxially reinforced with SiC monofilaments (SCS-6, Textron Specialty Materials, Lowell, MA) with or without an approximately 3  $\mu\text{m}$  thick carbon-silicon coating. Figure 1 shows a schematic cross

section of the fiber and the silicon-to-carbon ratio of the coating. The composites were made by nitriding preregs of the fibers and silicon powder. Details of the manufacturing process and microstructures can be obtained from earlier reports [16-18]. The fibers had a diameter of approximately 142  $\mu\text{m}$  and contained a central carbon core with a diameter of approximately 37  $\mu\text{m}$ . The carbon core represented approximately 6.8 % of the volume of the fibers. The composite with the coated fibers had a fiber volume fraction of 32 % and a density value of 2.17 g/cc. This value for density, when compared to the theoretical value of density of about 3.2 g/cc, implies a pore content of approximately 32 %. It is anticipated that the pores are located primarily within the matrix phase.

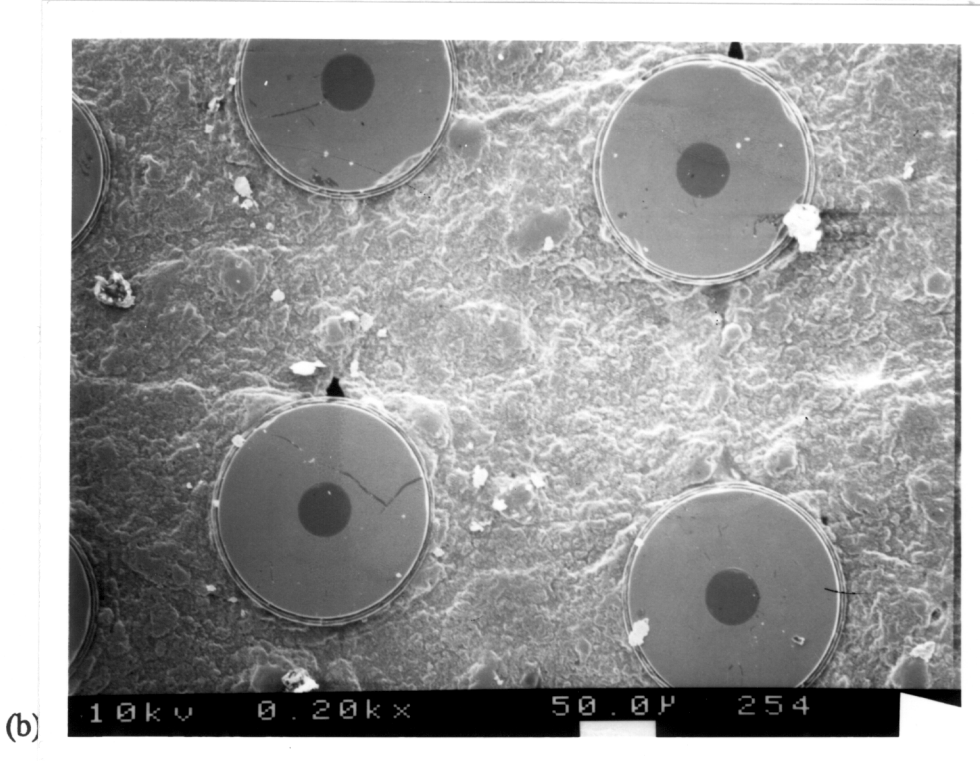
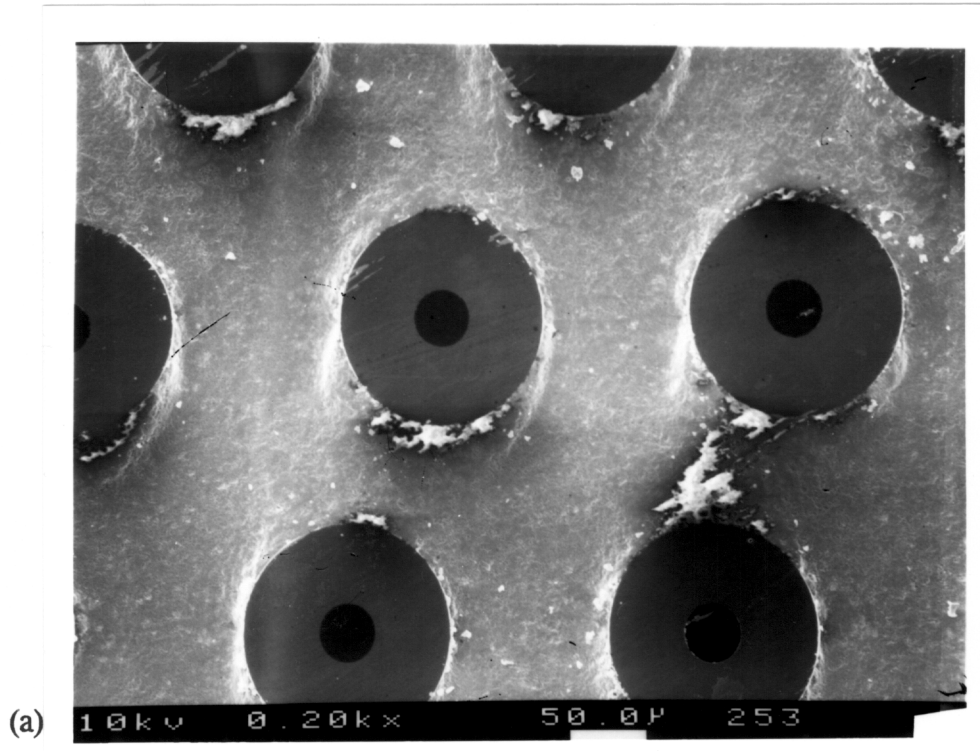
The corresponding values for the composite with the uncoated fibers were 38 vol. % fibers, a density of 2.45 g/cc and pore content of about 23 %. In order to facilitate the quantitative interpretation of the data, it was hoped that composite samples could be made with identical values of density and fiber volume fraction. Unfortunately, this could not be accomplished. However, this presents no problem, as explained in more detail later, if the thermal conductivity transverse to the fiber direction for perfect interfacial thermal contact is calculated from the corresponding value parallel to the fiber direction and compared with the experimental data. Any differences found will be indicative of the influence of an interfacial thermal barrier unaffected by other variables. Microstructures of the composites without and with the interfacial carbon coating are shown in figures 2a and 2b, resp. The corresponding details of the matrix-fiber interface without and with the carbon coating on the fibers are shown in figures 3a and 3b, resp.



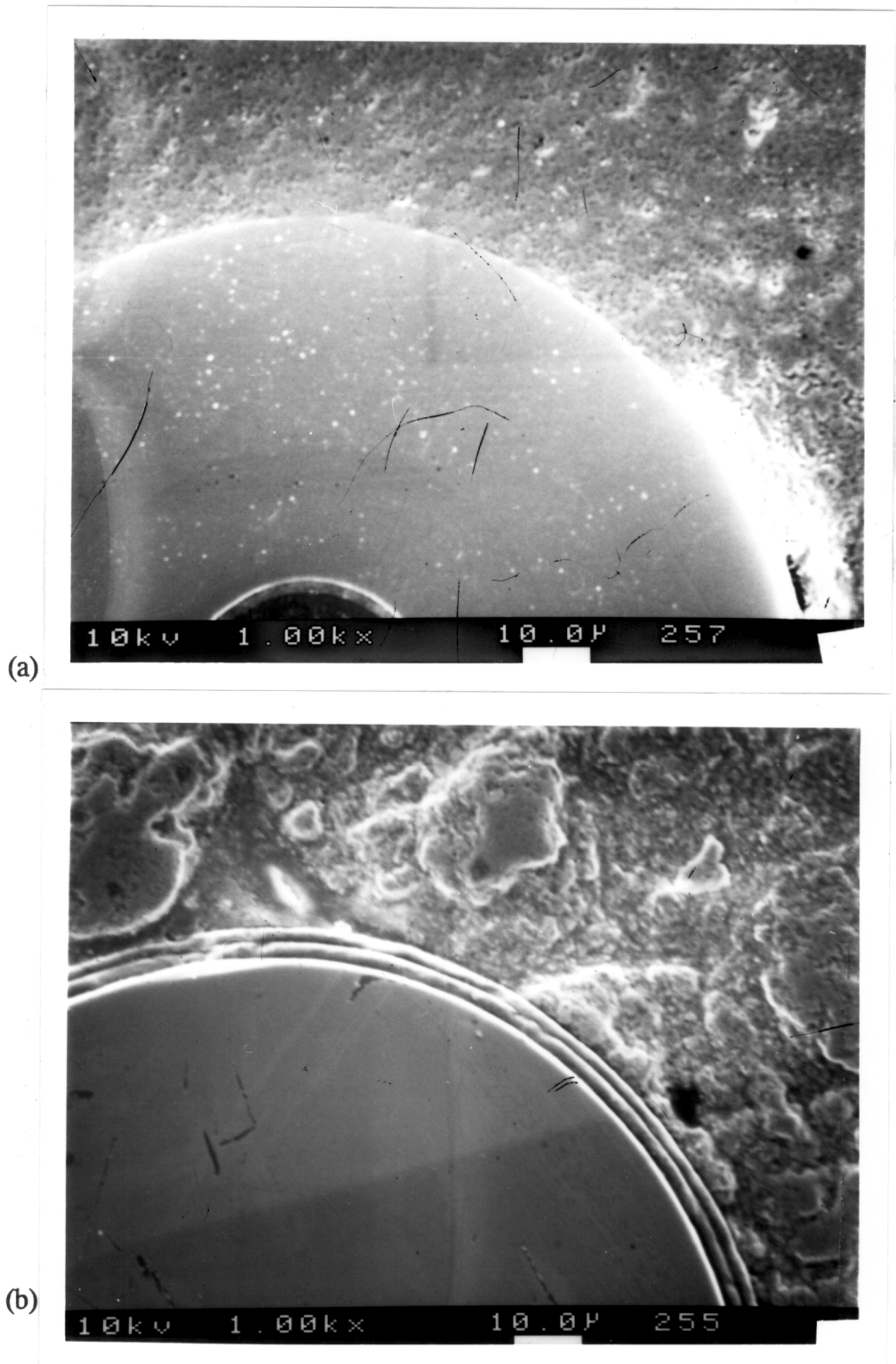
COATING COMPOSITION



**Fig. 1:** Schematic of SiC fiber showing the cross section and composition profile of the carbon coating.



**Fig. 2:** Scanning-electron-micrographs of uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride; (a) fibers without carbon coating and (b) with carbon coating.



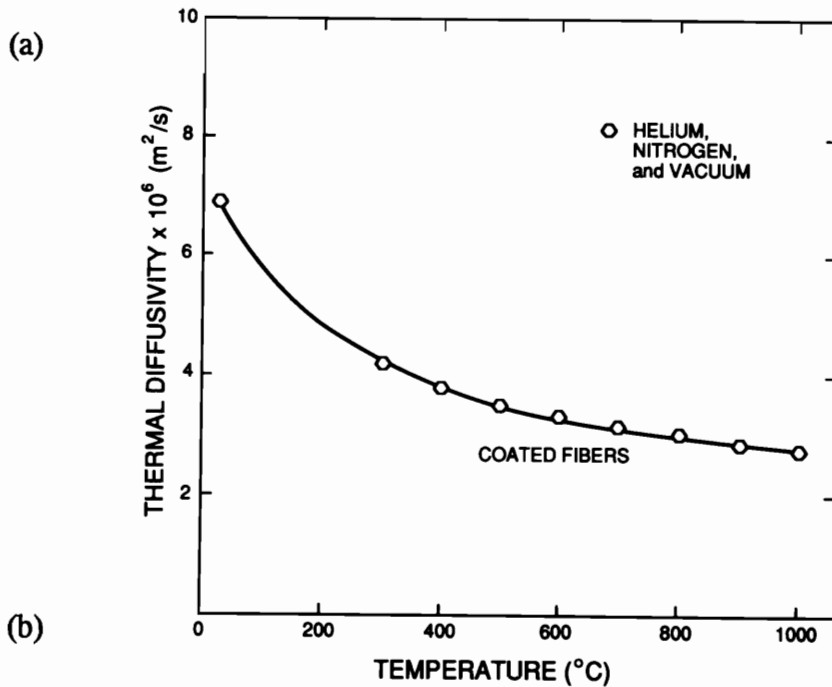
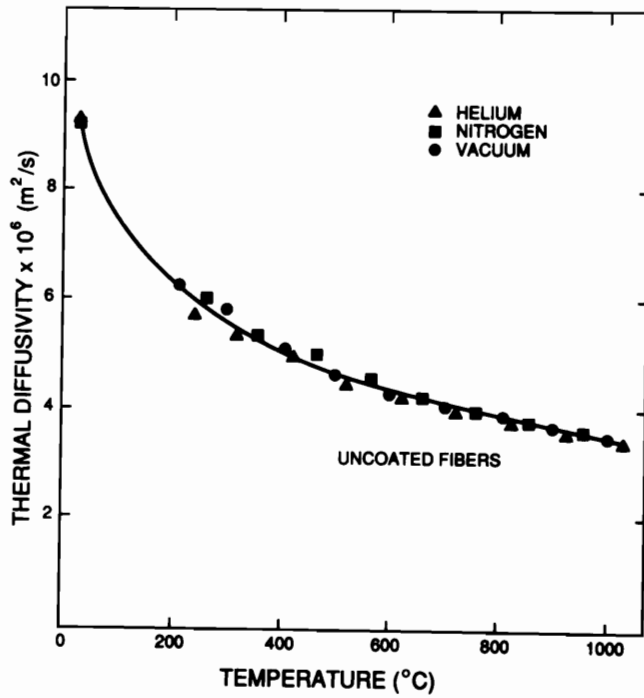
**Fig. 3:** Scanning-electron-micrographs of uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride showing details of interface; (a) without and (b) with carbon coating on fibers.

### **4.3.2 Experimental method.**

The effective thermal diffusivity of the composite samples was measured using the flash diffusivity technique [19,20], using approximately 8 x 8 mm square specimens with a thickness of approximately 2mm. The thermal diffusivity was measured along the 2 mm dimension. The experimental details have been presented in earlier reports [10-11,15]. In order to determine the role of the atmosphere in the interfacial heat transfer, the thermal diffusivity was determined in helium and nitrogen at atmospheric pressure and in vacuum at a fore-pump pressure of approximately 0.13 Pa. In order to determine the nature of gaseous diffusion along the interface, the changes in the value of thermal diffusivity were measured as a function of time as the atmosphere was changed from vacuum to nitrogen over a range of constant temperatures. The specific heat was measured by differential scanning calorimetry to 700 C and extrapolated to 1000 C, as guided by literature data. The thermal conductivity of the composite samples was calculated by multiplying the experimental value of the thermal diffusivity with the product of the density and the specific heat.

## **4.4 EXPERIMENTAL RESULTS, ANALYSIS, DISCUSSION AND CONCLUSIONS.**

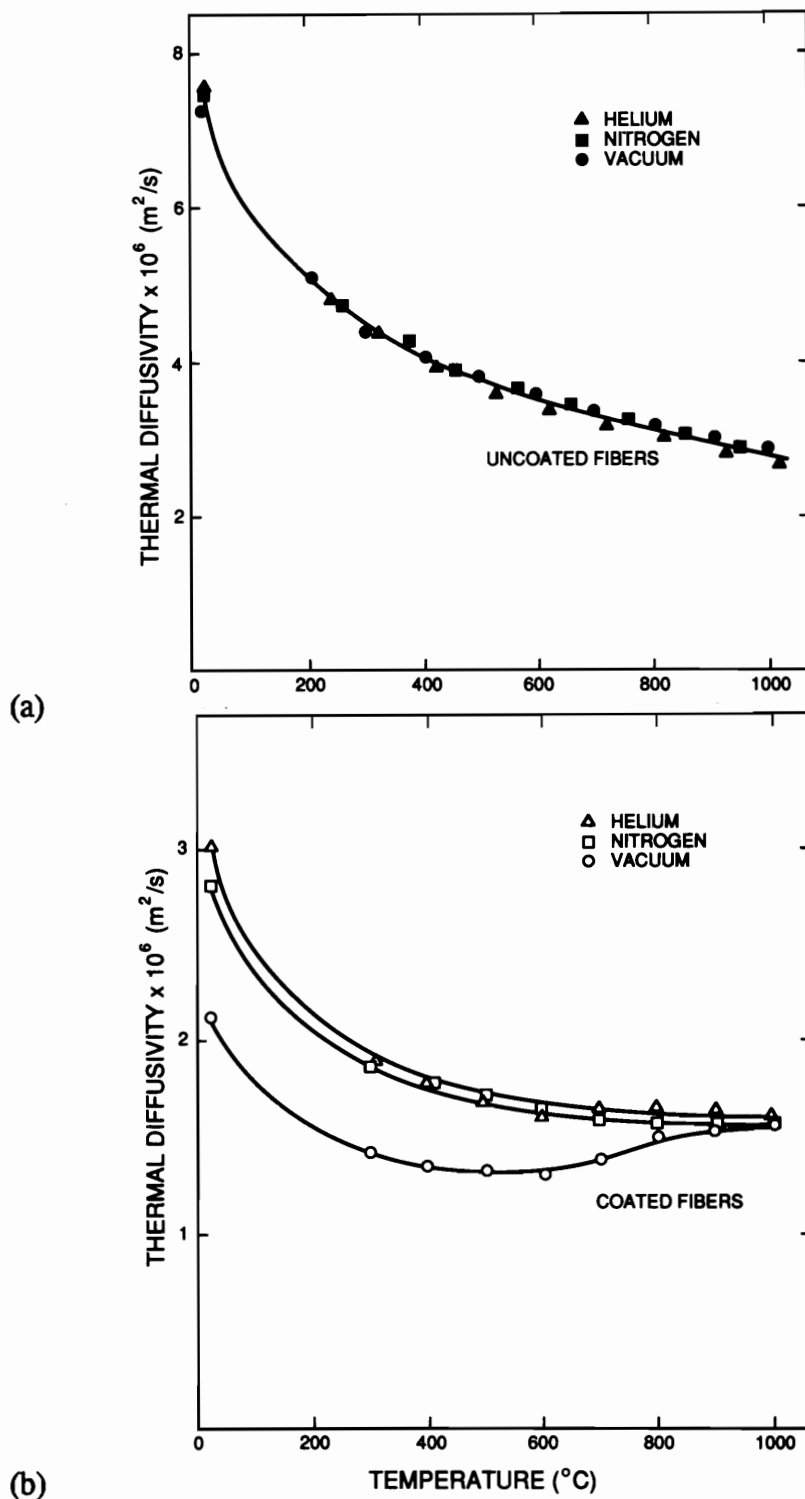
Figures 4a and 4b show the experimental data for the thermal diffusivity parallel to the fiber direction as a function of temperature in helium, nitrogen and vacuum for the composites with the uncoated and coated fibers, respectively. For both sets of data, the thermal diffusivity, within the experimental scatter in the data, is independent of the surrounding atmosphere. This result is expected, since the interface is not expected to



**Fig. 4:** Experimental data for the thermal diffusivity of uniaxial silicon carbide fiber reinforced reaction-bonded silicon nitride parallel to fiber direction in helium, nitrogen and vacuum, with, (a) fibers without carbon coating and (b) with carbon coating.

play a role in heat flow parallel to the fiber direction. The somewhat lower value of thermal diffusivity for the composite with the coated fibers compared with the corresponding value for the composite with the uncoated fibers can be attributed to the difference in their values of density and fiber volume fraction [21-24].

Figures 5a and 5b show the data for the thermal diffusivity transverse to the fiber direction as a function of temperature in helium, nitrogen and vacuum for the composites with the uncoated and coated fibers, respectively. Comparison of these sets of data shows that the thermal diffusivity at room temperature for the composite with the coated fiber is lower by as much as a factor of about three when compared to the corresponding data for the composite with uncoated fibers. This large difference cannot be explained on the basis of the differences in density alone. A possible explanation can be based on the observations that the thermal diffusivity of the composite with the coated fibers is a function of the test atmosphere. Because this effect of atmosphere is absent in the composites with the uncoated fibers and for heat flow parallel to the fibers in both composites, it cannot be attributed to gaseous heat transfer within the fibers or matrix. Clearly, for the composites with the coated fibers the atmosphere has access to the interface, evidence indicating the existence of an interfacial gap. The difference in the thermal diffusivity values between vacuum and nitrogen or helium for the composite with the coated fibers represents the contribution of gaseous heat conduction across the interface. In this respect, it is interesting to note that the relative differences in the thermal diffusivity for the three atmospheres decrease with increasing temperature to become insignificant as the temperature approaches the maximum temperature of about 1000 C for these experiments. Such a decrease is consistent with



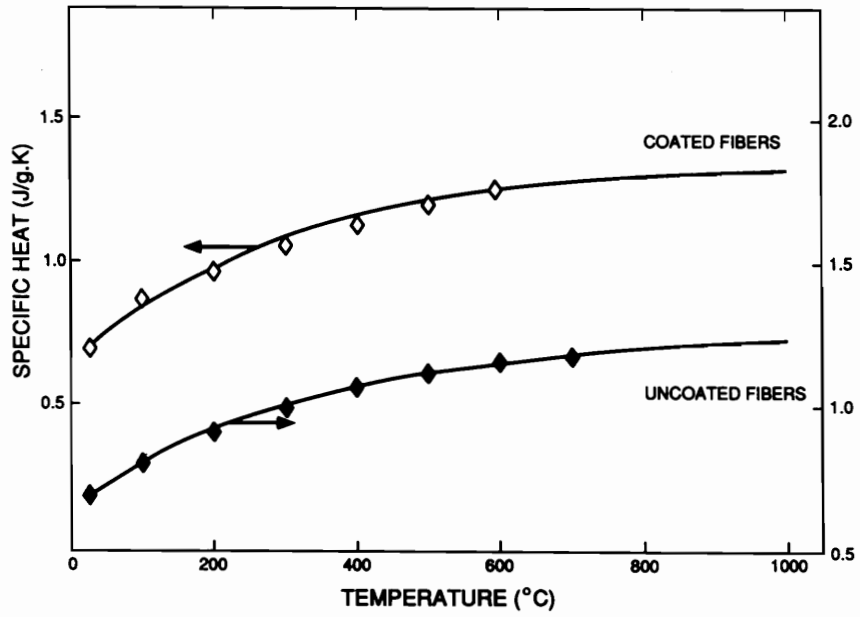
**Fig. 5:** Experimental data for the thermal diffusivity of uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride transverse to the fiber direction in helium, nitrogen and vacuum with, (a) fibers without carbon coating and (b) with carbon coating.

the existence of an interfacial gap resulting from the thermal expansion mismatch between the fibers and the matrix, as in this case with measured coefficients of thermal expansion of  $3.4 \times 10^{-6}$  for the matrix and  $4.6 \times 10^{-6} / ^\circ\text{C}$  for the fibers. On cooling from the nitriding temperature, this difference in thermal expansion results in tensile radial stresses at the interface. For the composites with the uncoated fibers it is speculated that the interfacial bond between the fibers and matrix is sufficiently strong to prevent interfacial debonding. In the composite with the coated fibers, as judged by studies of its mechanical behavior, interfacial debonding does occur usually within the coating itself and occasionally at the fiber-coating interface, indicative of a relatively weak interface, discussed in more detail later. Complete circumferential fracture along the interface for the above coefficients of thermal expansion would result in a mean gap size of the order of  $0.1 \mu\text{m}$  at room temperature. Reheating the composite back up towards the nitriding temperature results in crack closure and increased direct physical contact between the fibers and matrix and a corresponding decrease in the contribution of gaseous heat transfer across the interfacial gap.

Figure 6 shows the data for the specific heat of the composite samples reinforced with fibers without and with carbon coating. Comparison of these data show that the presence of the carbon coating on the fibers had little or no effect on the value of the specific heat.

For heat flow parallel to the fibers of a uniaxially reinforced composite, the effective thermal conductivity,  $K_{\text{eff}}$ , is:

$$K_{\text{eff}} = K_m V_m + K_f V_f + K_c V_c \quad (1)$$



**Fig. 6:** Specific heat of uniaxial silicon carbide fiber reinforced reaction-bonded silicon nitride with fibers with and without carbon coating. Curves above 700 C were extrapolated.

where  $K$  is the thermal conductivity,  $V$  is the volume fraction and the subscripts  $m$ ,  $f$  and  $c$  represent the matrix, fiber and the fiber core, respectively. For the composites of this study, the effect of the carbon coating is not reflected in equation 1. Because of its very small volume fraction, this introduces very little error.

The effective thermal conductivity of a matrix uniaxially reinforced with fibers of circular cross section perpendicular to the fiber axis is [12]:

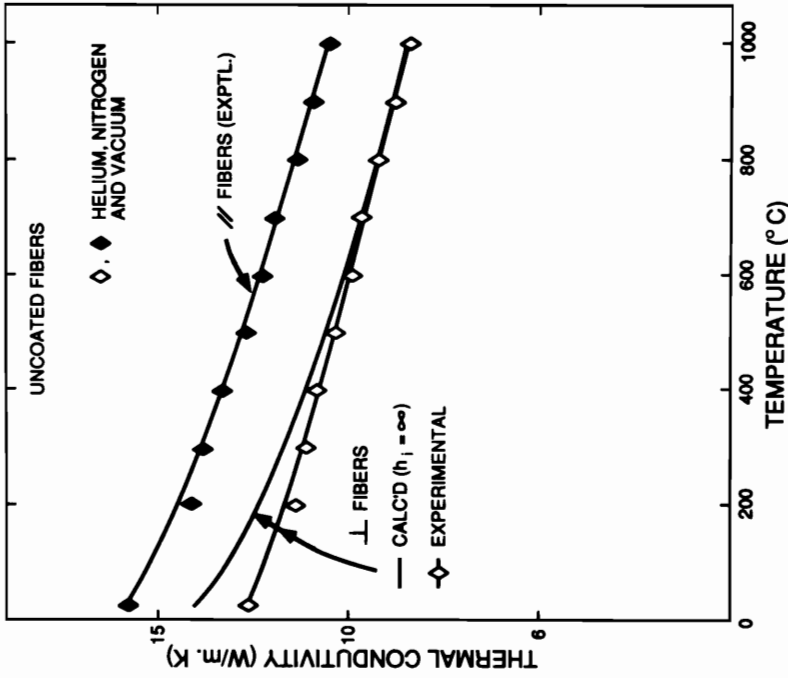
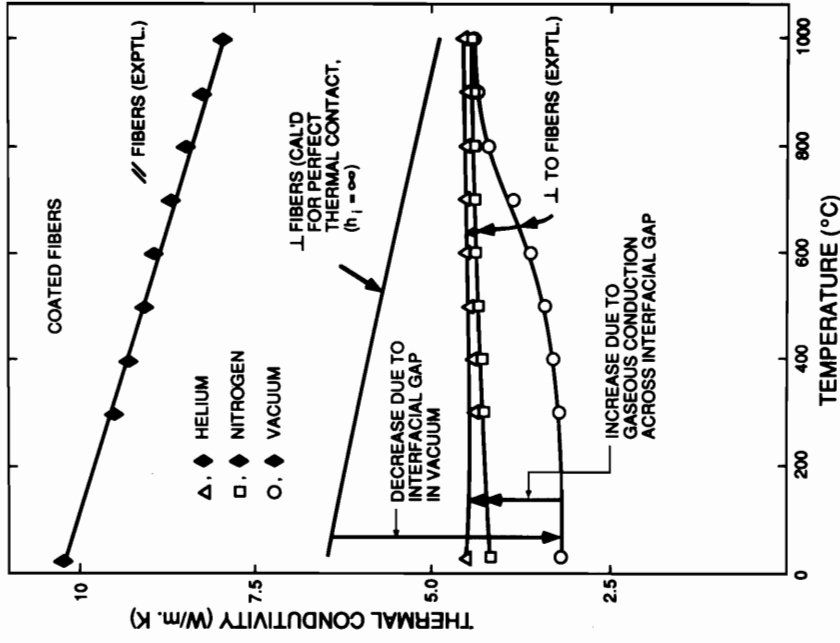
$$K_c = K_m \frac{\left[ \left( \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]}{\left[ \left( 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]} \quad (2)$$

where  $K$  and  $V$  represent the thermal conductivity and volume fraction, respectively. The subscripts  $c$ ,  $m$  and  $f$  refer to the composite, matrix and fiber phases, respectively,  $a$  is the fiber radius and  $h_i$  is the interfacial thermal conductance. Because the fibers in the composite of this study are composites in their own right, the quantity  $K_f$  in equation 2 was chosen to represent the effective thermal conductivity of the fibers, including the carbon core. Also, in equation 2, the presence of the carbon coating was considered an integral part of the interfacial conductance. The thermal conductivity of the matrix was calculated with the aid of equation 1 from the value of the thermal conductivity of the composite for heat flow parallel to the fiber direction. This calculation required values for the thermal conductivity of the carbon core and the silicon carbide fiber. From the direct correlation between Young's modulus and the thermal conductivity of carbon fibers along their direction as shown by Nysten et al [25], the thermal conductivity of the carbon core was estimated to be 29 W/m.K from its value of Young's modulus of 41 GPa at room temperature [26]. In the absence of

other information, the relative temperature dependence of the carbon core was assumed to be zero. This assumption introduces little error as the volume fraction of the core is quite small. The thermal conductivity of the silicon carbide was obtained in an earlier study [27] and found to be about 22.5 W/m.K at 25 °C, with a temperature dependence between 25 C and 1000 C, to a very good approximation, described by the linear equation:  $K_f = 22.5 [1 - 0.00025(T - 25)]$ , where T is the temperature in °C. With the above values for the carbon core and the silicon carbide of the fiber, the thermal conductivity of the matrix phase was calculated from the composite thermal conductivity by means of equation 1.

Using the thermal conductivity value for the matrix as established above, the effective thermal conductivity of the composite transverse to the fiber direction without a thermal barrier (i. e.,  $h_i = \infty$ ) was calculated using equation 2. This calculation also required a few simplifying assumptions. Firstly, the matrix and the silicon carbide phase of the fiber were assumed to be isotropic. Secondly, in view of the high anisotropy of the properties of carbon [28-30], the thermal conductivity of the carbon core in the fibers was assumed to be equal to zero. Accordingly, the effective thermal conductivity of the fiber transverse to its length was corrected for the presence of the core with the aid of equation 2, with  $K_f = 0$ . It should be noted that the above assumptions and calculations must be considered refinements only, with only minor effects on the final results as the volume fraction of the carbon core represents only a few percent of the total volume of the composite.

Figure 7a and 7b compare the experimental data for the thermal conductivity for both directions of heat flow with the calculated values for the thermal conductivity



(a)

(b)

**Fig. 7:** Comparison between thermal conductivity values measured parallel and transverse to the fiber direction and thermal conductivity values calculated from composite theory transverse to the fiber direction for a uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride with: (a) uncoated fibers and (b) coated fibers

transverse to the fiber direction for  $h_i = \infty$  (i. e., perfect interfacial contact) for the composite with uncoated and coated fibers, respectively.

For the composites with the uncoated fibers, the observed and calculated values for the thermal conductivity differ by at most some ten percent with a mean deviation of about five percent over the total temperature range. In view of the number of assumptions made in the calculations outlined above, this agreement must be considered quite good indeed. It appears reasonable to conclude that for the uncoated fibers, the nature of the interface between the fiber and the matrix is such that the degree of thermal contact is quite good. In contrast, for the composite with the coated fibers, a difference of a factor of about two is found between the observed values for the thermal conductivity transverse to the fiber direction at room temperature and the calculated values for  $h_i = \infty$ . This difference must be attributed to the lack of effectiveness of the carbon layer in transferring heat between the fiber and matrix, thereby lowering the effective thermal conductivity transverse to the fiber direction. It is expected that two effects play a role here, namely the thermal resistance of the carbon coating itself and the interfacial gap which results from the thermal expansion mismatch, with the latter probably playing the major role. It should be noted that in fig. 7a and 7b, the ratio of the calculated value of the thermal conductivity transverse to the fiber direction for  $h_i = \infty$  to the observed values of the thermal conductivity are not the same. This effect is due to the differences in the density and fiber volume fraction of the two composites.

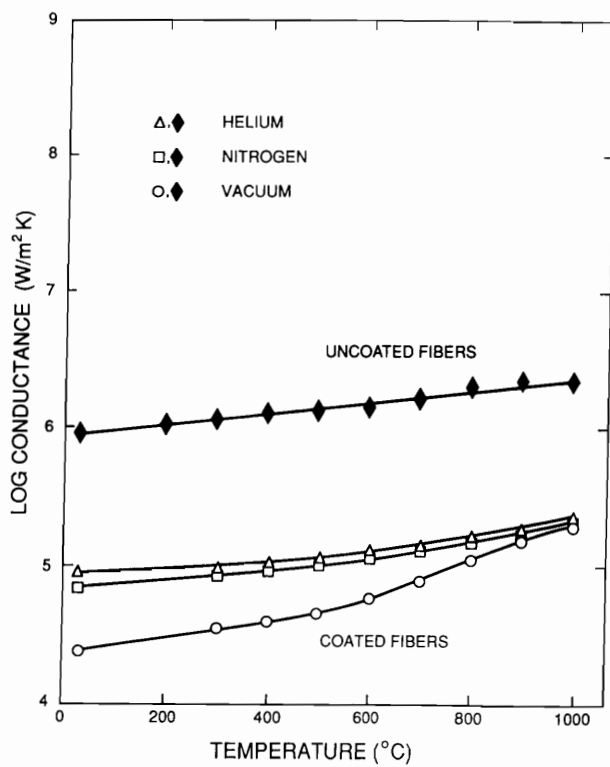
Referring to the data in fig. 7, it is interesting to note the differences in the relative temperature dependences for the various sets of data. With the exception of heat flow transverse to the fiber direction for the composite with the coated fibers, all other sets

of data show the negative temperature dependence expected for dielectric materials. In contrast, for the composite sample with the coated fibers, the thermal conductivity transverse to the fiber direction exhibits a temperature dependence which is near zero or even positive depending on the specific atmosphere. In these composites, the temperature dependence of the thermal conductivity of the individual components should not be affected by the coating. For this reason, it appears that the coating introduces a positive temperature dependence which more or less counteracts the negative temperature dependence of the thermal conductivity of the fibers and matrix. It is suggested here that the interfacial gap closure with increasing temperature is the primary factor which contributes to the positive temperature dependence of the interfacial thermal conductance. It is suggested that this same phenomenon is also responsible for the increased agreement with increasing temperature between the experimental and calculated data for heat flow perpendicular to the fiber direction as shown in fig. 7. In fact, near 1000 C the agreement is quite good.

Figure 8 shows the calculated values for the interfacial conductances. For the composite with the coated fibers, the conductances show the expected positive temperature dependence, which, as speculated earlier, results from the closure of the interfacial gap with increasing temperature. The conductance values in vacuum result from direct physical contact across the interface. The increase in the conductances in helium and nitrogen over the value in vacuum results from the contribution of gaseous heat transfer across the gap. Note that the conductance in helium exceeds the value for nitrogen, as expected from the corresponding differences in the values of the thermal conductivity for these two gases. It is also important to note that at room temperature the values for the conductances in vacuum and in nitrogen and helium differ by a factor

of about four. This suggests that at room temperature the gaseous heat transfer between the fiber and matrix represents some 80 % of the total heat transferred. As the gap closes with increasing temperature, accompanied by increased direct physical contact across the interface, the relative contribution of the gaseous heat transfer will decrease. As observed, this leads to a decrease in the differences in conductance values in the various gaseous environments. For the composite with the uncoated fibers the values for the thermal conductances are some order of magnitude above those for the composite with the coated fibers, as expected. However, as the calculation of the thermal conductances for the uncoated fibers are based on relatively small differences in the experimental values for the thermal conductivity and those for  $h_i = \infty$  their absolute magnitude and their temperature dependence must be regarded with some caution.

Differences in the thermal conductances due to the presence or absence of the carbon coating should be reflected in corresponding differences in the mechanical properties of the fiber-matrix interface. Indeed, for the composites with the carbon-coating the interfacial shear stress required for the debonding of the fiber- matrix interface was found to be about 10 to 18 MPa, to be reported in detail elsewhere [31]. For the same composites the stress required for interfacial sliding following debonding was measured to be 1 to 2 MPa. In contrast, for the composites without the carbon coating the stress required for interfacial debonding was estimated to be greater than 200 MPa. These values suggest an expected direct correlation between the interfacial mechanical properties of a composite and the interfacial thermal conductances based on direct physical contact at the fiber-matrix interface, i. e., the thermal conductances found in vacuum. Any gaseous contribution to the total thermal conductance is expected to show



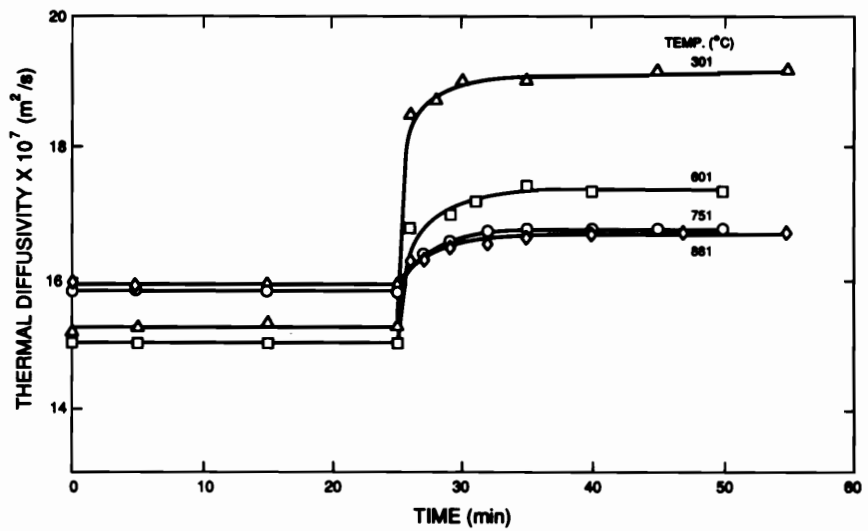
**Fig. 8:** Calculated values for the interfacial thermal conductances for uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride in helium, nitrogen nitrogen and vacuum for composites with uncoated and coated fibers.

a negative correlation, as such conductance is indicative of the absence of direct physical contact.

Figure 9 shows the data for the thermal diffusivity of the composite sample with the coated fibers as a function of time as the surrounding atmosphere is changed from vacuum to nitrogen at one atmosphere pressure for a range of values of constant temperature. Interesting to note is that the thermal diffusivity does not instantaneously take on the value obtained in nitrogen under steady-state conditions, but displays transient behavior analogous to that of the charging rate of a capacitor controlled by the electrical resistance of a circuit. Such an effect is to be expected if access of the nitrogen gas is controlled by its rate of diffusion along the interface from the outside surface of the specimen, so that the concentration of the gas within the interface increases gradually with time to reach a constant steady-state value. This will be reflected in a corresponding increase in the thermal diffusivity, due to an increased contribution of gaseous conduction. Of interest to note is that the time-period of the transient behavior increases with increasing temperature. This is also expected from a diffusion-controlled concentration of the gas phase in the interface, as the gap width decreases with increasing temperature.

The nature of gaseous diffusion along a narrow gap or capillary depends on the ratio between the gaseous mean-free-path,  $\lambda$ , and the width of the gap,  $d$ , referred to as the Knudsen number [32]:

$$N_k = \frac{\lambda}{d} \quad (3)$$



**Fig. 9:** Transient behavior in the thermal diffusivity of uniaxial silicon carbide fiber-reinforced reaction-bonded silicon nitride on changing the ambient from vacuum to nitrogen at one atmosphere.

For  $N_k \ll 1$ , the rate of diffusion is controlled by interatomic or intermolecular collisions, referred to as viscous diffusion [32]. In this case, the rate of diffusion is independent of the gap width. However, for  $N_k \gg 1$ , the rate of diffusion is controlled by the collisions between the atoms or molecules and the gap surfaces, with the rate of diffusion decreasing with decreasing gap width [32]. This type of diffusion is referred to as "molecular diffusion". As the gap width becomes of the order of the atomic or molecular size, the nature of the diffusional process is referred to as "configurational diffusion", with the rate of diffusion approaching zero as the gap width approaches zero. At atmospheric pressure the mean-free-path for nitrogen at room temperature can be calculated [33,34] to be approximately  $0.15 \mu\text{m}$ , which is of the order of the gap-width in these composites, as calculated earlier. For this reason, the nature of the interfacial diffusion at room temperature in the composites of this study is expected to be a function of the width of the gap. As the gap closes with increasing temperature, configurational diffusion will predominate. It is expected that the rate of diffusion of nitrogen into the interface will decrease with increasing temperature due to the associated gap closure. In turn, this will result in a longer time-period required for the thermal diffusivity to reach its steady-state value on changing the atmosphere from vacuum to one atmosphere of nitrogen, as observed.

In summary, the results of this study have shown that the presence of the carbon coating on the fibers of SiC fiber-reinforced reaction-bonded silicon nitride can significantly lower the effective thermal diffusivity transverse to the fiber direction by a factor of about two. At atmospheric pressure gaseous conduction across the interface appears to be the primary mode of heat transfer, as the result of fiber-coating-matrix debonding due to associated thermal expansion mismatches. The presence of such

debonding is manifested by significantly lower values of effective thermal diffusivity in vacuum than in nitrogen or helium at atmospheric pressure. The debonded interface is sufficiently narrow that on changing the surrounding atmosphere a significant time-period is required for the diffusion of the gas phase into or out of the interface.

## **ACKNOWLEDGEMENT.**

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## 5.0

### EFFECT OF FIBER ORIENTATION ON THE THERMAL CONDUCTIVITY OF A UNIAXIAL FIBER-REINFORCED COMPOSITE STRIP WITH INSULATED SIDES.

#### 5.1 ABSTRACT

An analysis was conducted of the effective thermal conductivity of a uniaxial fiber-reinforced composite strip with thermally insulated sides as a function of the angle between the fiber direction and the temperature gradient. It is shown that due to the constraints on the heat flow within the composite resulting from the insulated edges, the effective conductivity of the insulated strip can be significantly lower than the effective conductivity of an infinite medium of the same composite. This difference is a function of the angle between the fibers and the temperature gradient, and varies from zero for angles of  $0^\circ$  and  $90^\circ$  to a maximum at an angle which is a function of the ratio of the thermal conductivity of the composite parallel and perpendicular to the fiber direction. The anisotropic thermal conductivity of the insulated strip results in a temperature gradient transverse to the imposed temperature gradient, except for fiber angles of  $0^\circ$  and  $90^\circ$ .

## 5.2 INTRODUCTION

THE EFFECTIVE THERMAL CONDUCTIVITY OF COMPOSITE MATERIALS has been a topic of considerable theoretical interest for a wide variety of phase geometries [1-16]. Additional studies have also considered the effect of the existence of an interfacial thermal barrier [17-19]. In general, these studies have shown that the effective thermal conductivity of composites is a function of the phase distribution and the values of the thermal conductivity and volume fraction of the individual components. In the presence of an interfacial thermal barrier, the actual dimension of components within the composite becomes a variable as well. As far as these authors are aware, none of these analyses predict any influence of the over-all dimensions of the composite sample on the effective thermal conductivity, or have considered the possible effect of the thermal boundary conditions imposed on the outside surfaces.

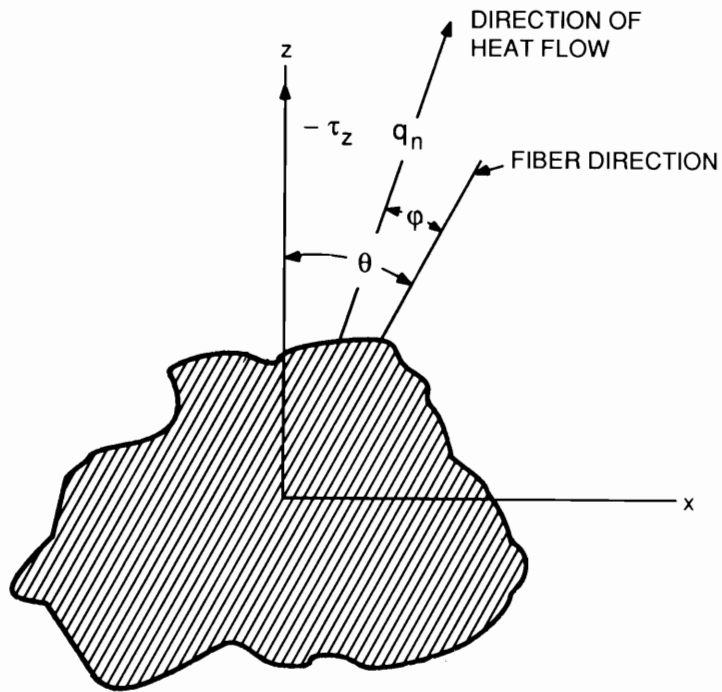
Uniaxial fiber reinforced composites, in general, are expected to exhibit highly anisotropic thermal conductivity. As pointed out by Nye [20], in anisotropic materials the direction of net heat flow need not correspond to the direction of the imposed temperature gradient. It should be pointed out, however, that this statement is strictly valid only for a material of infinite size. Effective thermal resistances for a thin single crystal rod with anisotropic thermal conductivity were presented by Carslaw and Jaeger [21]. Havis, Peterson and Fletcher [22], compared numerical and experimental data for the temperature distributions in a composite plate with thermally insulated edges of a thermally anisotropic composite. It was shown that the anisotropy in thermal conductivity, combined with the effect of the thermally insulated edges, created a significant distortion in the temperature distribution from the one expected for an

infinite plate. It was also shown that the effective thermal conductivity of the composite decreased strongly with increasing angle between the thermal gradient and the fiber direction from the value for heat flow parallel to the fiber direction. It is the purpose of this communication to present an analytical expression for the effective thermal conductivity of a uniaxially reinforced composite strip with insulated sides, as a function of fiber orientation.

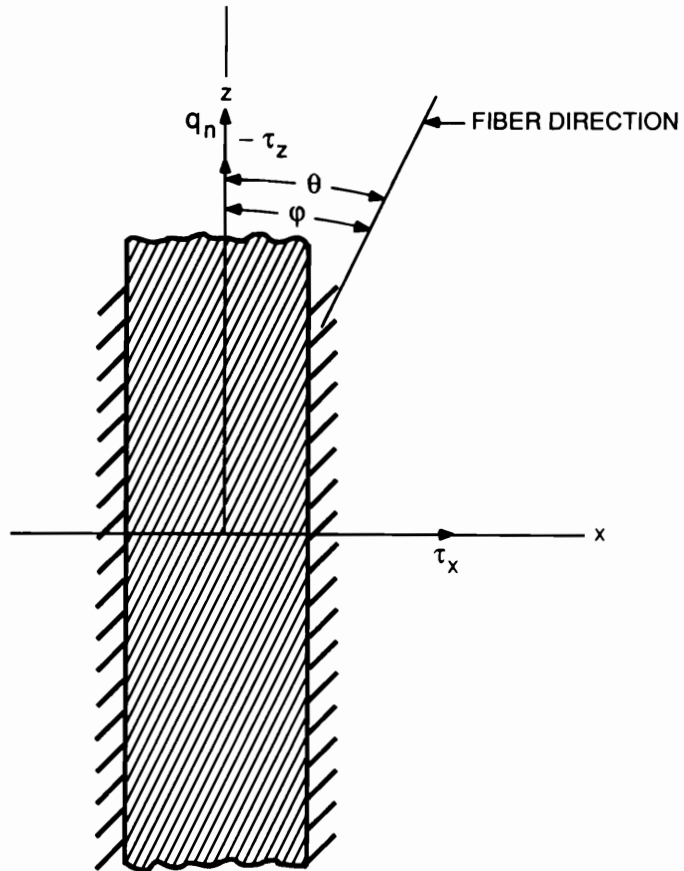
### 5.3 ANALYSIS

Figures 1 and 2 show a schematic of the composite plate infinite in extent and in the form of a long strip with insulated edges, respectively. For this analysis, a section of the strip far away from the ends will be considered, such that perturbations of the temperature distributions in the heat source and sinks need not be considered. The composite lies in the  $x$ - $z$  plane, with a temperature gradient,  $-\tau_z$ , applied along the  $z$ -axis. The thermal conductivity through the thickness of the plate will be assumed to be constant, which reduces the analysis to two-dimensional heat flow. The fibers are oriented at an angle  $\theta$  with the  $z$ -axis. In the infinite plate, the net heat flow occurs at an angle  $\psi$  from the fiber direction. The microstructure of the composite will be considered to be sufficiently small compared to the size of the plate or strip, such that the composite can be regarded as a homogeneous thermally anisotropic continuum.

The thermal conductivity of the plate can be defined in terms of the primary thermal conductivities,  $K_p$  and  $K_n$ , parallel and perpendicular to the fiber direction, respectively.  $K_p$  is given by the rule of mixtures:



**Fig. 1:** Infinite uniaxially fiber-reinforced composite plate subjected to temperature gradient at angle to fiber direction.



**Fig. 2:** Uniaxially fiber-reinforced composite strip with insulated sides subjected to temperature gradient at angle to fiber direction.

$$K_p = K_m V_m + K_f V_f \quad (1)$$

where  $K$  is the thermal conductivity,  $V$  is the volume fraction and the subscripts  $m$  and  $f$  refer to the matrix and fiber, respectively.

Taking into account the presence of an interfacial thermal barrier,  $K_n$ , for dilute volume fraction of circular fibers, after Hasselman and Johnson [17], is given by:

$$K_c = K_m \frac{\left[ \left( \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]}{\left[ \left( 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]} \quad (2)$$

The thermal conductivity of the composite plate without thermally insulated sides, as a function of direction is [20,22]:

$$K_{zz} = K_p \cos^2 \theta + K_n \sin^2 \theta \quad (3a)$$

$$K_{xx} = K_p \sin^2 \theta + K_n \cos^2 \theta \quad (3b)$$

$$K_{xz} = (K_p - K_n) \sin \theta \cos \theta \quad (3c)$$

For the infinite plate, the angle of net heat flow  $\psi$ , relative to the angle of the fibers, can be obtained from the components of heat flow parallel and perpendicular to the fiber direction:

$$q_p = -K_p \tau_z \cos \theta \quad (4a)$$

$$q_n = -K_n \tau_z \sin \theta \quad (4b)$$

The angle  $\psi$  can be obtained from:

$$\tan \psi = \left( \frac{K_n}{K_p} \right) \tan \theta \quad (5)$$

For the composite strip with insulated sides, the heat is constrained to flow along the temperature gradient such that  $\psi = \theta$ . Such constraint on the direction of heat flow can occur only by the development of a temperature gradient,  $\tau_x$ , transverse to  $\tau_z$ . At least qualitatively, the generation of such a transverse gradient is expected as the gradient along the fibers will be less than the gradient perpendicular to the fibers. In the limit, for fibers with thermal conductivity approaching infinity the fibers will be isothermal. This, for any angle of  $\theta$ , excepting  $0^\circ$  or  $90^\circ$ , will result in a transverse temperature gradient. The numerical results of Havis et al [22], also show the development of such a transverse temperature gradient.

The magnitude of the gradient  $\tau_x$  in terms of the gradient  $\tau_z$  can be derived by considering the contributions of both gradients to the heat flow parallel and perpendicular to the fiber direction, as follows:

$$q_p = -K_p \tau_z \cos \theta - K_p \tau_x \sin \theta \quad (6a)$$

$$q_n = -K_n \tau_z \sin \theta + K_n \tau_x \cos \theta \quad (6b)$$

Because the net direction of heat flow is parallel to the z-axis (i.e.,  $\theta = \psi$ ), the ratio of  $q_n/q_p = \tan \theta$ . This yields:

$$\tau_x = -\tau_z \left\{ \frac{[K_p - K_n]}{[K_n \cot \theta + K_p \tan \theta]} \right\} \quad (7)$$

It can be easily shown that despite the existence of the transverse gradient,  $\tau_x$ , the net heat flow in the x-direction equals zero.

The net heat flow,  $q_z$ , in the z-direction due to both gradients is given by:

$$q_z = -\tau_z (K_p \cos^2 \theta + K_n \sin^2 \theta) - \tau_x (K_p - K_n) \sin \theta \cos \theta \quad (8)$$

Substitution of  $\tau_x$  from equation 7 into equation 8 and recognizing that

$$K_z = -\frac{q_z}{\tau_z} \quad (9)$$

yields:

$$K_z = (K_p \cos^2 \theta + K_n \sin^2 \theta) - \left[ \frac{(K_p - K_n)^2 \sin^2 \theta \cos^2 \theta}{(K_p \sin^2 \theta + K_n \cos^2 \theta)} \right] \quad (10)$$

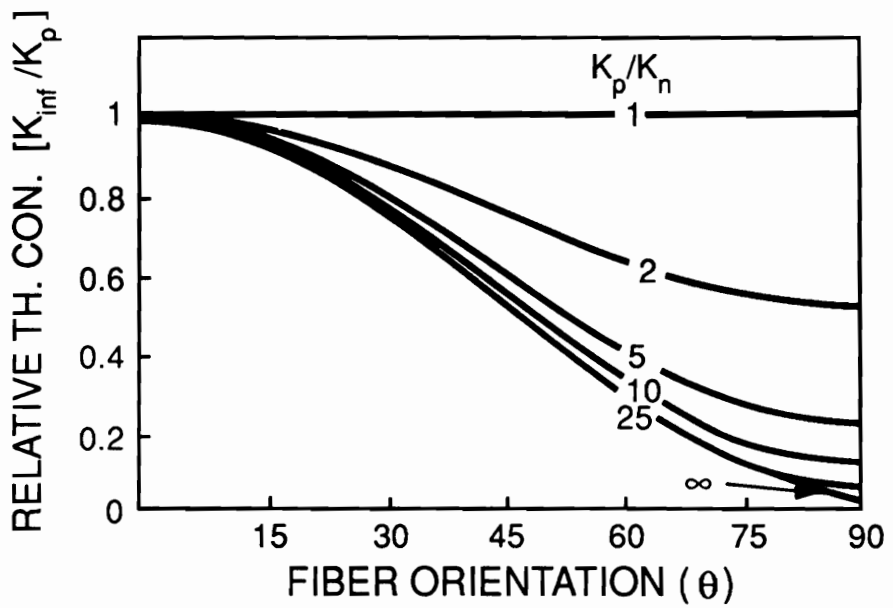
In equation 10, the first two terms represent the thermal conductivity along the z-axis for a composite plate of infinite extent. The second term represents the decrease in the thermal conductivity caused by the constraints on heat flow resulting from the insulated boundaries. Equation 10 can be rewritten in terms of the thermal resistivities:

$$K_z^{-1} = K_n^{-1} + (K_p^{-1} - K_n^{-1}) \cos^2 \theta \quad (11)$$

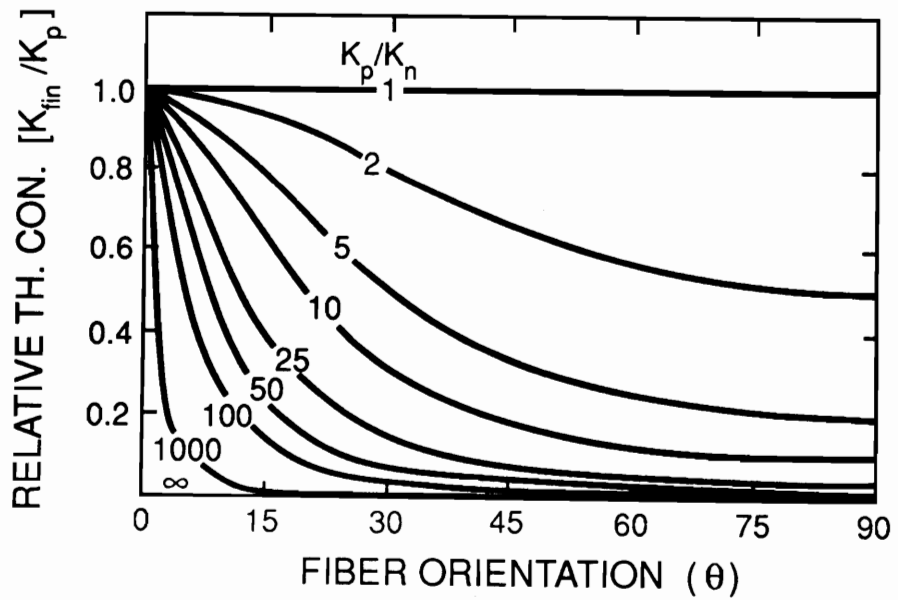
which is of the same general form as the equation for the effective thermal resistivity of a long thin rod presented by Carslaw and Jaeger [21].

Figures 3 and 4 compare the values for the thermal conductivity of the composite infinite in extent and the composite strip with insulated edges relative to the thermal conductivity parallel to the fiber direction as a function of the fiber angle for a range of ratios of thermal conductivity of the composite parallel and perpendicular to the fibers. In general, a comparison of figures 3 and 4 shows that the presence of the insulated edges lowers the thermal conductivity of the composite strip significantly, relative to the thermal conductivity of the composite infinite in extent. Figure 5 shows the actual numerical difference between the data of figures 3 and 4. This difference increases with the value of  $K_p/K_n$  for any given angle of the fibers. Furthermore, the angle for which the difference is a maximum decreases with increasing value of  $K_p/K_n$ , to reach a value of zero as  $K_p/K_n \rightarrow \infty$ , at which the value of the difference equals unity. It is anticipated that a similar effect can be found for other types of fiber-reinforced composites, such as those with a three-dimensional weave. For composite plates the effect of the insulated edges can be minimized by the use of laminated composites with good thermal coupling between neighboring laminates. This effect can even be eliminated altogether if the direction of the temperature gradient bisects the angle between the fibers in neighboring laminates.

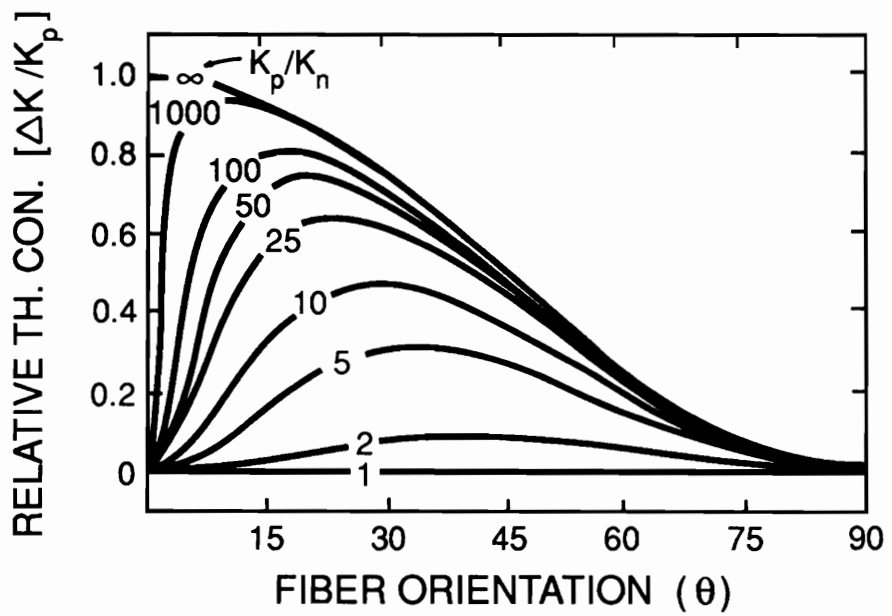
In summary, it is shown that the effective thermal conductivity of a uniaxially reinforced composite strip with thermally insulated sides can be significantly lower than the corresponding thermal conductivity of a composite plate infinite in extent.



**Fig. 3:** Dependence on fiber orientation of relative thermal conductivity of infinite composite plate for range of thermal conductivity ratios parallel and transverse to the fiber direction.



**Fig. 4:** Dependence on fiber orientation of relative thermal conductivity of insulated composite strip for range of thermal conductivity ratios parallel and transverse to the fiber direction.



**Fig. 5:** Dependence on fiber orientation of the difference in the relative thermal conductivity of infinite composite and insulated composite strip for range of thermal conductivity ratios parallel and transverse to the fiber direction as shown in figures 3 and 4.

## **ACKNOWLEDGMENTS**

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This paper titled

**ROLE OF SPECIMEN GEOMETRY IN THE EFFECT OF FIBER  
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UNIAXIAL CARBON FIBER-REINFORCED ALUMINO-BORO-  
SILICATE GLASS MATRIX COMPOSITE**

has been accepted for publication in  
**JOURNAL OF AMERICAN CERAMIC SOCIETY**

## 6.0

### **ROLE OF SPECIMEN GEOMETRY IN THE EFFECT OF FIBER ORIENTATION ON THE THERMAL CONDUCTIVITY OF A UNIAXIAL CARBON FIBER-REINFORCED ALUMINO-BORO-SILICATE GLASS MATRIX COMPOSITE**

#### **6.1 ABSTRACT**

A study concerning the effect of fiber orientation on the thermal conductivity of a uniaxial carbon fiber-reinforced borosilicate glass was conducted. For thin specimens, and thick specimens with specimen sides cut parallel to the fiber direction, the dependence of thermal conductivity on fiber orientation showed excellent agreement with theoretical behavior predicted for a composite infinite in extent. In contrast, the thermal conductivity data for rectangular thick specimens fell well below the data for the thin and angled specimens. For fiber orientation of  $45^\circ$  and higher, at which the heat was directed towards the sides of the specimen rather than the top, the thermal conductivity values showed excellent agreement with theoretical behavior predicted for a finite composite strip with insulated sides.

## 6.2 INTRODUCTION

The development of fiber-reinforced brittle matrix composites has led to major improvements in such properties as fracture toughness, brittleness, strength, etc. [1-6]. Generally, the thermal conductivity of the fibers exceed that of the matrix, so that increases in thermal diffusivity and/or conductivity of the composite are observed as well [7-11]. The thermal conductivity of fiber- or whisker reinforced composites has received a great deal of theoretical interest [11-18]. In general, the thermal conductivity of such composites has been shown to be a function of the thermal conductivity values and the volume fractions of the fibers and matrix, the fiber orientation and the degree of thermal contact at the fiber-matrix interface. The effective thermal conductivity of a uniaxial composite in any direction relative to the fibers can be calculated from the values of the thermal conductivity parallel and perpendicular to the fiber direction [18]. The above theories generally have assumed that the composite is infinite in extent and have not taken into account the possible effect of finite size of the composite specimen. As pointed out by Nye [19] and Carslaw and Jaeger [20], the net direction of heat flow within single crystals with anisotropic thermal conductivity does not necessarily coincide with the direction of the imposed temperature gradient. This should also be relevant for fiber- reinforced composites, which in general are expected to exhibit anisotropic thermal conductivity. Depending on the fiber angle, the presence of insulated boundaries parallel to the imposed temperature gradient can interfere with the net heat flow within the composite. In this respect, the recent analysis of Hasselman, et al [21] showed that depending on the orientation of the fibers, the effective thermal conductivity of a uniaxially reinforced composite strip of finite width can be a great deal less than the value for an infinitely large plate.

For a composite strip with insulated sides with a temperature gradient imposed along the length of the strip, the effective thermal conductivity along the length of the strip was derived to be [21]:

$$K_z = (K_p \cos^2 \theta + K_n \sin^2 \theta) - \left[ \frac{(K_p - K_n)^2 \sin^2 \theta \cos^2 \theta}{(K_p \sin^2 \theta + K_n \cos^2 \theta)} \right] \quad (1)$$

where  $K$  is the thermal conductivity, the subscripts  $z$ ,  $p$  and  $n$  refer to the composite and the directions parallel and perpendicular to the fiber direction, respectively, and  $\theta$  is the angle between the fiber direction and the temperature gradient. The thermal conductivity of the composite, parallel to the fiber direction is given by the rule of mixtures:

$$K_p = K_m V_m + K_f V_f \quad (2)$$

where  $K$  and  $V$  are the thermal conductivity and volume fraction, respectively and the subscripts  $p$ ,  $m$  and  $f$  represent the matrix and fiber, respectively.

The composite thermal conductivity,  $K_n$ , perpendicular to the fiber direction, including the effect of an interfacial thermal barrier for a dilute volume fraction of the fibers, as derived by Hasselman and Johnson [16], is:

$$K_c = K_m \frac{\left[ \left( \frac{K_f}{K_m} - 1 - \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]}{\left[ \left( 1 - \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) V_f + \left( 1 + \frac{K_f}{K_m} + \frac{K_f}{ah_i} \right) \right]} \quad (3)$$

where  $a$  is the fiber radius and  $h_c$  is the interfacial thermal conductance.

For an infinite composite plate, the thermal conductivity, unaffected by the presence of insulated edges is [17]:

$$K_c = K_p \cos^2 \theta + K_n \sin^2 \theta \quad (4)$$

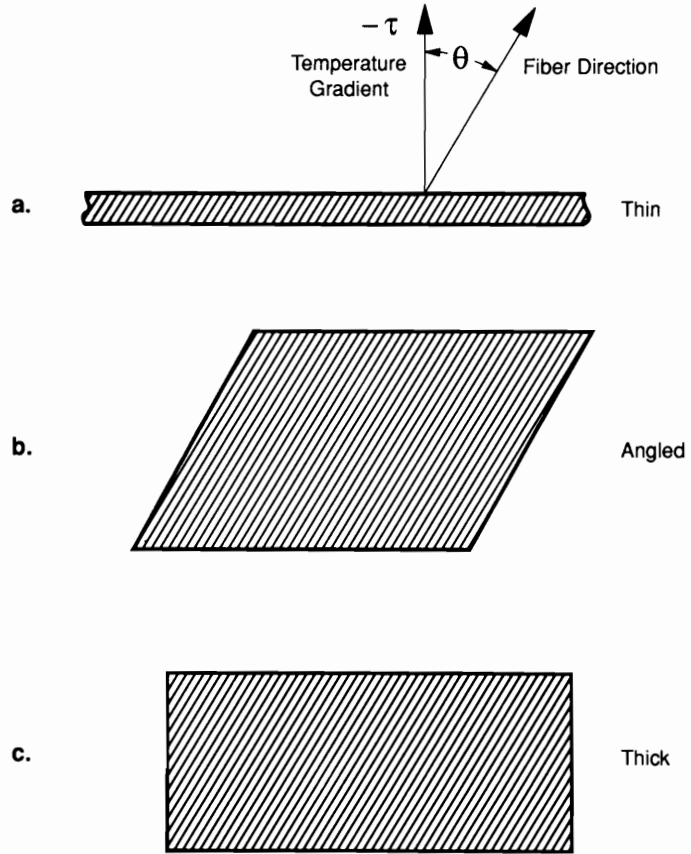
The angle  $\psi$  between the direction of net heat flow and the fiber direction is given by:

$$\tan \psi = \left( \frac{K_n}{K_p} \right) \tan \theta \quad (5)$$

Equation 5 indicates that for highly anisotropic composites with  $K_n/K_p \rightarrow 0$ , the direction of heat flow coincides with the direction of the fibers. In general, the direction of heat flow will occur at an angle  $\psi - \theta$  to the direction of the temperature gradient.

Comparison of equations 1 and 2 indicates that the second term on the right-hand side of equation 1 represents the decrease in the thermal conductivity of the composite, if heat flow within the composite is affected by the presence of insulated edges. The effect of the insulated edges on the effective thermal conductivity of fiber-reinforced

composites has implications for the thermal performance of such composites in design, as well as the effect of specimen geometry on measured values of the thermal conductivity. Let us consider the three specimen geometries shown in figure 1. The fibers are assumed to lie in the plane of the figure at an angle  $\theta$  to the imposed temperature gradient. The sample of figure 1a having width much greater than the thickness will be referred to as the "thin" sample. It is expected that in the center of this sample, far removed from the edges and associated effects, the effective thermal conductivity will be very close to the thermal conductivity value for an infinitely large composite, as expressed by equation 4. For the sample depicted in figure 1b, which will be referred to as the "angled" sample, heat flow will occur along the direction of the fibers. Because the edges are cut parallel to the fibers, they will not interfere with the flow of heat within the fibers. Again, it is expected that the thermal conductivity of this "angled" sample will also closely correspond to that given by equation 4. For the composite shown in figure 1c, which will be labelled as the "thick" specimen, the heat flow within the fibers is interrupted at the specimen edges. This condition formed the basis for the derivation of equation 1, for an infinitely long insulated strip. As a consequence, upon increasing the thickness of a composite specimen from the "thin" to the "thick" configuration, a decrease in the effective thermal conductivity is expected. Depending on the specimen thickness, this effect is expected to be small for small fiber angles relative to the temperature gradient, as most of the heat will be transported along the fibers to the front and back surfaces of the specimen. However, at high fiber angles, this effect is expected to be most pronounced, as the heat will be directed by the fibers to the side of the specimen rather than to the opposite surface. The experimental validation of this conclusion represented the objective of this study.

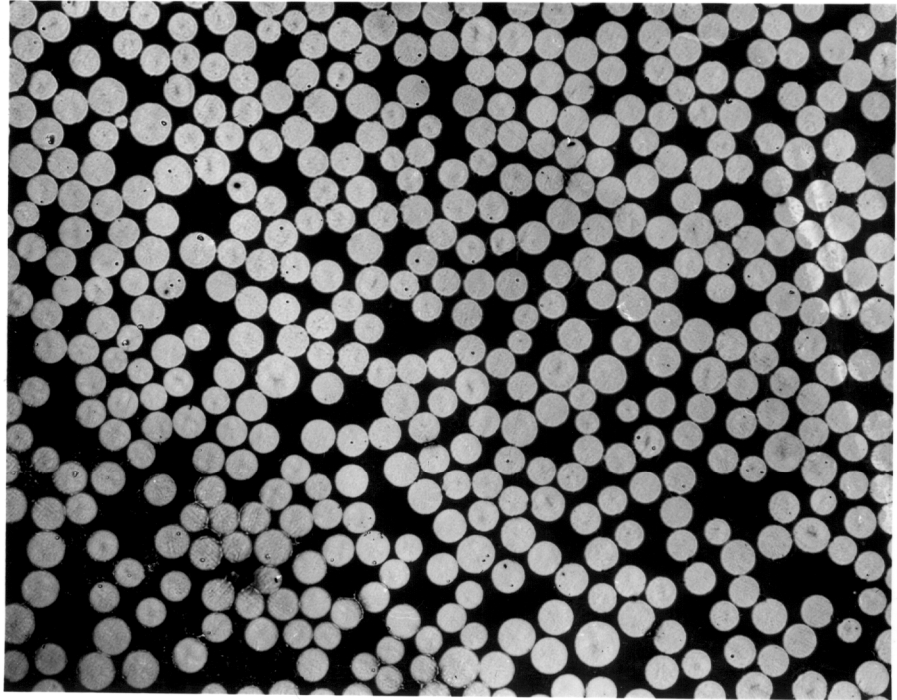


**Fig. 1:** Specimen geometries for measurement of thermal conductivity of uniaxial reinforced composite specimens: a. "thin", b. "angled" and c. "thick" specimen.

## 6.3 COMPOSITE AND EXPERIMENTAL APPROACH

The composite samples studied consisted of an alumino-boro-silicate glass(ABS-2) matrix uniaxially reinforced with Amoco P-55 carbon fibers. The composite density was 2.111 g/cc. An optical photomicrograph is shown in figure 2. The fiber diameter was of the order of 10  $\mu\text{m}$ . The fiber volume fraction was approx. 60 vol. %. Because of the close proximity of neighboring fibers, equation 3 may not be strictly valid. However, this will not affect the validity of equations 1 and 4. Three series of specimens with specimen geometries shown in figure 1 were cut from the larger composite block with a slow-speed diamond saw. The first series of specimens, which correspond to the "thin" samples of figure 1, were cut in the form of square platelets measuring approx. 8 x 8 mm with a thickness of approx. 2 mm over a range of values of fiber angle with respect to the sample plane. The second series of samples, which correspond to the "angled" samples of figure 1, were cut with the edges parallel to the fibers, again over a range of angles. The third series consisted of "thick" specimens measuring approx. 8 x 8 mm square by approx. 8 mm thick, over a range of angles between the fibers and the sample surfaces.

The heat conduction behavior of the samples at room temperature was obtained by measuring the thermal diffusivity, which, when multiplied by the volumetric heat capacity, yields the thermal conductivity. The thermal diffusivity was measured by the laser-flash technique [22]. The experimental details of this study were identical to those described elsewhere [7-10]. For this study, it is important to note that the IR-detector used to monitor the transient temperature of the rear face of the specimen, viewed a

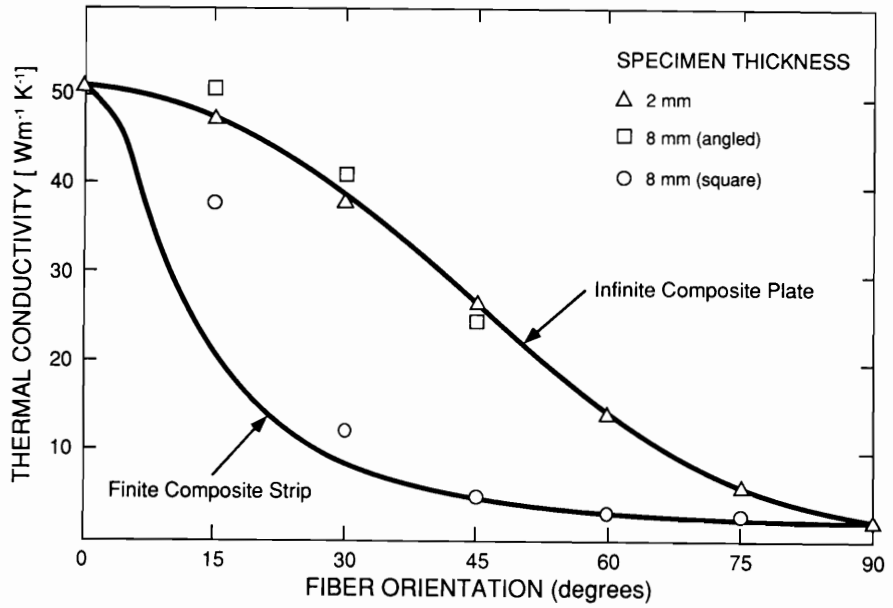


**Fig. 2:** Optical micrograph of section transverse to the fiber direction in uniaxial fiber-reinforced alumino-boro-silicate glass matrix composites.

circular area on the specimen surface approximately 4mm in diameter. The experimental data obtained for the "thin" and "angled" specimens were therefore not affected by any edge effects. In turn, this assured that the resulting values for the thermal conductivity would correspond to that given by equation 4. In calculating the thermal diffusivity from the transient temperature response, the thermal response of the sample was assumed to correspond to that of a homogeneous sample. The validity of this assumption was further assured because the area of the sample surface seen by the detector was much larger than the scale of the microstructure. The specific heat was measured by differential scanning calorimetry. The density of the composite was obtained from measured values of the volume and mass of a larger block of the composite.

## **6.4 RESULTS, DISCUSSION AND CONCLUSIONS.**

In figure 3, the experimental thermal conductivity for the three types of samples as a function of fiber angle, with the theoretically expected behaviors for the composite infinite in extent and the insulated strip of finite width are compared. The theoretical dependence was calculated from the thermal conductivity value for fiber angles of  $0^\circ$  and  $90^\circ$ , using equations 1 and 4. These results indicate that the values for the angular dependence of the thermal conductivity for the "thin" and "angled" samples, show excellent agreement with the theoretical behavior for the infinite composite. This is expected, as for these samples measured by means of the above procedures, the measured thermal response should not be affected by the presence of the edges of the specimens.



**Fig. 3:** Comparison of experimental data for the thermal conductivity of carbon fiber-reinforced alumino-boro-silicate glass matrix composite for "thin", "angled" and "thick" specimens as a function of fiber orientation with theoretically predicted behavior for an infinite composite plate and finite composite strip with thermally insulated edges.

In contrast, the data for the "thick" specimens fall well below those for the "thin" and "angled" specimens. This is particularly true at angles in excess of  $45^\circ$ , where the heat will be conducted by the fibers towards the side of the specimens, rather than directly towards the opposite face. For the higher fiber angles, the experimental data show excellent agreement with the theoretical behavior predicted for a finite composite strip with insulated sides. At fiber angles of less than  $45^\circ$ , the experimental data for the "thick" samples lie above those predicted by theory. This is to be expected, as at the lower fiber angles at least a fraction of the fibers will conduct heat from one side of the specimen to the other for the specific specimen thickness selected for this study. For this reason, the corresponding data for the thermal conductivity are expected to lie between the theoretical values for the composite plate infinite in extent and the composite strip of finite width with insulated sides. If for this study an even larger value of specimen thickness had been selected for the "thick" specimen, the fiber angle at which the experimental data agreed with the theoretical behavior for the insulated composite strip, would have been less than  $45^\circ$ .

In general, the excellent agreement between the experimental data for the "thin" and "angled" specimens for all fiber angles and the data for the "thick" specimens at angles of  $45^\circ$  and larger with the corresponding values predicted from theory provides support for the validity of the underlying theoretical principles. From a practical perspective, the observations of this study should be valid for other anisotropic composites and need to be taken into account not only in design, but also in the generation of experimental data.

## **ACKNOWLEDGMENT**

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## **7.0**

### **SUMMARY AND CONCLUSIONS**

A study carried out on the effect of an interfacial thermal barrier on the thermal diffusivity/conductivity of unidirectionally silicon carbide fiber reinforced reaction-bonded silicon nitride composites and the effect of fiber orientation on the effective thermal diffusivity/conductivity of carbon fiber reinforced borosilicate glass composites, led to the following conclusions.

#### **7.1 EFFECT OF INTERFACIAL THERMAL BARRIER**

- 1) The existence of an interfacial thermal barrier at the fiber-matrix interface for heat flow transverse to the fiber direction, strongly affected the thermal diffusivity/conductivity of all the composites studied, as predicted from theory.
- 2) Removal of the interfacial carbon coating by preferential oxidation of the as-made (reference) composites significantly reduced the thermal diffusivity/conductivity transverse to the fiber direction.
- 3) HIP'ing the as-made composites resulted in increased thermal diffusivity/conductivity of the composites in both transverse and parallel to the fiber direction. This increase was attributed to the densification of the matrix, increase in the thermal

conductivity of the fibers due to extensive growth of crystallites and increased physical contact at the fiber-matrix interface.

4) The thermal diffusivity/conductivity of the as-made composites with the interfacial carbon coating intact showed dependence on the type of atmosphere present. This observation was attributed to the formation of an interfacial gap at the fiber-matrix interface due to the thermal expansion mismatch of the fiber and matrix phase. The formation of an interfacial gap allowed access to gases at the interface, thereby incrementing the heat conduction due to gaseous heat transfer.

5) Similar atmospheric dependence of the thermal diffusivity/conductivity was also observed in the oxidized as well as HIP'd composites, indicative of the contribution of the gaseous heat conduction at the fiber-matrix interface. The composite with no carbon coating did not exhibit any atmospheric dependence for the transverse thermal conductivity as well as a very high value of interfacial shear strength, indicating very strong bonding between the fibers and the matrix.

6) Interfacial conductances calculated from measured values of the thermal diffusivities exhibited a positive temperature dependence for as-made as well as HIP'd composites. This phenomenon was attributed to the increased physical contact at the interface due to the closure of the interfacial gap with increasing temperature.

7) Removal of the interfacial carbon coating by oxidation caused a significant decrease (about one order of magnitude) in the interfacial conductances as compared to the as-made composites. This was a direct result of the decreased physical contact at the fiber-matrix interface. The interfacial conductance of the composites with no carbon

coating was an order of magnitude higher than the as-made composites due to strong bonding between the fiber and the matrix.

8) The relative values of the interfacial conductances in helium, nitrogen and vacuum for as-made, oxidized and HIP'd composites were consistent with the thermal conductivities of the three atmospheres, i.e. highest for helium, intermediate for nitrogen and lowest for vacuum.

9) The values of the interfacial conductances for all the composites studied spanned two orders of magnitude, the order of ascent being oxidized, as-made, HIP'd and the composite with no carbon coating. This observation is consistent with the extent of physical contact for each composite at the fiber-matrix interface.

In summary, the results of this study have established the important role an interfacial thermal barrier at the fiber-matrix interface can play in determining the transverse thermal diffusivity/conductivity of unidirectionally reinforced ceramic matrix composites. In view of the current trend in ceramic composites research of tailoring interfaces to achieve optimum interfacial mechanical properties, the corresponding thermal effects based on this study should be expected and accounted for. In addition, composites with interfacial gaps have exhibited atmospheric dependence of their thermal diffusivity/conductivity, thereby making it necessary to determine or predict their properties in different atmospheres for use in composite design.

## 7.2 EFFECT OF FIBER ORIENTATION

1) The analysis carried out on the effective thermal conductivity of a uniaxially reinforced composite strip with insulated edges as a function of the fiber angle with the temperature gradient showed that the presence of the insulated edges lowered the thermal conductivity considerably, relative to the thermal conductivity of a composite infinite in extent.

2) This difference was found to increase with an increase in the parallel to transverse conductivity ratio ( $K_p/K_n$ ) of the composite for any given angle of the fibers. The angle at which this difference was maximum decreased with increasing value of  $K_p/K_n$ .

3) Experimental investigation of this analysis was carried out on samples of carbon fiber reinforced aluminoborosilicate glass composite. The effective thermal conductivity of thin specimens and angled specimens with geometry such that their net direction of heat flow was parallel to the fiber direction showed excellent agreement with the expected behavior of an infinite composite plate. The effective thermal conductivity of the thick specimens was in excellent agreement with the values calculated from the analytical model for high fiber angles greater than  $45^\circ$ .

In summary, the results of this study have shown that the effective off-axis thermal conductivity of a uniaxially finite composite strip with insulated edges can be significant lower than the corresponding thermal conductivity of a composite plate infinite in extent. From a practical perspective these effects need to be taken into account not only for design purposes, but also for interpretation of experimental data.

# 8.0

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