Influence of fiber-matrix interphase on high temperature behavior of glass-ceramic matrix composites by Ramazan Kahraman

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University

Abstract:
The influence of the fiber-matrix interphase on the high temperature behavior of Nicalon fiber reinforced CAS-II glass-ceramic matrix composites has been investigated. Unidirectional and cross-ply laminates were studied from 20° up to 1000°C. Tensile testing at 1000°C in air lowered the longitudinal unidirectional strength to the stress level at which matrix cracking began to occur. Interfaces exposed along matrix cracks increased in bond strength, resulting in brittle composite fracture. The strength of crossplied composites was also severely reduced in 800°C air. Transverse plies cracked prior to 0° ply matrix cracking. However, embrittlement did not occur until the matrix in the 0° plies cracked.

Interphase oxidation did not appear to play a significant role in crack growth parallel to the fibers of transverse plies except near exposed edges. Oxygen did not appear to have penetrated the transverse cracks except directly on the specimen fracture surface. This was evidenced by a lack of bond strength changes along the transverse ply cracks. The surprising lack of apparent oxidation effects on 90&deg, ply cracking led to further investigation of crack growth parallel to the fibers using the double torsion test to measure the transverse fracture toughness (Glc) of unidirectional materials, and to look for evidence of environmental stress cracking. Glc did decrease moderately with increasing temperature (as does the bulk matrix), but no evidence of an interphase oxidizing effect on crack growth could be found. Cracks would not grow in the oxidizing environment at G1 values slightly below GIc, and oxidation did not occur on the part of the fracture surface which was cracked but not widely opened during the test.

The results of this study establish that oxidation does not take part in crack growth parallel to the fibers, except adjacent to exposed edges. Neither does oxygen enter 90° ply cracks in crossplied composites in sufficient quantity to produce oxidation embrittlement, at least up to the 0° matrix cracking strain. Matrix cracks in the 0° plies at higher strains do allow oxidation embrittlement of the 0° plies in unidirectional and crossplied composites. Contacts between fibers and matrix along the 90° ply cracks may locally seal-off and prevent further spread of oxygen. No such contacts and possible sealing-off occur along matrix cracks in the 0° plies, and oxygen is free to spread throughout the opened matrix crack to reach the carbon interphase regions.

INFLUENCE OF FIBER-MATRIX INTERPHASE ON HIGH TEMPERATURE BEHAVIOR OF GLASS-CERAMIC MATRIX COMPOSITES

by

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Dedicated to my mother, Hatice Sümer

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ABSTRACT

The influence of the fiber-matrix interphase on the high temperature behavior of Nicalon fiber reinforced CAS-II glass-ceramic matrix composites has been investigated. Unidirectional and cross-ply laminates were studied from 20° up to 1000°C. Tensile testing at 1000°C in air lowered the longitudinal unidirectional strength to the stress level at which matrix cracking began to occur. Interfaces exposed along matrix cracks increased in bond strength, resulting in brittle composite fracture. The strength of crossplied composites was also severely reduced in 800°C air. Transverse plies cracked prior to 0° ply matrix cracking. However, embrittlement did not occur until the matrix in the 0° plies cracked.

Interphase oxidation did not appear to play a significant role in crack growth parallel to the fibers of transverse plies except near exposed edges. Oxygen did not appear to have penetrated the transverse cracks except directly on the specimen fracture surface. This was evidenced by a lack of bond strength changes along the transverse ply cracks. The surprising lack of apparent oxidation effects on 90° ply cracking led to further investigation of crack growth parallel to the fibers using the double torsion test to measure the transverse fracture toughness (G_{Ic}) of unidirectional materials, and to look for evidence of environmental stress cracking. G_{Ic} did decrease moderately with increasing temperature (as does the bulk matrix), but no evidence of an interphase oxidizing effect on crack growth could be found. Cracks would not grow in the oxidizing environment at G_I values slightly below G_{Ic}, and oxidation did not occur on the part of the fracture surface which was cracked but not widely opened during the test.

The results of this study establish that oxidation does not take part in crack growth parallel to the fibers, except adjacent to exposed edges. Neither does oxygen enter 90° ply cracks in crossplied composites in sufficient quantity to produce oxidation embrittlement, at least up to the 0° matrix cracking strain. Matrix cracks in the 0° plies at higher strains do allow oxidation embrittlement of the 0° plies in unidirectional and crossplied composites. Contacts between fibers and matrix along the 90° ply cracks may locally seal-off and prevent further spread of oxygen. No such contacts and possible sealing-off occur along matrix cracks in the 0° plies, and oxygen is free to spread throughout the opened matrix crack to reach the carbon interphase regions.

INTRODUCTION

Glass-ceramic materials are ceramics produced by the controlled crystallization of appropriate glasses [1]. When these materials are fabricated, they are processed as glasses (while the materials are in a viscous form), then crystallized under controlled heat treatment conditions to achieve materials with superior toughness and high temperature strength [2]. They consist of a large proportion, typically 95 to 98 volume percent, of very small crystals, generally smaller than 1 micron, with a small amount of residual glass (amorphous) phase to make up a pore-free ceramic [1].

The recent development of ceramic or glass-ceramic matrix composites has been driven primarily by the need for high temperature structural materials for applications such as heat engines and space planes. While monolithic structural ceramics and glass-ceramics are also being developed to meet these needs, they have problems in structural applications due to their inherent brittleness. Glass-ceramic matrix composites offer potential to achieve high performance at high temperatures [3]. Considerable attention has been focused on (continuous or relatively long) fiber-reinforced glass-ceramics. The fiber addition increases toughness through crack deflection and fiber bridging behind the crack tip [3,4].

Ceramic matrix composites do not simply consist of a combination of reinforcement and matrix phases. More typically, either through fiber precoating or through reactions during processing, the resultant composites contain an interphase region separating the reinforcement and matrix phases that is very important in controlling the properties of the composite. Chemical compositions and processing conditions have a strong influence on the thickness of this interphase [3,5]. The main objective of this research was to develop a better understanding of the influence of the fiber-matrix interphase on high temperature behavior of multidirectional glass-ceramic matrix composites under the oxidizing conditions which exist in most potential applications.

BACKGROUND

Ceramic and glass-ceramic composites offer a great range of utility both on a high temperature basis as well as on other environmental considerations such as oxidation resistance, erosion, and chemical attack from acids, etc. [2,6]. The properties of these composites depend on the combination of the properties of starting materials and the fabrication procedure [3]. The fibers should not be greatly degraded during processing either by handling or by chemical reaction. Also, the resultant fiber-matrix interphase must have the characteristics necessary for optimum composite properties, as will be discussed in the following sections.

Mechanical Behavior of Ceramic Matrix Composites

Longitudinal Tensile Strength

In ceramic matrix composites (CMC's), the matrix failure strains are generally less than the fiber breaking strains [7,8,9]. The lower matrix failure strain indicates matrix failure prior to fiber failure. The possible failure modes for unidirectional CMC's are depicted in Figure 1 [10]. For strongly bonded systems, cracks formed in the matrix propagate through the interphase and the fibers without causing fiber-

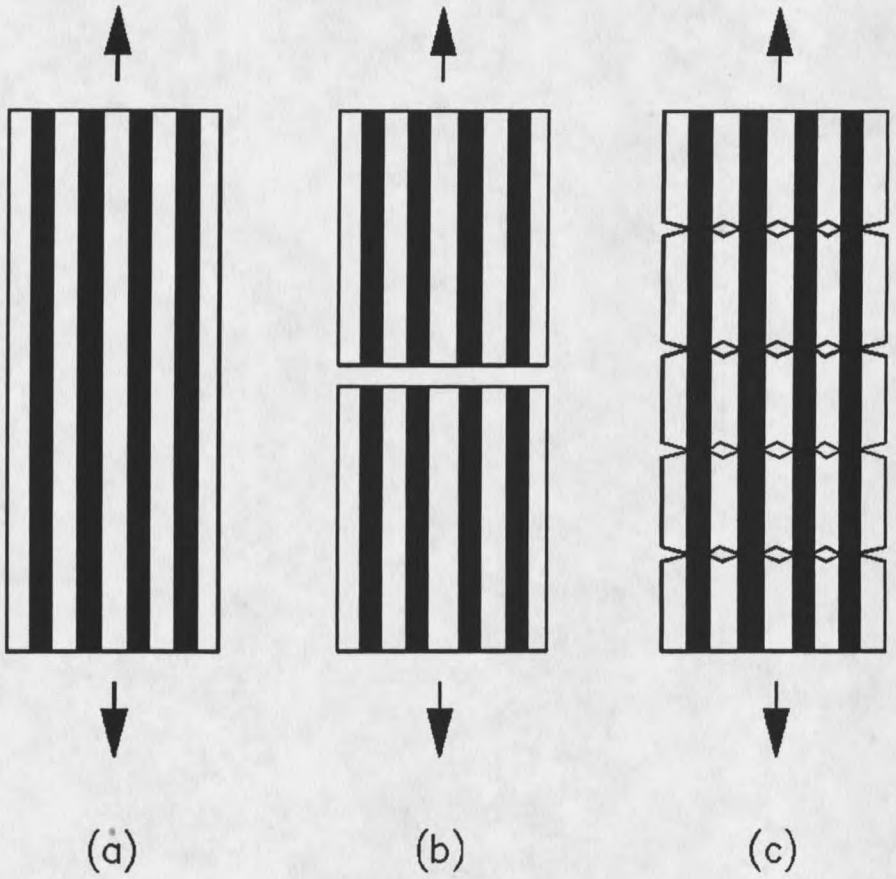

Figure 1. Failure processes in ceramic composites [10]: (a) before fracture; (b) simultaneous matrix and fiber fracture in a strongly bonded system; (c) multiple matrix cracking and fiber debonding prior to fiber failure in a weakly bonded system

matrix debonding as shown in Figure 1b [11]. Composite failure occurs at the matrix failure strain (ε_{mu}) by propagation of a single crack through the fibers. A linear stress-strain curve (Figure 2a) results due to the brittle nature of the fracture. Composite longitudinal strength (σ_{cL}) and modulus (E_{cL}) are expressed by the rule of mixtures [12]:

$$\sigma_{cL} = E_{cL}\varepsilon_{mu} \tag{2}$$

$$E_{cL} = E_f V_f + E_m V_m \tag{1}$$

where E_f : fiber modulus

V_f : fiber volume fraction

E_m : matrix modulus

V_m : matrix volume fraction ($1-V_f$)

Some strength enhancement is possible with high modulus fibers through the higher E_{cL}, but this is limited. The composite failure strain remains essentially unchanged from that of the unreinforced typically brittle matrix. In addition, longitudinal toughness (resistance to crack growth perpendicular to fibers due to a longitudinal stress) is not greatly enhanced over that of the matrix.

Stronger CMC's are possible in weakly bonded systems above a critical fiber volume fraction, V_{cr}. The dependence of composite strength on V_f is illustrated in Figure 3 [13]. If the fiber content is too low, the reinforcing fibers may be

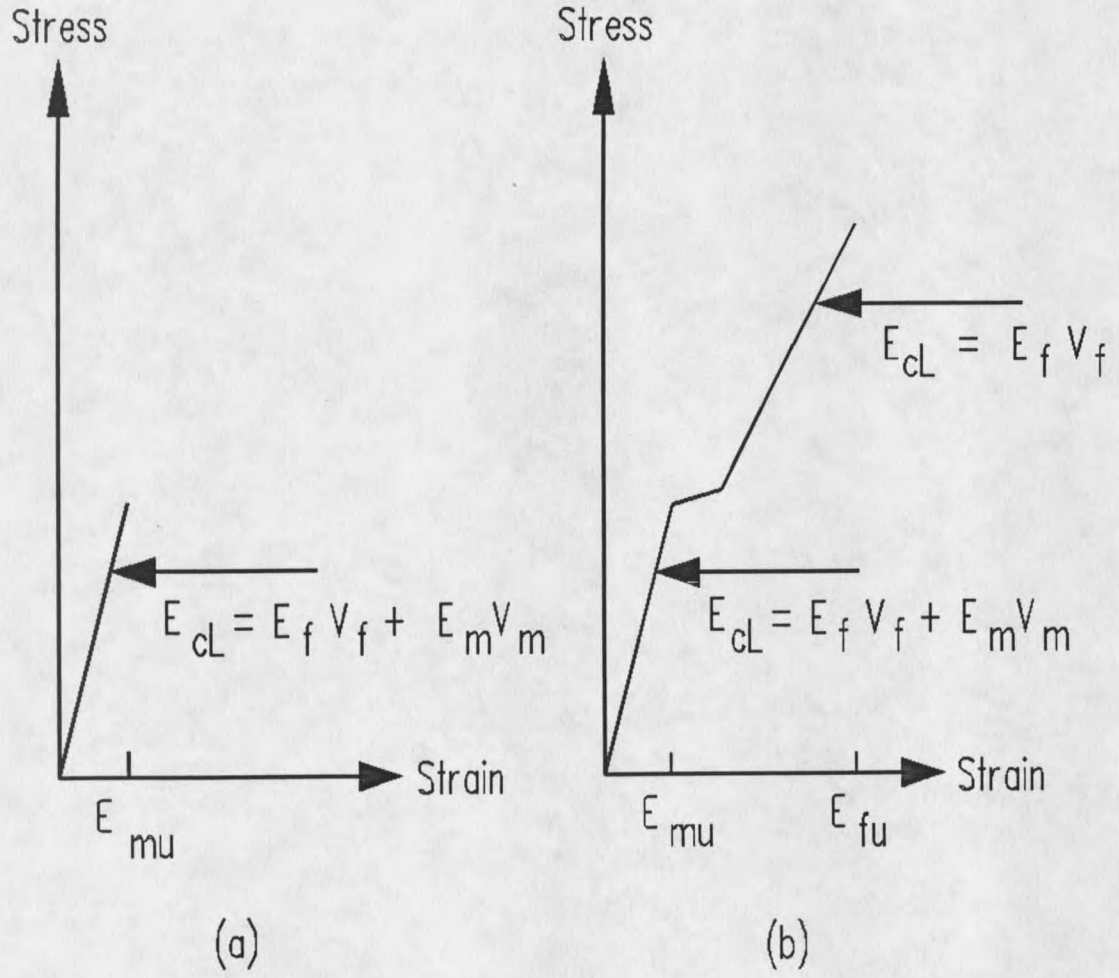

Figure 2. Model longitudinal tensile stress-strain behavior for fiber reinforced ceramic matrix composites [10]: (a) strongly bonded system; (b) weakly bonded system

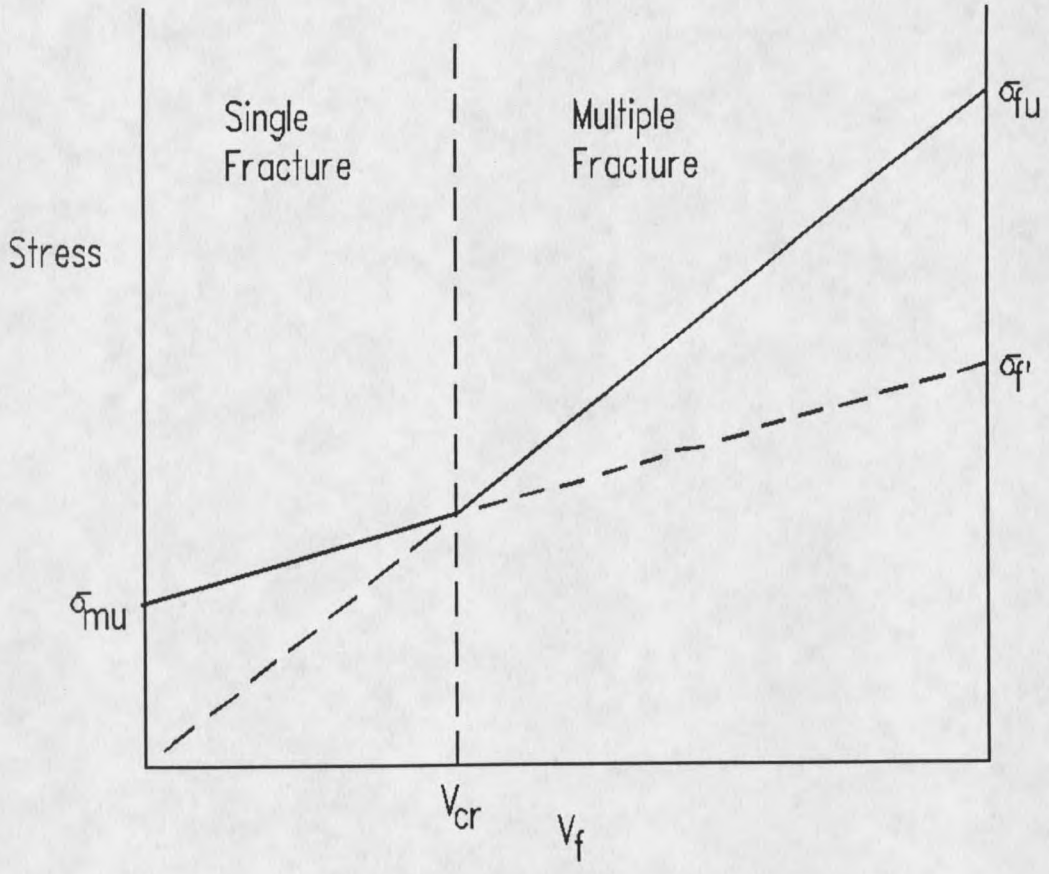

Figure 3. Dependence of composite strength on fiber content [13] (where σ_{mu} is matrix strength, σ_{fu} is fiber strength and $\sigma_{f'}$ is stress in the fiber at matrix fracture)

unable to support the total load carried by the composite when the matrix fails. Below V_{cr}, even in weakly bonded systems, composite strength is governed by the strength of the matrix. Failure occurs by single fracture, as described above.

Above V_{cr}, weakly bonded composites (Figure 1c) do not fail by the propagation of a single matrix crack [12,13,14]. The weak bond (or interphase) prevents spontaneous propagation of matrix cracks through adjacent fibers. After initial cracking of the matrix, the load is transferred to the fibers. The high fiber content allows support of the applied load, and multiple matrix cracking occurs with further stressing. The fiber volume fraction at the transition from single to multiple fracture is [12]:

$$V_{cr} = \frac{\sigma_{mu}}{\sigma_{mu} + \sigma_{fu} - \sigma_{f'}} \qquad (3)$$

where σ_{mu} : matrix strength

σ_{fu} : fiber strength

$\sigma_{f'}$: stress in the fiber at matrix fracture

Matrix cracking, accompanied by load transfer to the fibers, can continue until a saturation crack density level is achieved. After matrix crack saturation, the fibers bear almost all of the load. Failure of the composite occurs when the fracture strength of the fibers is exceeded.

The stress-strain curve for weakly bonded composites is non-linear, consisting of three distinct regions as shown in Figure 2b [13]. In the initial linear portion of the curve, the composite stress and modulus are described by the rule of mixtures. A deviation from linearity occurs at the matrix microcracking strain. Further load increase beyond the onset of microcracking causes additional matrix cracking and a permanent decrease in composite stiffness due to a decreased matrix contribution. The final linear regime of the stress-strain curve is governed primarily by fiber properties. Failure of the ideal composite material occurs at an ultimate tensile strength approximated by the product of fiber strength and fiber volume fraction ($\sigma_{fu}V_f$). The ultimate composite failure strain, ε_{cu}, is increased over that of the unreinforced matrix and is (approximately) equivalent to that of the reinforcing fibers.

Longitudinal Toughness

The toughness (for cracks perpendicular to fibers) of CMC's cannot be expressed in terms of conventional fracture mechanics parameters (i.e. critical stress intensity factor) since failure does not occur by the growth of a single crack. While the toughness cannot be readily quantified, the resistance to notches and flaws is greatly increased if the fiber-matrix bond is weak, and then the behavior parallels

that of tough reinforced plastics [3,11]. If the interfacial bond is strong, the longitudinal toughness can be as low as that of the monolithic matrix, since a single planar crack grows through the fibers and matrix [5,11,12].

Transverse Properties

In most theoretical and experimental treatments of ceramic matrix composites, only the improvements in longitudinal properties over the monolithic matrix materials are highlighted. Little coverage is given to transverse properties of these composites. The transverse properties of uniaxially reinforced ceramics depend on the toughness of the matrix and interface directly, with little benefit of effects like fiber bridging, as will be discussed in the following section.

The poor transverse properties of some unidirectionally reinforced ceramics limit their use, since there are few engineering applications where transverse stresses are not encountered [10,14]. The resistance to crack growth parallel to the fibers is especially a determining factor for the useful design stress range since cracking parallel to the fibers is usually the initial form of damage in multidirectional composites [15]. This cracking process has been associated with the (transverse) fracture toughness, defined by the critical strain energy release rate, G_{Ic}

[16,17], which will be discussed in detail later.

Interface (or Interphase) Effects on Composite Properties

The fiber-matrix interphase plays a critical role in transferring loads in a composite. Figure 4 [11] illustrates three critical aspects of glass and ceramic matrix composite behavior which depend strongly on the interphase. The off-axis and shear properties (Figure 4a) such as shear strength, transverse tensile strength and transverse toughness are expected to correlate directly with fiber-matrix bond strength if other parameters remain unchanged [11,14].

Figures 4b and 4c illustrate the effect of the interphase on composite longitudinal toughness. As noted earlier, if the interphase is too strong, then, when matrix cracks form normal to the fibers, they can propagate through the fibers, giving brittle behavior similar to that in monolithic glasses and ceramics [5,11,12,18,19]. A sufficiently low fiber-matrix bond strength will increase flaw tolerance by allowing fiber debonding during crack propagation perpendicular to the fibers (fiber bridging) and/or by deflecting matrix cracks parallel to the fibers [3,11,12].

The pattern in glass and ceramic matrix systems without strong bonding of forming matrix cracks normal to the locally debonded fibers is indicated in Figure 4c. The stress at which significant matrix cracks form in unidirectional specimens

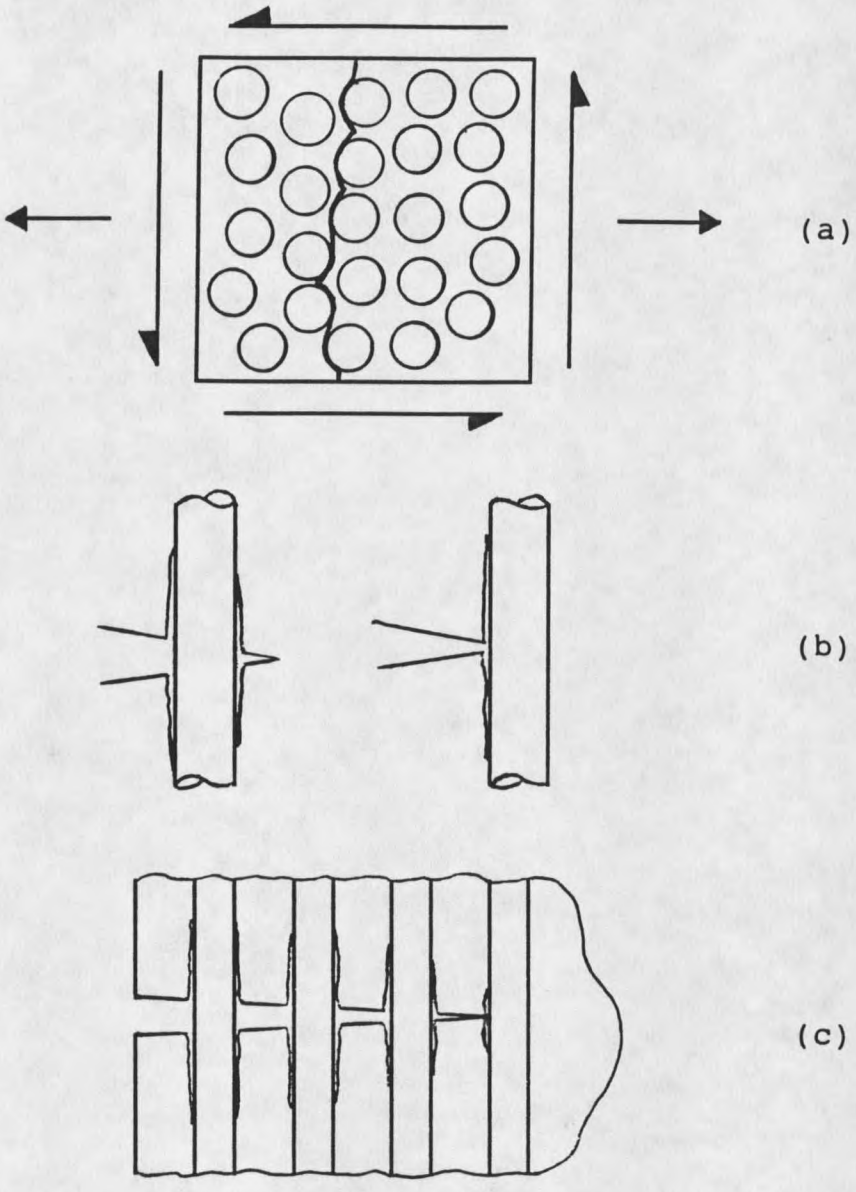

Figure 4. Interface dominated properties [11]: (a) off-axis and shear strength; (b) flaw tolerance (debonding or matrix crack deflection to prevent matrix crack penetration through the fibers); (c) resistance to the growth of matrix cracks in longitudinal tension: propagation of matrix crack with bridging fibers

loaded in tension parallel to the fibers limits their practical use conditions. As described earlier, the opening of large matrix cracks is resisted in part by work done against friction as the matrix slides relative to the unbroken, bridging fibers. Thus, both the tendency to initiate debonding and the subsequent resistance to sliding of the matrix relative to the fibers appear to be two important factors in determining the working stress range of some ceramic matrix materials.

As anticipated, the maintenance of a low interfacial bond strength is critical to achieving composite toughness in the direction of fibers. However, while providing the desired (longitudinal) toughness, this also causes low off-axis composite strength and the need for multiaxial fiber reinforcement for most engineering applications.

Interphase in Nicalon Reinforced Glass-Ceramics

As described earlier, by choosing high-strength, relatively high-modulus, continuous (or relatively long) fibers and incorporating them into matrices, high-strength and tough composites can be created if the fiber-matrix interphase is weak enough to divert and/or bridge cracks. The ultimate strength of such a composite is then controlled by the in-situ fiber strength, and a composite tensile strength well beyond that associated with matrix cracking can be achieved [3]. The

Nicalon-fiber-reinforced lithium-aluminosilicate (LAS) glass-ceramic (Nicalon/LAS) system has met these requirements through the development of a carbon-rich fiber-matrix interphase during processing, and with no deterioration in fiber strength [2,3].

The invention of the continuous polymer-derived SiC based fiber Nicalon (Nippon Carbon Company, Tokyo, Japan) has permitted the development of high-temperature, high-performance ceramic or glass-ceramic matrix composites [2,3,5,20]. Nicalon, with an average tensile strength and elastic modulus of 1920 MPa [21] and 193 GPa [2,20,21] respectively, has a unique nonstoichiometric chemistry that makes it particularly suited to the development of high-strength glass-ceramic matrix composites. Initially, composites with excellent strength were achieved using glass matrices. To achieve the highest levels of temperature resistance, however, the use of crystallized LAS matrices proved most advantageous [2,20]. By densifying (to remove porosity) the composites while the matrix is amorphous and of low viscosity and then crystallizing (ceraming) afterwards, it is possible to produce a very refractory composite with high strength and toughness [2].

Chemical reactions can occur between the fiber and matrix during processing of Nicalon reinforced glass-ceramics, producing the carbon-rich interphase region [3,5,18,20]. The strength of the fiber-matrix interphase and the resulting

composite mechanical properties are significantly influenced by the formation of such interphase regions [18]. The carbon-rich layer of moderate strength effectively limits load transfer between the matrix and the strong fiber either by cohesively failing or adhesively separating from the fiber or the matrix. The carbon-rich layer forms a bond strong enough for load transfer, yet weak enough to debond readily and allow fiber bridging during crack propagation [5,22]. The layer is either nonexistent or carbon-poor in composites that exhibit little toughness [22].

Environmental Effects

Nicalon reinforced glass-ceramic matrix composites with a well developed carbon interphase exhibit excellent longitudinal toughness and crack deflecting ability at room temperature [3,5,20,23]. However, reductions of strength and strain to failure (in the fiber direction) have been observed when testing at temperatures as low as 400°C [24].

The testing of the Nicalon/LAS system in air at 700°C or above has lowered composite tensile strength to the stress level at which matrix cracking begins to occur [25]. Similar embrittlement has been reported for Nicalon/BMAS (barium-magnesium-aluminosilicate) [26] and Nicalon/CAS (calcium-aluminosilicate) [27] composites upon testing in air at temperatures exceeding 800°C. In contrast to room temperature