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Fracture of aluminum phosphate-alumina matrix silicon carbide fiber reinforced laminated composites

Lee Hong, Ph.D.
University of Nevada, Reno 1962
The dissertation of Hong Li is approved:

[Signature]

Dissertation Advisor

[Signature]

Department Chair

[Signature]

Dean, Graduate School

University of Nevada

Reno

February 1992
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Fracture of Aluminum Phosphate/Alumina Matrix
Silicon Carbide Fiber Reinforced Laminated Composites

by Hong Li

Chairperson of the advisory committee: Professor Richard C. Bradt
Mackay School of Mines
University of Nevada, Reno

The fracture of SiC/Al₂O₃-AlPO₄ cementitious matrix, 2D woven fabric, laminated composites was investigated from room temperature to 1200 °C. The differences in the mechanical properties were studied in terms of (i) the carbon coating on the fibers and (ii) temperature. A significant result of this thesis was the major effect of the matrix bond phase transition of the AlPO₄ on the fracture resistance. A distinct transition of the fracture from toughened-to-embrittled was observed at 600 °C for the three composites. For temperatures below 600 °C, the carbon coating promotes a weak interfacial bonding at the fiber/matrix interface. Consequently, fiber debonding and fiber pull-out contribute to the rising R-curves of the composites. At temperatures above 600 °C, the thermally induced clamping stresses on the fibers are large, while the effect of the carbon coating is insignificant. As a result, the interfacial bonding at the fiber/matrix interface is very strong. The lack of the fiber debonding and fiber pull-out result in a flat R-curves for these composites.
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1. Introduction and Statement of the Problem

Within the past two decades, studies of the fracture of monolithic single phase ceramics and multiphase ceramics have attained a maturity that now permits many fracture phenomena to be quantitatively described\[1-7\]. The predominant fracture initiating flaws have been identified and the fundamental mechanics and statistics related to their effects have been determined. In addition, the crack growth resistance exhibited by common ceramic microstructures has been modeled in terms of: microcrack toughening\[8-10\], transformation toughening\[11-12\], crack deflection toughening\[13\] and grain bridging toughening\[14-15\]. This progress has been extended to ceramic matrix composites which are reinforced by short fibers or whiskers\[16-22\], continuous fibers\[23-31\], particulates and particles\[32-42\].

For fiber reinforced ceramic matrix composites (FRCMC's), the subsequent development of micromechanical models has resulted in an improved understanding of the toughening mechanisms, relating the increases in the fracture toughness and the crack growth resistance to the mechanical properties of the reinforcements and to the interfacial characteristics of the fiber/matrix interface. Except for the energy consumed in the fracture of the matrix and fibers, the crack growth resistance of ceramic matrix composites is now attributed to several other energy consumption sources including the fiber debonding and the fiber pull-out. However, the most significant energy dissipation takes place during the fiber pull-out, which has been characterized as a wake region effect. In the wake region, behind an advancing crack tip, there exists a counter stress field (compressive) to that for the crack propagation. It results from the frictional shear stresses on the fibers as they are pulled out of the matrix\[43-57\]. For any given composite system that is composed of a fiber reinforcement and a matrix, the fracture resistance relies on the microstructural design.
and the optimization of the fiber/matrix interface characteristics. A weak interfacial bonding appears to be desirable to enhance crack growth resistance.

With the development of FRCMC's, there exists the need for greater understanding and development of micromechanical models to quantitatively describe and to specify fracture phenomena and parameters, such as the fracture toughness ($K_{IC}$), the general crack growth resistance (R-curve) and the total work of fracture (WOF). Existing models, however, are firmly based on well established linear elastic fracture mechanics (LEFM). For FRCMC's, there are no standards available to determine the fracture resistance parameters as a consequence of the difficulties presented by the nonlinearity which is present in those composites, where LEFM theory is simply not suitable. A related factor is the R-curve behavior of fiber reinforced composites, for the rising R-curve behavior of FRCMC's also creates uncertainty in the specification of the instability of fracture with respect to the conventional determination of the fracture toughness, $K_{IC}$. In glass and many monolithic ceramics, the minimum geometry factor ($Y_{min}$) corresponds to the instability point, yielding the fracture toughness ($K_{IC}$) for these brittle solids which do not have rising trends in terms of the crack growth resistance, but exhibit flat R-curve behavior. For materials which exhibit a rising R-curve, the degree of the aforementioned uncertainty is related to the specimen size and geometry[54,55]. Despite of this dilemma, Jenkins et al[56] have developed a 3-D finite element method for the chevron-notched three-point-bend specimen test, which has been applied successfully to both monolithic ceramics and to whisker reinforced ceramic composites[56].

Cementitious bonding of ceramics is well known as a fabrication technique for cementitious bonded refractories have long been commercially utilized in the ceramic industry on the basis of the advantages of energy savings and higher fabrication productivity. The unique attraction of this fabrication method for FRCMC's is the
possibility of room temperature consolidation processing. Production of the composite at room temperature protects the as-fabricated FRCMC's from any high temperature degradation of the mechanical properties during fabrication, especially those of the reinforcement fibers. There are numerous reports of studies of phosphate bonded monolithic alumina[57-65]. However, with respect to FRCMC's, there are no published studies of the processing or the mechanical properties of phosphate bonded composites.

Fracture of a variety of fiber reinforced ceramic composites is experiencing continual investigation. The studies of unidirectional fiber reinforced laminated composites can be found elsewhere[51-53]. There is little information on woven fabric laminated FRCMC's[66-69]. This is surprising for the latter has more practical applications because of their planar mechanical properties in two orientations, the two weave directions. Another potential advantage of woven fabric laminated FRCMC's is that their resistance to fracture may be enhanced by the additional interactions between the laminae during crack propagation. Therefore, it is essential to understand the fracture phenomena of woven fabric composites for potential engineering applications.

SiC fiber reinforced ceramic matrix composites are one of the most popular for both academic research and engineering applications because of the high temperature strength and oxidation resistance of commercially available SiC fibers, such as Nicalon fibers. Phosphate bonded alumina in the AlPO₄-Al₂O₃ system has been also extensively studied and exhibits good mechanical properties at elevated temperatures. Therefore, for this thesis, continuous Nicalon SiC fiber reinforced AlPO₄-Al₂O₃ matrix, woven fabric 2D laminated composites have been selected for study. It is well established that a significant toughening mechanism for the fiber reinforced ceramic matrix is fiber frictional pull-out during fracture of the composite. Therefore, the interfacial bonding at the fiber/matrix interface is very important. Fortunately, the interfacial bonding can be controlled during processing and
hence optimized by proper composite processing practice and fabrication. For this study, to evaluate interfacial effects on the mechanical properties of the composites, different thicknesses of pyrolytic carbon coatings (three) were applied to the SiC fiber surfaces prior to composite fabrication.

To summarize the aforementioned aspects associated with the development of FRCMC's, the objectives of the present research are: (i) to study the fracture behavior of SiC fiber reinforced ceramic matrix composites fabricated by the phosphate bonding refractory method, which are in the form of 2D woven fabric laminates, (ii) to investigate the effects of a pyrolytic carbon fiber surface coating on the mechanical properties of these composites, including the fracture toughness ($K_{IC}$), the modulus of rupture (MOR), the crack growth resistance (R-curve) and the total work of fracture (WOF), and (iii) to determine the effects of temperature on the above mentioned properties from room temperature through 1200 °C in air. To evaluate these composites, two different fracture test methods were used, including (i) chevron notched three-point-bend specimen, and (ii) the unnotched three-point-bend specimen of flexural strength MOR-specimen.
II. Review of Literatures

Development of continuous fiber reinforced cementitious ceramic matrix composites began in earnest following the successes of whisker reinforced ceramics and fiber reinforced ceramic matrix composites which were fabricated by chemical vapor infiltration. Advantages of utilizing a cementitious material to consolidate the matrix for fiber reinforced ceramic matrix composites are: (i) that the bonding between the fiber and the matrix is achieved at or near room temperature, (ii) the initial bonding is not achieved by thermally stimulated diffusion, (iii) thermal degradation of the reinforcements at elevated temperatures is avoided during the composite fabrication, and (iv) the energy requirements and the costs of composite manufacturing can be significantly reduced. Cementitious matrix ceramic composites thus have considerable appeal and potential.

Roy[70] has recently summarized developments of fiber reinforced cementitious ceramic matrix composites utilizing calcium silicate cement matrices. Some of the mechanical properties of these types of composites are summarized in Table 2.1. The flexural strengths are generally below 100 MPa and the fracture toughness values are only about 2.0 MPa-m$^{1/2}$. The magnitudes of these properties are somewhat disappointing, showing little improvement in their fracture toughness and less in their flexural strengths, compared with dense monolithic cements. It is obvious that there exists a need for better performance in terms of the aforementioned mechanical properties. To achieve a better design of a composite, understanding the reinforcement, matrix, and the interface between them is crucial. The following sections review the current understanding features on the mechanical behavior of fiber reinforced ceramic matrix composites.
Table 2.1

Mechanical Properties of Macrodefect-Free Cementitious Fiber Composites, after Roy [70]

<table>
<thead>
<tr>
<th>Fibers</th>
<th>1 MOR/KIC</th>
<th>5 MOR/KIC</th>
<th>10 MOR/KIC</th>
<th>15 MOR/KIC</th>
<th>20 MOR/KIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>93.1/-</td>
<td>85.3/-</td>
<td>70.2/-</td>
<td>75.3/-</td>
<td>60.8/-</td>
</tr>
<tr>
<td>Glass</td>
<td>84.0/1.66</td>
<td>79.1/1.17</td>
<td>79.4/1.74</td>
<td>81.0/1.88</td>
<td>84.5/1.85</td>
</tr>
<tr>
<td>Glass</td>
<td>78.5/2.30</td>
<td>80.8/2.38</td>
<td>100.6/2.41</td>
<td>110.0/2.48</td>
<td>88.0/2.13</td>
</tr>
<tr>
<td>Polymer</td>
<td>70.0/1.66</td>
<td>54.8/-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>91.0/2.68</td>
<td></td>
<td>122.9/3.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>94.2/2.51</td>
<td>103.3/-</td>
<td>126.8/2.81</td>
<td>100.3/-</td>
<td></td>
</tr>
<tr>
<td>Kevlar</td>
<td>83.3/2.09</td>
<td>93.0</td>
<td>89.0</td>
<td>58.3</td>
<td></td>
</tr>
</tbody>
</table>

*: Flexural strength, MPa. @: Fracture toughness, MPa-m¹/²
1: Fiberfrax, kolon ceramic fiber, Carborundum Co.
2: Cem-Fil alkali resistant, Pilkington Reinforcement limited
3: Collated fibrillated polypropylene fibrous reinforcement, Forta Corporation
4: Carbon Fiber, Zoltek Corporation
5: Polycrystalline alumina fiber, Saffil, ICI Products
6: Kevlar Aramid pulp, Du Pont Co.
2.1 Materials and Mechanical Properties

2.1.1 Silicon Carbide Fibers

Continuous SiC fiber reinforced ceramic matrix composites are promising for applications with specific demands for a combination of high specific elastic modulus, high specific strength, light weight and good thermal stability. Research of continuous SiC fibers has been in progress for nearly three decades. Following the development of the carbon fiber pyrolysis technique, study of the polymer pyrolysis processing of other ceramic materials began in the early 60's. Chantrell and Popper[71] in England were one of the first to suggest the concept of ceramics from polymer pyrolysis in print. However, in the case of SiC fibers, Yajima and his colleagues in Japan completed the pioneering work[72-76]. Some of the current processes for commercial SiC fiber fabrication are based on the early patents of Yajima and his colleagues[77-78]. The resulting SiC fiber is called Nicalon. It is a β-SiC and is commercially produced by the Nippon Carbon Company.

As summarized by Yajima[76], the synthesis of continuous Nicalon SiC fibers involves five steps through the polymer pyrolysis processing. The base material, or starting polymer is a polycarbosilane. The pyrolysis processing proceeds as follows: (i) removal of the low molecular weight components from the polycarbosilane at about 300 °C for 1 hr. in N₂ gas, (ii) fiber spinning of continuous polycarbosilane fibers at a temperature of 350 °C, (iii) curing the fibers in air at about 200 °C, and (iv) the pyrolysis of the cured fibers at temperatures between 1200 °C and 1300 °C in an inert gas atmosphere, or in a vacuum to yield the final product, continuous SiC fibers.

When Nicalon fiber is produced by the above fabrication technique, the fibers contain excess free carbon as well as some SiO₂. Based on the data published by Yajima[76], the molar ratio of SiC : C : SiO₂ is either 1 : 0.78 : 0.22 or 1 : 0.98 : 0.32.
depending on the preparation methods of the starting polymer, as the same type of polycarbosilane polymer was used for each. The oxygen originates from the curing process in air, which slightly oxidizes the SiC on its surface. Yajima also noted that the free carbon, even when the final SiC fibers are heated in air at 1250 °C for three days, still exists at a fairly high level as SiC : C : SiO₂ = 1 : 0.59 : 0.46. The microstructure of Nicalon fiber has been proposed by Laffon et al.[79]. A schematic model shows the presence of the mixture of β-SiC crystallite, SiCₓOᵧ (x+y=4) and aromatic carbon as depicted in Figure 2.1.

Both the tensile strength and the Young’s modulus of the Nicalon SiC fibers are of interest for the fiber reinforcement of various matrices, both ceramic and metallic. The Nicalon fiber has unique properties. Figure 2.2 illustrates the tensile strength and Young’s modulus of the Nicalon fiber versus its heat treatment temperature, that is the pyrolysis temperature for the conversion from polycarbosilane to silicon carbide. When the thermal decomposition is completed at 800 °C to 900 °C, the strength increases. Above 1000 °C, there is a structural change in the fiber from an amorphous state to a crystalline one (β-SiC) and at 1200 °C the tensile strength achieves a maximum. At temperatures above 1300 °C, the crystallization of β-SiC is continuous and grain growth proceeds slowly, during which the weight loss due to evolution of CO gas results in a decrease of the fiber strength. Similar trends for the Young’s modulus of the Nicalon fiber have also been reported, from 400 GPa to 150 GPa, at the thermal decomposition temperatures from 800 °C to 1300 °C by the same research group[72,74].

2.1.2 Thermal Stability of Nicalon SiC Fibers

As a candidate for high temperature applications, the fibers should remain inert in the oxidizing atmospheres of operating conditions. However, because SiO₂ is
Figure 2.1 A schematic of the structure of a Nicalon fiber illustrating the various materials which are present. There is no specific orientation relative to the fiber length [79].
Figure 2.2 Mechanical properties of Nicalon SiC fibers cured in (●) vacuum and (○) N₂ flow, and heat-treated in the range 400 to 1300 °C [72,74].
thermodynamically more stable than SiC at high temperatures. SiC is oxidized almost instantly when exposed to an O₂ environment. Fortunately, the oxide layer is a protective one, which increases the oxidation resistance of the SiC itself. Several models have been developed to describe the oxidation of SiC. The oxidation process of SiC appears to be controlled by (i) the inward diffusion rate of oxygen through the SiO₂ scale[80,81] or by (ii) the desorption of CO from the SiC-SiO₂ interface[82,83]. This oxidation process follows a parabolic relationship[84,85] and the oxidation product is either a mixture of the amorphous and crystalline forms of SiO₂, or a monophasic form, which varies with the oxidation temperature[80-85]. Yavuz and Hench[83] have studied the low temperature oxidation of SiC. In contrast to the previous models, their results suggest that there develops an intermediate layer from the oxidation reaction. It has been identified as a ternary phase, Si-O-C, which separates the SiC and the SiO₂ scale. Their study suggests that at low temperatures (<1000 °C), the Si-O-C phase occurs after a brief incubation period and at the expense of the Si-C bonds at the SiC surface.

Mah et al[84] have studied the thermal stability of Nicalon fibers at temperatures greater than 1200 °C in different atmospheres. For the case of an air heat treatment at 1200°C, a decrease of the fiber strength by about 30% has been reported. They also used X-ray diffraction analysis to identify that grain growth occurred during the heat treatment. An initial grain size of 1.6 nm grew to 8.0 nm near the fiber surface. The observed mechanical property degradation was related to the result of the evaporation of CO and the β-SiC grain growth. However, this thermal degradation is substantially recovered after heat treatment at 1300 and 1400 °C as the result of the formation of a thicker SiO₂ film on the fiber surface. Chaim[87] recently reported the study of Nicalon fibers that had been heat treated at 1200 °C in air. He observed the formation of a SiO₂-tridymite layer on the fiber surface at high oxygen partial pressures.
Although SiC fibers can benefit from the formation of the passive layer of SiO\textsubscript{2} at high temperatures, from the point of view of a fiber reinforced ceramic matrix composite, this oxidation layer will promote interfacial bonding between the fiber and the matrix. This strengthening of the interfacial bond is not desirable, as it is for the case of the strength of an individual fiber. Thus there is merit to inhibit the oxidation of the Nicalon fibers and to prevent its contribution to the increased fiber/matrix bonding.

2.1.3 Aluminum Phosphate Cements and Bonding

According to Wygant\textsuperscript{[88]}, if two constituents other than water react to form the cementitious material, the mechanism of bond formation is called chemical or reaction bonding. Reaction bonded materials offer important energy savings by eliminating the need for high temperature processing. Commercial phosphate bonded refractories are one type of reaction bonded ceramic. Aluminum phosphate binders have been extensively studied\textsuperscript{[58,61-64]}. These bonds are achieved through the chemical reaction between phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) and alumina (Al\textsubscript{2}O\textsubscript{3}) which yields monoaluminum phosphate also known as MAP, which is Al(H\textsubscript{2}PO\textsubscript{4})\textsubscript{3}. The reaction can be written as:

\[
\text{Al}_2\text{O}_3 + 6 \text{H}_3\text{PO}_4 \rightarrow 2 \text{Al} (\text{H}_2\text{PO}_4)_3 + 3 \text{H}_2\text{O} \quad (2-1)
\]

This bonding process can be directly applied to alumina powders by mixing with MAP, Al(H\textsubscript{2}PO\textsubscript{4})\textsubscript{3}, which is capable of reacting with the alumina, according to the following reactions\textsuperscript{[89]}:

\[
\text{Al} (\text{H}_2\text{PO}_4)_3 + \text{Al}_2\text{O}_3 \rightarrow 3 \text{AlPO}_4 + 3 \text{H}_2\text{O} \quad (2-2)
\]

and

\[
\text{AlPO}_4 \text{H}_n + \text{Al}_2\text{O}_3 \rightarrow 3 \text{AlPO}_4 \quad (2-3)
\]
These reactions depend on (i) the concentrations, (ii) the curing time, (iii) relative humidity, (iv) the curing temperature, and (v) the surface area of the reactants, i.e. the alumina, in this case. However, the stability of the resulting bonds is controlled by the $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ratio. A typical commercial phosphate binder has a $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$ ratio of about 4.3, which is stabilized, as compared with the unstable ones with a ratio of less than 2.3, and those which are metastable and have a ratio of between 2.3 and 3.0.

In the early 1950's, studies of phosphate bonded refractories were systematically reviewed and investigated by Kingery[57-59]. For phosphate bonded alumina, Kingery[58] reported that the effect of temperature on strength is unusual in that all values of the modulus of rupture are greater than the strength after initial drying. This phenomenon is directly related to the monoaluminum phosphate bond content which increases with an increase in temperature. Weight loss also increases through 800 °C with the formation of aluminum metaphosphate, Al(PO$_3$)$_3$, and the liberation of H$_2$O.

Gonzales and Halloran[61,62] have extensively studied the mechanical properties of phosphate-bonded alumina refractories as a function of firing temperature from 300 to 1200 °C. The microstructure of phosphate-bonded refractories changes dramatically with increased firing temperature as a result of the continued reaction between the alumina grains and the phosphate binder. For firing samples at 300 °C, the fracture was exclusively intergranular, as the alumina grains were coated with a filmy phase, presumably the aluminum phosphate binder. The aggregate grains were usually covered with this film, suggesting cohesive failure of binder. For firing at 600 °C, the fracture mode is similar to that at 300 °C, although the individual grains appear to be more distinct as a result of the more complete reaction with the phosphate binder. However, after firing at 900 °C, the fracture mode becomes a mixed transgranular and intergranular one, in which the cracks propagate at the binder/aggregate interface, i.e. adhesive failure of the binder. For the
material fired at 1200 °C, the bonding between the grains is very strong and the fracture mode is fully transgranular. Table 2.2 summarizes the room temperature flexural strengths from the above investigation. As a consequence of the continuous change in the microstructure and bonding between the matrix grains and the binder, the strength is initially increased with firing temperature through 1000 °C. It is apparent that an increase in strength is associated with the development of a more fully bonded microstructure. Above 1000 °C, the strength decreases significantly.

2.1.4 Phase Transformations of Aluminium Ortho-Phosphates

As the cementitious bond develops AlPO₄, it is pertinent to review the phase transitions of this compound which is known as Berlinite. Beck[91] has extensively studied those phase transformations. The phase transformations of AlPO₄ can be described as:

\[
\begin{align*}
815±4°C & \quad 1025±50°C & \quad >1600°C \\
\text{Berlinite} & \quad \text{Tridymite} & \quad \text{Cristobalite} & \quad \text{Molten AlPO}_4 \\
586±2°C & \quad 93±3°C & \quad 130°C & \quad 210±5°C \\
\alpha & \quad \beta & \quad \beta_1 & \quad \beta_2 & \quad \beta
\end{align*}
\]

These can be directly compared with the phase transformations of silica (SiO₂), which are:

\[
\begin{align*}
860°C & \quad 1470°C & \quad >1710°C \\
\text{Quartz} & \quad \text{Tridymite} & \quad \text{Cristobalite} & \quad \text{Molten SiO}_2 \\
573°C & \quad 117°C & \quad 163°C & \quad 220-270°C \\
\alpha & \quad \beta & \quad \beta_1 & \quad \beta_2 & \quad \beta
\end{align*}
\]

These transformations subsequently result in abrupt volume changes and variations in the thermal expansions of AlPO₄ and SiO₂. The thermal expansions for the various phases of AlPO₄ have been previously measured and are summarized in Table 2.3[91,93].
Table 2.2

Flexural Strengths of Phosphate-Bonded High Alumina Refractories[61-62]

<table>
<thead>
<tr>
<th>Firing Temperature (°C)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃ Plastic</td>
</tr>
<tr>
<td>300</td>
<td>25.8 ± 1.9</td>
</tr>
<tr>
<td>600</td>
<td>29.4 ± 2.2</td>
</tr>
<tr>
<td>800</td>
<td>29.8 ± 2.1</td>
</tr>
<tr>
<td>1000</td>
<td>38.7 ± 2.8</td>
</tr>
<tr>
<td>1200</td>
<td>24.9 ± 2.0</td>
</tr>
<tr>
<td>1400</td>
<td>2.4 ± 0.1</td>
</tr>
</tbody>
</table>
Table 2.3
Thermal Expansion Values for the Phases of AlPO$_4$ and SiO$_2$[91-93]

<table>
<thead>
<tr>
<th>Phase</th>
<th>α-Quartz</th>
<th>β-Quartz</th>
<th>α-Cristobalite ( x 10^{-6} /°C )</th>
<th>β-Cristobalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>RT-583</td>
<td>583.2</td>
<td>RT-200</td>
<td>200-500</td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>13.3</td>
<td>-2.5</td>
<td>18.8</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>RT-573</td>
<td>573.2</td>
<td>RT-220</td>
<td>220</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>13.3</td>
<td>-2.5</td>
<td>8.8</td>
<td>4.5</td>
</tr>
</tbody>
</table>
2.1.5 Fiber Coatings and Related Interfacial Bonding of the Fiber/Matrix

Ceramic-fiber composites have been attracting increasing technical interest because of their increased fracture toughness and the absence of catastrophic failure upon reaching their maximum load-carrying capability. The high crack growth resistance (CGR) of these composites has been associated with the limited extent or degree of the interfacial bonding between the fibers and the matrix, which facilitates fiber pull-out and crack bridging as the major source of the increased crack growth resistance. The beneficial effects of a weak interfacial layer have led to investigations of composites with coated fibers. The most common choices for fiber coatings have been boron nitride (BN) and carbon[94-99].

Rice et al. [94] have studied the effects of a BN coating on the mechanical properties of SiC fiber and Al₂O₃ fiber reinforced SiO₂ matrix composites. Testing at room temperature and at 1000 °C revealed that there exist substantial improvements of both the flexural strengths and fracture toughnesses for the coated fiber reinforced composites over the uncoated fiber composites. Corbin et al. [96] addressed the role of the coating thickness on SiC filament reinforced RBSN (reaction bonded Si₃N₄), in which RBSN was reinforced with SiC filaments coated with 1 µm and 3 µm amorphous carbon films. They reported that both the flexural strength and the total work-of-fracture improved significantly as the thickness of the carbon coating was increased from 1 µm to 3 µm.

Goettler and Faber [46] studied the surface coating effect for glasses reinforced by SiC fibers by varying the coating thickness and the coating compositions. They found that the interfacial shear strength of the fiber/matrix interface was decreased by reducing the amount of free carbon available at the surface of the fiber. For a pure carbon coating (0.5 µm), the interfacial shear strength was higher than two other CVD coated (by varying the Si/C ratio in the coatings) SiC fiber reinforced glasses. A similar result occurred for lower
Si/C nano CVD coatings. Lehman and Doughan[99] investigated the carbon coating effect on Al₂O₃/glass composites. Comparing carbon coated Al₂O₃/glass with the uncoated Al₂O₃/glass, the flexural strengths increased by more than 100%.

Rahaman et al.[100] have measured the interfacial shear stress for both untreated and oxidized SiC fiber reinforced cordierite matrix composites as well as for a matrix composed of cordierite with 15% vol SiC whiskers. The study demonstrated that the debonding and the frictional sliding shear stresses for these composites were significantly increased over those for the oxidized SiC fiber reinforced composites. Their investigation revealed that the oxidation of the SiC fiber surface enhances the bonding between the fiber and the matrix. This is further confirmed in the same study for the different sintering temperature of processed untreated SiC fiber reinforced composites. For these composites, the debonding and the frictional sliding shear stress increase with an increase of the sintering temperature and the sintering time. This is because the sintering results in increased oxidation of the SiC fiber surface and promotes stronger chemical and mechanical bonding at the interface.

Burn and Singh [101] have studied the effects of thermal expansion mismatch and fiber coatings on the fiber/matrix interfacial shear stresses in SiC fiber reinforced mullite ceramic matrix composites. They have reported that compared with the mullite matrix reinforced by an uncoated SiC fiber, the presence of a BN coating can significantly reduce the interfacial bonding between the fiber and the matrix. This causes a reduction of the debonding stress and also of the interfacial frictional stress. For the composite, the thermal expansion coefficient of the SiC fiber is only slightly less than that of the mullite matrix. However, the coating thickness had little effect on the frictional stress. For the same situation of fiber coating, the composite of a SiC fiber and SiO₂ glass matrix has also been studied, showing no effect of the fiber coating on the interfacial bonding, nor on the interfacial stress. This is probably because the thermal expansion coefficient of the fiber is
so much greater than that of the SiO$_2$ matrix that the fibers separate from the matrix during the cooling process of the composite fabrication.

These experimental investigations conclude that the fracture related mechanical properties of fiber reinforced ceramic matrix composites can be controlled through the microstructural design of the interfacial bond between the fibers and the matrix.

2.2 Continuous Fiber Reinforced Ceramic Matrix Composites

Fiber-reinforced ceramic matrix composites (FRCMCs) have attracted a great deal of attention for use in high temperature structural applications. The primary reason for these efforts lies in the assumption that strong ceramic fibers can prevent catastrophic brittle failure by providing various energy dissipation processes during crack extension. To achieve the goal of an optimal design for such types of composites, both the elastic behavior and the fracture processes of a given composite system must be fully analyzed. It is now well accepted that for any given composite system, the individual mechanical properties of the fibers and the matrix are fixed and the design of such a composite is dictated by tailoring the fiber/matrix interface properties. For a fiber-reinforced laminate composite, the mechanical properties also depend on the detailed geometry/configuration of the design. The aforementioned properties are discussed with respect to the current understanding of the elastic properties and fracture behavior of continuous fiber-reinforced ceramic matrix composites.

2.2.1 Elastic Properties of Laminated Composites

Laminates are fabricated in such a manner that they respond mechanically as single layer materials. A schematic representation of a laminated composite is illustrated in Figure 2.3. The bonds between the laminae in a laminated composite are often assumed to be
Orthotropic lamina with its principal material axes oriented at angle $\theta$ with reference coordinate axes.

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\tau_{xy}
\end{bmatrix} =
\begin{bmatrix}
\bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{16} \\
\bar{Q}_{12} & \bar{Q}_{22} & \bar{Q}_{26} \\
\bar{Q}_{16} & \bar{Q}_{26} & \bar{Q}_{66}
\end{bmatrix}
\begin{bmatrix}
\epsilon_x \\
\epsilon_y \\
\gamma_{xy}
\end{bmatrix}
\]

Figure 2.3 Geometry of multilayered laminate [102]
One of the most important advantages of fibrous composites is that their anisotropic properties can be controlled very effectively by altering the materials and manufacturing process. The elastic properties of a laminated composite have been derived by applying Hooke's Law to laminate theory and can be found in many textbooks [102,103]. In general, for a laminated composite, the elastic properties can be expressed in a form of Hooke's Law as:

\[
\begin{bmatrix}
N_i \\
M_i \\
N_{\epsilon}
\end{bmatrix}
= \begin{bmatrix}
A & B \\
B & D
\end{bmatrix}
\begin{bmatrix}
\epsilon^0 \\
\kappa
\end{bmatrix}
\]

(2.4)

where \(\epsilon^0\) is the mid-plane strain and \(\kappa\) is the laminate curvature. \(N\) and \(M\) are the force and the moment resultants, respectively, and are expressed as:

\[
N_r = \int_{-h/2}^{+h/2} \sigma_r dz \quad (r = x, y, xy) \tag{2.4a}
\]

and

\[
M_r = \int_{-h/2}^{+h/2} \sigma_r z \, dz \quad (r = x, y, xy) \tag{2.4b}
\]

The \(r\) can be any of the \(x, y\) and \(xy\) in the \(x-y-z\) Cartesian coordinate system. The \(A, B, D\) are the extensional stiffness matrices, which can be expressed as:

\[
A_{ij} = \sum_{k=1}^{n} (Q_{ij})_k (h_k - h_{k-1}) \tag{2.4c}
\]

and

\[
B_{ii} = \frac{1}{2} \sum_{k=1}^{n} (Q_{ij})_k (h_k^2 - h_{k-1}^2) \tag{2.4d}
\]

and

\[
D_{ii} = \frac{1}{6} \sum_{k=1}^{n} (Q_{ij})_k (h_k^3 - h_{k-1}^3) \tag{2.4e}
\]
in which \((Q_{ik})_k\) are the stiffness matrices of the \(k\)-th layer.

For most FRCMC's, the applications involve an elevated temperature environment and hence an important factor which must be considered is the thermal stress state within the composite. By considering the thermal stresses, Equation (2-4) can be expanded into the form:

\[
\begin{bmatrix}
N_i \\
M_i
\end{bmatrix} = \begin{bmatrix}
A \\
B
\end{bmatrix} \begin{bmatrix}
\mathbf{E} \\
\mathbf{k}
\end{bmatrix} \begin{bmatrix}
NT \\
MT
\end{bmatrix}
\]

where \(NT\) and \(MT\) are thermal force and thermal moment resultants, respectively. These are expressed in the form of:

\[
N_{iT} = \Delta T \sum_{k=1}^{n} (Q_{ii})_k \{\alpha_r\}_k (h_k - h_k^0) \quad (r = x, y, xy) \quad (2-5a)
\]

and

\[
M_{iT} = \frac{1}{2} \Delta T \sum_{k=1}^{n} (Q_{ij})_k \{\alpha_r\}_k (h_k^2 - h_k^0 h_k^0) \quad (r = x, y, xy) \quad (2-5b)
\]

The \(\{\alpha_r\}_k\) is the coefficient of thermal expansion of the \(k\)-th layer for the laminated composite. According to Equation (2-5), it is evident that the load carrying capacity of the composite can be significantly reduced by the presence of thermal stresses. However, it is important to realize that the laminate theory as represented by Equations (2-4) or by Equations (2-5) are based on the assumption that there exists perfect elastic bonding between the fibers and the matrix, as well as between adjacent lamina. Influences of the thermal expansion mismatch between the fibers and the matrix, and of interfacial properties on the overall load carrying capacity of the laminated composite are not included in Equations (2-5).
It is evident that the elastic properties of the laminate can be affected by many factors. Exclusion of the manufacturing variables, these include: (i) the individual elastic properties of each component of the composite, (ii) the volume fraction of each component, (iii) the fiber orientation within the lamina, (iv) the stacking symmetry or sequence of each lamina in the laminate, and (v) the temperature of application or measurement.

To enhance the effectiveness of the reinforcement by incorporating long continuous fibers, a woven fabric laminate is often applied. For this situation, the wavy nature of the fiber weave affects the elastic properties of the laminate. Luo and Chou[104] have theoretically treated the effects of the fiber weave configuration on the elastic properties of flexible laminated composites. Their concepts should also be applicable to inflexible composites with certain modifications. Ishikawa et al.[105,106] have proposed an analytical model to describe the stiffness of 2-D woven fabric composites by considering the effects of local coupling.

2.2.2 Strengths of Fiber Reinforced Ceramic Matrix Composites

Applying the rule of mixtures to fiber reinforced ceramic matrix composites, the bulk strength of the composite is considered to be composed of three main contributions: the strength of fibers, the strength of the matrix and the strength of the fiber/matrix interface. Although it is important to realize the importance and the role of the fiber/matrix interface for the crack growth resistance of a composite, in general, the analysis of the bulk strength of the composite is under the assumption of perfect bonding between the fiber and the matrix. Therefore, the most influential factors are attributed to the intrinsic properties of the fiber and the matrix.

For FRCMCs, cracks generally initiate in the brittle matrix which is comparably weaker than the fibers. In terms of the stress for initial matrix cracking (σm), an
expression for unidirectional fiber composites has been developed by Aveston et al\[107\]. It is:

\[
\sigma_m = \frac{\pi \tau (K_{ICm})^2 (1-V_m)^2 E_f V_f^2}{E_f (1 - V_f)} 1/3
\]

Hence the stress for the initiation of the matrix crack is affected by (i) the interfacial shear strength, \(\tau\), (ii) the fracture toughness and the Poisson's ratio of the matrix, \(K_{ICm}\) and \(V_m\), (iii) the Young's modulus, the volume fraction and the radius of the fiber, \(E_f, V_f\) and \(r\), and (iv) the Young's modulus of the composite, \(E_m\). This relationship has been verified by Coyle et al\[108\] for a Nicalon fiber reinforced polycrystalline Al\(_2\)O\(_3\) matrix composite.

Although initial cracking occurs in the matrix, this does not automatically result in the catastrophic failure of the composite because of the high crack growth resistance of fiber reinforced composites. For the failure of the composite, it is necessary to break a bundle of the fibers after the matrix crack has initiated. The strength of the composite is therefore controlled by the strength distribution of the fibers and the fiber bundles. It is well documented that the strengths of the fibers can be described by a modified Weibull statistical distribution function for fiber reinforced composites\[109,110\]:

\[
P(\sigma) = 1 - \exp\left(\frac{-2 \pi \tau^m \left(\frac{2L}{\sigma_o^m}\right)^{m+1}}{m+1}\right)
\]

where \(\sigma_o\) is the mean fiber strength in the units of [stress x length\(^{-2/m}\)], \(m\) is the Weibull modulus, \(r\) and \(L\) are the fiber radius and length, respectively, and \(\tau\) is the frictional stress at the fiber/matrix interface. According to Equation (2-7), it is evident that both the gage length of the fibers and the interfacial stress affect the measured strengths of composites.
In terms of the fiber bundle strength, Corton[111] has developed the expression:

\[
\frac{\sigma_b}{\sigma_a} = \left( \frac{m \sigma}{1} \right)^{1/m} \left( \Gamma(1 - 1/m) \right)
\]  \hspace{1cm} (2.8)

where \(\sigma_b\) is the bundle strength of the fibers and \(\sigma_a\) is the average strength when the same length of fiber is tested individually. The \(\Gamma\) is the tabulated gamma function and \(m\) is the Weibull modulus. Application of the fiber bundle model as defined by Daniels[112] practically prohibits its application to estimating the strength of a composite. Once a fiber in a bundle breaks, that fiber is assumed to carry no more load whatsoever; while in actuality, a broken fiber in a composite regains its load within a short distance from the break. By considering the above, Schwieter and Steif[113] have derived an expression for the composite strength (\(\sigma_{\text{comp}}\)) as it varies with the fiber volume fraction, \(V_f\), as:

\[
\sigma_{\text{comp}} = V_f \left\{ \frac{1}{N_T} \sum_{j=1}^{N_I} (\sigma_{Ij}) + \frac{1}{N_T} \sum_{j=1}^{N_B} (\sigma_{Bj}) \right\}
\]  \hspace{1cm} (2.9)

where \(N_T\) is the total number of fibers in the specimen, \(N_I\) is the number of fibers in the specimen that are intact, and \(N_B\) is the number of fibers in the specimen that are broken. \(\sigma_{Ij}\) represents the tensile stress carried by the \(j\)-th intact fiber at the plane of a matrix crack; consistent with the generalization of equal load sharing, \(\sigma_{Ij} = \sigma_I\) for all \(j\) fibers. \(\sigma_{Bj}\) is the tensile stress carried by the \(j\)-th broken fiber at the plane of the matrix crack. According to Equation (2.9), the contribution of broken fibers to the strength of the composite must be considered when the interfacial shear strength between the fiber and the matrix is high.
2.3 Fracture

2.3.1 Linear Elastic Fracture Mechanics of Brittle Solids (LEFM)

For an ideal solid, the theoretical cohesive strength can be described by the interatomic force-separation law. It can be approximated by a function that exhibits three properties: (i) an initial slope that relates to the elastic modulus E, (ii) a total work of separation that corresponds to a surface energy, γ, and (iii) a maximum value that represents the interatomic cohesive force. Because the exact mathematical form makes little difference in the final result, it is convenient to use a sine function, which can be expressed as[114]:

\[ \sigma(x) = \left( \frac{E \gamma}{b} \right)^{1/2} \sin \left( \frac{E b}{\gamma} \frac{x}{b} \right) \]  \hspace{1cm} (2.10)

where \( b \) represents the equilibrium interatomic spacing and \( x \) denotes the displacement from the equilibrium separation distance. It follows that the theoretical cohesive strength is the maximum value of \( \sigma(x) \). It is:

\[ \sigma_{\text{th}} = \left( \frac{E \gamma}{b} \right)^{1/2} \]  \hspace{1cm} (2.11)

This prediction is experimentally observed to be considerably in excess of the measured strengths of bulk materials, often by a factor of 1,000 or more.

Griffith[115] traced this discrepancy to the existence of crack-like flaws, the presence of which renders the material far from the concept of an ideal and perfect solid. For brittle, Griffith-type materials, the surface energy, \( \gamma \), is the only mechanism for dissipating energy. For an elliptical shaped crack with a critical dimension, \( a \), the measured failure strength, \( \sigma_{\text{failure}} \), is:
where \( P \) is the applied load and \( C \) is the compliance. Griffith's energy balance statement of the critical condition for crack extension is then

\[
\dot{G} = R
\]

(2.17)

where \( R \) represents the material's resistance to crack growth.

In order to avoid the mathematically awkward strain energy release rate, a global parameter, Irwin [117] specified a local crack-tip parameter, namely the stress intensity factor \( K \). The final formulation is expressed as:

\[
\dot{G} = K^2 / E' \tag{2.18}
\]

where \( E' = E \) for a condition of plane stress and \( E' = E/(1-\nu^2) \) for the condition of plane strain.

### 2.3.2 Crack Growth Resistance or R-curve Behavior and Fracture Stress

For a crack to propagate, it must satisfy the energy criterion in the fracture process[119]. Figure 2.4 depicts the relationship between the strain energy release rate, \( G \), and the crack extension, \( \Delta a \). Two types of crack growth resistance curves or R-curves are illustrated in Figure 2.4, the flat R-curve and the rising R-curve. Based on the Griffith fracture criterion that fracture occurs for a critical flaw size for a given material, the origin of the axis of the strain energy release rate \( (\dot{G}) \) is translated to the position of the preexisting crack length, \( a_0 \). The dashed lines are constructed according to the Griffith criterion and Irwin's similarity relationship[117]. The line for a Griffith crack with a crack length of \( 2a_c \) is described by:
Figure 2.4 Universal representation of the fracture criterion [119].
\[ G = \sigma^2 \pi a / E' \quad \text{and} \quad (E' = E/(1-\nu^2)) \quad (2.19) \]

in which \( \sigma \) is the applied stress. The slope of the line is expressed by \((\sigma^2 \pi / E')\).

The physical significance of Figure 2.4 can be described as follows. By loading the crack from zero stress to \( \sigma_1 \), the \( G \)-value increases from 0 to A which is less than the crack growth resistance, \( R_c \), for the initiation of the fracture, thus indicating no crack extension. A further increase of the applied stress to a critical level, \( \sigma_c \), raises the \( G \)-value to the point C, where \( G = R_c \) is satisfied. At that point, catastrophic brittle fracture occurs for the material having the flat R-curve, for \( G > R_c \). However, for the material exhibiting a rising R-curve, catastrophic fracture will not occur for \( G < R_c \) and the crack extends in a stable fashion. Failure of the rising R-curve material does not occur until the applied stress reaches the \( \sigma_f \)-value, at which point, the following relations:

\[ \frac{\delta G}{\delta a} = \frac{\delta R}{\delta a} \quad \text{and} \quad G = R \quad (2.20) \]

are satisfied. The importance of a rising R-curve is that stable crack extension is maintained to a limited extent without catastrophic failure and can often extend to a higher applied stress levels than for a flat R-curve.

To further address the rising R-curve, Figure 2.5 depicts a schematic relationship, revealing the dependence of fracture stress, \( \sigma_f \), on the rising form of R-curve as described by Sakai and Bratli. Three different R-curves are denoted by the lines, a, b, and c. Each has its own steady state toughness, \( R_s \), but the same \( R_c \) for the initiation of crack growth. As shown in Figure 2.5, the fracture stress of each is obtained by the same procedures as previously described for Figure 2.4. The slopes of the dashed straight lines for these materials reveal that the fracture stresses are in the order of: \((\sigma_f)_b > (\sigma_f)_a > (\sigma_f)_c\).
Figure 2.5 Dependence of fracture stress on the rising behavior of R-curve [6].
However, the steady-state saturation R-curve toughness values are in the order of $(R_{c})_{a} > (R_{c})_{b} > (R_{c})_{c}$. This scheme for the strength-toughness relationship clearly illustrates that the highest steady state toughness, $(R_{c})_{c}$, does not always yield the highest strength of fracture stress, $\sigma_{f,c}$, when rising R-curve behavior exists. For this reason, the experimental determination of the rising R-curves for ceramics is significant and essential, not only to the microstructural design of ceramics, but also for their structural applications in design as well.

2.3.3 Fracture of Continuous Fiber Reinforced Ceramic Matrix Composites

In contrast to the catastrophic failure of brittle solids, fiber reinforced ceramic matrix composites (FRCMCs) exhibit a non-catastrophic fracture process. Figure 2.6 (a) schematically presents an idealized stress-strain curve for a typical "tough" ceramic matrix composite[118]. This curve consists three fracture regions: (i) a linear elastic region which precedes the initial matrix cracking (BMC), (ii) a nonlinear region, within which stress and strain increase due to additional matrix macrocracking (AMC), and finally (iii) a large nonlinear region, within which stress decreases with an increase of strain, accompanying both fiber fracture (FF) and extensive fiber pull-out. Crack growth in these composites is controlled by the wake region behind the crack tip front.

The typical composite fracture process has been addressed in detail by Jenkins et al.[19] and is shown in Figure 2.6 (b). A plot of the external load versus the displacement at the peak load clearly reveals a sawtooth-like crack propagation pattern. The initial change in the compliance of the composite is related to the initiation of the matrix crack. The matrix crack is then arrested by the fibers, which recovers some compliance for the composite. At the sawtooth maximum, the point $b_{0}$, fiber breakage occurs and follows by an arresting at the point $a_{1}$. At this moment of crack arrest, the remaining fibers
Figure 2.6 (a) Idealized stress-strain behavior of ceramic fiber/ceramic matrix composite [123] and (b) Upper portion of load vs. displacement curve [19].
ahead of the crack halt the crack extension and the stress increases until the next event takes place. The cycle of crack propagation and arrest continues until the complete destruction of the integrity of the composite. Two factors have been previously discussed regarding the crack arrest: (i) the fiber debonding and (ii) the fiber frictional pull-out, which is characterized by the following wake region effect. The size of the effective wake region, in general, is large in comparison with the very small critical crack length in a brittle solid.

As a consequence of the nonlinear behavior of the composite as just discussed, the hypotheses of linear elastic fracture mechanics (LEFM) are no longer directly applicable. Simple Griffith theory cannot be applied to describe the fracture of those composites since the surface energy as previously specified is no longer the dominant factor in controlling crack growth. This nonlinear behavior has been described in terms of the concept of rising R-curve behavior as previously described and detailed in elementary fracture mechanics texts such as the one by Broek[119]. The crack growth resistance is evaluated in terms of the strain energy release rate as a function of either the crack length (a) or the crack extension (Δa). Unfortunately, this approach is dependent on test specimen geometry. Therefore, for a basis of comparison, it is important to compare similar composites by consistently applying the same fracture test method and identical specimen geometry to obtain meaningful results.

2.3.4 Toughening Mechanisms of Continuous Fiber Reinforced Ceramic Matrix Composites

One philosophy for toughening brittle ceramics is to create microstructures in which the pure Griffith theory no longer dictates fracture behavior, thus the preexisting flaws do not dominate the fracture process. Such engineering ceramics have a higher crack growth resistance, during the process of which the strain energy release rate accompanying crack extension increases. This increasing resistance of a material to crack extension has been
characterized as rising R-curve behavior. There are several aspects of rising R-curve behavior which must be considered. First, processing-related flaws can be present without leading to the failure of the material. Second, the range or scatter in strengths may be considerably reduced. Third, the R-curve form is not an intrinsic material property, but dependent on the test specimen geometry or the specific failure mode of an artifact.

2.3.4 a General Features of R-curves

There appear to be at least three types of R-curves that have been observed through experimental measurements. Figure 2.7 illustrates the three representative rising R-curves for actual ceramic materials in which no phase transformations are involved. It also illustrates several flat R-curves. Figure 2.7 (a) presents the measured crack growth resistance for fine grain size specimens of Si₃N₄ and SiC polycrystalline ceramics in terms of the instantaneous stress intensity factor, $K_R[56]$. It is evident that the crack extension against a constant fracture resistance as described by $K_R$ yields a flat R-curve, for these ceramics. For materials having a flat R-curve, the fracture processes are usually catastrophic and appear very brittle.

Figures 2.7 (b) and (c) illustrate the measured crack growth resistances for a polycrystalline graphite and an Al₂TiO₅[9]. Another type of R-curve is evident as initially the $K_R$ increases sharply with crack extension, but soon reaches a saturation value of $K_R$ which is independent of further crack extension. These are both characterized as rising R-curves. Polycrystalline ceramic materials exhibiting rising R-curves resembles a semi-brittle material, as their fracture processes may involve an initially stable crack growth, but subsequently brittle fracture when $\frac{\delta G}{\delta (\Delta a)} > \frac{\delta R}{\delta (\Delta a)}$. 
Figure 2.7 Three types of R-curves: Flat R-curves for fine grain Si$_3$N$_4$ and SiC [56] (a), Rising R-curves for an isotropic polycrystalline graphite, an Al$_2$TiO$_5$-ceramic[9] (b-c) and Rising R-curve for a SiC fiber reinforced CVI ceramic composite [120] (d).
Figure 2.7 (d) illustrates another type of rising R-curve, one for a SiC fiber reinforced SiC matrix composite[120]. Its crack growth resistance is characterized in terms of the strain energy release rate, G, which has a parallel physical significance to the use of the \( K_R \) value, for both are related by the material elastic modulus through Irwin's similarity relation in Equation (2-18). In contrast to the rising R-curves shown in Figures 2.7 (b) and (c), for the fiber reinforced composite, this rising R-curve has a different trend. The R-value gradually and continually increases with crack extension. For this type of rising R-curve, it appears that there exists no saturation level for the crack growth resistance. The composites possessing this type of rising R-curve are not brittle; their fracture proceeds in a stable fashion.

2.3.4 b Toughening Mechanisms for Rising R-curve in FRCMC's

Experimental evidence of the rising R-curve behavior of ceramics has lead to several micromechanical models. Figure 2.8 illustrates a schematic representation of toughening processes for fiber reinforced ceramic matrix composites as suggested by Wells et al[121], Sakai[122] and Shah and Ouyang[123]. For FRCMC's, the related toughening mechanisms, or bridging mechanisms, has been attributed to at least four different contributions: (i) the new surface area created by the matrix crack extension, (ii) the new surface area created by debonding at the fiber/matrix interface, both within the wake region and at the crack tip front, (iii) fiber bridging in the wake region behind the crack tip front, and (iv) frictional fiber pull-out in the wake region.

For these toughening mechanisms, it is important to realize that the fiber debonding occurs not only within the following wake region, but also at the crack tip front. The debonding region in front of the crack tip has been described as a frontal process zone (F.P.Z.) by Sakai[122]. This debonding is a prerequisite for toughening to be effective for
Figure 2.8  (a) Schematic diagram of composite fracture ahead of notch [121-123] and (b) a model for crack bridging with a frontal process zone (f.p.z.) and the following wake region [122].
The debonding of the fiber/matrix not only blunts the advancing crack tip, but also creates a following wake region to effectively reduce the stress intensity factor at the crack tip. Finally, it provides an environment for the fiber pull-out. It appears that the most significant contribution to the rising R-curves of FRMC's originates in the counter stress resulting from the fiber pull-out in the following wake region.

2.4 Engineering Design of Fiber Reinforced Ceramic Matrix Composites

Toughening of fiber reinforced ceramic matrix composites (FRCMC's) has also been reviewed by Evans and Marshall[124]. A preexisting crack without bridging fibers (e.g. notched by a saw) initially grows in the matrix without breaking fibers. A bridging zone, or following wake region, subsequently develops behind the advancing crack front, thus resulting in increasing closure tractions from the fibers as the crack extends. Consequently, the applied stress intensity factor which is required for continued crack growth increases, and the crack growth is dictated by an increasing crack growth resistance, a rising R-curve.

To obtain and optimize the rising R-curves of FRMC's, Evans et al.[124,125] have summarized those critical parameters which must be considered. For the reinforcement, it is desirable to have a fiber with a high average strength ($\sigma_a$), but with a wide strength distribution, i.e. a low Weibull modulus ($m$). For a tough composite, it is also essential to achieve a weak fiber/matrix interfacial bonding, (mechanically and chemically) and to promote a low coefficient of friction between the two newly debonded created surfaces. The former enables the ease of debonding of the fiber and the matrix, while the latter affects the position of fibers when they are fractured and hence the length of pull-out during bridging of the newly created surfaces in the following wake region.
2.4.1 Factors Related to Fiber Debonding

It is well known that fiber debonding and pull-out are the primary criteria for the toughening process of a fiber reinforced composite. The debonding conditions for a fiber-ceramic matrix system have been clearly specified by Evans et al [125] and by He and Hutchinson[126]. Figure 2.9 presents those parameters which are important for fiber reinforced ceramic matrix composites[125,126]. In terms of the fracture surface energies of the fiber ($\Gamma_f$) and the interface ($\Gamma_{if}$), the criterion for fiber debonding instead of fiber fracture is that the strain energy release rate of the interface ($G_{ic}$) is significantly small compared with that of the fiber ($G_{fc}$). The ratio of $G_{ic}$ to $G_{fc}$ should be equal to, or less than, 1/4 for the condition where there exists no elastic mismatch between the fiber and the matrix as shown in Figure 2.9 (a). This can be affected by the elastic mismatch between the fiber and the matrix, which Dundurs[127] has characterized by the parameter:

$$\alpha = \frac{E_f - E_m}{E_f + E_m} \tag{2-21}$$

where $E$ is the plane strain tensile elastic modulus, $E = E/(1 - \nu^2)$ and the subscripts f and m refer to the fiber and the matrix, respectively. It is evident that the Dundurs parameter ($\alpha$) is important regarding the debonding criterion when there exists elastic mismatch between the fiber and the matrix.

In general, however, the stress condition can be arbitrary in orientation to the fiber axial direction. It introduces a second important factor associated with fiber debonding, namely the phase angle of loading ($\psi_i$):

$$\psi_i = \tan^{-1} \left( \frac{k_1}{k_2} \right) \tag{2-22}$$
Figure 2.9 (a) Crack front debonding diagram indicating the range of relative interface fracture energy, $\Gamma_\alpha/\Gamma_\beta$. (b) Trends in phase angle, $\Psi_\alpha$, at the debond crack. (c) Effect of interface orientation on the debonding requirements [125-126].
where the $k_1$ and $k_2$ are the imaginary and real components of the stress intensity factor at debonding. Figure 2.9 (b) depicts the relationship between the elastic mismatch of the fiber/matrix and the phase angle of loading at the crack tip for debonding. For the woven fabric composite, the fibers usually have a finite inclination angle ($\theta$) with respect to the crack plane in the matrix. According to the model proposed by Evans and He\textsuperscript{125}, illustrated in Figure 2.9 (c), for the woven fabric composite, the condition for the fiber debonding must vary from one position to another since the relative fracture surface energy ($\Gamma_{/\Gamma}$) changes with the angle $\theta$ for a given fiber/matrix system, or a fixed Dundurs parameter ($\alpha$).

### 2.4.2 Factors Related to Fiber Frictional Pull-out

Although the debonding process is a necessary condition for the toughening of fiber reinforced ceramic matrix composites, the major contribution to the toughening, or the rising $R$-curve behavior originates from the fiber frictional pull-out. Based on the statistical nature of the fiber strength, the locations of fiber breakage govern the pull-out distribution, which can, in principle, be determined from the stresses on the fibers ahead of the matrix crack and in the wake region. Thouless et al\textsuperscript{54} have presented the probability of fiber failure in the form of:

$$
\omega (z, t) = \frac{\frac{2\pi r^m}{\sigma_0^{\infty}}}{(t - 2\pi z/r) \exp \left\{ - \left( \frac{t}{\Gamma} \right)^{m+1} \right\}}
$$

$$
\Gamma = \left( \frac{\sigma_0^{\infty} \tau (m+1)}{2\pi r^2} \right)^{m+1}
$$
where \( z \) is the distance from the matrix crack plane, \( \tau \) is the stress acting on a fiber between the crack plane, and \( \tau \) is the interfacial shear strength assumed to be constant. The \( \sigma_0 \) and \( m \) are related to the Weibull statistics of the fibers as defined by Equation (2-7). According to Equation (2-23), a cumulative fiber pull-out density, \( \Omega(h) \), for the fiber pull-out length less than \( h \), is:

\[
\Omega(h) = 2 \int_0^h \left( \omega(z, \tau) \right) \, dz \, dt
\]  

(2-24)

In terms of the mean fiber pull-out length, \( <h> \), it can be expressed in the form of (54):

\[
<h> = \frac{r \Sigma}{2 \tau (m+1)} \left[ \frac{\tau^{m+1}}{m+1} \right] \Gamma \left( \frac{m+2}{m+1} \right)
\]  

(2-25)

where \( \Gamma \) is the tabulated gamma function and \( \Sigma \) is defined by:

\[
\Sigma = \left[ \frac{\Lambda_0 \, S_0 \, \tau^{m+1}}{2 \pi \, r^2} \right] ^{1/(m+1)}
\]  

(2-25a)

where \( \Lambda_0 \) and \( S_0 \) are scale parameters which have the units of stress and area, respectively. The \( m \) is the Weibull modulus of the fibers.

Figure 2.10 illustrates both measured and calculated distributions of fiber pull-out lengths as a function of the heat treatment time at 800 °C for the Nicalon fiber/LAS matrix composite[54]. It is evident that the theoretical calculations in this case are consistent with the experimental results. An important feature, as shown in Figure 2.10, is that there is a significant reduction of the fiber pull-out lengths in the range between 10 and 50 \( \mu \text{m} \) for the
Figure 2.10 Histograms indicating trends in fiber pull-out length with heat treatment at 800 °C for Nicalon fiber/LAS matrix composite [125].
composite heat treated for longer times, 8 and 16 hrs comparing with the 4 hr case. This demonstrates the crucial effect of the variation of the interfacial bonding on the fiber pull-out.

According to Equation (2.25), fiber pull-out is strongly affected by both the properties of the fiber and the interface. The contribution of the fiber can be related to the fiber strength distribution, m, as described by the Weibull modulus. Low m-values are associated with longer fiber pull-out lengths. When the m-value approaches infinity, the fiber pull-out length approaches zero. The fiber pull-out length is also related to the fiber radius, r. It is suggested that larger diameter fibers are relatively easier to pull out than smaller diameter fibers, for the \( \langle h \rangle \) is proportional to \( r^{m+1/m-1} \). In addition, the interfacial shear strength \( \tau \) between the fiber and the matrix plays a significant role, for the fiber pull-out length, \( \langle h \rangle \), is related to \( 1/\tau^{m+1/m-1} \). Hence, a stronger fiber/matrix interface makes it more difficult to achieve fiber pull-out.

2.4.3 Thermal Stress Effects on Fiber Debonding and Fiber Pull-out

For application of FRCMC's at elevated temperatures, thermal stresses from either the thermal expansion mismatch between the fibers and the matrix or a volume change as the result of a phase transformation, or both, can exert a significant effect on the mechanical properties of FRCMC's. Recently, Cao et al [129] have studied the effects of thermal residual stresses on several composites analyzing six different matrices reinforced by Nicalon fibers. Under the assumption that the thermal residual stresses do not involve any phase transformations or crystallization in glasses of the matrices, they have applied the model of Budiansky et al [130] to calculate the thermally induced stress normal to the fiber/matrix interface, \( \sigma_F^T \), and the residual stress in the matrix parallel to the fiber axis, \( \sigma_T^R \). These residual stresses can be expressed as:
where $\lambda_1$ and $\lambda_2$ are functions of the fiber volume fraction, $V_f$, and the elastic properties of the fiber: $(E_f, \nu_f)$, the matrix: $(E_m, \nu_m)$ and the composites, $E$, which are described in the forms of:

$$
\lambda_1 = \frac{1 - (1 - \frac{E}{E_f})(1 - \nu_f)/2 + (1 - \nu_f)(\nu_m - \nu_f)/2 - (E/E_f)[\nu_f + (\nu_m - \nu_f)V_f(E_f/E)]^2}{(1 - \nu_m)[1 + \nu_f + (\nu_m - \nu_f)V_f(E_f/E)]}
$$

and

$$
\lambda_2 = \frac{1 - (1 - \frac{E}{E_f})/2(1 + \nu_f) + (1 + \nu_f)(\nu_m - \nu_f)/2}{1 + \nu_f + (\nu_m - \nu_f)V_f(E_f/E)}
$$

and

$$
\varepsilon = (\alpha_f - \alpha_m) \Delta T
$$

where $\alpha_f$ and $\alpha_m$ are the coefficients of linear thermal expansion for the fiber and the matrix, respectively.

By applying Equations (2-26), Cao et al[128] have reported that high compressive residual stresses normal to the Nicalon fibers, $\sigma_{\perp}^T$, relate to high shear fiber sliding stresses; while the axial residual stresses, $\sigma_{\parallel}^T$, do not affect the sliding stresses, but may attribute to fiber debonding. They have also reported that the carbon layer on the Nicalon
fibers reduces the sliding stress. According to their results, thermal residual stresses from composite fabrication and thermally induced stresses from the application of the composite at elevated temperatures affect the fiber debonding and pull-out and hence alter the rising R-curves of the composite. With respect to the design and application of FRCMC's, it is critical to consider the effect of thermally induced stresses.

2.4.4 Thermal Expansion of Composites

The thermal expansions of composite materials have been theoretically modelled by Turner[131] and Schapery[132]. According to these models, the coefficient of thermal expansion of a composite is affected by several parameters, namely, weight (W_i) or volume (V_i) fraction of each component, the coefficients of thermal expansion of the components (\alpha_i), the Young's moduli of the components (E_i) and the density of each component (\rho_i). In general, their models can be presented as follows:

Turner's Model:

\[ \alpha_{\text{comp}} = \sum \frac{\alpha_i E_i (W_i/\rho_i)}{E_i (W_i/\rho_i)} \]  \hspace{1cm} (2-27)

Schapery's Model:

\[ \alpha_{\text{comp}} = \sum \frac{\alpha_i E_i V_i}{E_i V_i} \]  \hspace{1cm} (2-28)

The differences in these two models relate to the different views of the contributions of each component of a composite material. Turner's model[131] emphasizes contribution of thermal expansion of each component in terms of weight fraction, while Schapery's model addresses that in terms of volume fraction. Fundamentally, there is no differences between
the two models. As the thermal expansion is usually measured for a sample's length or its volume rather than some weight fraction, the form of Schapery's model[132] is often preferred from an experimental viewpoint.

According to these models, it is clear that any differences and changes of an individual component will consequently reflect on the variations in performance of the composite, on both the macroscopic scale and the microscopic scale. Macroscopically, the thermal expansion of the composite will change accordingly and microscopically, microcracking in matrix or at the interface between two components will occur. In addition, the interfacial bonding may also vary to accommodate the changes within the composite. Relative to the composites in this study, Table 2.4 summarizes several properties of each component, including Al₂O₃, AlPO₄-quartz form, AlPO₄-cristobalite form and the SiC fibers, which are used for the three composites used in this study. From an viewpoint of better engineering design of FRMCs, it is important to fully understand the effects of these properties of each individual component on the bulk performance of the composite.
Table 2.4
Physical Properties and Thermal Expansions of Al$_2$O$_3$, AlPO$_4$ and SiC

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
<th>$\gamma$ (J/m$^2$)</th>
<th>$K_{IC}$ (MPa-m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.90</td>
<td>403</td>
<td>0.26</td>
<td>35</td>
<td>3.6</td>
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<tr>
<td>AlPO$_4$</td>
<td>2.62</td>
<td>83.4</td>
<td></td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td>SiC</td>
<td>2.55</td>
<td>206</td>
<td>0.19</td>
<td>8.12</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Thermal Expansion:

<table>
<thead>
<tr>
<th>Phase</th>
<th>99%Al$_2$O$_3$</th>
<th>SiC</th>
<th>AlPO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$T ($^{\circ}$C)</td>
<td>CTE ($\times 10^{-6}$$/^{\circ}$C)</td>
<td>$\Delta$T ($^{\circ}$C)</td>
<td>CTE ($\times 10^{-6}$$/^{\circ}$C)</td>
</tr>
<tr>
<td>RT-200</td>
<td>7.0</td>
<td>3.6</td>
<td>RT-583</td>
</tr>
<tr>
<td>RT-300</td>
<td>6.7</td>
<td>3.8</td>
<td>583</td>
</tr>
<tr>
<td>400-600</td>
<td>8.3</td>
<td>4.6</td>
<td>RT-200</td>
</tr>
<tr>
<td>RT-600</td>
<td>7.6</td>
<td>4.3</td>
<td>200 - 500</td>
</tr>
<tr>
<td>700-1000</td>
<td>9.5</td>
<td>5.0</td>
<td>500</td>
</tr>
<tr>
<td>RT-900</td>
<td>8.1</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>RT-1200</td>
<td>9.0</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>RT-1500</td>
<td>10.2</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>
III. Experimental Procedures

3.1 Materials

Three commercially woven fabric 2-D laminated composites were obtained for this study#. They were in the form of panels approximately 450 mm x 195 mm x 8 mm. Figure 3.1 shows the 2D woven fiber configuration of the composites. The reinforcement for these composites was Nicalon silicon carbide (β-SiC) continuous fibers (Nippon Carbon Company, Tokyo, Japan) and the cementitious matrices were composed of a mixture of fine alumina (Al₂O₃) and aluminum phosphate (AlPO₄). According to the supplier’s data, for these three composites, the volume fraction of the fibers is 45%, and that of the matrix is 45% in the ratio of 17% Al₂O₃ to 28% AlPO₄. The volume fraction of porosity of the composites is about 10%. The three composites can be distinguished by the different amounts of pyrolytic carbon coating on the fibers, which were coated prior to the composite fabrication. Therefore, for simplicity, throughout this thesis the three composites are denoted as SiC-I, SiC-II and SiC-III, in the order of increasing pyrolytic carbon levels.

3.2 Sample Preparation from the As-Received Panels

To conduct thermal expansion measurements and fracture tests, proper sample dimensions are required. To produce valid test specimens, each composite panel was mounted on a glass plate by using a glycol phthalate glue (crystal bond 509 adhesive) for diamond sawing. The mounting was done at about 100 °C for about 30 min., followed by air cooling. After the mounted panel was completely cooled, it was placed onto the magnetized working stage of commercial surface grinder and sawed using a 0.25 mm thick

# Aluminum Company of America, Alcoa Technfcal Center, PA 15069, U.S.A.
Figure 3.1 A panel of Nicalon fiber reinforced alumina-aluminum phosphate matrix, 2D woven fabric, laminated composite. (white color shows the matrix and black color shows the fibers)
diamond wafer blade. Cooling liquid was applied to the panel during the cutting process.

For thermal expansion measurements, samples were cut into 2" in lengths. The dimensions of the square cross section of the specimen were dictated by the thickness of the panel and were about 7.5 mm x 7.5 mm. For the chevron-notched three point bending test, specimens were cut into 63 mm x 7.5 mm x 7.5 mm bars. For the unnotched three-point bend flexural strength tests, samples were cut into 36 mm x 3.8 mm x 3.8 mm bars.

3.3 Linear Thermal Expansion Measurements

Thermal expansion measurements were completed to ascertain the dimensional changes during both the heating and cooling cycles as well as to confirm the presence of the AlPO₄ phase transitions. An Orton automatic recording dilatometer was used. Specimens were exposed to air during these measurements. The heating rate was 3 °C/min for measuring from room temperature to 1000 °C, the maximum working temperature of the dilatometer. After the temperature reached 1000 °C, the specimen was furnace-cooled.

Each of the three as-received composites were used for thermal expansion measurements. During the measurements, a trace of linear thermal expansion percentage versus temperature was recorded. The automatically recorded chart of linear thermal expansion versus temperature allows direct determination of the thermal expansion coefficient of the composites. The coefficients of thermal expansion (CTE) were determined from the recorded slopes during the heating cycle by applying Equation (3.1):

\[
\alpha = \frac{\Delta L / L_0}{\Delta T}
\]

\[
\text{Equation (3.1)}
\]
where $\alpha$ is the thermal expansion coefficient, $\Delta L$ is the dimensional change, or the percentage linear thermal expansion, 0.1 is the expansion multiplier for the dilatometer setting, $L_0$ is initial specimen length and $\Delta T$ is the temperature change in °C.

### 3.4 X-ray Powder Diffraction

The phase contents of the three as-received composites (SiC-I, SiC-II and SiC-III) were determined by the X-ray powder diffraction method. The X-ray source was monochromatic Cu-Kα radiation. The scanning 2θ angle was from 20° to 70° at a scanning rate of 2°/min and a chart speed of 1 in/min. For these composites, the specimens were those in the as-received condition and, heat treated in air at 400 °C and 1200 °C for 3 hours each. Hence, these powders are representative of the specimens undergoing the fracture testing. For the X-ray diffraction pattern analysis, Bragg’s Law was applied in the form:

$$\lambda = 2d \sin \theta,$$

where, knowing $\lambda$, the wavelength of Cu-Kα (1.542 Å) and the 2θ angle of reflection, the d-spacing can be calculated for the diffraction peaks. By comparing the calculated d-spacings with the standard JCPDS data file as a reference, the phases in each composite could be identified. For each identified phase, at least three substantial peaks were matched with the JCPDS references.

### 3.5 Mechanical Testing

There are several methods which have been applied to the measurement of the fracture toughness of brittle materials, including the chevron-notched specimen, a double cantilever beam, the double torsion specimen and a single-edge-notched beam. These techniques are usually applied depending on the information which is desired to be obtained. To simultaneously evaluate the fracture toughness ($K_{IC}$), the $R$-curve ($G_c$) and the
total work-of-fracture (WOF), the chevron notched three-point-bend specimen test has unique characteristics. By using this method, the aforementioned fracture related parameters can be obtained from a single (P-u) curve. The technique promotes controlled stable crack propagation, for the stress level to initiate a crack is very low due to the extremely high stress concentration near to the apex of the chevron and the stored elastic energy prior to the crack initiation is hence low. For these reasons, that method was used in this thesis study.

3.5.1 Chevron-Notched Three-Point Bend Specimen Test

As just described, to simultaneously obtain the fracture parameters (KIC, Gf, and WOF) for the composites, the chevron-notched three-point-bend test specimen was used. The specimens were fractured at room temperature to 1200 °C at 200 °C intervals. At each temperature, ten individual specimens were tested for each of the three composites.

3.5.1.a Testing Apparatus:

For the fracture test, a universal Instron testing machine (Instron Corp., MA, USA) was used. It is a screw driven commercial testing machine which is equipped with a temperature controlled furnace. Elevated temperature testing was done using a refractory-lined furnace heated by eight vertical SiC elements, fashioned to form a cylindrical hot zone, approximately 100 mm in diameter and 200 mm in length. The tests were done near to the center of the hot zone. A schematic of the furnace setup is shown in Figure 3.2. Power for the SiC heating elements was provided from two individual units with each source delivering power to four of the heating elements. The testing temperature was measured using a Pt/Pt, 13%-Rh (Type R) thermocouple housed within the lower SiC tube of the test fixture with the sensing bead located just below the specimen. All testing was completed in air.
Figure 3.2 Schematic diagram of the universal test machine equipped with an elevated temperature furnace [128].
For the test fixture, the top ram was a dense sintered alpha silicon carbide (α-SiC) rod with a diameter of 25 mm and a length of 300 mm. A knife edge was machined at the center of one end. The lower portion of the fixture was a circular tube, of the same dense SiC having an outside diameter of 42 mm and an inside diameter of 35 mm with a length of 350 mm. Knife edges were machined into one end of the tube, 40 mm apart to obtain the lower span for the three point bending test. The test machine compliance is determined by the silicon carbide test fixture plus the test machine itself. It was equal to 0.5 µm/kg over the testing temperature range[128]. The testing cross head speed was maintained at 0.01 mm/min for all testing. Each sample was thermally stabilized in the hot zone at the testing temperature for 30 min prior to the actual test.

Figure 3.3 illustrates the configuration for the test. The major span, S, was 40 mm. For all of the chevron-notched specimens, the lengths of specimens were 65 mm with a square shaped cross section of 7.5x7.5 mm². For all notched specimens, the initial ratio (a₀ over W) was 0.44.

3.5.1.b Data Recording:

To determine the aforementioned properties for the fracture characterization of these composites, the load-displacement curve was recorded during each test. Load-displacement (P-u) plots were obtained from the load point displacement (LPD) trace record on a strip chart by using the formula:

\[
\frac{\text{(chart reading) x (cross head speed)}}{\text{chart speed}} \times \text{displacement (u)} = \frac{1}{(3-3)}
\]

This trace was then converted to a non-dimensional compliance plot using a 3-D finite element program, the details of which are described elsewhere by Jenkins et al[56, 128].
Figure 3.3 Schematic diagram of the fracture test configuration for the chevron-notched three-point-bend specimen.
3.5.1.c Fracture Toughness

Once the crack initiates, for any applied stress state, the instantaneous stress intensity factor, $K_{Ii}$, can be calculated from the formula (55,133):

$$K_{Ii} = \frac{P_i Y_i(\alpha_i)}{BW^{1/2}}$$  \hspace{1cm} (3-4)

where $P_i$ is the instantaneous load. Equation (3-4) holds for a general notch geometry, although the shape correction factor curve, $Y_i(\alpha_i)$, is different for different notch geometries, such as the chevron-notch and a straight-notch.

A schematic for the calculation of the geometric parameter, $Y_i(\alpha_i)$, is shown in Figure 3.4. The compliance for a particular load is obtained by using:

$$C = \frac{u}{P}$$  \hspace{1cm} (3-5)

where $C$ is the compliance, $u$ is the displacement corresponding to a particular load $P$ on the load displacement plot (Figure 3.4). The geometric parameter, $Y_i(\alpha_i)$, is then calculated by applying Equation (3-6):

$$Y_i(\alpha_i) = \frac{1}{2} \left( \frac{dC}{d\alpha} \right) \left( \frac{\alpha_i - (\alpha_n)}{\alpha_1 - \alpha_n} \right)$$  \hspace{1cm} (3-6)

where $\alpha_i$ is the normalized instantaneous crack length ($a_i$) by the specimen width ($W$) at the instantaneous load $P_i$, $\alpha_1$ is the final crack length ($a_1$) to the width ratio and $\alpha_n$ is the initial crack length ($a_n$) to the width ($W$) ratio, which is 0.44 as previously noted. $dC/d\alpha$ is the slope of the non-dimensional compliance curve.
Figure 3.4 Schematic diagram showing the relationship between the specimen compliance and the geometric factor.
Under the specific condition where the maximum applied test load ($P_{max}$) is observed, the plane strain fracture toughness $K_{IC}$ can be defined, according to Munz[133] and Munz et al[55], as:

$$K_{IC} = \frac{P_{max} Y_{min}(\alpha_n)}{BW^{1/2}}$$

in which $Y_{min}(\alpha_n)$ is the minimum value of $Y(\alpha)$ for a given $\alpha_n$. Hence, numerical analysis to determine the $Y(\alpha)$ must be adopted to determine $Y_{min}(\alpha_n)$. Jenkins et al[56] have developed a finite element method to calculate the $Y_{min}(\alpha_n)$ from the experimentally recorded ($P-u$) plot. According to Equation (3-7) as proposed by Munz et al[55,133], a criterion for the fracture toughness calculation is based on the condition of $P_{max}$ and $Y_{min}(\alpha_n)$. Although this is not theoretically unambiguous due to the presence of the rising R-curve behavior of the composites, nevertheless, in practice it is within a reasonable margin for the prediction of the fracture toughness since it underestimates $K_{IC}$ by using the smaller value of $Y_{min}(\alpha_n)$ rather than $Y_{c}(\alpha)$, that is the condition where the instability of crack propagation occurs for the toughened ceramic matrix composite.

The fundamental source of fracture information is the load-displacement record of the fracture event, the ($P-u$) plot. There are at least two ways which can be utilized to record the ($P-u$) data: (i) directly from the loading frame recorder as load point displacement (LPD) and (ii) as crack mouth opening displacement (CMOD) through a laser-based strain gage system as discussed by Jenkins[128]. The former was used in this study.

3.5.1.4 Crack Propagation Resistance, or R-Curve:

R-curves are well described by Broek [119] in his elementary text as the resistance to crack propagation with crack extension. Physically, it is characterized by the
instantaneous strain energy release rate that describes the instantaneous relationship between the externally applied energy input ($\Delta U_r$) versus the variation of newly created fracture surfaces ($\Delta A_r$) as shown in Figure 3.5. In practice, the $G_r$-value is calculated by using Equation (2-16) as:

$$G_r = \frac{1}{2B} \int \frac{dC}{da}$$

It is known that a damaged composite cannot go back to the origin when it is unloaded as shown in Figure 3.5. By applying Equation (2-16), the above concern can be neglected, for the experimentally measured change of the compliance ($dC$) with the crack extension (da) records the real situation for the damaged composite.

3.5.1.e. Total Work-of-Fracture:

The total work-of-fracture was calculated based on the definition by Nakayama[133] and Tattersall and Tappin[134]:

$$\text{WOF} = \frac{\int \text{P du}}{2\Delta T}$$

where $\int \text{P du}$ is the area under the (P-u) curve which is total energy consumed to fracture the chevron area of dimension $2\Delta T$. A schematic representation is shown in Figure 3.6. The integration of the area under the (P-u) curve was done by using the computer program after Jenkins[128].
Figure 3.5 Schematic diagram for the R-curve calculations [128].

Figure 3.6 Schematic diagram for the total work-of-fracture calculation [128].
3.5.2 Three-Point Bend Specimen Test

To measure the flexural strengths or the rupture of modulus (MOR) for the composites, unnotched specimens were used. Ten specimens were broken at each testing temperature, the same as that for the chevron-notched three-point-bend test, from room temperature to 1200 °C at 200 °C intervals. For the flexural tests, the same universal Instron apparatus was used. However, the test SiC fixture was changed to a smaller major span of 29 mm. The cross head speed was 0.01 mm/min. Each sample was thermally stabilized at the testing temperature for 30 min prior to testing. The configuration of the MOR test is similar to that shown in Figure 3.3, but the specimens were not pre-notched. The major span was 29 mm. The lengths of all specimens were 36 mm with a squared shaped cross section of 3.6x3.6 mm².

To determine the MOR, the maximum load, \( P_{\text{max}} \), at fracture of the specimen was used. The strength or MOR was then calculated from the formula:

\[
\text{MOR} = \frac{3}{2} \left( \frac{P_{\text{max}} L}{b h^2} \right) \tag{3.10}
\]

where \( L \) is the major span in mm, \( b \) and \( h \) are specimen width and thickness, respectively. The reported value of the MOR is the average based on sample size of ten and the range is the 95% confidence interval as estimated by the "t" distribution.

3.6 EDS Analysis of the Fiber/Matrix Interface

The fiber/matrix interfaces of the three composites, both as-received and after heat treatment at 1200 °C for three hours, were analyzed by energy dispersion spectroscopy (EDS) using the JEOL-JSM-840 A scanning electron microscope. Specimens were those which were previously mechanically tested and their fracture surfaces were used.
specimen surfaces were first cleansed in an ultrasonic cleaner and the mounted on an aluminum substrate using a conducting adhesive. The fracture surfaces were then lightly coated with a Au-Pd coating layer prior to the EDS analysis. The EDS signals were obtained from the fiber/matrix interface with about a 0.5 µm diameter electron beam. The amount of the carbon coating and the resolution of the EDS for carbon necessitated a 10 KeV excitation voltage for the analysis.

3.7 SEM Fractography of Fracture Surfaces

The fracture surfaces of specimens from both the chevron-notched tests and the flexural strengths or MOR tests were subjected to SEM fractography. The fractured sample surfaces were cleansed in an ultrasonic cleaner and mounted on an aluminum substrate using a conducting adhesive and then coated with a Au-Pd coating layer to enhance observation in the SEM. Fractographic studies were conducted by using the JEOL-JSM-840 A scanning microscope. The excitation voltage was 20 KeV for the fracture surface analysis. The working distance (WD) varied from 13 mm to 39 mm to achieve the best contrast of the fracture surface images. Various magnifications were selected to address each specific feature and issue.
IV. Results and Discussion

Three SiC reinforced cementitious matrix composites with increasing amounts of carbon coating on the reinforcing fibers were utilized to analyze the fiber/matrix interfacial effects on their fracture. In order to fully examine and explain the differences as well as similarities for the three composites in terms of the measured mechanical properties: $K_{IC}$, MOR, $G_f$ and the WOF, the following sections address those individual topics.

4.1 Specimen Characterization

X-ray diffraction analysis was utilized for the identification of the phases in the three as-received composites. This established a baseline for the detection of future possible reactions for specimens after testing at elevated temperatures. The scanning $2\theta$ angular range was from $20^\circ$ to $70^\circ$. The diffraction peaks were identified from the JCPDS references.

Figure 4.1 presents the X-ray diffraction patterns for the three as-received composites within the $2\theta$ angle range between $20^\circ$ and $70^\circ$. All of the X-ray diffraction peaks were identified. Table 4.1 summarizes the experimental X-ray diffraction information for the three composites in the as-received condition and the related matching data from JCPDS references within the X-ray scanning range ($2\theta$ angle) from $20^\circ$ to $70^\circ$. Comparing the experimental results with the JCPDS references, for these three composites, there appear to exist four primary phases: $\beta$-SiC, $\alpha$-$\text{Al}_2\text{O}_3$, $\text{AlPO}_4$ (quartz form) and $\text{AlPO}_4$ (cristobalite form). According to the information provided by the manufacturer, the reinforcement is Nicalon fiber, identified as the $\beta$-SiC phase and the matrix material is a mixture of $\alpha$-$\text{Al}_2\text{O}_3$ and $\text{AlPO}_4$ where the latter exists in two crystalline modifications, the quartz and cristobalite forms, $\text{AlPO}_4(q)$ and $\text{AlPO}_4(c)$. 
Figure 4.1 X-ray powder diffraction patterns of the three composites in the as-received condition.
Table 4.1
Primary Mineralogical Phases Detected in the As-Received Composites

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</table>

@ from X-ray data; # from JCPDS cards; q = quartz from; c = cristobalite form
X-ray diffraction patterns for the three composites after heat treating at 400 °C for three hours were also obtained. The powders used for that X-ray diffraction analysis were extracted from the chevron-notched tested specimens at 400 °C, the use of which enables a direct study of any possible phases change during the fracture test at that temperature. Figure 4.2 illustrates the X-ray diffraction patterns for the three composites. Table 4.2 summarizes the X-ray results for the three composites. Comparing Figure 4.2 with Figure 4.1, the X-ray patterns are identical. In terms of the normalized X-ray diffraction intensities for both the as-received and the 400 °C heated conditions, shown in Tables 4.1 and 4.2, there are no indications of any phase changes.

Figure 4.3 illustrates the 1200 °C-3 hr diffraction patterns for the three composites. The resulting X-ray data summarized in Table 4.3 reveals significant differences in the X-ray diffraction patterns. There are substantial increases in the intensities of the AlPO₄(c) peaks and a decrease in the AlPO₄(q) peaks. Therefore it must be concluded that there occurs a phase conversion from AlPO₄(q) to AlPO₄(c) for the matrix during the exposure at 1200 °C.

From the analyses of the experimental X-ray diffraction data, it is evident that there exist differences in the contents of the AlPO₄(c) phase for both the as-received composites and after exposure at 1200 °C. Table 4.4 summarizes the estimated amounts of the quartz and cristobalite forms of AlPO₄ in terms of their normalized maximum intensities at the 2θ angles of 26.0° and 21.2°, respectively. It suggests that the amounts of the AlPO₄(c) phase is approximately identical for the SiC-I and the SiC-II in the as-received condition. For the as-received SiC-III, the amount of the AlPO₄(c) phase is slightly higher.

In terms of the temperature effects, Table 4.4 also confirms that there is no phase conversion of AlPO₄(q) to AlPO₄(c) at temperatures below 400 °C. Austin[142] has
Figure 4.2 X-ray powder diffraction patterns of the three composites in the 400 °C-3 hr heat treated condition.
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@ from X-ray data; # from JCPDS cards; q = quartz from; c = cristobalite form
Figure 4.3 X-ray powder diffraction patterns of the three composites in the 1200 °C-3 hr heat treated condition.
Table 4.3
Primary Mineralogical Phases Detected in the 1200 °C Treated Composites

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@ from X-ray data; # from JCPDS cards; q = quartz; c = cristobalite form
Table 4.4

X-Ray Powder Diffraction Analysis of Phases of AlPO₄-Quartz Form and AlPO₄-Cristobalite Form in the Matrix of SiC/Al₂O₃-AlPO₄ Composites (*)

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<th>SiC-III</th>
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<td>AlPO₄(q) (%); AlPO₄(c) (%)</td>
<td>AlPO₄(q) (%); AlPO₄(c) (%)</td>
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<td>90; 10</td>
<td>84; 16</td>
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* The percentage values are based on the normalized X-ray diffraction intensity peaks at 2θ angles equal to 26.0° and 21.2° for AlPO₄(q) and AlPO₄(c), respectively.
shown that there occurs some phase conversion of AlPO$_4$(q) to AlPO$_4$(c) for temperatures between 600 and 1000 °C for very long heat treatment times, more than 100 hr. For this reason, the phases of the three composites within that temperature range between 600 and 1000 °C were not investigated in this study. However, for the three composites tested at 1200 °C for 3 hr, the phase conversion of AlPO$_4$(q) to AlPO$_4$(c) is substantial as evident from Table 4.4 as well as in Table 4.3. This phase conversion is also more substantial for the SiC-III than for either SiC-I or SiC-II, which is believed to be related to the differences in the initial contents of the AlPO$_4$(c) in the three as-received composites.

### 4.2 Pyrolytic Carbon Coating on the Fibers

From the results of the X-ray diffraction analyses, it can be concluded that the three composites are very similar in terms of their phase compositions. For the study of the interfacial effect on the toughening of these composites, the surfaces of the Nicalon fibers were precoated with different amounts of pyrolytic carbon. It is known that the surface of the Nicalon fiber is higher in carbon with respect to silicon so that with the carbon coating being used, it is difficult to quantitatively analyze the differences in carbon from the applied coating. However, it is possible to qualitatively assess the carbon contents for the three composites.

To characterize the differences in the carbon coatings, energy dispersive spectroscopy (EDS) analysis was performed on the vicinities of the fiber/matrix interface regions for the three composites. The investigation focused on the interfacial region between the fiber and matrix for the as-received specimens and those tested at 1200 °C. The former is to establish the baseline for the differences in the carbon content in the vicinity of the fiber/matrix interface and to ascertain the temperature effect on the carbon coating, which may be expected to oxidize during air exposure at 1200 °C.
Figure 4.4 presents the EDS patterns of the fiber/matrix interfaces of the three as-received composites. For the SiC-I, the carbon is readily detected along with oxygen, aluminum, silicon and phosphorus, as well as the gold and platinum from the specimen SEM coating. These elements are from either the reinforcing fiber or the matrix which have previously been identified by the X-ray diffraction analysis. The carbon, however, can be from either the SiC fiber or the carbon deposition on the fiber surface, even from both sources.

EDS analyses were also performed on the SiC-II and SiC-III composites as illustrated in Figure 4.4. In general their EDS patterns are quite similar to that for the SiC-I. However, it is important to observe that the carbon peak for the SiC-II is significantly higher than that for the SiC-I, while the EDS pattern for the SiC-III shows an even higher carbon level than that of the SiC-II. Again, this detected carbon could originate from both sources, for the EDS beam was focused at the fiber/matrix interface.

Figure 4.5 illustrates the EDS analyses for the fiber/matrix interfaces of the same three composites after exposure to air at 1200 °C for three hours. The EDS patterns show that the fiber/matrix interfacial carbon peaks are substantially decreased as represented by their intensities. Since the carbon coating on the fiber surfaces readily accesses the oxygen in the air, compared with the carbon in the SiC fiber, it must be concluded that the observed reduction of the carbon peak intensities can be attributed to the high temperature oxidation of the fiber carbon coatings in the composites.

Comparing the resulting EDS analyses shown in Figures 4.4 and 4.5, the question of the carbon sources is resolved. For the three as-received composites, the variation of the intensities of the carbon peaks is directly related to the amount of the pyrolytic carbon coating on the Nicalon fibers, as shown in Figure 4.5. As result, it is clear that the major
Figure 4.4 EDS analyses of the three composites at their fiber/matrix interfaces (as-received). Note the increase of the carbon intensity from the first to the third composite. The x are the peaks from the Au-Pd coating.
Figure 4.5 EDS analyses of the three composites at their fiber/matrix interfaces (1200 °C, 3 hr.). Note the carbon intensities are reduced. The x are the peaks from the Au-Pd coating.
differences in these three composites is characterized by the initial amount of the pyrolytic carbon coating on the Nicalon fibers. Based on the intensity level of the carbon peak, the amount of the pyrolytic carbon coating increases in the order: SiC-I : SiC-II : SiC-III.

4.3 Linear Thermal Expansion Analysis

Figure 4.6 illustrates the thermal expansion traces from room temperature to 1000 °C for the three composites. Both the heating and cooling cycles are presented. Several features that are obvious in Figure 4.6 are of interest. First, the general trends of the linear thermal expansion during the heating and cooling cycles are similar for the three composites. It is evident that there is a temperature region between about 550 and 700 °C where the linear thermal expansion increases significantly. A factor contributing to the observed increase is the α-β phase transformation of the AlPO₄-quartz form as discussed by Beck [91]. The contribution from the preexisting AlPO₄-cristobalite phase in the matrix appears to be insignificant, for the volume increase associated with the α-β phase transformation of the AlPO₄(c) form occurs at about 200 °C, which is not observed.

Figure 4.6 also reveals that the heating and cooling cycles do not coincide, illustrating the thermal expansion hysteresis of the three composites. The cooling trace is significantly below the heating one for the three composites. For the SiC-I, as the temperature decreases, the specimen returns to its original length at about 150 °C. For both the SiC-II and SiC-III, the original specimen lengths were not achieved even when those specimens were completely cooled to room temperature. This suggests that a permanent dimensional change occurs for both SiC-II and SiC-III composites during heating to 1000 °C. The observed thermal expansion hysteresis of the three composites may be a consequence of a configuration change of the woven fibers and slippage of the fibers due to the thermal expansion mismatch between the fiber and the matrix. Other possibilities
Figure 4.6 Linear thermal expansion measurements for (a) SiC-I, (b) SiC-II, and (c) SiC-III from 30 to 1000 °C (as-received).
relate to microstructural changes of the matrix and microcracking in the composites as reported by other researchers[136-138].

There exist three main temperature regions as revealed by the slopes of the linear thermal expansion versus temperature. During the heating cycle for the three composites, these temperature regions can be defined as RT-583 °C, 583-700 °C and 700-1000 °C. For the cooling cycle, a linear expansion persists in the higher temperature range of 1000-700 °C. However, as the temperature decreases further during the furnace cooling, there exists a distinctive nonlinear region for the linear thermal expansion versus temperature relating to the large hysteresis.

The coefficients of linear thermal expansion (CTE) can be determined by using Equation (3-1). Table 4.5 summarizes the measured CTE values corresponding to the heating cycle for the three composites. The CTE remains constant to 586 °C. At 586 °C the CTE increases substantially due to the $\alpha \rightarrow \beta$ phase transformation of AlPO$_4$(q). Then the CTE decreases in the temperature region from 700 to 1000 °C to a level close to the initial CTE value for the low temperature region (RT-586 °C). Comparing the CTE values throughout the temperature range of the measurement, the results are mixed in terms of the highest value and the lowest value. In the temperature region of the $\alpha \rightarrow \beta$ phase transformation of the AlPO$_4$(q) occurring, the CTE value of the SiC-I composite is the lowest, while that of the SiC-III composite is the highest and that of the SiC-II composite is intermediate.

Compared with the CTE values summarized in Table 2.3 for each of the individual phases: $\beta$-SiC, $\alpha$-Al$_2$O$_3$, AlPO$_4$(q) and AlPO$_4$(c), the measured CTE values of the three composites are lower than those of $\alpha$-Al$_2$O$_3$, AlPO$_4$(q) and AlPO$_4$(c), but higher than that of $\beta$-SiC. This can be explained in terms of the various factors from a composite point of
Table 4.5

Coefficients of Thermal Expansion of the SiC/Al₂O₃-AlPO₄ Composites

<table>
<thead>
<tr>
<th>Temperature Range (°C)</th>
<th>Coefficient of Thermal Expansion (x 10⁻⁶ /°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiC-I</td>
</tr>
<tr>
<td>Experimentally Measured:</td>
<td></td>
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<tr>
<td>RT - 586</td>
<td>4.76</td>
</tr>
<tr>
<td>586- 700</td>
<td>7.05</td>
</tr>
<tr>
<td>586 - 1000</td>
<td>4.17</td>
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<tr>
<td>Calculated (Appendix A):</td>
<td></td>
</tr>
<tr>
<td>RT - 586</td>
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</tr>
<tr>
<td>586*</td>
<td>5700</td>
</tr>
<tr>
<td>586 - 1000</td>
<td>6.52</td>
</tr>
</tbody>
</table>

# dimensional increase resulting from the α-β phase transformation of the AlPO₄ (q).
Hsueh and Becher [139] have studied the thermal expansion behavior of fiber reinforced ceramic matrix composites (FRCMC's). They have assumed that there exists little difference in the Young's modulus and Poisson's ratio between the reinforcement and the matrix. Therefore, the CTE of the composite is directly associated with those of the individual phases and their volume fractions, which can be estimated by the rule of mixtures [131, 132].

Table 4.5 also summarizes the calculated CTE values for the three composites by using the rule of mixture as described by Schapery [132] (Appendix A). It is evident that the estimated CTE values are not consistent with the measured CTE values. For the temperature regions of RT-586 °C and 700 - 1000 °C, the calculated CTE values are much higher than the measured. However, for the temperature region of 586-700 °C, the experimental CTE values are substantially lower than the estimated. For the former, the overestimation from the rule of mixture may be associated with the effect of the α-β phase transformation of the AlPO₄-cristobalite form. Its contribution to the CTE values of the three composites may not be so significant as it is predicted. For the latter, the α-β phase transformation of the AlPO₄-quartz form must be dominant.

Eckel and Bradt [140] have reported the thermal expansions of alumina fiber, mullite fiber and Nicalon SiC fiber reinforced CVD SiC matrix laminate/2-D woven composites. For the alumina fiber reinforced composites, they found significant deviations between the measured CTE values and those calculated by the rule of mixtures. However, there was good agreement of the CTE values between the measured and calculated values for both the mullite fiber and SiC fiber reinforced composites. Those results were related to the thermal expansion mismatch between the fiber and the matrix. For the former, the expansion of the alumina fiber is nearly twice that of the SiC matrix, which creates interfacial tensile stresses large enough to disrupt the interfacial bonding. Consequently, the extent of the thermal
expansion contribution from the alumina fibers is significantly reduced. This thermal expansion mismatch effect, or disruption of the interfacial bonding, on the resulting bulk thermal expansion of the composite is not taken into account in the usual rule of mixtures calculations.

Li and Bradt[141] have theoretically analyzed the internal micromechanical stresses within a SiC inclusion-reinforced alumina matrix composite. The results indicate that for a reinforcement volume fraction of \( V_f = 0.3 \) there exists about a 400 MPa internal tensile stress in the alumina matrix and a highly compressive internal stress within the range of 500 to -1700 MPa in the SiC inclusions. Of course, this calculation is under the assumption of a strong bonding developed at the inclusion/matrix interface. Nevertheless, this level of thermoelastic internal stresses is high enough to disrupt the interfacial bonding, as it is known that the interfacial bond strength for a typical ceramic/ceramic composite must be only about 20 MPa, or less, if the composite is expected to be toughened by the reinforcement and these composites are toughened.

For the three composites measured in this study, the reinforcements are the SiC fibers and the matrices contain the \( \text{Al}_2\text{O}_3 \). The interface of the fiber/matrix still experiences the tensile stress as the result of the thermal expansion mismatch between the fiber and the matrix. Therefore, the factor attributing to the lower experimental CTE values is probably similar. Another possibility may involve the presence of \( \text{AlPO}_4 \) (q) and \( \text{AlPO}_4 \) (c) phases in the matrices of the three composites. As shown in Table 2.3, the phase transformations actually decrease the CTE values of the \( \text{AlPO}_4 \) (q) and \( \text{AlPO}_4 \) (c) phases, especially for the \( \text{AlPO}_4 \) (q) phase, although the volume change due to the \( \alpha \rightarrow \beta \) phase transformation of the \( \text{AlPO}_4 \) (q) is significant. As result, the measured bulk CTE values for the three composites are lower than the theoretical rule of mixture values.
4.4 Fracture

To understand the fracture behavior of these FRMC's, it is important to realize that it not only depends on the intrinsic properties of the reinforcing fiber and the matrix, but also is strongly affected by the fiber/matrix interfacial bonding. For a better understanding of the fracture process of a FRMC, the effect of temperature on the interface must be considered to fully characterize the fracture process. To address these factors, the mechanical tests were designed so that the specimens were fractured at 200°C temperature intervals from 30 to 1200 °C. The parameters which were measured to characterize the fracture behavior of these composites are: (i) the fracture toughness, $K_{IC}$, (ii) the crack growth resistance, or R-curve, (iii) the total work-of-fracture, WOF, and (iv) the modulus of rupture, MOR (or flexural strength). To evaluate the first three parameters (i-iii), the chevron-notched three point bending specimen method was utilized. The flexural strength or MOR was measured by using an unnotched three point bending specimen.

4.4.1 Load – Displacement Records

To determine the fracture toughnesses, or $K_{IC}$ values, chevron-notched specimens were prepared and then tested by the three-point-bend method. The load (P) versus load-point displacement (u) traces from room temperature to 1200 °C were recorded and analyzed. Figures 4.7 (1a-4c) illustrate typical experimental traces at RT, 400, 600 and 1000 °C for the three composites. A common and obvious characteristic for all three is that the fracture process is a non-catastrophic one, characterized by the long tail trace of the (P-u) curve after crack initiation. This is a typical response of many composites to crack growth. In addition, several other characteristics of the (P-u) traces merit individual discussion.
Figure 4.7 Load - displacement curves, (P-u), for the three composites tested at 30, 400, 600 and 1000 °C. The test results at 1200 °C are not shown for they were catastrophic brittle failure.
For the composites tested at room temperature in their as-received condition, shown in Figures 4.7 (a-1c), the maximum load, $P_{\text{max}}$, at which composite fracture initiates, increases in the order: SiC-I : SiC-II : SiC-III. Once $P_{\text{max}}$ is reached, there occurs a sudden decrease in the load carrying capacity of the composite. However, crack extension is arrested and then a second form of crack extension occurs. This process directly reflects the crack growth resistance of the composite. The SiC-I appears to have the lowest resistance to crack growth as indicated by the shorter tail of the $(P-u)$ curve shown in Figure 4.7 (a-b). By the same measure, the SiC-II and SiC-III both have a higher crack growth resistances as revealed by the significantly longer tails of their $(P-u)$ curves. In addition, the decrease in the load carrying capacity for the SiC-I is perhaps not as continuous as that for SiC-II and that for SiC-III, at least on the scale of these records.

When the testing temperature is increased to 400 °C, the $(P-u)$ plots as illustrated in Figures 4.7 (2a-2c) reveal two distinct differences with respect to the room temperature results (plots). First, the initiation load of fracture, $P_{\text{max}}$, for the SiC-II is significantly reduced to level nearly equal to that for the SiC-I, but the $P_{\text{max}}$ for the SiC-III is not quite so significantly reduced. Second, the trends of the reduction of the load carrying capacity for the SiC-II and SiC-III become less continuous similar to that of the SiC-I at room temperature. This represents a reduction of the crack growth resistance of these composites.

For the testing temperature of 600 °C, as shown in Figures 4.7 (3a-3c), the $P_{\text{max}}$ values for all three of the composites decrease and the differences in $P_{\text{max}}$ among the three composites are negligible. Furthermore, fracture becomes less stable as indicated by the very short tails of the $(P-u)$ plots as shown in Figure 4.7 (3a-3b). The crack growth resistance is even more reduced when the composites are tested at 1000 °C. Figures 4.7 (4a-4c) illustrate that at 1000 °C, the three composites are much more brittle.
From the above discussion of the (P-u) traces, it is evident that the fracture behavior, or the crack growth resistance, varies from one composite to another, as well as with temperature for each of the composites. These (P-u) plots can be further analyzed to quantitatively describe the crack growth resistance, including the fracture toughnesses (K\text{IC}), the R-curves (G\text{R}) and the total work-of-fracture values (WOF).

### 4.4.2 Fracture Toughnesses

From the experimental (P-u) curves, the sets of (P\text{r}, u\text{r}) values can be converted into (P\text{r}, \alpha\text{r}) values by using Equation (3-5). Then the geometric factors, Y(\alpha\text{r}), can be obtained according to Equation (3-6). Once the geometric factors, Y(\alpha\text{r}), are determined, the fracture toughnesses, K\text{IC}, can be estimated by applying the P\text{max} and Y\text{min} criterion as:

\[
K_{IC} = \frac{P_{\text{max}} Y_{\text{min}}(\alpha_{r})}{BW^{1/2}}
\]

from which the detailed procedures have been previously discussed.

Figure 4.8 represents the calculated fracture toughnesses, the K\text{IC} values from room temperature to 1200°C for the three composites. The error bars represent the 95% confidence intervals based on the test sample size of ten and calculated by the statistical t-distribution. Several features are evident in Figure 4.8. First, the general trend persists for all three of the composites that their fracture toughnesses decrease with an increase of the testing temperature. Perhaps an exception occurs for the fracture toughnesses at 1200 °C, which appear to be slightly higher than those at 1000 °C. These results will be addressed in
Figure 4.8 Fracture toughness, $K_{IC}$, of the chevron notched specimens of the SiC-I, SiC-II and SiC-III, tested at temperatures from 30 to 1200 °C.
two different temperature regions, below 600 °C and above 600 °C. At temperatures below 600 °C, the SiC-I has the lowest toughnesses, the SiC-II is intermediate in fracture toughness and the SiC-III has the highest $K_{IC}$-values. However, above 600 °C, the fracture toughnesses of the three composites are not as distinguishable as at the lower temperatures. When the 95% confidence intervals are considered, the $K_{IC}$-values at temperatures of 600 °C and above are practically the same.

The results presented in Figure 4.8 are significant in two respects. First, it is evident that by altering the interfacial bonding between the Nicalon fibers and the Al$_2$O$_3$-AlPO$_4$ cementitious matrix, the fracture toughness can be significantly improved. At room temperature, the toughness increases from about 7 MPa-m$^{1/2}$ to 10.5 MPa-m$^{1/2}$, nearly a 50% increment for the SiC-II and to 14.9 MPa-m$^{1/2}$, about a 100% increment, for the SiC-III with respect to the fracture toughness value for the SiC-I. Second, the extent of toughening improvement of these composites is significantly reduced by testing at elevated temperatures. However, to gain further insight to the temperature effect on the brittleness of these fiber reinforced composites, the crack growth resistances, the R-curves, of the three composites must be considered in detail.

4.4.3. Modulus of Rupture

To fully describe the fracture properties of a composite, it is equally important to evaluate the strength of that composite. In general, the strength ($\sigma_f$) and fracture toughness ($K_{IC}$) of materials are related by $\sigma_f = K_{IC} \gamma(\alpha) c^{-1/2}$ where $c$ is the size of the critical flaw.

In this study, the flexural strength, or modulus of rupture (MOR) was measured by using the three-point bending method. The maximum load, $P_{max}$, at which the fracture initiates was recorded to calculate the flexural strength by applying the strength of materials formula:

$$\sigma_f = \frac{6P_{max}}{bd^2}$$
Figure 4.9 presents the results of the MOR versus testing temperature along with the 95% confidence intervals for the three composites.

In general, the MOR values and their temperature dependencies are similar for all three of these composites. Strengths also appear to be rather insensitive to the testing temperature, although there exists some data fluctuation. For each individual composite, averaging all of the MOR values obtained for the seven testing temperatures yields, for the SiC-I: 139 MPa, for the SiC-II: 161 MPa and for the SiC-III: 133 MPa (Appendix C). Comparing these MOR values, it appears that the SiC-II is slightly stronger than the SiC-I and the SiC-III. However, the differences are not very substantial. Although these composites have used the same Nicalon fibers in their reinforcement and the flexural strengths of fiber reinforced ceramic matrix composites are predominantly governed by the fibers, it is important to realize that the matrix and the fiber/matrix interfacial bonding may also contribute to the strength.

The results suggest that the flexural strengths are nearly independent of the testing temperature for the range of room temperature to 1200°C. This trend indicates that the flexural strengths of these composites are dominated by the flexural strength of the Nicalon fiber bundles. It is consistent with the reported experimental results for the strengths of the SiC fibers[74], which shows no significant decrease over the same temperature range. Fitzer and Pfeiffer [142] have studied the bending strengths of silica glass matrix reinforced by Nicalon fibers at both room temperature and 1200°C. They reported that the flexural strength of the composites slightly increases at 1200°C, which they related to the stronger interfacial bonding between the fiber and the matrix, for the matrix contains 12 mol% ZrO₂.
Figure 4.9: Modulus of rupture, MOR, of the unnotched specimens of the SiC-I, SiC-II and SiC-III, tested at temperatures from 30 to 1200 °C.
It is evident that the flexural strengths of these composites are lower than the tensile strengths of the Nicalon fibers. It can be related to the 2D woven fabric architecture of these composites. In this configuration, only half of the total fiber bundles are used to carry an externally applied load; while the calculation of the flexural strength takes the total cross section as a load carrying area. Broman and Prewo[25] have studied the flexural strengths of SiC fiber reinforced glass matrix composites, the fiber orientations of which are either 0° or 0°/90°. They reported that for the testing from room temperature to 1000 °C, the bending strengths of the 0°/90°-composite are only about half of those for the 0°-composite. This confirms that the dominant factors of the fiber strengths and fiber orientations, which directly relate to the performance of the composite. Another possibility can be related to the concept of Schuwert and Steiff[113]. In their model as shown in Equation (2-9), the calculation of the strength of the composite must consider contributions from the broken fibers; while the flexural tests in this study only consider the maximum load and the first fiber bundle breakage. Consequently, the measured flexural strengths, or MOR values are significantly lower.

Comparing the results shown in Figures 4.8 and 4.9, there exists no correlation between the fracture toughnesses (KIC) and the flexural strengths (MOR) below 600 °C, although it is generally expected for brittle solids, as previously mentioned. This may be related to the rising R-curve behavior of the FRMCs. The measured KIC-values in this case are based on the (Pmax-Ymin) criterion. Prior to an applied load level reaching Pmax, a nonlinear (P-u) behavior already exists, implying a certain degree of matrix cracking and fiber debonding. For the measurement of the MOR, the flexural strength is determined by the Pmax which results in the failure of the fiber bundles of the composite. The composite has an elastic linear behavior before failure occurs. For these reasons, it is not unexpected
that there is little or no correlation between the fracture toughness values and the flexural strengths for these three composites below 600 °C.

However, the fracture toughness values for the measurements above 600 °C, are generally consistent with the flexural strengths, both of which are about constant and temperature independent. This further implies that since the composites become more brittle at elevated temperatures, their (P-u) relationships are more or less elastic linear at an applied load level up to \( P_{\text{max}} \), similar to a monolithic ceramic. In this situation, the resulting measured fracture toughnesses are consistent with the measured flexural strengths for the composites, which is shown in parts of Figures (4.8)-(4.9) at temperatures above 600 °C.

### 4.4.4 Fracture Surfaces of MOR-Specimens

To further analyze the fractures of these MOR-specimens, Figure 4.10 shows the MOR-specimen side surfaces of these composites when broken at room temperature. Two distinguishing features are evident. For both the SiC-I and the SiC-II, the fracture path is composed of many sections of matrix cracking followed by fiber breakage. Since the MOR values are determined by the load at which the first bundle of fibers is broken, the resulting values should reflect that major contribution to the strengths of the fibers. For the SiC-III, however, the fractography reveals that the fracture path of the composite is a type of interlaminar one. This interlaminar failure prior to the fiber bundle breakage reveals that the resulting MOR value is also associated with the interfacial bonding between the fibers and the matrix. Furthermore, EDS analyses indicated that the carbon coating on the fiber surfaces used for the SiC-III composite is thicker, the weaker interfacial bonding at the fiber/matrix interface in the SiC-III must be responsible for the observed interlaminar fracture.
Figure 4.10 Scanning electron micrographs of the three-point-bend specimens (side view) tested at 30 °C. The cracks initiate from bottom towards the top in a nonbrittle fashion for SiC-I and SiC-II; while only delamination is observed for SiC-III.
The argument for the effect of the fiber/matrix interfacial bond on the flexural strengths of the composites is also supported by other experimental evidence. As shown in Figure 4.9, the MOR values of the composites may increase slightly at the higher testing temperatures (600-1000 °C). Figure 4.11 illustrates the SEM fractographic study of the three composites at 1200 °C. It reveals that their fracture patterns are similar, the processes of which involve matrix cracking and fiber breakage with little, or even without any delamination of these composites.

To summarize the above fractography, the following conclusions are reached. For the specimens at low temperatures, the fractures of the three composites are mainly controlled by a weak mechanical coupling between the fiber and the matrix, which is related to the carbon coating on the fibers. Their fracture processes involve the matrix cracking, delamination at the fiber/matrix interface and fiber breakage. For the specimens at elevated temperatures, strong thermal clamping stresses control the interfacial bonds at the fiber/matrix interface. The fracture processes of the three composites involve matrix cracking and fiber breakage without delamination at the fiber/matrix interface.

4.4.5 Crack Growth Resistance, or R-curves

By converting the (P, a) curves to (P, a) results, the crack growth resistance (\(\tilde{G}_f\)), or R-curves, can be determined by using Equation (2-16):

\[
\tilde{G}_f = \frac{1}{2B} \frac{1}{P^2} \frac{dC}{da} \quad (2-16)
\]
Figure 4.11 Scanning electron micrographs of the three-point-bend unnotched specimens (side view) tested at 1200 °C. The three composites fail in a brittle fashion.
The calculated $G_t$ values (kJ/m$^2$) correspond to the instantaneous crack propagation resistance for a specific crack extension, $\Delta a$ (mm). By plotting the $G_t$ value versus $\Delta a$, the R-curves can be determined at the different testing temperatures for the three composites.

Figure 4.12 illustrates the experimental R-curves for the SiC-I composite tested at temperatures from room temperature to 1000 °C. Since the tests at 1200 °C involved catastrophic-like failure, no consistent ($G_t$ - $\Delta a$) results could be obtained. Several features are apparent. First, the rising R-curves are predominant at the lower testing temperatures ($T < 600$ °C) as shown in Figure 4.12 (a). At the higher testing temperatures ($T > 600$ °C) shown in Figure 4.12 (b), increases of the R-curves are substantially reduced, yielding a nearly constant crack growth resistance, or flat R-curve.

Figure 4.13 illustrates typical experimental R-curves for the SiC-II composite tested over the same temperature range. There appears a substantial improvement in terms of the increase of the R-curve for the lower testing temperatures for the SiC-II shown in Figure 4.13 (a) when compared with the SiC-I shown in Figure 4.12 (a). However, at the higher testing temperature range shown in Figure 4.13 (b), similar, nearly flat, R-curves result. There are no distinguishing features between the SiC-II and the SiC-I in the high temperature regime.

Figure 4.14 illustrates the experimental R-curves for the SiC-III for the same temperature range, from 30 to 1000 °C. It is evident that at the lower testing temperatures, as shown in Figure 4.14 (a), the rising R-curves of the SiC-III composite are the highest of the three. The flat nature of the R-curve at the higher testing temperatures, as shown in Figure 4.14 (b), is, however, similar to that for the SiC-I and SiC-II composites.

At the lower testing temperatures, it is evident that the extent of the R-curve increases are in the order of: SiC-I : SiC-II : SiC-III. The SiC-I has the lowest resistance to
Figure 4.12 Strain energy release rate, $\psi$, of the chevron notched specimens of the SiC-I, tested at temperatures: (a) 30 to 400 °C and (b) 600 to 1000 °C.
Figure 4.13 Strain energy release rate, \( \dot{\gamma}_t \), of the chevron notched specimens of the SiC-II, tested at temperatures: (a) 30 to 400 °C and (b) 600 to 1000 °C.
Figure 4.14 Strain energy release rate, $\dot{\gamma}_r$, of the chevron notched specimens of the SiC-III, tested at temperatures: (a) 30 to 400 °C and (b) 600 to 1000 °C.
crack extension, while the SiC-III exhibits the highest resistance. At elevated testing temperatures (>600 °C), however, the three composites have similar, flat R-curves. Although there exists experimental scatter in these R-curves, the conclusion can be reached that the rising nature of the R-curves decreases with an increase in the testing temperature from room temperature through 600 °C and generally is flat from 600 to 1000 °C.

The varying extent of the rising R-curves for these three composites when tested at low temperatures indicates differences in the degree of toughening by the continuous fiber reinforcement. From the X-ray diffraction analyses of the composites, the three are of similar phase composition. Manufacturing information indicates that the architecture and the types of fiber and volume percentages of both the fibers and the matrices in the three composites are identical. For the testing temperature regime below 600 °C, the differences in the rising R-curves for the three composites must be related to the differences in the thickness of the carbon coatings on the fiber surfaces and the role of that coating on the fiber/matrix interfacial bonding. However, at elevated temperatures, the thermal stresses play an important role governing the interfacial bonding in terms of the matrix clamping of the fibers and therefore affects fiber debonding and fiber pull-out.

To further clarify the role of the fiber/matrix interfacial bonding on the crack growth resistance, or the rising R-curves. Table 4.6 summarizes the calculated thermally induced stresses, $\sigma_T^F$ normal to the fiber surface and $\sigma_T^T$ parallel to the fiber axis, from 200 to 1000 °C (Appendix B). As revealed in Table 4.6, $\sigma_T^T$ has a negative sign, revealing compressive stresses on the fibers from the matrix at the fiber/matrix interface. $\sigma_T^T$ has a positive sign, indicating longitudinal tensile stresses on the fibers. It is apparent that at room temperature, thermally induced stresses are zero and at 200 °C, these stresses are also still low. The level of $\sigma_T^T$ does not provide significant constraint on the fibers. For those conditions, the thickness of the carbon coating is a dominant factor promoting the fiber
Table 4.6

The Calculated Thermally Induced Stresses on the Fiber Surfaces of the SiC-I, SiC-II and SiC-III Composites (Appendix B)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>normal to fiber surface</th>
<th>parallel to fiber axis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{2T}$ (MPa)</td>
<td>$\sigma_{0T}$ (MPa)</td>
</tr>
<tr>
<td>200</td>
<td>-59.0</td>
<td>37.1</td>
</tr>
<tr>
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<td>1576.0</td>
</tr>
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</tr>
<tr>
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<td>1634.5</td>
</tr>
<tr>
<td>1000</td>
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<td>1649.7</td>
</tr>
</tbody>
</table>

* An additional stresses resulting from the $\alpha$-$\beta$ phase transformation of the AlPO$_4$(q) have been considered in the estimations at 586 °C and above, which is about 1576 MPa (Appendix B).
debonding and pull-out. The three composites exhibit toughening as the results of easy fiber debonding and pull-out, yielding significantly rising R-curves. For less carbon coating on the fibers such as the case of the SiC-I composite, the R-curves have a smaller rising trend. Increasing thickness of the carbon coating results in a significant improvement in the rising trends of the R-curves.

For testing at 400 °C, the thermal stresses increase considerably. Both the carbon coating and $\sigma^T$ appear to affect the rising R-curves. Based on the fact that the rising R-curves still exist with certain degrees of reductions, as shown in Figures 4.12(a)-4.14(a), it becomes evident that the effect of thermal clamping stresses on the fibers increases and that of the beneficial role of the carbon coating decreases. Despite the presence of the compressive thermal stresses on the fibers, the differences in the R-curves among the three composites are still affected by their initial carbon coatings. The thicker carbon coating can reduce the effectiveness of these thermal clamping stresses on the fibers better than the thinner carbon coating. This is confirmed by the experimental R-curves shown in Figures 4.12(a)-4.14(a), in which the extents of rising R-curves increase in the order of SiC-I, SiC-II and SiC-III.

It is noted that the $\gamma_k$ values for all three composites when tested above 600 °C, as shown in Figures 4.12(b)-4.14(b), are substantially reduced, exhibiting nearly flat R-curves. For the tests at 600 °C, the nearly flat R-curves can be related to the very high level of thermally induced clamping stresses, $\sigma^T$, on the fibers, as shown in Table 4.6. The $\alpha$-$\beta$ phase transformation of the AlPO$_4$-quartz form doubles the compressive clamping stresses on the fibers. The fibers are very tightly clamped by the surrounding matrix material, which makes it impossible for fiber debonding and fiber pull-out. This clamping stress not only relates to the thermal expansion mismatch between the fibers and the matrix, but also involves the $\alpha$-$\beta$ phase transformation of AlPO$_4$-quartz form at
temperature 586 °C [91]. At that temperature, the radial clamping stress substantially increases to about 1580 MPa, which is more than 70% of the strength level of Nicalon fibers, about 2200 MPa. This estimated clamping stress resulting from the phase transformation is comparable with those calculated by Li et al [141], which range from 500 to 1700 MPa. The estimated magnitudes of the clamping stresses are in good agreement with the trends of the experimentally measured fracture toughnesses and the R-curves as shown in Figures 4.8 and Figures 4.12(b)-4.14(b), respectively. Above the phase transformation temperature, the clamping stresses on the fibers suddenly increase to a level of 1700 MPa. Because of these very high clamping stresses on the fibers, the fiber debonding appears impossible and consequently no fiber pull-out process occurs during the fracture of the three composites. It must be concluded that at 600 °C and above lower fracture toughnesses and nearly flat R-curves for the three composites are directly associated with the high clamping stresses on the fibers from the matrix, in which the effect of the α-β phase transformation of AlPO₄-quartz is dominant at the 586 °C.

To summarize the above discussions, for the SiC/Al₂O₃-AlPO₄ composites, the rising trends of the R-curves are controlled by two primary factors. Below the temperature of the α-β phase transformation of AlPO₄-quartz form, the effect of the carbon coating on the fibers is dominant. Low thermal clamping stresses and weak interfacial bonding resulted from the presence of the carbon coating to create an environment that favors the fiber debonding and fiber pull-out. Above the phase transformation temperature, the thermal and phase transformation induced compressive stresses on the fibers play a dominant role and the high clamping stresses of the matrix on the fibers make the carbon coating ineffective, preventing fiber debonding and pull-out. The high levels of clamping stresses result from volume increases due to the thermal expansion differences between the
matrix and the fiber and the α-β phase transformation of the AlPO₄(q). As a result, all three composites exhibit nearly flat Γ curves at 600 °C and above.

4.4.6 Total Work-of-Fracture

Parallel to the evaluation of the R-curve behavior for these three composites, the total work-of-fracture (WOF) values were measured by applying:

\[ WOF = \frac{\int P \, du}{2A_T} \]  

(3-9)

to the load displacement curves by simply integrating the area under the (P-u) curves. Figure 4.15 illustrates the total work-of-fracture values versus the testing temperatures for the three composites. It is apparent that there exist consistent differences between the WOF values for the three composites and that they compare favorably with the results for the R-curves and the fracture toughness values. The similarities are self evident. The rising R-curves and the high fracture toughnesses of the composites result in a larger area under the (P-u) curve during the fracture test, revealing that more applied external energy is needed for crack extension, i.e. a higher value of the total work-of-fracture.

Similar to the other tests, two temperature regimes can be readily defined for the measured WOF values, one from room temperature to 600 °C (low temperature) and another from 600 °C to 1200 °C (high temperature). The distinguishing features of the WOF values over the above defined temperature regions can be directly correlated with the experimentally determined R-curves and explained in terms of the carbon coating and the thermal clamping stresses, plus the phase transformation effects as previously discussed.

As shown in Figure 4.15, for the SiC-I, the WOF values are the lowest of the three composites throughout the entire range of testing temperatures. For the SiC-I, the
Figure 4.15 Total work-of-fracture values from the chevron-notched specimens of the composites from 30 to 1200 °C. Note that the results reveal two temperature regions, one below 600 °C and the other above 600 °C.
maximum WOF value occurs in the as-received condition. Increases in the testing temperature subsequently reduce the WOF values. For the SiC-II and the SiC-III, similar trends are observed; but the magnitudes of the WOF values for both are significantly greater for temperatures below 600 °C. Differences in the total work-of-fracture values of these three composites cannot be clearly distinguished at temperatures above 600 °C. It is consistent with both the measured $G_c$ and $K_{IC}$ values for that temperature regime.

Dominant factors affecting the total WOF values for these three composites are the same as those which affect the R-curves, namely (i) the differences in the carbon coatings in the low temperature regime, and (ii) induced clamping stresses from both the thermal expansion differences and the AlPO$_4$ $\alpha$-$\beta$ quartz phase transformation in the high temperature regime. At low temperatures ($T < 600$ °C), the weak interfacial bonding enables the fibers to detach themselves from the surrounding matrix. Consequently, the fiber debonding and fiber pull-out consumes extra energy during crack extension, creating greater crack growth resistance, or larger $G$-values and hence yielding larger values of the total work-of-fracture.

At high temperatures ($T > 600$ °C), the interfacial bonding between the fiber and the matrix becomes much stronger due to the presence of the high clamping stresses on the fiber surfaces. Consequently the debonding of the fibers from the matrix becomes more difficult. The matrix crack cannot be blunted by the debonding mechanism and as a result, the stress intensity at the crack tip is high enough to further fracture the adjacent fibers. Because the fiber fracture is co-planar with the matrix fracture, there is no fiber pull-out and neither is an opposing stress field generated by the bridging fibers in the wake region. For this situation, the composites act as rigid monolithic solids and the crack propagation does not require extra external energy, yielding low crack growth resistance (low $G$-values) and hence lower values for the total work-of-fracture.
4.4.7 Fracture Surfaces of the Chevron-Notched Specimens

To gain further insight to the fracture processes of these three composites at the different test temperatures, a detailed fractography study that is complementary to the measurements is necessary. Figure 4.16 depicts a general view of the fracture surfaces of the chevron-notched specimens of the three composites. The loading of the specimens for these fracture surfaces was from the base of the chevron as depicted in Figure 4.16, hence the crack initiated from the apex of the chevron and proceeded to the base. As illustrated in Figure 4.16, it appears that the chevron tips are sharp, the radii of which are generally less than 100 µm, since the tip area covers only few fibers, each of which is about 12 µm in diameter.

Macroscopically, the fracture surface follows the chevron cross section from the apex to the base of the chevron for each of the three composites. After crack initiation, the crack propagates with a subsequent breakage of individual fiber bundles which experience a tensile stress condition, layer by layer. However, those fiber bundles whose axial directions are perpendicular to the applied tensile stress, do not appear to be affected and the integrity of those fibers remains during the fracture process, as clearly shown in Figure 4.16. To fully understand the differences in the fiber debonding and fiber pull-out among these three composites, it is necessary to observe each fracture surface in detail. Scanning electron microscopy (SEM) was applied to the fracture surfaces of the three composites for specimens tested at the different temperatures.

Figure 4.17 illustrates the fracture surfaces of the chevron-notched specimens of the three composites fractured at room temperature. Comparing the three, it is evident that the extent of fiber pull-out from the matrix and the fiber pull-out length increase in the order: SiC-I : SiC-II : SiC-III. Those differences reflect their interfacial bond strengths. This
Figure 4.16 Scanning electron micrographs of the fracture surfaces of the chevron-notched specimens of the three composites, tested at 600 °C.
Figure 4.17 Fracture surfaces of the chevron-notched specimens of the three composites, tested at 30 °C: (a) side view showing fiber pull-out and (b) face view of the crack tip region.
observation is consistent with the previous results. Combining these observations with the earlier measurements, it must be concluded that the fiber debonding and pull-out increases from the SiC-I to the SiC-III and that is directly associated with the level of the fiber carbon coating on the three composites at room temperature.

Figures 4.18 depicts the fracture surfaces of the three composites after testing at 400 °C. For the SiC-I, there is much less fiber debonding and fiber pull-out. Instead, the Nicalon fibers appear to fracture in a fashion co-planar with the matrix without any fiber pull-out. This indicates an increase of the interfacial bond strength between the fibers and the matrix. Since the profile of the fiber/matrix interface is distinct, indicating no chemical reaction at the interface, the interfacial bond strength increase must be associated with an increase of the mechanical clamping of the fibers by the matrix as a result of the thermal expansion differences between the fiber and the matrix.

Similarly, for the SiC-II as shown in Figure 4.18 in comparison with Figure 4.17, it is evident that both the number and the length of the pull-out fibers are also substantially reduced. Again, this must be a result of the interfacial bond strengthening by the thermal clamping stresses from the expansion mismatch of the fibers and the matrix. It also reveals that the fiber/matrix bonding of the SiC-III remains fairly weak as shown by the large amount of fiber pull-out, although the testing temperature (400°C) does affect the interfacial bond strength, as indicated by the reduced number of fiber pull-out events.

The effects of the strength of the interfacial bond on the fracture of the three composites is further confirmed by the fractography of the three composites tested at 600 °C, as shown in Figure 4.19. It is evident that as the testing temperature increases the fiber pull-out process during fracture decreases. At 600 °C, the SiC-II fracture is identical to the SiC-I in terms of the fracture surfaces morphology as well as the fracture toughness, crack
Figure 4.18 Scanning electron micrographs of the fracture surfaces of the chevron-notched specimens of the three composites, tested at 400 °C. Only the SiC-III composite exhibits significant fiber pull-out.
Figure 4.19  Scanning electron micrographs of the fracture surfaces of the chevron-notched specimens of the three composites tested at 600 °C. Note the absence of fiber pull-out.
growth resistance, or the R-curves and the total work-of-fracture values. For the SiC-III, the process of fiber pull-out is also substantially diminished. These observations indicate that the SiC-III composite fractures similarly to the SiC-I and SiC-II at 600 °C. With respect to the measured properties (KIC and WOF), the three composites are practically indistinguishable, as previously shown in Figures 4.8 and 4.15. The absence of fiber debonding further confirms that the clamping stresses on the fibers are very high.

At all temperatures above 600 °C, the fracture modes of the three composites are completely brittle as evidenced by the planar fractures shown in Figure 4.20, which illustrates the fracture surfaces of the three composites tested at 1000 °C. For these composites, the advancing crack propagates through the matrix and the fibers on the same plane, the cross sectional plane of the chevron. At 1200 °C, the fracture appearance is the same as shown in Figure 4.21. For these fracture surfaces, there is no pull-out of the fibers, neither is there any debonding between the fiber and the matrix, which was observed in the composites as shown in Figure 4.21. According to the EDS analyses previously discussed, this planar fracture and the loss of the fiber/matrix debonding process may be partially associated with the loss of the carbon coating. However, the dominant factor is the high clamping stresses on the fibers as a result of thermal expansion mismatch between the fibers and the matrix as well as the phase transformation of the AlPO4(q). The loss of carbon and the possible chemical reaction at the fiber/matrix interface just enhances the bonding.

Although X-ray powder diffraction analyses of specimens exposed to high temperatures do not reveal any new phase formation in the three composites, the oxidation of the SiC fibers is readily promoted by the oxidative loss of the carbon coating which serves a chemical reaction barrier preventing the fibers from reacting with oxygen as well as with the matrix. Figure 4.22 illustrates the vicinity of the fiber/matrix interface region on
Figure 4.20 Scanning electron micrographs of the fracture surfaces of the chevron notched specimens of the three composites tested at 1000 °C. Note the absence of fiber pull-out.
Figure 4.21 Fracture surfaces of the chevron-notched specimens of the three composites, tested at 1200 °C: (a) side view showing the absence of fiber pull-out and (b) face view of the crack tip region. Compare with Figure 4.17.
Figure 4.22 Scanning electron micrographs revealing (a) a distinct the fiber/matrix interface and (b) the glassy features of some of the fiber/matrix interfaces for the SiC-III composite, tested at 1200 °C.
a fracture surface for the SiC-III composite tested at 1200 °C. Two features are apparent. At some regions of the fiber/matrix interface, the SEM image of the boundary appears almost as distinct as that in the composites tested at lower temperatures. However, in other regions of the fiber/matrix interface, the SEM image of the boundary between the fiber and the matrix disappears. The morphology seems to be a glassy one. The lack of a distinct interfacial boundary indicates that there may be some chemical reaction occurring between the fiber and the matrix. The reaction probably contributes to a stronger interfacial bonding between the fibers and the matrix.

To summarize the above fractographic studies of the three composites tested at different temperatures, it is concluded that the carbon coating on the fibers promotes weak fiber/matrix interfacial bonding. Thicker carbon coating results in extensive fiber debonding and fiber pull-out, while thinner carbon coating yields less fiber debonding and pull-out. The effect of carbon coating on the fiber debonding and pull-out decreases with an increase of the test temperature. Above 600 °C, the effect high clamping stresses on the fibers are dominant, yielding no fiber debonding and fiber pull-out.

By combining the information from the EDS analyses, the fracture measurements, the calculated thermal stresses on the fibers, and the observations from the SEM fractography study, the following conclusions can be reached. The fracture character of these composites can be described in two different regions:

1. A) For the specimens at temperatures less than 600 °C,

(1) The thickness of the carbon coating on the fibers has a significant effect on the fracture of the three composites. For the thin carbon coating, the composite fails with less fiber pull-out than for the thicker carbon coated fiber composite. The extent of fiber pull-out:
increases and the distribution of the lengths of the pullout fibers appears to be wider for the thicker carbon coatings.

2) Because of the existence of the precoated carbon film on the fibers, there is only weak mechanical interlocking without any direct chemical bonding between the fiber and the matrix. Consequently, there exists extensive fiber/matrix debonding prior to fiber fracture and pull-out.

3) The thermally induced stresses on the fibers from the matrix are not high enough to contribute to a strong fiber/matrix interfacial bond. Consequently, the interfacial bonding between the fiber and the matrix is controlled by the thickness of the carbon coating.

As the result of the lack of fiber/matrix bonding, all of the composites fail in a non-brittle fashion that is characterized by a series of fracture processes including: matrix cracking followed by fiber breakage and debonding and finally fiber pull-out. These processes increase the crack growth resistance of the composites, yielding strongly rising R-curves at temperatures below 600 °C. The extent of rising R-curve trend is related to the amount of fiber pull-out, the distribution of the lengths of fibers pulled out and the friction between the fiber and the matrix. It is clear that the interfacial bond strength has a significant effect on the rising R-curve behavior of the three composites.

B) For the specimens at temperatures equal to or greater than 600 °C.

1) The clamping stresses on the fiber surfaces are high, which originates from the thermal expansion mismatch between the fibers and the matrix, plus the α-β phase transformation of AlPO₄₋₁.⁴

2) Benefits of the carbon coating for the weaker interfacial bonding at the fiber/matrix interface are negated. The resulting strong mechanical coupling between the
fiber and the matrix prohibits fiber debonding. Consequently, the stress intensity at the crack tip of the matrix is high enough to fracture the adjacent fibers, the fractures of the three composites are quite brittle.

3) As a consequence of the high temperature carbon oxidation reaction, the loss of carbon coating on the fiber surfaces can promote the chemical coupling between the fibers and the matrix, yielding even stronger interfacial bonds at the fiber/matrix interface.

As the result of the increased fiber/matrix coupling, all of these composites fail in a brittle fashion that is characterized by a fracture processes of matrix cracking and subsequent fiber breakage. These two processes do not increase the crack growth resistance of these composites and they exhibit nearly flat R-curves. It is evident that the clamping stresses on the fiber surfaces are detrimental to the mechanical performance of these composites.
V. General Relationship Governing the Fracture of the SiC Fiber Reinforced Al₂O₃-AlPO₄ Cementitious Ceramic Matrix Composites

As previously addressed for the crack growth resistance or the rising R-curve characteristics, it is evident that for these three composites studied, two primary factors affect their rising R-curves below 600 °C: (i) the pyrolytic carbon coatings and (ii) temperature. It is desirable to develop a general relationship to describe those effects on the fracture of this type of cementitious composite. Further exploration of such a relationship is necessary for a better understanding of the toughening mechanisms of these types of composites in general.

5.1 Models to Describe the Rising R-curve Behavior

The toughening mechanisms of fiber reinforced ceramic matrix composites (FRCMC's) have been quantitatively addressed by Osmani et al. [144]. For a composite possessing perfect interfacial bonding, the crack growth resistance can be expressed as:

\[ \tilde{G}_r = 2 \left( V_f \gamma_f - V_m \gamma_m \right) \]  \hspace{1cm} (5-1)

where \( V \) and \( \gamma \) are the volume fractions and surface energies for the fiber (f) and the matrix (m), respectively. For a composite having weak bonding, but for which the Weibull modulus of the fiber strengths is very high, the crack growth resistance is increased and may be expressed in the form of:

\[ \tilde{G}_f = \tilde{G}_r + V_f \tau \sigma_f^{1/3} E_f / 3 \]  \hspace{1cm} (5-2)

where \( \tilde{G}_f \) is the crack growth resistance, \( \tau \) is the interfacial shear stress at the fiber/matrix interface, \( \sigma_f \) and \( E_f \) are the fiber strength and Young's modulus, respectively, and \( r \) is the
fiber radius. This expression is further expanded for a fiber reinforced composite with weak interfacial bonding when the Weibull modulus of the fiber strengths is lower. The crack growth resistance is then further increased and may be described by:

$$G_2 = G_1 + V_1 \tau h^2 / 3 \pi r$$  \hspace{1cm} (5.3)

where $h$ is the fiber pull-out length. According to Equation (5.3), both $\tau$ and $h$ can significantly contribute to an increase of the crack growth resistance, $G_2$. However, it is known that an increase in $\tau$ also reduces the fiber pull-out length, $h$, as well as $G_1$ as shown in Equation (5.2). Therefore, a weak fiber/matrix interfacial bonding is desirable to promote rising R-curves in fiber reinforced composites.

Campbell et al.[21] have recently proposed a general rising R-curve relationship in terms of:

$$M \dot{G}_r = V_1 L_{d1} \frac{\sigma^2}{E} - E \varepsilon_0 \Gamma h^2 - \frac{4 \Gamma h^2}{r + 1} V_1 h^2 - \frac{2 V_1 \tau h^2}{r}$$  \hspace{1cm} (5.4)

where $L_{d1}$ is the fiber debonding length, $E$ is the Young's modulus of the composite, $\varepsilon_0$ is the misfit strain which causes the interface to be in residual compression, $\Gamma$ is the surface energy of the interface, and the other terms are as previously defined. In this model, the first term is a bridging contribution that derives from the stored elastic strain energy. The second term is the loss of residual strain energy caused by matrix crack extension and debonding. The third term reflects the new surface area created by fiber debonding, and the fourth term is the fiber pull-out contribution, dissipated through the frictional sliding at the interfaces.
In terms of the contribution of the fiber pull-out process to a rising R-curve, the two models as described by Equations (5.3) and (5.4) are very similar. That is, in fact, a primary factor for the toughening of ceramic matrix composites. In this study, the experimentally measured R-curves also confirm that the degree of fiber debonding and pull-out significantly affect rising R-curves. Based on the extensive data from this study, the aforementioned factors can be further investigated with regard to their roles affecting the rising R-curves. However, only a general empirical relationship can be established since any analytical approach must involve the knowledge of (i) temperature related diffusion processes at the interface, (ii) oxidation of the carbon coating layer, and (iii) the thermal induced stress conditions that include factors of the thermal expansion mismatch between the fibers and the matrix, and the phase transformation of AlPO₄, etc. Nevertheless, an empirical engineering approach to the experimental data is certainly useful to physically describe the observed rising R-curves and to compare the results with the existing models.

5.2 An Empirical Relationship for the Crack Growth Resistance

According to the experimentally determined R-curves for the three composites, as depicted in Figures 4.12 to 4.14, it appears that the trends of these R-curves are exponentially proportional to the crack extension. To further support this observation, Figure 5.1 illustrates the experimental R-curves and the related regression R-curves generated by using an exponential function of crack extension. That function is:

\[ \Delta G_f = \gamma_a \exp \left( \frac{\Delta a}{\Delta a} \right). \]  

(5.5)

It is evident that for all three composites, the exponential regression analyses yield acceptable results for the correlation coefficients, \( r^2 \), range from 0.70 to 0.85, not only for the room temperature R-curves, but also for the high temperature, flat R-curves. At room temperature, the rising R-curves are substantial and increase in the order: SiC-1, SiC-1!
Figure 5.1  Regression analyses of the R-curves for the SiC I, SiC II, and SiC III tested at (a) 30 and (b) 1000 °C.
and SiC-III. At 1000 °C, however, the R-curves become significantly flatter for all three composites. Earlier results reveal that this is related to the fiber/matrix interfacial bond strength. Combining the regression analyses with the aforementioned models suggests that the following relationship for the total crack growth resistance:

\[ \frac{\dot{\gamma}}{\dot{\gamma}_0} = \gamma G_i + \gamma G_r \exp \left\{ \xi \Delta \right\} \]  

(5-6)

where \( \gamma G_i \) is related to an initial crack growth resistance when no fiber pull-out occurs and \( \gamma G_r \) denotes the fiber pull-out contribution to the rising R-curve behavior, although the detailed format of that relationship needs to be more firmly established in terms of the aforementioned toughening related factors: the interfacial bonding, the temperature, and the extent of fiber pull-out.

Sakai and Bradt[6] have summarized in their review that there exist three types of R-curves for monolithic and composite ceramic materials. These are schematically illustrated in Figure 5.2. Comparing Figure 5.1 with 5.2, it is evident that the experimental results and resulting regression analyses, as shown in Figures 4.12-4.14 and Figure 5.1, are consistent with the trend described by the dashed line in Figure 5.2. The crack growth resistance increases with crack extension in a cumulative fashion. However, the effect of temperature on that specific rising R-curve trend deserves further explanation.

On the basis of the success of the previous exponential analyses for the three composites at room temperature and 1000 °C. Figure 5.3 illustrates the resulting regression R-curves for the three composites when tested at temperatures to 1000 °C. Table 5.1 summarizes the parameters \( \gamma G_a \) and \( \xi \) for the regression lines as described by Equation (5-5). Again, these regression analyses yield the correlation coefficients (\( r^2 \)) from 0.7 to 0.9. Although some of these coefficients are just within the satisfactory margin.
Figure 3.2 Schematic diagram showing three types of R-curves in monolithic polycrystalline ceramics and ceramic based composites [6].
Figure 5.3 Resulting R-curves from applying regression analyses to the experimental \( y_i \) values for (a) SiC-I, (b) SiC-II, and (c) SiC-III at temperatures from 30 to 1000 °C.
Table 5.1

R-Curve Parameters of SiC/Al₂O₃-AlPO₄ Composites as a Function of Testing Temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SiC-I $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
<th>SiC-II $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
<th>SiC-III $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
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</table>

--------------- the $\alpha$-$\beta$ phase transformation of AlPO₄(q)  ------------------

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SiC-I $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
<th>SiC-II $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
<th>SiC-III $G_a$ (kJ/m²) $\xi$ (mm⁻¹)</th>
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<td>0.05 1.31</td>
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</table>
the trends of the resulting R-curves are consistent with the experimental results in Figures 4.12-4.14. As shown in Table 5.1, it is apparent that at lower temperatures (< 600 °C) the R-curve coefficients, \(G_c\), vary with the specific composite and the temperature. At 600 °C and above, the \(G_c\) values are independent of the composites and temperature. For the \(G_c\) values, there are no systematic trends regarding the composites and temperatures. It appears that at 800 °C and above the \(G_c\) values increase in the order: SiC-I, SiC-II and SiC-III, although the physical significance is unclear. Each of the two parameters will be addressed in further detail.

For the SiC-I, Figure 5.3 (a) depicts the \(G_c\) values for the testing temperatures to 1000 °C. These appear to converge to a constant value at the initial stage of crack extension, \(\Delta a=0\). It indicates the initiation energy of the crack not involving the fiber pull-out. For further crack propagation, the \(G_c\) values of the composite are higher for the lower testing temperatures than for elevated temperatures. In addition, the \(G_c\) values for the higher testing temperatures do not vary significantly.

For the SiC-II, Figure 5.3 (b) depicts the \(G_c\) values revealing similar trends as for the SiC-I. However, the extent of the R-curve increase is substantial greater at the lower temperatures than for the SiC-I. These results reflect the experimental observations of the R-curves as a function of testing temperature as shown in Figures 4.12-4.14. The initial \(G_c\) value for room temperature is slightly higher, which may be related to a small amount of fiber debonding at the interface, in addition to the matrix cracking.

The SiC-III is shown in Figure 5.3 (c), for which the resulting regression R-curves follow the experimental R-curves previously presented in Figure 4.14. Even a more significant rising R-curve trend is evident, as shown in Figure 5.3 (c). The \(G_c\) values are distinguishable at the initial stages of crack extension. However, at elevated temperatures.
the rising R-curves are substantially reduced and flat R-curves appear to be an adequate description of the resistance of the composite to crack growth. Similarly, the higher \( G \)-values for low temperatures at the initial stage of crack extension may involve some fiber debonding.

The R-curve regressions naturally mirror the experimental R-curves, although the experimental data scatter yields low correlation coefficients. There should be no problem to utilize the resulting regression R-curves to establish a general relationship for the toughening of this type of composite.

### 5.3 A Proposed Empirical Relationship for the Rising R-curves

Two distinct types of R-curves have earlier been identified for these three composites. The R-curves at the lower temperatures, from room temperature through 600°C, indicate substantial increases with crack extension, while those at the higher temperatures above 600°C are generally quite flat. It is evident that the toughening-to-embrittlement transition has a direct effect on the R-curves. For the toughened composites \( T<600°C \), the \( G \)-values increase with crack extension, yielding a strong rising R-curve. For the embrittled composites \( T>600°C \), the \( G \)-values are constant, small in magnitude and essentially independent of the extent of crack extension, yielding flat R-curves.

Reviewing the results of the regression analyses as summarized in Table 5.1, there must exist a relationship between the parameters, \( G_i \) and \( \xi \), and temperature. Physically, the \( G_i \) value must have the units of energy per unit area according to Equation (5.5), for \( \alpha \) is related to the strain energy release rate. The \( \xi \) value must have the units of \( \text{length}^{-1} \), for the units of all exponential terms must be dimensionless.

As previously mentioned, for the three composites at the lower temperatures, Table 5.1 reveals the \( \xi \)-values ranging from 0.53 to 1.31 \( \text{mm}^{-1} \) for the three composites, which
to not appear to have any systematic relationship to the testing temperature, or to the individual composites. However, according to Equation (5.5), the \( \xi \)-values must be physically related to crack extension and hence to the fiber pull-out process during the fracture of these composites. According to its positive contribution to the crack growth resistance, \( \Delta G \), and its range of distribution, it must be associated with the energy of fiber sliding at the fiber/matrix interfaces, per unit length. Hence the \( \xi \)-values are affected by (i) the applied stress to pull-out the fiber per unit length, \( \sigma_{\text{pullout}} \langle h \rangle \), (ii) the initial interfacial shear resistance, \( \tau_0 \), for the as-received composite, and (iii) the thermally induced compressive stress, \( \mu \Delta \sigma^T \), as addressed earlier. Because the fiber pull-out is proportional to the applied stress, \( \sigma_{\text{pullout}} \), but inversely related to the interfacial shear resistance, \( \tau_m \), as well as to the compressive thermal stress, \( \Delta \sigma^T \), therefore, a simplest form of the \( \xi \)-value can be expressed in the form of:

\[
\xi = \frac{\sigma_{\text{pullout}} \langle h \rangle}{\tau_m - \mu \Delta \sigma^T}
\]

where \( \langle h \rangle \) is the average fiber pull-out length, \( \mu \) is the coefficient of friction of the fiber/matrix interface. In Equation (5.7), it must be realized that \( \Delta \sigma^T \) comes from not only the thermal expansion mismatch between the fiber and the matrix, but also may from the previously discussed phase transformation of AlPO\(_4\)(a). For the SiC fiber sliding on the surface of Al\(_2\)O\(_3\), \( \mu \) is about 0.15[145]. The shear resistance, \( \tau_m \), of a SiC/LAS composite has been reported to be about 20 MPa [142]. For the \( \mu \) and \( \tau_m \) values of the composites in this study, which are unknown, the above values will be used for the estimation of stresses for fiber pull-out.

To further confirm Equation (5.7), it is constructive to estimate the \( \sigma_{\text{pullout}} \langle h \rangle \) for the fiber pull-out when the composites are tested at different temperatures. Although the initial interfacial shear strength, \( \tau_m \), is unknown, for the most of FRCMC's, its magnitude
is about 20 MPa. The coefficient of friction of the fiber/matrix interface, $\mu$, can be assumed to be about 0.15. In terms of the thermally induced clamping stresses on the fibers, the $\Delta \sigma^T$ are equal to the estimated $\sigma^T$-values as summarized in Table 4.6. As previously discussed, the $\xi$-values are not well characterized in terms of either the carbon coating or the testing temperature. Therefore, for approximately estimating $\sigma_{\text{pullout}}$ values at a given temperature, average values of the $\xi$-values for the three composites tested at each given temperature have been used. Table 5.2 summarizes the estimated values of $\sigma_{\text{pullout}}$ for the three composites. It reveals that the values of $\sigma_{\text{pullout}}$ increase nearly one order of magnitude, from about 30 MPa-mm$^{-1}$ to about 220 MPa-mm$^{-1}$ when the testing temperature crosses that for the $\alpha$-$\beta$ phase transformation of the AlPO$_4(q)$. This is directly associated with an increase in the fiber clamping stresses that increase more than ten times from 120 MPa to 1700 MPa as presented in Table 5.2. It implies that below the phase transformation temperature, the interfacial shear resistance is small and the fibers can be pulled out with much less external force, but that above the transformation temperature, the interfacial shear resistance increases significantly and hence for the fiber pull-out, the external force must be much larger. This conclusion is consistent with the earlier SEM fractographic studies of the fracture surfaces for the three composites, which supports the results from the assumptions used in Equation (5.7).

As previously, for the three composites at the lower temperatures, Table 5.1 also reveals the $G_a$-value decreases with increasing test temperature. At a given
Table 5.2

Estimated Average Applied Stress for Fiber Pull-Out, $\sigma_{\text{pull-out}}$, for SiC Reinforced Al$_2$O$_3$-AlPO$_4$ Cementitious Matrix Composites (*).

<table>
<thead>
<tr>
<th>$\Delta T$ (°C)</th>
<th>$\Delta \sigma_T$ (MPa)</th>
<th>$\xi_{\text{average}}$ (mm$^{-1}$)</th>
<th>$\sigma_{\text{pull-out}}$ (MPa-mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200-25</td>
<td>-59.0</td>
<td>0.94</td>
<td>28.6</td>
</tr>
<tr>
<td>400-25</td>
<td>-126.4</td>
<td>0.85</td>
<td>33.1</td>
</tr>
</tbody>
</table>

---------- the $\alpha$-$\beta$ phase transformation of AlPO$_4$(q) ----------

| 586            | -1576.0                 | -----                          | -----                           |
| 600-25         | -1765.2                 | 0.74                          | 210.7                           |
| 800-25         | -1669.2                 | 0.74                          | 200.0                           |
| 1000-25        | -1702.0                 | 0.91                          | 250.1                           |

(*) The interfacial shear resistance: $\tau_0 = 20$ MPa, and the coefficient of friction of the fiber/matrix interface: $\mu = 0.15$. 
temperature, the \( G_a \)-values also increase in the order: SiC-I > SiC-II > SiC-III. At elevated temperatures (\( T > 600 \, ^\circ C \)), the \( G_a \)-values for these composites also decrease with increasing temperature. However, the magnitudes are considerably reduced and are practically identical. To define the proper function of the \( G_a \)-value as it varies with temperature, further analysis of the results is necessary. Figure 5.4 represents a plot of the regression estimated \( G_a \)-values versus temperature, revealing that \( G_a \) decreases with an increase in temperature. The nonlinearity appears different for each individual composite for the temperature range below 600 \( ^\circ C \), a trend which is well described by an exponential relationship. The correlation coefficients range from 0.85 to 0.98. That relationship for the \( G_a \)-values is described by:

\[
G_a = \Gamma \exp\left(-\frac{\eta}{T}\right)
\]  

(5-8)

where \( \Gamma \) is the energy per unit area and \( T \) is the temperature. The \( \eta \) has the units of (Kelvin)\(^{-1}\). Table 5.3 summarizes the resulting \( \Gamma \)- and \( \eta \)-values for the three composites when tested at the temperatures from 30 to 1000 \( ^\circ C \). The \( \Gamma \)-values are 0.42, 0.83 and 16.47 kJ/m\(^2\), and the \( \eta \)-values are 2.12 \( \times 10^{-3} \), 2.60 \( \times 10^{-3} \) and 6.03 \( \times 10^{-3} \) K\(^{-1}\) for the SiC-I, SiC-II and SiC-III. Comparing the regression results, both the \( \Gamma \)-values and the \( \eta \)-values increase in the order: SiC-I, SiC-II and SiC-III.

Several additional features can be noted in Figure 5.4. Below 600 \( ^\circ C \), the \( G_a \)-values for the SiC-I are the smallest, the SiC-II has intermediate \( G_a \)-values and those for the SiC-III are the largest. The trends of these resulting exponential curves in Figure 5.4 are consistent with the experimental data, in which the variation of the \( G_a \)-value versus temperature is flat for the SiC-I, but very steep for the SiC-III. Also, the regression analysis yields a temperature of 600 \( ^\circ C \), for which the three curves coincide. The regression analysis also suggests that the \( G_a \)-value is independent of the composite at
Figure 5.4 Regression analyses of the $\dot{\gamma}_a$ values for SiC-I, SiC-II and SiC-III, tested at temperatures from 30 to 1000 °C.
Table 5.3

Resulting Regression Analyses of the $G_v$ values in the Form of Equation (5.8) for the SiC-I, SiC-II and SiC-III. Tested at Temperatures 30 to 1000 °C

<table>
<thead>
<tr>
<th>Composites</th>
<th>SiC-I</th>
<th>SiC-II</th>
<th>SiC-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{r}$ (kJ/m²)</td>
<td>0.42</td>
<td>0.83</td>
<td>16.47</td>
</tr>
<tr>
<td>$\eta$ (K⁻¹)</td>
<td>$2.12 \times 10^{-3}$</td>
<td>$2.60 \times 10^{-3}$</td>
<td>$6.03 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
temperatures above 600 °C. This must be associated with the phase transformation induced high clamping stresses on the fibers, as discussed earlier.

As shown in Table 5.3, the $\Gamma$-values vary significantly for these three composites, but are constant for a given composite and independent of temperature. It is likely that the $\Gamma$-value is associated with the number of density of fibers which experience debonding, $N_f$, the fiber debonding length, $L_{d0}$, and the debonding energy of each individual fiber for the composites, $\Gamma_f$. Since the energy consumed in the fiber debonding relates to the newly created surface area of fiber/matrix interface, the total surface area of the fiber debonding can be expressed as $A_d = 2\pi \xi \sum (L_d/k)$ where $k = 0 - N_f$. With respect to the total fracture surface area, $2A_{fr}$, the $\Gamma$-value can be expressed as:

$$\Gamma = \frac{A_d}{A_{fr}} \xi \pi \Gamma_f \sum \frac{L_d}{A_{fr}}$$

Because the $\Gamma$-values are independent of temperature, Equation (5-9) suggests that the differences in the estimated $\Gamma$-values originate from the variations of the carbon coatings in these three composites. For the SiC-I composites, the thickness of the carbon coating is less than those for the SiC-II and SiC-III composites. As a result, for the as-received condition, the degree of fiber debonding for the SiC-I composite is much less than that for the SiC-II, while the extent of fiber debonding for the SiC-II is further less than that for the SiC-III. The $\Gamma$-values appear to be well correlated with the carbon coatings on the fibers.

It is also known that fiber debonding is primarily determined by the fiber/matrix interfacial bond strength. For the effect of temperature on the interfacial bond strength, the use of an effective interfacial bond strength should be adequate for the interfacial bond may involve both chemical and mechanical couplings. The chemical coupling results from
chemical and diffusion reactions between the fiber and the matrix, while the mechanical coupling, in this case, comes from thermally induced compressive stresses on the fibers. For these three composites, the chemical coupling does not appear to be an important factor as addressed earlier. The temperature effect on the effective interfacial bond strength originates from the thermal stresses due to the thermal expansion differences in the fiber and the matrix as well as to the phase transformation previously discussed. Apart from the aforementioned thermally induced stresses as described by Equation (5-7), for these composite systems, it appears that there exists another factor related to temperature, which is described by the term of $\exp(-\eta T)$ in Equation (5-8).

As summarized in Table 5.3, it is evident that the $\eta$-values are all similar, but increase in the order: SiC-I, SiC-II and SiC-III. According to Equation (5-8), it is apparent that a large $\eta$-value has more a negative contribution to the R-curve increase and that the $\eta$-values are associated with the temperature effect, which must relate to the thermally induced volume changes of the matrix. Based on the experimental results of the R-curves, the SiC-III is the least susceptible to elevated temperature degradation, which contradicts its large $\eta$-value in this regard. The major differences in the three composites are their carbon coatings on the fiber surfaces, which cannot be directly related to the large $\eta$-value of the SiC-III. The only remaining choice is the differences in the contents of the $\alpha$-AlPO$_4$-cristobalite phase in the three composites. As summarized in Table 4.4, for the three as-received composites, the relative amounts of the $\alpha$-AlPO$_4$-cristobalite phases are also similar, but do increase in the order of SiC-I, SiC II and SiC-III, too. This is in agreement with the order of the $\eta$-values and may be related.

Although the $\alpha$-AlPO$_4$-cristobalite phase contents in the three as-received composites are small, their role governing the fracture of the three composites may be significant as the thermally induced volume changes in these composite systems also create
compressive stresses on the fibers, resulting in a positive contribution to the effective interfacial bond strength, but a negative contribution to the crack growth resistance. On this basis, the proportionality between the amount of the $\alpha$-AlPO$_4$-cristobalite phase and the $\eta$-value can be proposed. Therefore, it may be concluded that the $\eta$-value may be physically related to the effect of thermally induced volume change of the matrix on the R-curve increase. The units of $\eta$ are expected to be the same as the coefficient of thermal expansion.

To summarize the above discussions, the total crack growth resistance of the three composites can be generalized, by substituting Equations (5-7), (5-8) and (5-9) into Equation (5-6), yielding:

\[
\bar{G}_t = G_0 + \pi \tau \Gamma \sum_{k=0}^{N_i} \left( L_a / A_{tot} \right) \exp \left( -\eta \Gamma \right) \exp \left( \frac{\left| \sigma_{\text{peeling}} / <h> \left( \eta - \mu \Delta T \right) \right|}{\Delta a} \right)
\]

(5-11)

It is clear that the crack growth resistance, as expected by the rising R-curve of these composites, is composed of two primary contributions. The first relates to the composite having a perfect interfacial bonding as described by Osmani et al[144]. The second part relates to the toughening contributions from the fiber debonding and the fiber pull-out.

As shown in Figure 5.4, at temperatures above 600°C, the $G_0$ values of these three composites are practically identical, about 30 J/m$^2$ obtained by extrapolating the horizontal line to the vertical axis, which can be defined as $G_0$. This constant $G_0$-value physically relates to the flat R-curves of the three composites at elevated temperatures. This is the case as described by Osmani et al[144] and shown in Equation (5-11). For these three composites, the $G_0$-value can be also estimated by Equation (5-11). Utilizing the data from Table 2.4, the estimated $G_0$-value is 24 J/m$^2$. Although the estimated $G_0$-value from
Equation (5-1) is slightly lower than that extrapolated from Figure 5.4. It is not unexpected since in the calculation it is assumed that fibers are perfectly bonded with the matrix plus the high Weibull modulus of the fiber strengths. In practice, these two assumptions are not 100% valid for the three composites. Therefore, the $G_f$ value in Equation (5-6) or (5-11) is equal to that described by Equation (5-1). As a result, Equation (5-11) can be further expanded as:

$$
G_r = 2(V_f\gamma_f + V_m\gamma_m)
$$

$$
+ \pi r \Gamma \sum_{k=1} \frac{(L_d/A_{int})_k \exp[-\eta T]}{L_d} \exp\left\{ \frac{\sigma_{pullout}/\langle h \rangle}{(\tau - \mu \Delta \sigma T)} \right\} \Delta a
$$

(5-12)

According to the above empirical relationship, a brittle ceramic body can be toughened, or reinforced, by incorporating fibers. As suggested by Equation (5-12), however, there may exist some limitations regarding the temperature of the composite application in practice. The extent of the composite toughening is controlled by (i) the bulk composite properties, and (ii) the effective interfacial bond strength. The latter is strongly temperature dependent as revealed by the second term of Equation (5-12).

The conclusion from this empirical crack growth resistance model is in good agreement with the models of Osmani et al[144] and Campbell et al[21]. In their toughening models, the extent of the fiber toughening is proportional to the length of fiber debonding[21] and length of fiber pull-out[21,144]. In addition, for a given crack growth resistance, the fiber pull-out is inversely associated with the interfacial shear strength[21,144], as demonstrated in Equation (5-12). Both the temperature effect on the effective interfacial bond strength and the thermally induced stresses on the fiber surfaces are incorporated in Equation (5-12).
Addressing the terms defined in Equation (5-12) with respect to the experimental observations, several consistencies are evident. First, carbon coatings on the Nicalon fibers can be used to make a substantial improvement in the ceramic matrix toughening by introducing a weak fiber/matrix interface. Under this condition, fracture of the composites exhibits significant fiber debonding and pull-out. The resultant rising R-curves are substantial. The variation of the amount of carbon level on the fiber surface consequently results in differences in the extent of toughening for the three composites. Second, the rising R-curve trend is substantially diminished as a result of large thermal induced clamping stresses on the fiber surfaces. As a consequence, the strong interfacial bonding yields much less or even no fiber debonding and fiber pull-out, without which the crack growth resistance of the three composites is significantly reduced, yielding the nearly flat R-curves at temperatures of 600 °C and above.

To conclude the above analysis, the toughening relationship expressed in Equation (5-12) is consistent with both the experimental results of this study and the previously published fiber toughening models[21,144]. This empirical relationship combines two fundamental aspects regarding the fiber reinforced ceramic matrix composite. It reveals that the brittle matrix ceramics can be toughened by introducing fibers and that the extent of the fiber reinforcement not only depends on the interfacial bond strength through an initial microstructural design including the fiber coating, but also closely relates to the application temperature which may have an influential effect (generally detrimental) on the ceramic toughening mechanisms. This appears to be particularly true for composites where the matrix has a higher thermal expansion than that of the reinforcing fibers.
VI. Summary and Conclusions

Fracture properties of the continuous Nicalon SiC fiber reinforced Al₂O₃-AlPO₄ matrix, 2D woven fabric, laminated composites were studied from room temperature to 1200 °C. Chevron-notched and unnotched three-point-bend specimens were tested. Fracture was characterized in terms of the fracture toughnesses, the flexural strengths, the strain energy release rate and the total work-of-fracture. The effects of both pyrolytic carbon coatings on the fiber surfaces and temperature on fracture were investigated.

6.1 Fracture Toughnesses

The fracture toughnesses were determined for the composites from room temperature to 1200 °C by using the chevron-notched three-point-bend specimen test. A $P_{\text{max}}-Y_{\text{min}}$ criterion was applied. At room temperature, the fracture toughnesses for these as-received composites increase from 7.1 MPa-m$^{1/2}$ to 14.9 MPa-m$^{1/2}$, which is about a 100 % increase through improved processing. At temperatures below 600 °C, the fracture toughnesses increased in the order of the thickness of the pyrolytic carbon coatings. For all three, the fracture toughnesses decreased with increasing temperature between room temperature to 600 °C. At the higher temperatures of 600 °C and above, there are not any distinguishing features in the fracture toughness for these three composites.

The fracture toughnesses of the three composites at $T < 600$ °C were related to the levels of the carbon coatings on the surfaces of the Nicalon fibers. The carbon coating promotes a weak interfacial bonding between the fiber and the matrix, which allows the fiber debonding and subsequent pull-out. As the result, the stress intensity at the crack tip is reduced, resulting in higher fracture toughnesses. However, at temperatures above 600 °C, the clamping stresses on the fibers were large enough to prevent the fibers from
debonding. These clamping stresses originated from both the thermal expansion mismatch between the fiber and the matrix and the \( \alpha-\beta \) phase transformation of AlPO\(_4\)-quartz form. Consequently, the fracture toughnesses of the three composites were substantially reduced.

6.2 Modulus of Rupture

The flexural strengths or the MOR values of the three composites were measured from room temperature to 1200 °C. The MOR does not change significantly over this temperature range, although there are some data fluctuations among the three composites. It is concluded that the MOR is generally constant for all three composites. Since the flexural strengths of the composites were measured in terms of the maximum load, the measured MOR values are directly related to the strengths of the bundles of Nicalon fibers at that temperature.

The MOR values do not exhibit any characteristic of the carbon coatings on the fibers. At first, the result may appear inconsistent with the fracture toughnesses which were measured for the three composites. A factor is the rising R-curve behavior of the composites. The effect is further confirmed when the results of both measurements are compared at temperatures above 600 °C. For that temperature regime, the composites are brittle as a result of the strong fiber/matrix interfacial bonding which is related to the high thermally induced clamping stresses on the fiber surfaces. The major contribution to that clamping stresses is the \( \alpha-\beta \) phase transformation of the AlPO\(_4\)-quartz form. Consequently, the measured flexural strengths and the fracture toughnesses of the three composites are consistent above 600 °C because the fracture toughness measurements at 1 - 600 °C do not involve fiber debonding and the composites exhibit nearly flat R-curves.
6.3 Crack Growth Resistance, R-curves

Using the chevron-notched fracture test, the crack growth resistance, or the R-curve, of the three composites were also determined as a function of temperature from room temperature to 1000 °C. The R-curve trends were characterized in terms of strain energy release rate versus crack extension. In the lower temperature regime (T < 600 °C), all of the composites exhibited various degrees of rising R-curves. However, the extents of the rising R-curves decreased with increasing temperature. The SiC-I has the lowest crack growth resistance, the SiC-II is an intermediate and the SiC-III has the highest crack growth resistance curves. It directly relates to the thickness of the carbon coating on the fibers and its role on fiber pull-out. The thicker carbon coating results in a weaker fiber/matrix interfacial bonding, which promotes the fiber debonding and pull-out, yielding a greater R-curve increase.

The effect of temperature on the R-curves was explained in terms of the roles of both the carbon coating on the fibers and thermally induced clamping stresses on the fibers and its role on the fiber/matrix interfacial bond strength. At the temperatures below 600 °C, the thermal clamping stresses are low and the carbon coating assumes a key role in controlling the bonding at the fiber/matrix interface. The weak interfacial bonding, as revealed by the SEM fractography study, resulted in extensive fiber/matrix debonding and pull-out. At 600 °C and above, the effect of the thermal clamping stresses on the fibers is dominant, which increases the fiber/matrix interfacial bond strength significantly as the result of the α-β phase transformation of the AlPO₄-quartz form. The stronger interfacial bond strengths were estimated and also confirmed by the SEM fractography that revealed decreases in both the fiber debonding and the fiber pull-out with an increase of temperature. The role of the carbon coating is insignificant regarding the R-curves of these composites above 600 °C.
6.4 Total Work-of-Fracture

The total work-of-fracture (WOF) was also determined as a function of temperature from room temperature to 1200 °C, using the chevron-notched three-point-bend specimen method. For the three composites, the general trend revealed that the WOF decreases with an increase in temperature, which is consistent with the experimental results for the fracture toughnesses and the R-curve trends.

At temperatures below 600 °C, the total work-of-fracture was significantly higher, which relates to both the fiber debonding and pull-out and is consistent with the rising R-curves. In this temperature region, the effect of carbon coating thickness is a primary one. The total work-of-fracture values increased in the order of the carbon coating thicknesses for the three composites. At 600 °C and above, the WOF values were similar for all three composites and their magnitudes were much lower than those at the lower temperatures. These were related to the flat R-curves as the result of much stronger interfacial bond strengths which increased the interfacial shear resistances at the fiber/matrix interface.

Based on the results of this study, it can be concluded that for cementitious bonded matrix, SiC fiber reinforcement may have excellent fracture resistance at low temperatures if the fiber/matrix interfacial bonding is optimized. However, the crack growth resistance may change dramatically with temperature increases. In the case of the Al₂O₃-AlPO₄ matrix reinforced with continuous SiC fibers, a transition temperature of toughened-to-embrittled occurs at about 600 °C. For better design of these FRCMC's for applications at elevated temperatures, the concept of an effective interfacial bond strength is a very important factor.
6.5 A General Description of the Rising R-curves

According to the experimental R-curves for the three composites, an empirical relationship of the rising R-curve behavior was generalized, in which several primary factors were defined with the consideration of both the experimental results in this study and previously published toughening models for fiber reinforced ceramic matrix composites. This general relationship not only reflects a good consistency with the experimental results for the three SiC/Al₂O₃-AlPO₄ composites, but also suggests additional factors to be considered regarding the design of tougher fiber reinforced ceramic matrix composites.

The fracture of SiC/Al₂O₃-AlPO₄ cementitious matrix, 2D woven fabric, laminated composites was investigated. The differences in the mechanical properties were studied in terms of (i) the carbon coating on the fibers and (ii) temperature. A significant result of this thesis was the major effect of the matrix bond phase transition of the AlPO₄ on the fracture resistance. A distinct transition of the fracture from toughened to-embrittled is observed at 600 °C for the three composites. For temperatures below 600 °C, the carbon coating promotes a weak interfacial bonding at the fiber/matrix interface. Consequently, fiber debonding and fiber pull-out contribute to the rising R-curves of the composites. At temperatures above 600 °C, the thermally induced clamping stresses on the fibers are large, while the effect of the carbon coating is insignificant. As a result, the interfacial bonding at the fiber/matrix interface is very strong. The lack of the fiber debonding and fiber pull-out result in the flat R-curves of the composites.
VII. Suggestions for Future Research

The promising results of the Nicalon SiC fiber reinforced Al$_2$O$_3$-AlPO$_4$ matrix laminated composites have proven the potential of the cementitious phosphate bonding concept in the fabrication of fiber reinforced ceramic matrix composites. However, as with all research, as many new questions have arisen as have been answered. The large differences in the fracture resistances of these three composites and their lower crack growth resistance at elevated temperatures present many topics for future research.

For fiber reinforced ceramic matrix composites, it is essential to optimize the interfacial bond strength during the processing of the composite. It is one of the most important aspects of these composites needs to be further investigated. This study suggests that the fracture toughness, the crack growth resistance and the total work-of-fracture can be stabilized at higher temperatures if the fiber surface coating is properly controlled to provide desirable interfacial bonding. The desirable interfacial bonding must be achieved through a thermally stable fiber coating which promotes modest mechanical coupling and at the same time prohibits diffusional bonding. At elevated temperatures, for this cementitious composite system, the thermally induced clamping stresses on the fibers are significant. These stresses are related to (i) thermal expansion mismatch between the fiber and the matrix and (ii) the α→β phase transformation of AlPO$_4(q)$. The carbon coating fails to counter the effects of the thermal expansion on the interfacial bond, resulting in a strong interfacial bond and brittle-like composites. To further extend the composite application temperature without loss of fracture toughness and crack growth resistance, other coating materials or a duplex coating method should be investigated. However, the effect of the AlPO$_4(q)$ α→β transition may be difficult to overcome.
Theoretical models for the crack growth resistance of fiber reinforced ceramic matrix composites are presently somewhat speculative and empirical. These can be further developed with additional experimental results. Based on this research, an empirical model of the toughening of fiber reinforced ceramic cementitious matrix composites has been presented. This model relates the effects of fiber toughening to several parameters. Those parameters are temperature dependent and also compete with one another. For better understanding of the toughening processes, quantitative relationships among these factors must be established.

A significant result of this thesis was the major effect of the matrix bond phase transition of the AlPO₄ on the fracture resistance. This illustrates the need for future research addressing different cementitious matrices. Very likely, every different matrix will have its own peculiar characteristics.
VIII. References


[58] W.D. Kingery, "Fundamental Study of Phosphate Bonding in Refractories: II."


Appendix A

Calculation of the Coefficients of Thermal Expansion of the Composites

The CTE values of the composites were calculated by using Equation (2.28).

(1) CTE of the matrix only:

\[
\alpha_m = \frac{\alpha_{\text{Al}_2\text{O}_3} E_{\text{Al}_2\text{O}_3} V_{\text{Al}_2\text{O}_3} + \alpha_{\text{AlPO}_4} E_{\text{AlPO}_4} V_{\text{AlPO}_4} + \alpha_{\text{SiPO}_4} E_{\text{SiPO}_4} V_{\text{SiPO}_4} \times \alpha_{\text{SiPO}_4} E_{\text{SiPO}_4} V_{\text{SiPO}_4}}{(E_{\text{Al}_2\text{O}_3} V_{\text{Al}_2\text{O}_3} + E_{\text{AlPO}_4} V_{\text{AlPO}_4} + E_{\text{SiPO}_4} V_{\text{SiPO}_4})}
\]

where

(a) \( V_{\text{Al}_2\text{O}_3} = 0.38 \) and \( V_{\text{AlPO}_4} = 0.62 \)

(b) Assume that \( E_{\text{AlPO}_4} = E_{\text{AlPO}_4} = E_{\text{AlPO}_4} \)

(c) Based on results from the X-ray diffraction analyses as shown in Table 4.4:

<table>
<thead>
<tr>
<th></th>
<th>SiC-I</th>
<th>SiC-II</th>
<th>SiC-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{\text{AlPO}_4} )</td>
<td>0.57</td>
<td>0.56</td>
<td>0.52</td>
</tr>
<tr>
<td>( V_{\text{SiPO}_4} )</td>
<td>0.05</td>
<td>0.06</td>
<td>0.10</td>
</tr>
</tbody>
</table>

RT to 586°C:

\[
\alpha_m (RT \rightarrow 586°C) = \frac{[7.6 \times 403 \times 0.38 + 13.8 \times 83.4 V_{\text{AlPO}_4} + 0.2 \times 83.4 V_{\text{SiPO}_4} \times 10^b]}{[403 \times 0.38 + 83.4 \times 0.62]}
\]

<table>
<thead>
<tr>
<th></th>
<th>SiC-I</th>
<th>SiC-II</th>
<th>SiC-III</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_m )</td>
<td>0.07</td>
<td>0.06</td>
<td>0.98 \times 10^{-b} (1/K°C)</td>
</tr>
</tbody>
</table>
Due to the $\alpha$–$\beta$ phase transformation of the AlPO$_4$ (q), a dimensional change is estimated from a 0.5% dimensional increase due to the $\alpha$–$\beta$ phase transformation of the SiO$_2$ (q) [91], which is:

\[
\frac{\Delta L}{L_{\text{AlPO}_4}} = \frac{\Delta L}{L_{\text{SiO}_2}} \times (V_{\text{mol/AlPO}_4} / V_{\text{mol/SiO}_2})
\]

\[
= (1.005 x \times 122.0 / 3.9) / (60.1 / 2.2)
\]

\[
= 0.0057
\]

where $V_{\text{mol/AlPO}_4}$ and $V_{\text{mol/SiO}_2}$ are the molar volumes of AlPO$_4$ and SiO$_2$, respectively.

586°C to 1000°C:

\[
\alpha_{m,(586-1000°C)} = \frac{[9.5 \times 403 \times 0.38 + (-2.5) \times 83.4 \times V_{\text{AlPO}_4(q)} - 0.0 \times 10^{-6}]}{[403 \times 0.38 + 83.4 \times 0.62]}
\]

\[
\begin{array}{ccc}
\text{SiC-I} & \text{SiC-II} & \text{SiC-III} \\
= 6.52 & 6.53 & 6.57 \times 10^{-6} \quad (1/°C)
\end{array}
\]

(ii) CTE of the composites (matrix + fibers):

\[
\alpha_c = \frac{\alpha_{\text{mat}} V_m + \alpha_f E_f V_f}{(E_m V_m + E_f V_f)}
\]

where Young's modulus of the matrix is calculated using the rule of mixtures:

\[
E_m = V_{\text{Al}_2\text{O}_3} / E_{\text{Al}_2\text{O}_3} + V_{\text{AlPO}_4} / E_{\text{AlPO}_4}
\]

\[
= 0.38 / 403 + 0.62 / 83.4 \times 8.4 \times 10^{-1} \quad (\text{GPa}^{-1})
\]

\[
E_m = 119.1 \quad (\text{GPa})
\]
RT to 586 °C:

\[ \alpha_{v, \text{RT-586°C}} = \frac{[ \alpha_m x 119.1 x 0.45 - 3 x 206 x 0.45 ] x 10^6}{[ 119.1 x 0.45 - 206 x 0.45 ]} \]

\[
\begin{array}{ccc}
\text{SiC-I} & \text{SiC-II} & \text{SiC-III} \\
6.04 & 6.04 & 6.01 x 10^{-6} (1^\circ \text{C})
\end{array}
\]

at \( T = 586^\circ \text{C} \):

Since the volume fractions of the AlPO_4(q) are about the same for the three composites, the average value, 0.55, was used in the calculation.

The volume change of the AlPO_4(q) over the matrix at the phase transformation is:

\[ \Delta \alpha_{AlPO_4} \Delta \alpha_{V_m} = 3 \alpha L \Delta L / L \rho \Delta \alpha_{V_{AlPO_4}} V_{AlPO_4} / V_m \]

\[ = 3 x 0.0057 x [ ( 0.55 x V_m ) / V_m ] \]

\[ = 0.0094 \]

586 °C to 1000 °C:

\[ \alpha_{v, 586-1000^\circ \text{C}} = \frac{[ \alpha_m x 119.1 x 0.45 + 5.0 x 206 x 0.45 ] x 10^6}{[ 119.1 x 0.45 + 206 x 0.45 ]} \]

\[
\begin{array}{ccc}
\text{SiC-I} & \text{SiC-II} & \text{SiC-III} \\
5.56 & 5.56 & 5.58 x 10^{-6} (1^\circ \text{C})
\end{array}
\]
Appendix B

Calculation of Thermally Induced Stresses Normal to the Fiber Surface and Parallel to the Fiber Axis

The stress values in the composites are calculated by using Equation (2-26), except for the situation where there is the α-β phase transformation of the AlPO₄(α) involved.

(i) Thermally induced strain on the fibers:

\[ \varepsilon_{f,m} = (\alpha_f - \alpha_m) \Delta T \]  (without phase transformation)

\[ \varepsilon^{\alpha-\beta}_{f,m} = \Delta V^{\alpha-\beta}_{AlPO_4(m)} V_m \]  (with phase transformation)

Because the CTE values of the matrix, \(\alpha_m\), are about the same for the three composites over the given temperature ranges (Appendix A), the average values of \(\alpha_m\) are used in the following calculations.

\[ \varepsilon_{f,m} (\text{586 C}) = (4.3 - 0.04) \times 10^{-6} \times \Delta T = -4.74 \times 10^{-6} \Delta T \]

\[ \varepsilon^{\alpha-\beta}_{f,m} (\text{586 C}) = -1.17 \times 10^{-6} \Delta T \]

\[ \varepsilon_{f,m} (\text{586-1000 C}) = (5.0 - 6.54) \times 10^{-6} \times \Delta T = -1.54 \times 10^{-6} \Delta T \]

(ii) Young's modulus of the composites (fibers + matrix)

\[ E_c = V_m / E_m + V_f / E_f \]

\[ = 0.45/119.1 + 0.45/206 = 6.0 \times 10^{-3} \text{ (GPa)} \]

\[ E_c = 167.7 \text{ (GPa)} \]
(iii) $\lambda_1$ and $\lambda_2$ parameters (Equation 2.26):

$$E_c / E_r = 167.7 / 206 = 0.81 \text{ and } E_r / E_c = 206 / 167.7 = 1.23$$

$$\lambda_1 = \frac{1 - (1-0.81)(1-0.19)/2 + (1-0.45)(0.26-0.19)/2 - [0.19 + (0.26-0.19) x 0.45 x 1.23]^2}{(1-0.26) [ 1 - (0.19 + (0.26-0.19) x 0.45 x 1.23 )]}
= 0.99$$

$$\lambda_2 = \frac{1 - [(1-0.81) / (1+0.19) x 2] + (1+0.45)(0.26-0.19)/2}{1 + 0.19 + (0.26-0.19) x 0.45 x 1.23}
= 0.79$$

(iv) The stresses on the fibers:

RT to 586 °C:

$$\sigma_2^T = \frac{0.79 \cdot 206}{0.99 \cdot 167.7} \left[ \frac{0.45}{1 - 0.26} \right] \times 119.1 \times (-4.74 \times 10^6) \Delta T$$

$$= -337.1 \times 10^3 \Delta T \text{ (MPa)}$$

$$\sigma_{II}^T = \frac{1}{2 \times 0.99} \left[ \frac{1}{1 - 0.26} \right] \times 119.1 \times (-4.74 \times 10^6) \Delta T$$

$$= -211.9 \times 10^3 \Delta T \text{ (MPa)}$$

at $T = 586 \degree \text{C}$:

$$\sigma_2^{\alpha-\beta} = \varepsilon^{\alpha-\beta}_{/586 \degree \text{C}} E_c$$

$$= -0.0094 \times 167.7 \times 10^3 = -15866 \text{ (MPa)}$$
\[ \sigma_{\alpha-\beta} = \sigma_{\alpha-\beta} \]

\[ = -1576 \text{ (MPa)} \]

586°C to 1000°C:

\[ \sigma_T^\alpha = \frac{0.79}{0.99} \left( \frac{206}{167.7} \right) \left( \frac{0.45}{1 - 0.26} \right) x 119.1 x (-1.54 x 10^{-6}) \Delta T \]

\[ = -120.2 x 10^{-3} \Delta T \text{ (MPa/°C)} \]

\[ \sigma_T^\beta = \frac{1}{2 x 0.99} \left( \frac{1}{1 - 0.45} \right) x 119.1 x (-0.91 x 10^{-6}) \Delta T \]

\[ = -75.6 x 10^{-3} \Delta T \text{ (MPa/°C)} \]
Appendix C-1

Measured Mechanical Properties of Nicalon SiC Fiber Reinforced Alumina-Aluminum Phosphate Matrix, 2D Woven Fabric, Laminated Composite (SiC-1)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$K_{IC}^{\alpha}$ (MPa-m$^{\alpha/2}$)</th>
<th>MOR$^{\alpha}$ (MPa)</th>
<th>WOF$^{\alpha}$ (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>7.05 ± 1.22</td>
<td>128.6 ± 15.4</td>
<td>0.77 ± 0.19</td>
</tr>
<tr>
<td>200</td>
<td>6.77 ± 1.31</td>
<td>128.3 ± 14.1</td>
<td>0.52 ± 0.10</td>
</tr>
<tr>
<td>400</td>
<td>5.22 ± 0.83</td>
<td>144.0 ± 20.5</td>
<td>0.31 ± 0.10</td>
</tr>
<tr>
<td>600</td>
<td>5.03 ± 0.92</td>
<td>124.0 ± 10.0</td>
<td>0.25 ± 0.12</td>
</tr>
<tr>
<td>800</td>
<td>3.62 ± 0.78</td>
<td>137.0 ± 7.0</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>1000</td>
<td>2.91 ± 0.39</td>
<td>147.5 ± 16.6</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td>1200</td>
<td>5.93 ± 2.37</td>
<td>159.8 ± 4.0</td>
<td>0.33 ± 0.19</td>
</tr>
</tbody>
</table>

$^{\alpha}$ numbers are averages of ten samples with 95% confidence in t-distribution.
# Appendix C-2

Measured Mechanical Properties of Nicalon SiC Fiber Reinforced Alumina-Aluminum Phosphate Matrix, 2D Woven Fabric: Laminated Composite (SiC-II)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$K_{IC}$ (MPa-m$^{1/2}$)</th>
<th>MOR (MPa)</th>
<th>WOF (kJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10.49 ± 0.69</td>
<td>157.9 ± 13.9</td>
<td>2.71 ± 0.46</td>
</tr>
<tr>
<td>200</td>
<td>11.78 ± 1.12</td>
<td>168.0 ± 17.3</td>
<td>2.64 ± 0.88</td>
</tr>
<tr>
<td>400</td>
<td>6.73 ± 0.59</td>
<td>180.8 ± 9.3</td>
<td>1.04 ± 0.09</td>
</tr>
<tr>
<td>600</td>
<td>6.29 ± 0.56</td>
<td>149.4 ± 6.1</td>
<td>0.62 ± 0.10</td>
</tr>
<tr>
<td>800</td>
<td>4.25 ± 0.40</td>
<td>159.6 ± 12.6</td>
<td>0.39 ± 0.06</td>
</tr>
<tr>
<td>1000</td>
<td>3.19 ± 0.26</td>
<td>141.3 ± 8.7</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>1200</td>
<td>5.76 ± 1.03</td>
<td>172.3 ± 11.3</td>
<td>0.45 ± 0.11</td>
</tr>
</tbody>
</table>

Numbers are averages of ten samples with 95% confidence in t-distribution.
Appendix C-3

Measured Mechanical Properties of Nicalon SiC Fiber Reinforced Alumina-Aluminum Phosphate Matrix, 2D Woven Fabric, Laminated Composite (SiC-III)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>K&lt;sub&gt;IC&lt;/sub&gt; (MPa-m&lt;sup&gt;1/2&lt;/sup&gt;)</th>
<th>MOR (MPa)</th>
<th>WOF (kJ/m&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14.91 ±1.16</td>
<td>127.8 ±13.8</td>
<td>4.02 ±0.57</td>
</tr>
<tr>
<td>200</td>
<td>15.71 ±2.85</td>
<td>114.9 ±9.4</td>
<td>3.41 ±0.78</td>
</tr>
<tr>
<td>400</td>
<td>15.32 ±1.52</td>
<td>129.8 ±6.6</td>
<td>3.79 ±0.42</td>
</tr>
<tr>
<td>600</td>
<td>5.71 ±0.87</td>
<td>129.3 ±13.1</td>
<td>0.43 ±0.06</td>
</tr>
<tr>
<td>800</td>
<td>4.83 ±0.69</td>
<td>150.7 ±18.0</td>
<td>0.28 ±0.03</td>
</tr>
<tr>
<td>1000</td>
<td>5.10 ±0.76</td>
<td>154.0 ±18.1</td>
<td>0.27 ±0.03</td>
</tr>
<tr>
<td>1200</td>
<td>6.85 ±1.01</td>
<td>127.3 ±9.0</td>
<td>0.48 ±0.08</td>
</tr>
</tbody>
</table>

@ numbers are averages of ten samples with 95% confidence in t-distribution.
VITA

Hong Li

PERSONAL


EDUCATION

<table>
<thead>
<tr>
<th>Degree</th>
<th>Field</th>
<th>Institution</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph D</td>
<td>Metallurgical Engineering</td>
<td>Mackay School of Mines, University of Nevada, Reno</td>
<td>May 1992</td>
</tr>
<tr>
<td>MS</td>
<td>Materials Science and Engineering</td>
<td>University of Washington, Seattle</td>
<td>December 1989</td>
</tr>
<tr>
<td>BS</td>
<td>Ceramic Science and Engineering</td>
<td>NYS College of Ceramics, Alfred University, Alfred</td>
<td>May 1987</td>
</tr>
<tr>
<td>BE</td>
<td>Mechanical Engineering</td>
<td>Shanghai Maritime Institute, Shanghai, P.R. China</td>
<td>July 1982</td>
</tr>
</tbody>
</table>

RESEARCH AREAS

Ph D Dissertation:

Fracture of Aluminum Phosphor/Alumina Matrix, Silicon Carbide Fiber Reinforced Laminate Composites. Advisor: Dr. Richard C. Bradt

Master Thesis:

Microhardness Anisotropy and a Normalized Meyer's Law for Single Crystal Rutile. Advisor: Dr. Richard C. Bradt

Bachelor Theses:

(1) Yittria Partially Stabilized Zirconia and its Fracture Toughness by Using Indentation Method (Alfred)

(2) Application of High Strength Bolt in a Joint of Steel Structure (Shanghai)

EXPERIENCE

Research Assistant, Mackay School of Mines, University of Nevada, Reno, NV
April 1990 - January 1992

Thermal and coating effects on fracture of ceramic matrix composites
Elastic/plastic properties of single crystals and polycrystalline ceramics
Research Assistant University of Washington, Seattle, WA December, 1988 - March, 1990

Mechanical properties of fiber reinforced ceramic matrix composites
Microhardness anisotropies of single crystals

Assistant Engineer Bureau of Nanjing Harbor, Nanjing, P.R. China August, 1982 - July, 1985

In charge of purchase and maintenance of diesel transportation machines
In charge of design of coal dust precipitation systems

PERSONAL ORGANIZATION

American Ceramic Society
American Society of Metals International
Minerals, Metals and Materials Society

TECHNICAL PUBLICATIONS


[2] "Microhardness Anisotropy of Single-Crystal Cassiterite (SnO2)"


[4] "Microhardness Anisotropy and the Indentation Load/Size Effect in MgO-xAl2O3 Spinel Single Crystals"


[6] "Microhardness Anisotropy on the (010) Cleavage Plane of Single-Crystals of Bi2S3 and Sb2S3"

[7] "Knoop Microhardness Anisotropy of Single-Crystals Aragonite (CaCO3)"
The Microhardness Indentation Size/Load Effect (ISE) in Hard Ceramic Materials

[9] "The Indentation Size/Load Effect in Rutile and Cassiterite Single-Crystals"

[10] "The Indentation Size/Load Effect on the Microhardness of Fused Silica"

**Manuscripts in Preparation**


[16] The Indentation Size Effect in WC-Co Alloys