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Processing and Properties of an Alumina Composite Fiber

A Dissertation Presented to
the faculty of the School of Engineering and Applied Science
University of Virginia

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy (Materials Science and Engineering)

by
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August 1999
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Abstract

High temperature metal matrix composites have superior properties to many of the metal alloys currently used in high temperature aerospace structures. However, because of the high cost of their fiber reinforcements, these high temperature composites have not been widely used to date. Here a composite fiber processing approach has been developed to create a low cost reinforcement for high temperature composites. The approach extends the "hybrid" fiber concept of Cantonwine and Deve (1994) who reinforced Ti 6Al 4V with a low-cost, multifilament alumina tow infiltrated with a carbon matrix. To avoid the problems of high temperature oxidation inherent with the carbon matrix, this thesis explores the development of an all oxide composite fiber. The composite fiber consisted of a high strength Nextel™ 610 alumina fiber tow and a highly porous alumina matrix. A slurry casting process was developed for incorporating the matrix into the fiber tow. Composite fiber processing consisted of four stages: slurry infiltration, fiber shaping, solvent evaporation and sintering. Using an alumina slurries with carefully tailored viscosities and particle volume fractions ($d = 0.5 \, \mu m$), two methods for infiltration were successfully developed. During the evaporation of the slurry solvent, shrinkage pores were identified as a significant problem and resulted in large voids within the porous alumina matrix. A systematic process development effort resulted in methods for avoiding these voids, but at the expense of a reduced filament packing density (34%). The filament packing density should be maximized to maximize the stiffening and strengthening potential of the composite fiber. A continuous sintering technique was developed to partially sinter the porous matrix. During this sintering stage, filament grain growth, filament-to-filament, particle-to-filament and particle-to-particle contact growth all occurred. The role of grain growth and each bonding mechanism upon the stress/strain response and ultimate strength of the alumina composite fiber was investigated. It was found that grain growth and filament-to-filament sintering caused a decrease in the single filament and bundle strength. Filament-to-filament sintering had an especially strong effect on the bundle strength because bonded filament clusters failed when the weakest filament within the cluster failed and because shear stresses could be induced at the filament-to-filament bond-line as the fila-
ments were locally bent or twisted during tensile loading. Finite element modeling was used to confirm the presence of these shear stresses. Within the alumina composite fiber, particle-to-filament sintering had the most important effect on mechanical behavior. Particle-to-filament sintering increased the resistance to fiber/matrix debonding and sliding. This at first served to increase the load transfer efficiency of the matrix, but it also increased the shear resistance of the interface and eventually resulted in a decrease in fiber strength and an embrittlement of the composite fiber. Composite fibers of this type hold significant promise as a reinforcement for high temperature metal matrix composites provided ways are found to increase the filament packing density.
Dedication

This dissertation is dedicated to my precious daughter, Grace Cullen Cantonwine, who died on March 23, 1999, the day she was to be born. She will always hold a special place in the hearts of her mother and father.
Acknowledgments

I would like to first thank the Air Force for their support of this work under a AFOSR URI grant (#F49620-93-1-0359) and the Virginia Space Grant Fellowship. I would also like to thank my advisor, Prof. Haydn Wadley, for giving me the opportunity to work on the composite fiber approach for processing continuous reinforced composites, and the other members of my committee, Prof. Frank Wawner, Prof. Marek-Jerzy Pindera, Prof. Carl Herakovich and Prof. Dana Elzey for their efforts in guiding this research and for their insightful comments of the resulting dissertation. I would especially like the thank Marek for his thorough reading of the initial dissertation drafts, Dana for his open door policy and Carl for having enough faith in the composite fiber processing approach to commit a university research initiative program to the development of an alumina composite fiber reinforced nickel-based metal matrix composite. Although we learned first hand that the processing of high temperature metal matrix composites is difficult, the final conclusion for the composite fiber processing approach, I believe, is a hopeful one.

In addition to my advisor and committee members, many others have helped me throughout the years. Those included Willie Shoupe, Tommy Eanes and Peter Schare who helped with the design and building of the experimental setup and James Demerest who helped with the finite element analysis. I would especially like to thank Herve Deve for his collaborations while I worked at 3M and Dave Wilson for his many interesting discussions about the properties of the Nextel™ 610 alumina fiber and for providing me with materials.

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List of Symbols

\( v_f, v_{fb} \) - velocity; \( f \)-fluid, \( fb \)-fiber

\( k, k_n, k_p \) - permeability, \( n \)-normal, \( p \)-parallel

\( \eta, \eta_s, \eta_l, \eta_r \) - viscosity, \( s \)-slurry, \( l \)-liquid, \( r \)-relative

\( \Delta P, \Delta P_c, \Delta P_g \) - change in pressure, \( c \)-capillarity, \( g \)-gravity

\( l \) - length

\( h, h_c \) - height, \( c \)-coating

\( t \) - time

\( \tau, \tau_{xy}, \tau_{yz} \) - shear stress

\( \tau_s \) - sliding resistance

\( \tau_d \) - debond strength

\( V_{pd} \) - powder volume fraction

\( V_{cr} \) - critical volume fraction

\( K_H \) - hydrodynamic volume constant

\( P \) - pore volume fraction

\( V_p \) - pore volume
$S_p$ - pore surface area

r, r_f, r_c, r_m$ - radius, f-fiber, c-capillary tube, m-meniscus

$V_{f_{max}}$ - maximum packing density of fiber bundle

$\rho_l, \rho_s, \rho_r$ - density, $l$-liquid, $s$-slurry, $r$-relative

$\kappa$ - curvature

$\gamma_{sv}, \gamma_{lv}, \gamma_{se}, \gamma_s$ - surface energy, $sv$-surface/vapor, $lv$-liquid/vapor, $se$-surface/environment, $s$-slurry

$S_d$ - relative surface area of solid phase

$x$ - neck radius

$y$ - sintering shrinkage

$\chi$ - neck growth rate

$y$ - shrinkage rate

$L_i$ - initial length

$\Delta L$ - change in length

$S_i$ - initial surface area

$\Delta S$ - change in surface area

$U_E, U_s, U_m, U_{tot}$ - energy, $E$-strain, $s$-surface, $m$-mechanical, $tot$-total

$c, c_o, c_{sf}$ - crack length, $o$-initial, $sf$-final

$G$ - strain energy release rate

$R_o, R_{se}$ - crack resistance, $o$-inherent, $se$-environment
$K_I$ - stress intensity (mode I)

$E, E_f, E_m, E_c$ - Young's modulus, f-fiber, m-matrix, c-composite

$\nu$ - Poisson's ration

$E'$ - modulus, plane stress ($E$), plain strain ($E(1-\nu^2)$)

$T_o, T_e, T_{gb}$ - toughness, o-inherent, e-environment, gb-grain boundary

$\psi$ - crack geometry factor

$\sigma, \sigma_r, \sigma_u, \sigma_a, \sigma_f, \sigma_b, \sigma_m, \sigma_c$ - stress, r-residual, u-ultimate, a-applied, f-fiber, b-bundle, m-matrix, c-composite

$\alpha$ - coefficient of thermal expansion (CTE)

$\Delta\alpha$ - change in CTE

$T$ - temperature

$\Delta T$ - change in temperature

$g, g_c$ - grain size, c-spontaneous microcracking

$K_o$ - threshold toughness

$K_{IC}$ - fracture toughness

$\sigma_o$ - Weibull reference stress

$L_o$ - Weibull reference length

$m$ - Weibull modulus

$L$ - gauge length

$N$ - number of tests
$\varepsilon, \varepsilon_b$ - strain, $b$-bundle

$\varepsilon_{fail}$ - failure strain

$\sigma_{fail}$ - failure stress

$\sigma_b^{\text{max}}$ - bundle strength

$\sigma_c^{\text{max}}$ - composite strength

$\sigma_{mc}$ - matrix cracking stress

$V_{fail}$ - fraction of failed filament

$n$ - number of filaments

$V_f, V_{fe}$ - volume fraction, $f$-fiber, $fe$-filament ends

$\Gamma_i, \Gamma_f, \Gamma_m$ - fracture energy, $i$-interface, $f$-fiber, $m$-matrix

$\tau_d$ - debond strength

$\tau_s$ - sliding stress

$l_{in}$ - ineffective length

$\sigma_{\text{froen}}$ - Rosen’s prediction of fiber strength

$\sigma_{\text{curtin}}$ - Curtin’s prediction of fiber strength

$\sigma_{\text{cur}}$ - Curtin’s characteristic strength

$\Theta, \Theta_{\text{max}}$ - fiber slack parameter, $\text{max}$-maximum

$g(\varepsilon)$ - probability density function

$\phi_i, \phi_{\text{max}}$ - filament alignment angle, $\text{max}$-maximum
\( \varepsilon_i \) - strain of misaligned filaments

\( C_i \) - number of filaments in a cluster of type \( i \)

\( \bar{x} \) - mean diffusion distance

\( Q \) - activation energy

\( R \) - gas constant

\( D \) - diffusivity

\( D_0 \) - pre-exponential term for diffusivity

\( A_j \) - mirror constant
CHAPTER 1 Introduction

Silicon carbide filament reinforced titanium matrix composites and some other metal matrix composites (MMCs) have higher specific modulus, specific strength and creep resistance than any metal or alloy used in aerospace structures [1]. However, the high cost of MMCs has limited their utilization. According to a Department of Defense analysis, MMCs will not be widely considered for use in civil aircraft structures until the finished component price drops to less than $1,100/kg [2]. Currently, SiC monofilaments are manufactured via a slow chemical vapor deposition process that results in a fiber cost of approximately $11,000/kg [3]. Assuming a composite consisted of 30% fiber by weight, the cost of this SiC fiber alone in a composite would be $3,300/kg. Once the matrix, manufacturing, machining and inspection costs are factored in, SiC fiber reinforced composites cost $5,000 (or more) per kilogram.

The cost of high temperature composites could be significantly lowered if widely available, inexpensive multifilament strands or fiber tows were used instead of a monofilament. Currently, a high strength Al₂O₃ fiber tow is available from 3M for $1,100/kg [4], an order of magnitude less than the SiC monofilament. They are also less stiff and strong and unfortunately, more difficult to fabricate into a high temperature MMC compared to
their monofilament counterparts. This difficulty with processing is a result of the difference in the filament diameters. Typically SiC monofilaments have a diameter between 100 and 140 μm whereas the filaments in a tow have a diameter of approximately 10 μm. The difficulties arise in trying to get the matrix alloys in between the 10 μm filaments while still maintaining a uniform filament distribution [5-7]. Higher costs are also incurred when coatings must be applied to the much larger surface area of the smaller diameter filaments [7].

The most successful technique for manufacturing composites from fiber tows utilizes pressure casting which is typically used with aluminum matrix composites [5]. However, the high melting temperatures required for metals like highly reactive titanium and nickel alloys cause filament damage prior to and during infiltration [6]. Another possible route to a uniform filament distribution is to deposit the matrix material onto each filament via physical vapor deposition (PVD). Kieschke et. al at 3M produced such a titanium matrix composite using a vapor deposition process, but the effort were abandoned because of difficulties with spreading the filaments and the high cost of the complex interface coatings needed to protect the filaments during subsequent processing steps [7].

To circumvent some of these processing difficulties, 3M explored a novel “hybrid” composite fiber approach for fabricating a titanium matrix composite [8]. In this approach, the filaments of a tow were gathered together and held in place by a carbon binder to create an alumina/carbon composite fiber. The metal matrix was then applied around this composite fiber to create a hierarchical composite structure (see figure 1.1). As a proof of concept, a titanium composite manufactured using this approach had a specific modulus 50% greater than the base alloy and an ultimate strength between 0.7 and 1.4 GPa [9]. The measured strength of the alumina/carbon composite fibers prior to consolidation was approximately 1 GPa.
Figure 1.1 Microstructure of a titanium matrix composite reinforced with alumina/carbon composite fibers [9].

This hierarchical microstructure in some ways mimics the microstructure of natural structural bio-composites such as bamboo (see figures 1.2). A cross section of the bamboo is shown in figure 1.2a. On the microstructural level, bamboo is a collection of vascular bundles surrounded by matrix tissue. Figure 1.2b shows the vascular bundles are dense fibers packed tightly together while the matrix tissue has an open cell, sponge-like structure [10,11]. Other natural materials such as muscle tissue [12] also exhibit a hierarchical microstructure. The observation of these structures in nature shows that the microstructure produced by the composite fiber approach can be successfully used in load bearing materials.
Figure 1.2 The microstructure of bamboo [11]. The vascular bundles are a collection of stiff, dense fibers while the matrix material is more like an open cell foam.

Besides using fiber which costs less than the SiC monofilaments, the composite fiber approach also reduces cost by avoiding expensive coating systems. The binder essentially replaces the role of the coatings which are usually applied to protect the filaments and promote crack deflection and sliding. Similar to a fiber coating, the binder must be chemically compatible with the filaments (to avoid reactions) and weak enough to promote crack deflection. If both the fiber and binder are chemically incompatible with the surrounding matrix, then a coating may be required for the perimeter of the composite fiber but not around each individual filament.

The motivation for the research of this thesis stemmed from interest in extending the use temperatures of MMCs to above 900 °C while limiting costs by utilizing the composite fiber processing approach. At these temperatures titanium matrices are not a candidate
because of oxidation problems [13]. Oxidation issues will also eliminate carbon as a potential binder. Therefore, oxidation resistant filaments, binders and matrices are required.

There are two families of high temperature tow fibers; SiC and oxide based. 3M manufactures oxide based fibers designated Nextel™ (440, 550, 610, and 720). The Nextel™ 440 and 550 fibers were primarily designed for high temperature thermal application [4], and the Nextel™ 610 and 720 fibers, as reinforcements in structural composites; 610 for high strength and 720 for high creep resistance [14]. The SiC fibers (the most familiar being the Nicalon family [15]) typically have better high temperature creep properties [14] but may oxidize under certain conditions [16]. Therefore, to focus on systems which are chemically stable in high temperature oxidation environments, the fiber used in this work was from the oxide based family. The specific fiber chosen was Nextel™ 610.

The Nextel™ 610 fiber is 99.5% alumina with a grain size of less than 100 nm [17,18]. Besides the low cost ($1100/kg), Nextel™ 610 is a high strength fiber. The average single filament strength of Nextel™ 610 is greater than 3 GPa which is comparable to some SiC monofilaments [19]. The second advantage is that this fiber is almost purely α-alumina, and the vast literature on alumina can be utilized to predict diffusion controlled processes as well as mechanical properties. The disadvantage of the Nextel™ 610 is its restriction to temperatures below 1000 °C because of limited creep resistance [20].

In order to avoid protective coatings for the individual filaments, the binder must be compatible with the filaments so that reactions do not occur. The binder must result in a weak fiber/binder interface to promote crack deflection and maximize toughness. Potential oxidation resistant binders include porous oxides like Y₂O₃, ZrO₂, and Al₂O₃ [21] (dense oxides will not promote crack deflection), montazite (LaPO₄) [22] and shealite (CaWO₄) [23]. While montazite and shealite are fully dense and deform readily in shear
creating the desired weak interfaces, these materials are currently not widely available. To avoid reactions which might result in the creation of new phases like mullite, a highly porous $\text{Al}_2\text{O}_3$ was chosen as the binder.

A porous alumina binder could be introduced into a fiber tow by physical vapor deposition (PVD), chemical vapor deposition (CVD), sol-gel processing or slurry casting. Since both CVD and PVD will increase cost because of either high capital costs or very slow processing rates, sol-gel processing and slurry casting were down-selected as potential processing routes. Slurry casting is a simple process using readily available materials. A slurry is made by mixing powder into a liquid. The slurry is then cast, dried and sintered. If full density is required the sintering process can be quite severe (for alumina sintering temperatures are often greater than 1600 °C [45]. However, for the purposes here, porosity is desired to promote crack deflection and sintering can be limited to much lower temperatures. Conversely, sol-gel processing involves the polymerization of a metal organic compound followed by a conversion reaction to alumina [29]. The polymerization process occurs via hydrolysis which means the atmosphere must be controlled for both the sol and gel states [29]. In addition, there is typically a large volume change associated with the conversion to alumina [35] which may mean multiple infiltration processes to get enough alumina into the filament to hold them together. For example, the volume of a commercially available aluminum butoxide (Gelest) would decrease 95% during its conversion to alumina. In contrast, the volume change during slurry drying can be as little as 20%. To avoid having to control the atmosphere in the sol-gel process and limit number of infiltration steps, slurry casting was chosen as the process to infiltrate the Nextel™ 610 tows with a highly porous alumina binder, thus creating an alumina composite fiber.

This thesis concentrates upon exploring and understanding how to fabricate an alumina composite fiber using a slurry casting process and how the room temperature
stress/strain response is affected by that process. The process consists of an infiltration stage where the slurry is introduced into the multifilament tow; a shaping stage where the tow is drawn through a shaping die; a drying stage where the liquid in the slurry is removed and a sintering stage where diffusional mechanisms cause bonding and grain growth within the filament. The effects of high temperature sintering on failure will be investigated in some detail.

Figure 1.3 shows the important microstructural features of an alumina composite fiber. The binder will initially have a granular structure due to the slurry process. When temperature increases, three different sintering phenomenon can occur simultaneously: particle-to-particle contact growth; particle-to-filament contact growth; and filament-to-filament contact growth. Grain growth within the alumina filaments which can cause strength degradation can also occur. Filament-to-filament sintering will alter the fiber surface which potentially can cause surface defects and a decrease in strength. This will also provide a ready pathway for filament cracks to transfer from one to another. Particle-to-filament sintering may also alter the filament surface but more importantly will likely control the interface properties between the fiber and porous binder. If the interface properties become too strong the composite toughness and strength can be degraded. In addition, the amount of particle-to-particle sintering will ultimately control how the matrix fails which can be important if composite failure occurs from the propagation of a single matrix crack. The main objective of the thesis then was to isolate the effect of each diffusional phenomenon so that their significance for the mechanical properties might be better understood.
Figure 1.3 Schematic illustration of the microstructure of the porous alumina composite fiber.

This thesis begins by examining our current understanding of the mechanical behavior of alumina single filaments, filament bundles and ceramic matrix composites (Chapter 2). Chapter 3 describes the development of a process for fabricating alumina composite fibers. The development of the methodology for mechanical testing is described in chapter 4. Chapters 5 and 6 then explore the effects of sintering on the mechanical properties of single filament and dry (uninfiltrated) tows, respectively. The effects of sintering on the alumina composite properties are then explored in Chapter 7. A discussion of the results and their implication for composites made with alumina composite fibers is given in chapter 8. It includes suggestions for future work. The final chapter summarizes the important findings and primary conclusions of the research.
CHAPTER 2 Background: Mechanical Properties of Alumina and Ceramic Composites

The expected mechanical performance of an alumina composite fiber can be understood from a review of the mechanical properties of single filaments, filament bundles, and ceramic matrix composites. Specifically, the tensile stress/strain response of alumina and ceramic composites are discussed concentrating on understanding and predicting failure.

2.1 Tensile Failure of Alumina

The theoretical strength of a crystalline material has been predicted to be approximately one tenth its Young’s modulus [54]. Since, the Young’s modulus of alumina is around 400 GPa [55], its theoretical strength is predicted to be about 40 GPa. This is an order of magnitude higher than the strongest commercially manufactured alumina [56]. The reason for this discrepancy was explained first by Griffith [57] who made the same
observation for glass. Griffith recognized that failure in brittle solids occurs at a stress lower than the theoretical strength because of the propagation of pre-existing flaws.

To establish a terminology used extensively through the text, the thermodynamics of Griffith's analysis are presented. The total energy, $U_{tot}$, of a cracked body under stress is the sum of the mechanical energy associated with the applied loads, $U_m$, and the energy associated with the creation of new crack surfaces, $U_s$:

$$U_{tot} = U_m + U_s$$  \hspace{1cm} (2.1)

Differentiating equation (2.1) with respect to a change in crack length, $dc$ and setting equal to zero gives a criterion for equilibrium crack growth.

$$\frac{dU_{tot}}{dc} = \frac{dU_m}{dc} + \frac{dU_s}{dc} = 0$$  \hspace{1cm} (2.2)

It has also been shown that the change in the mechanical energy with crack extension is independent of loading conditions. Therefore assuming a "fixed grips" loading condition, the change in mechanical energy can be equated with the change in the elastic strain energy [54].

$$\frac{dU_m}{dc} = \frac{dU_E}{dc}$$  \hspace{1cm} (2.3)

Therefore, equilibrium can be defined as a balance between the negative of the change in strain energy and the change in surface energy:

$$\frac{dU_s}{dc} = -\frac{dU_E}{dc}$$  \hspace{1cm} (2.4)
By convention the driving force for crack extension is defined as the negative of \(\frac{dU_E}{dc}\) or the strain energy release rate, \(G\). Conversely the resistance to crack extension, \(R_o\), is defined as \(\frac{dU_f}{dc}\). Therefore the definition of equilibrium can be rewritten as:

\[
G = R_o
\]

where \(R_o = 2\gamma_{sv}\); \(\gamma_{sv}\) is the surface energy \((J/m^2)\) of the fracture surface in a vacuum.

For mode I fracture, the strain energy release rate can be equated to the stress intensity factor, \(K_I\):

\[
G = \frac{K_I^2}{E'}
\]

Where \(E'\) is the Young’s modulus \((E)\) for plane stress and \(E/1-\nu^2\) for plane strain where \(\nu\) is Poisson’s ratio. The intrinsic fracture toughness of a material, \(T_o\), is likewise related to \(R_o\):

\[
R_o = \frac{T_o^2}{E'}
\]

The onset of equilibrium crack growth can now be restated in terms of stress intensity factors and toughness:

\[
K_I = T_o
\]

More generally, when the toughness is affected by other mechanisms besides surface energy (e.g. plasticity):

\[
K_I = T
\]
In a perfectly brittle material, the toughness has a single characteristic value directly related to energy required to create new surfaces. A plot of toughness versus crack length or a T-curve is shown in figure 2.1.

The stress intensity factor is related to the crack length, \( c \), and applied stress, \( \sigma_a \), via:

\[
K_I = \psi\sigma_a\sqrt{\pi c}
\]  

(2.10)

where \( \psi \) is a factor which depends on the geometry of the crack and specimen. A plot of \( K_I \) versus crack length for two different applied stresses is also shown in figure 2.1.

![T-curve diagram](image)

**Figure 2.1** T-curve for a perfectly brittle material with two K-curves representing two different applied stresses (\( \sigma_l \) and \( \sigma_u \)). \( c_o \) is the initial crack length. \( c_{cr} \) is the crack length required to cause catastrophic failure when the applied stress is \( \sigma_l \).

The failure criteria for unstable crack growth can now be defined. First, the Griffith equilibrium condition must be satisfied. This will occur whenever the K-curves intersect the T-curve. For instance, at the lower stress in figure 2.1, the K-curve intersects the T-curve at \( T < T_o \). Although \( K_f = T \), it can easily be seen that for an increment \( dc \), T
increases more than $K$ and the crack can not extend. Therefore an important second criteria becomes:

$$\frac{dK_I}{dc} > \frac{dT}{dc} \quad (2.11)$$

For the higher stress case in Figure 2.1, both failure criteria are met and the material fails catastrophically. The stress intensity factor at which catastrophic failure occurs is also known as the critical stress intensity factor or fracture toughness, $K_{Ic}$, and the ultimate strength, $\sigma_u$, is then defined as:

$$\sigma_u = \frac{K_{Ic}}{\psi \sqrt{\pi c_{cr}}} \quad (2.12)$$

where $c_{cr}$ is the critical crack size.

The majority of materials, including ceramics, are not perfectly brittle [54,58]. This results from other mechanisms besides surface energy resisting crack extension. In metals plastic deformation dominates the resistance [58] while in ceramics mechanisms such as microcracking, crack deflection, stress induced phase transformations and grain bridging may increase the crack resistance [54]. These additional mechanisms create a rising T-curve (also know as rising R-curve behavior) which results in $K_{Ic}$ being greater than $T_o$, the toughness associated with surface creation (see Figure 2.2). Materials with rising T-curves can exhibit stable or subcritical crack growth below the ultimate strength.
2.1.1 Fracture toughness of alumina

Although no plastic deformation occurs at the crack tip [54], alumina can exhibit a rising T-curve [59,60,61]. A rising T-curve typically results from frictional forces that arise when grains slide past one another in the crack tip wake [54,59]. It has also been shown that this shielding effect decreases as the grain size decreases and become negligible at grain sizes less that 2.5 μm [59]. Since the grain size of Nextel™ 610 is less than 0.1 μm, the grain bridging mechanism is unlikely to be significant during fracture, and the toughness of the Nextel™ 610 can be assumed to be the intrinsic toughness, $T_o$, of alumina.

Using the relationship in equation (2.7), the intrinsic toughness can be related to the surface energy: $T_o = \sqrt{2\gamma_{sv}E}$. The surface energies of various crystallographic planes in alumina have been reported to be from 1-3 J/m$^2$ [62,63], and $E'$ in plane strain is 420 GPa ($E = 400$ GPa, $v = 0.23$ [55]). The predicted intrinsic toughness would be from 0.9 to 1.6
MPa $\sqrt{\text{m}}$ which is significantly less than the measured $T_o$ for alumina: 2.5-3.0 MPa $\sqrt{\text{m}}$ [54,59,60,64]. The corresponding fracture energy obtained from the measured $T_o$ values is between 7.4 and 10.7 J/m²; up to a factor of three above expectations. This discrepancy was realized by Wiederhorn [63] in his work on the fracture of sapphire. He concluded that irreversible or nonconservative effects such as heat generation must be activated in addition to the creation of new surfaces. Other causes may be associated with additional fracture surface area from meandering cracks through grain boundaries or ledges.

2.1.2 Fracture Surface Features

The features of a fracture surface that are typically observed in ceramics are schematically shown in figure 2.3 [54,170]. The initial defect has a crack depth of $c_o$ and if sub-critical cracking occurs the critical crack depth is defined as $c_{cr}$. When subcritical cracking is not present $c_{cr}$ will be equivalent to $c_o$. During catastrophic failure the initial crack propagation creates a smooth mirror region. Eventually a transition occurs from the smooth mirror region into a rougher mist region. The boundary of the transition is represented by $r_m$ in figure 2.3. The mist region then changes into an even rougher hackle region and after the hackle region macroscopic crack branching occurs [170]. The boundary between the mist and hackle regions is $r_{st}$ and the boundary between the hackle-macroscopic crack branching region is $r_h$. The cause of the different regions is suspected to be related to the kinetic energy of the propagating crack [54].

Ideally a fracture surface feature indicating the critical crack size, $c_{cr}$, would be present and could be used in equation (2.12) along with the measured strength or fracture stress, $\sigma_u$, to calculate the fracture toughness, $K_{IC}$. Unfortunately, the only features present are the initial defect size and the mirror-mist, mist-hackle or hackle-crack branching.
boundaries. It has been shown experimentally that the product of the fracture stress and the square root of the boundary distance is equal to a constant [170]:

\[ \sigma_u r_j^{1/2} = A_j \]  

(2.13)

where \( r_j \) is the distance to a particular boundary and \( A_j \) is the corresponding mirror constant. Once the mirror constant is known, the fracture stress can be predicted directly from measurements of the mirror-mist, mist-hackle or hackle-crack branching boundaries. This technique has been used to calculate the in situ failure stress of filaments within fully dense composites [119].

Figure 2.3 Schematic of the mirror-mist-hackle regions around a strength limiting defect (\( c_0 \)). After Mecholsky and Freiman [170].
2.1.3 Grain size effects on the failure of alumina

Given that toughness increases with increasing grain size [59], it is somewhat surprising that the strength of alumina decreases with increasing grain size [65-71] (see figure 2.4) Recall from equation (2.12), if the fracture toughness increases with grain size, the pre-existing flaw size also must increase to cause a decrease in strength. Therefore, the pre-existing flaw size must be related to the microstructure.

Pre-existing flaws in alumina result from either processing or spontaneous microcracking [54]. Spontaneous microcracking occurs along grain boundaries and is a natural result of the residual tensile stress between grains after cooling from the high processing temperatures [54]. These residual stresses arise in alumina because of anisotropy in the coefficient of thermal expansion (CTE) [55]. The residual stress between grains can be calculated from [54]:

\[ \sigma_r = \frac{E \Delta \alpha \Delta T}{2(1 + \nu)} \quad (2.14) \]

Where \( \Delta \alpha \) is the difference in CTE along the principal crystal axes. For alumina \( \Delta \alpha \approx 8 \times 10^{-7} \text{ C}^{-1}, \nu = 0.23 \) and \( E = 400 \text{ GPa} \) [55]. For a \( \Delta T \) of 1400 °C, the residual stress would be approximately 200 MPa. More detailed analyses revealed that the residual stress within grains increased with increasing grain size [72].
Figure 2.4 Orowan-Petch plot of strength vs. $g^{-1/2}$. The data points for alumina are from biaxial strength tests (Chantikul et al. [59]). The Petch branch's were determined for four different flaw sizes.

Spontaneous microcracking can be predicted from a model assuming a penny shaped flaw within the grain boundary whose diameter scales with the grain size. If a scaling factor, $\beta$, is defined as the ratio of the crack size to the grain size, equation (2.10) can be shown to result in a critical grain size, $g_c$, for spontaneous microcracking is [54]:

$$g_c = \frac{\pi}{4\beta} \left( \frac{T_{gb}}{\sigma_r} \right)^2$$

(2.15)

Where $T_{gb}$ is the grain boundary toughness. If $\beta$ is assumed to be 0.5, $T_{gb} = 2.75$ MPa $\sqrt{m}$ [59] and $\sigma_r = 200$ MPa, then the critical grain size is about 300 $\mu$m. This is about an order of magnitude greater than the smallest grain size (35 $\mu$m [59]) where spontaneous microcracking has been observed. The reason for this large error in the prediction is uncertain.
but may be due to the critical flaw being a crack at a triple point rather than along a grain face. The observed microcracks typically extend 2-3 grain diameters before arresting in areas of residual compression [54]. The strength of alumina can then be related to the grain size, \( g \), by substituting \( 2g \) for \( c \) in equation (2.12).

\[
\sigma_u = \frac{K_{Ic}}{\psi \sqrt{2\pi g}}
\]  

(2.16)

Plots of strength versus the inverse square root of grain size are referred to as Orowan-Petch plots (see figure 2.4) [54]. The Orowan branch [73] describes the behavior when the strength is inversely proportional to the grain size (equation (2.16)) and the slope would be \( K_{Ic}/\psi \sqrt{2\pi} \). The Petch branch describes the behavior when the strength is essentially insensitive to grain size. This occurs at small grain sizes where spontaneous microcracking does not occur. The origin of failure in this branch has been the subject of much speculation. The initial physical explanation was based on dislocation pileup at grain boundaries [74]. However, plastic deformation is limited in non-cubic materials like alumina [54]. Subsequent interpretations hypothesized that the region exhibited “Griffith” behavior with the strength controlled by extrinsically created flaw, for example from machining or processing [68,70,71]. Therefore assuming \( K_{Ic} \) is constant with grain size (at small grain size this is a reasonable assumption), the Petch branch can be represented as horizontal lines in the \( \sigma-g^{-1/2} \) plots; (see figure 2.4). The predicted strength is then only a function of the extrinsic flaw size.

2.1.4 Subcritical crack growth

In the analysis of the Orowan-Petch plots, it was implicitly assumed that the T-curve of alumina was flat as shown in figure 2.1. However, alumina can exhibit rising T-curve behavior [54] thus resulting in subcritical cracking. For example, subcritical cracking can
occur in alumina under certain environmental conditions [77]. The important role of environmentally assisted, subcritical cracking in ceramics was first recognized in static fatigue experiments for glass [75,76]. Orowan [75] found that glass in moist air had one third the strength of glass in a vacuum. Static fatigue is a phenomenon in brittle materials where the material survives the initial loading but fails under a sustained load after an extended time. Referring again to section 2.1.1, a crack may only propagate when both failure criteria (equations (2.9) and (2.11)) are met. The initial loading in static fatigue experiments can be represented by the lower K-curve in figure 2.1 (i.e. no initial crack growth). The only way for catastrophic failure to occur is for the T-curve to be lowered such that it follows the lower K-curve until the second intersection at $c_{sf}$. Evidence of moisture being an important variable caused Orowan to hypothesize that the environment at the crack tip lowered the surface energy, effectively lowering toughness.

Further evidence of the environmental contribution to subcritical cracking can be found by measuring crack velocity ($v$) as a function of the stress intensity factor, $K$, for different levels of relative humidity. Weiderhorn [77] has measured crack velocities in sapphire using double-cantilever beam test specimens. The results plotted versus the applied strain energy release rate, $G$, (figure 2.5) show that the crack velocity increases rapidly with relative humidity.
Figure 2.5  a) Measured crack velocity in sapphire versus the applied strain energy release rate, $G$ [77]; b) Schematic of a typical crack velocity, $v$ versus stress intensity factor, $K$ curve [54]. recall $G \propto K^2$. 

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Figure 2.5a shows that Weiderhorn's data can be characterized by three distinct regions of crack velocity behavior. The crack velocity plotted versus the stress intensity factor will also exhibit a similar profile (figure 2.5b). The threshold toughness, $K_o$, represents the limit to which the toughness, $T_e$, can be lowered by the environment

\[
K_o = T_e = (E'R_{se})^{1/2} = (E'2\gamma_{se})^{1/2}
\]  

(2.17)

where $\gamma_{se}$ and $R_{se}$ are the surface energy and fracture resistance within the environment ($\gamma_{se} < \gamma_{sv}$). Region I depends on applied stress, temperature and chemical concentrations at the crack tip [54] and is usually modeled as a thermally activated process [78]. Region III represents the behavior in a vacuum, and implies that at these crack velocities the transport of the environmental species can not keep up with the crack tip [54]. Region II is essentially a bridge between region I and Region III. The velocity is constant and is thought to be controlled by a transport process such as diffusion of the chemical species [54,78]. Because of the rate dependence of the crack velocity during environmentally assisted subcritical cracking, Charles [79] and Evans [78] showed that susceptible ceramics exhibit a decrease in strength with a decrease in strain-rate.

In addition to static fatigue tests, subcritical cracking has also been detected under dynamic loading conditions by a fractography approach [81-85]. The critical crack size can be calculated from the measured strength by rearranging equation (2.12):

\[
cr = \frac{1}{\pi} \left( \frac{K_{lc}}{\psi \sigma_u} \right)^2
\]  

(2.18)

If the critical crack size is larger than the identified defect which caused failure then the crack must have initially propagated subcritically. With this approach, Kirchner and co-workers found that subcritical cracking could occur around internal defects in alumina during dynamic loading even at temperatures as low as -196 °C [84]. Because of the tem-
perature and location of the defects, it seems unlikely that environmental effects caused the observed subcritical cracking, but they provided no clear explanation for the mecha-
nism.

As discussed in section 2.1.3, spontaneous microcracking can occur in alumina at grain sizes above 30 \( \mu \text{m} \). This is essentially a form of subcritical crack growth. When the residual stress state is such that spontaneous microcracking does not occur, the tensile stresses can still contribute to subcritical cracking because of the principle of superposition [54]. In addition elastic anisotropy can cause induced stresses within misoriented grains [86]. These elastic mismatch stresses have been shown to cause stress singularities at grain boundary triple points [86]. Microcracking ahead of the crack tip may then occur followed by linkage to cause crack growth.

2.1.5 Alumina fiber strength

The previous sections have described alumina’s sensitivity to defects. This sensitivity to defects means that alumina and ceramics in general are only as strong as their weakest defect (i.e. weakest link statistics). Since these are statistical in nature, the result is a distribution of strengths. For design and modeling purposes the strength can be fitted to a Weibull distribution [58]. Weibull [87] defined a probability of failure which increased as the tested volume increased. If \( P_f \) is the probability of failure, then the cumulative Weibull distribution function is:

\[
P_f = 1 - \exp \left( -\frac{V}{V_o} \left( \frac{\sigma}{\sigma_o} \right)^m \right)
\] (2.19)
where $\sigma_f$ is the applied filament stress. $\sigma_o$ and $m$ are the Weibull reference stress and modulus, respectively, $V$ is the volume being tested and $V_o$ is a reference volume at which $\sigma_o$ and $m$ were previously measured.

If the variation in fiber diameter is small, the volume terms reduce to the tested length of the fiber:

$$P_f = 1 - \exp\left(-\frac{L}{L_o}\left(\frac{\sigma_f}{\sigma_o}\right)^m\right)$$  \hspace{1cm} (2.20)

The Weibull parameters, $\sigma_o$ and $m$, can then be determined experimentally by conducting single filament tests at a reference gauge length, $L_o$. The measured strengths for a set of $N$ tests are sorted and assigned an integer, $i$, representing their position. The probability of failure is then calculated for each strength using the relationship [88,89].

$$P_f = \frac{i - 0.5}{N} \quad i = 1 \ldots N$$  \hspace{1cm} (2.21)

The Weibull modulus, $m$, is determined by finding the slope of $\ln(\ln(1/(1-P_f)))$ versus $\ln(\sigma_f)$, and the reference stress, $\sigma_o$, is the stress at the probability of failure, 0.63. As an example, the probability of failure for an Al$_2$O$_3$ fiber made by 3M (Nextel 610) is shown in figure 2.6. The Weibull distribution is clearly a good approximation of the strength data of this system.
Figure 2.6 Probability of failure versus applied stress for as-received Nextel™ 610 single filaments. The data points correspond to measurements made during this work. The solid line is the best fit to the data using the Weibull function given by equation (2.20).

2.1.6 The Ideal Fiber Bundle

The failure strength of a collection of filaments falls between the extremes of the Weibull distribution. To predict the stress/strain response of filament bundles, Daniels [90] and later Coleman [91] developed the ideal bundle model. An ideal fiber bundle is a collection of \( n \) independent fibers oriented in a parallel array. When stress is applied to the bundle, it is assumed to be evenly distributed to all the fibers. At a stress much lower then the mean failure strength, the first fiber will fail. This fiber becomes completely ineffective and the load it once carried is then assumed to be evenly redistributed over the
remaining \((n - 1)\) fibers. This concept is called global load sharing because the released load is shared “globally” with all the remaining fibers.

The bundle stress, \(\sigma_b\), is defined as the load divided by the initial area of all the filaments. The bundle stress will be equivalent to the filament stress until filament failure begins. At that point the single filament stress become larger than the bundle stress. As defined by Daniels [90] and Coleman [91], the ideal bundle stress is:

\[
\sigma_b = \sigma_f (1 - P_f)
\]  

where \(\sigma_f\) is the applied stress in an unbroken filament and \(P_f\) is the probability of failure which can be determined from the Weibull distribution using equation (2.20). The probability of failure is equivalent to the fraction of filaments that have failed. Equation (2.22) is therefore a simple rule of mixtures model. Daniels and Coleman assumed that the number of filaments \((n)\) in the bundle was large. What constitutes “large” will be discussed later.

By substituting equation (2.20) into equation (2.22) and using Hooke’s law for the fiber stress, the bundle stress can be written as a function of strain, \(\varepsilon\).

\[
\sigma_b = E_f \varepsilon \exp \left( -\frac{L}{L_o} \left( \frac{E_f \varepsilon}{\sigma_o} \right)^m \right)
\]  

(2.23)

Where \(E_f\) is the modulus of the fibers. The maximum bundle strength, \(\sigma_{b, max}\), occurs when \(\frac{d\sigma_b}{d\varepsilon} = 0\). The strain at the failure of the bundle is:

\[
\varepsilon_{fail} = \frac{\sigma_o (L_m)}{E_f \left( \frac{L_o}{L} \right)}^{1/m}
\]  

(2.24)
Invoking Hooke's law, the stress in the unbroken filament when the bundle fails is:

\[ \sigma_{\text{fail}} = \sigma_o \left( \frac{L_m}{L_o} \right)^{-1/m} \]  

(2.25)

The bundle strength is then found by substituting equation (2.24) into equation (2.23):

\[ \sigma_b^{\text{max}} = \sigma_o \exp \left( -\frac{1}{m} \left( \frac{L}{L_o} \right)^{-1/m} \right) \]  

(2.26)

A plot of equation (2.23) is shown in figure 2.7 using the Weibull parameters for as-received Nextel™ 610 filaments. Since the exponential term in equation (2.23) is equivalent to the fraction of unbroken fibers, the Young's modulus of an ideal bundle is that of the filaments until filament fracture begins. The initial nonlinearity in the stress/strain response comes about as filaments begin to fail which in effect decrease the stiffness of the bundle. The fraction of filaments that have failed at ultimate strength of the bundle, \( V_{\text{fail}} \), can be found by substituting equation (2.25) into equation (2.20):

\[ V_{\text{fail}} = 1 - \exp \left( -\frac{1}{m} \right) \]  

(2.27)

For \( m = 10 \), \( V_{\text{fail}} = 0.095 \). The bundle stress then gradually decreases as the exponential term in equation (2.23) decreases faster than the increase in filament stress \((E \varepsilon)\). The gradual nonlinear decrease from the ultimate strength can only be observed in a strain controlled tensile test.
Figure 2.7 Predicted stress/strain response of an ideal bundle. $E_f = 380$ GPa, $\sigma_o = 3.37$ GPa; $m = 11.0$; $L_o = 25$ mm.

The assumption of the number of filaments, $n$, being "large" was considered by Phoenix and Raj [92]. They modeled a fiber bundle without making this assumption and defined the bundle strength, $\sigma^\text{max}_b(n)$, as a function of the number of filaments:

$$\sigma^\text{max}_b(n) = \sigma^\text{max}_{\text{bideal}}(1 + \Delta(n)) \tag{2.28}$$

where $\sigma^\text{max}_{\text{bideal}}$ is the ideal bundle strength and $\Delta(n)$ is a function of the number of filaments, $n$, and the Weibull modulus, $m$:

$$\Delta(n) = 0.9962n^{-2/3}(m + 1)^{-1/3 - 1/3(m + 1)} \exp\left(-\frac{1}{3(m + 1)}\right) \tag{2.29}$$
As one can see in figure 2.8, this term will be approximately 0.01 for a bundle with 200 filaments ($m=10$). Since the number of filaments in the Nextel$^\text{TM}$ 610 tow is approximately 400 and $m$ is around 11, $\Delta(n)$ is essentially zero.

![Graph showing $\Delta(n)$ vs. Number of Filaments in Bundle]

Figure 2.8 Phoenix and Raj's prediction of $\Delta(n)$ for $m = 10$. The number of filaments in a bundle can be considered "large" when $n > 200$.

2.1.7 Gauge Length issues with fiber testing

The power of the Weibull probability function is that the strength distribution can be predicted for any given gauge length, $L$, once the Weibull parameters have been determined. This is especially important in predicting composite strength where an effective gauge length (see section 2.2.4) is defined. For both metal and ceramic matrix composites, this effective gauge length is around 2 mm (see page 47) whereas filament testing is typically performed at gauge lengths of 25 mm.
Unfortunately, a number of researchers have noted that the predicted strength distribution at gauge lengths other then the reference gauge length are not accurate [93-96]. Problems can arise in the calculation of the Weibull modulus, $m$. Often the value of the Weibull modulus can be significantly different depending on the technique used in the calculation.

The technique described in section 2.1.5 is referred to as the single gauge length (SGL) technique. However, the Weibull modulus can also be determined by testing at multiple gauge lengths and plotting the natural logarithm of the average strength versus the natural logarithm of the gauge length. This relationship can be seen by taking the double logarithm of equation (2.20) and rearranging to give:

$$
\ln \sigma_f = -\frac{1}{m} \ln L + \frac{1}{m} \ln \ln \left( \frac{1}{1 - P_f} \right) + \ln \sigma_o + \frac{1}{m} \ln L_o \tag{2.30}
$$

The average strength by definition occurs when $P_f$ equals 0.5, therefore the last three terms in the above equation are constant (a specific $L_o$ must be assumed). The slope of the plot, $\ln \sigma_f$ versus $\ln L$, is $-1/m$. The Weibull modulus calculated with the multiple gauge length (MGL) approach can be twice that calculated via the SGL technique [56,94].

As an example, consider the results of Lavaste for FP DuPont alumina filaments [94]. The Weibull parameters for the FP DuPont fiber using both the SGL and MGL techniques are given in Table 2.1. To test the assumption that the bundle properties at one gauge length can be predicted from single filament strengths at another gauge length, the bundle strength is predicted using equation (2.26) with $L$ equal to 5 mm (see Table 2.2). Since the SGL technique will most accurately describe the strength distribution at that gauge length, the prediction of the bundle strength using the SGL technique at 5 mm will be considered the closest to reality; it is therefore shaded in the table.
Table 2.1: Weibull Parameters for FP Alumina [94]

<table>
<thead>
<tr>
<th>Tested Gauge Length (mm)</th>
<th>SGL ( L_o ) (mm)</th>
<th>SGL ( \sigma_o ) (GPa)</th>
<th>SGL ( m )</th>
<th>MGL ( L_o ) (mm)</th>
<th>MGL ( \sigma_o ) (GPa)</th>
<th>MGL ( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5</td>
<td>1.91</td>
<td>4.30</td>
<td>5</td>
<td>1.82</td>
<td>10.6</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>1.67</td>
<td>6.20</td>
<td>25</td>
<td>1.63</td>
<td>10.6</td>
</tr>
<tr>
<td>75</td>
<td>75</td>
<td>1.58</td>
<td>4.06</td>
<td>75</td>
<td>1.50</td>
<td>10.6</td>
</tr>
<tr>
<td>150</td>
<td>150</td>
<td>1.38</td>
<td>3.55</td>
<td>150</td>
<td>1.29</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 2.2: Prediction of Ideal Bundle Strength @ \( L = 5 \) mm

<table>
<thead>
<tr>
<th>Tested Gauge Length (mm)</th>
<th>SGL Bundle Strength (GPa)</th>
<th>MGL Bundle Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.07</td>
<td>1.32</td>
</tr>
<tr>
<td>25</td>
<td>1.37</td>
<td>1.38</td>
</tr>
<tr>
<td>75</td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>150</td>
<td>1.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

First consider the SGL bundle strength predictions. As the tested gauge length increases, the prediction at 5 mm becomes progressively worse. Even at 25 mm the bundle strength is predicted to be 28% higher than that predicted at 5 mm. The predictions from the MGL technique are much more consistent, but they all overpredict the predicted response at 5 mm by about 25%.
The results are slightly better when predicting the bundle strength at the longer gauge lengths, 25, 75 and 150 mm (see Tables 2.3, 2.4 and 2.5). Again, the shaded cell is considered the most accurate prediction. The SGL predictions from the 25, 75 and 150 mm tests compare well to the most accurate prediction while the prediction using the 5 mm tests underpredicts the response by 20 - 30%. The MGL technique constantly overpredicted the response, though the predictions at 25 mm were reasonable.

### Table 2.3: Prediction of Ideal Bundle Strength @ $L = 25$ mm

<table>
<thead>
<tr>
<th>Tested Gauge Length (mm)</th>
<th>SGL Bundle Strength (GPa)</th>
<th>MGL Bundle Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.74</td>
<td>1.14</td>
</tr>
<tr>
<td>25</td>
<td>1.06</td>
<td>1.19</td>
</tr>
<tr>
<td>75</td>
<td>1.15</td>
<td>1.21</td>
</tr>
<tr>
<td>150</td>
<td>1.21</td>
<td>1.11</td>
</tr>
</tbody>
</table>

### Table 2.4: Prediction of Ideal Bundle Strength @ $L = 75$ mm

<table>
<thead>
<tr>
<th>Tested Gauge Length (mm)</th>
<th>SGL Bundle Strength (GPa)</th>
<th>MGL Bundle Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.57</td>
<td>1.03</td>
</tr>
<tr>
<td>25</td>
<td>0.89</td>
<td>1.07</td>
</tr>
<tr>
<td>75</td>
<td>0.87</td>
<td>1.09</td>
</tr>
<tr>
<td>150</td>
<td>0.88</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 2.5: Predictions of Bundle Strength @ L = 150 mm

<table>
<thead>
<tr>
<th>Tested Gauge Length (mm)</th>
<th>SGL Bundle Strength (GPa)</th>
<th>MGL Bundle Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.49</td>
<td>0.96</td>
</tr>
<tr>
<td>25</td>
<td>0.79</td>
<td>1.0</td>
</tr>
<tr>
<td>75</td>
<td>0.74</td>
<td>1.02</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>0.94</td>
</tr>
</tbody>
</table>

The results suggest that it is difficult to predict the bundle strength at very small gauge lengths (< 5 mm) using either the SGL or MGL techniques, but reasonable predictions can be made at the higher gauge lengths. Since the effective gauge lengths are typically less than 5 mm, the composite models described in section 2.2.4 will tend to overpredict the ultimate composite strength.

2.2 Ceramic Matrix Composites

In the early 1970's, strong and stiff commercially available graphite fibers were used to reinforce glass and glass-ceramic matrices [1,97-99]. The advantages of these matrices were their relatively low processing temperatures and castability. Though some of the basic behavioral mechanisms were identified during this period [99], oxidation issues restricted the use temperatures of graphite. In the late 1970's, the development of the more oxidation resistant SiC Nicalon fiber in Japan [15] created the potential for an increase in operating temperature. In addition to glass and glass-ceramic matrices [100-103], other processes to infiltrate a matrix between the fibers were developed: chemical vapor infiltration (CVI) [168] and slurry casting processes followed by CVI or sol-gel infiltration [169].
However, it has recently become clear that even with protective coatings the SiC fiber cannot withstand the high temperature oxidizing environments that exist in the desired applications [104-109].

To avoid oxidation problems, oxide-oxide composites are now being investigated [110,111]. Oxide based fibers like NextelTM 610 and 720 have strength properties comparable to those of SiC based fibers [17,56] and improved creep properties compared to previous oxide fibers [112-113]. The matrix technology developed with the graphite and SiC fiber can be used with these oxide fibers, but the development of coating systems which are compatible with the fiber, matrix and environment has been a significant undertaking [111,21-23]. Currently weakly bonded dense coatings like montazite [22] and shealite [23] and strongly bonded porous coatings like ZrO₂ [21] have been developed to provide the desired weak interfacial properties. The porous coating concept has also been expanded to create ceramic composites with an entirely porous matrix [110].

2.2.1 Stress/Strain Response of Unidirectional Reinforced Composites

The porous matrix of the alumina composite fiber is expected to have a much lower strain to failure than the fully dense alumina filaments. A schematic of the stress/strain response for this type of ceramic matrix composite where matrix cracking is expected prior to failure of the composites is shown in figure 2.9. The initial Young's modulus of the composite can be predicted using the rule of mixtures [114]

\[ E_c = V_f E_f + (1 - V_f) E_m \]  

(2.31)

where \( E_f \) and \( V_f \) are the Young's modulus and the volume fraction of filaments, respectively and \( E_m \) is the Young's modulus of the matrix. The nonlinearity in the response and failure mechanisms will be discussed in the following paragraphs.
Figure 2.9 Schematics of the stress/strain response of a ceramic composite and the type of deformation occurring at each stage.

There are two distinct types of fracture mechanisms in ceramic matrix composites (CMCs) where matrix cracking is expected. Failure can be designated as either matrix crack dominated [115] (figure 2.10) or fiber fracture dominated [115-122] (figure 2.11). The matrix crack dominated failure mechanisms occur from the propagation of a single matrix crack through both matrix and filaments. In the fiber dominated mechanism multiple matrix cracks can propagate through the composite without causing fiber failure.

Two modes of matrix crack dominated failure can occur (figure 2.10). The mode designated "brittle" occurs when an approaching matrix crack penetrates through a strong
interfacial bond into the fibers. Once the crack reaches a critical length the composite will undergo catastrophic failure. The “Brittle-tough” mode occurs when the crack tip does not penetrate the fibers and the fibers fail in the wake. The increase in toughness results from a reduction of crack tip stresses due to traction forces imposed on the crack surfaces [123].

Figure 2.10 Matrix Crack dominated failure mechanisms. a) single matrix crack, b) single matrix crack with some filament shielding in the wake.

When the fiber-matrix interfaces are very “weak”, matrix cracks may deflect along the interface effectively blunting the crack-tip at the fiber matrix interface. Multiple matrix cracks may then propagate through the entire sample without causing fiber failure. Composite failure will then be dominated by the failure of the fibers instead of the failure of the matrix.
Fiber Fracture Dominated

**Figure 2.11** Fiber fracture dominated mechanism. a) local load sharing, b) global load sharing.

The two modes of mechanisms by fiber dominated failure are seen in figure 2.11. when matrix cracks deflect along the interface a short distance and the sliding resistance is large [117] “tough-brittle” behavior occurs. In this case, the load or stress of a broken fiber is concentrated in neighboring unbroken filaments. These neighboring filaments now have a higher probability of failure compared to the filaments that are far away. Filament failure then localizes around the fracture surface of the composite and flat fracture with short pull-out lengths ensues [120].

For composites failing via the global load sharing mechanism, interface debonding is easy and the sliding resistance is low. In this “tough” composite, the weak interface properties promote the “global” redistribution of stress from a failed filament to the remaining unbroken filaments. Fiber failure then occurs at random locations and due to shear-lag
reloading fibers may fail in more than one location. This type of failure is characterized by multiple matrix cracking and large pull-out lengths [119, 124].

The schematic in figure 2.9 also shows that if the composite fails by a fiber fracture dominated mechanism, then the cyclic response of the composite after matrix cracking exhibits a hysteresis and some permanent deformation, $\varepsilon_p$ [119].

2.2.2 Prediction of Matrix Cracking

Aveston, Cooper and Kelly [99] first analyzed the matrix cracking problem by comparing characteristic strain-to-failure of both the matrix ($\varepsilon_{m^*}$) and the filament ($\varepsilon_{f^*}$). They stated that if the filament stress within a composite at the filament failure strain ($V_f E_f \varepsilon_{f^*}$) was greater than the composite stress at the matrix failure strain ($E_c \varepsilon_{m^*}$) then multiple matrix cracking would occur. In the alumina composite fibers fabricated for mechanical testing, $V_f = 0.34$, $E_f = 380$ GPa [14], $E_m = 30$ GPa [157], and $\varepsilon_{f^*} = 0.007$. Therefore, the criterion for multiple matrix cracking in the alumina composite fiber would be $\varepsilon_{m^*} < 0.006$. Given that the matrix is only a slightly sintered alumina, the failure strain is expected to be well below this criterion.

The analysis of He and Hutchinson [125] and Budiansky [127] for matrix cracking within a composite are based on fracture mechanics and will be used to predict interface debonding and the stress at the onset of matrix cracking. He and Hutchinson [125] investigated whether a crack approaching an interface would deflect and determined that deflection occurs when the ratio of the fracture energy of the interface to that of the fiber
\( \frac{\Gamma_i}{\Gamma_f} \) is less than a critical value. In the absence of any elastic mismatch between the fiber and matrix, the matrix crack deflection criteria is:

\[
\frac{\Gamma_i}{\Gamma_f} < 0.25
\]  

(2.32)

A plot of the fracture energy ratio versus elastic mismatch, \( \alpha \), is shown in figure 2.12.

![Diagram](image)

Figure 2.12 Diagram of the criteria for matrix crack deflection up the interface: \( \alpha = \frac{(E_f' - E_m')}{(E_f' + E_m')} \) [126]. \( E' \) in plain strain is \( E/(1-\nu^2) \).

The critical stress at which matrix cracking occurs without causing catastrophic failure was determined by Budiansky et al. [127] for the three specific cases shown in figure 2.13. The maximum critical stress occurs in case (a) where the debonded filaments do not slip.
or bonded filament do not debond. In this case assuming no residual stress in the matrix, the stress in the composite when matrix cracking occurs is [127]:

\[
\sigma_{mc}^{(a)} = E_c B \left( \frac{6 V_f E_f}{(1 - V_f)^2 E_c (1 + \nu_m)} \right)^{1/4} \left( \frac{\Gamma_m}{r_f E_m} \right)^{1/2}
\]  

(2.33)

where \( r_f \) is the fiber radius, \( \nu_m \) is the Poisson's ratio of the matrix and \( B \) is a function of only the fiber volume fraction:

\[
B = \left( \frac{2(1 - V_f)^3}{-6 \log V_f - 3(1 - V_f)(3 - V_f)} \right)^{1/4}
\]  

(2.34)

Figure 2.13 Mechanisms of steady-state matrix cracking under tensile loading [127]
The minimum cracking stress was predicted to occur for case (b) where the fibers are not bonded to the matrix and may slip. Again assuming no residual stresses in the matrix, the composite stress at the onset of matrix cracking is [127]:

$$\sigma_{mc}^{(b)} = E_c \left( \frac{6 V_f^2 E_f \tau_s}{(1 - V_f)E_m E_c} \right)^{1/3} \left( \frac{\Gamma_m}{r_f E_m} \right)^{1/3}$$

(2.35)

The stress at which cracking occurs in case (c) lies in between cases (a) and (b) [127].

2.2.3 Interface Properties

Since, the determination of crack deflection and matrix cracking stress are a function of the fracture energy of the interface, $\Gamma_i$, and the sliding resistance, $\tau_s$, a direct measurement of these properties has been developed based upon fiber pullout [128] or pushout tests [129-132]. Because the experimental procedures are easier, the pushout test has been more widely used. A schematic of the pushout test is shown in figure 2.14. As the applied load is increased, a debond crack initiates along the interface. Debonding can occur at the bottom-face when bending stresses are induced [132]. To avoid bending stresses the ratio, $t/h$, must be less than two [132]. When bending stresses are avoided the interface will begin to debond at top-face and propagate down [131]. The sliding resistance is measured once a debond crack has propagated through the entire length of the interface contained in the sample. An schematic of an interface stress versus displacement curve is shown in figure 2.15.
**Figure 2.14** A schematic diagram of a fiber pushout test

**Figure 2.15** Idealized interface stress versus displacement curve for a pushout test.
Normally sliding between the fiber and matrix is modeled using a Coulombic friction law [131]:

$$\tau_s = \mu \sigma_r$$  \hspace{1cm} (2.36)

where $\mu$ is the coefficient of friction and $\sigma_r$ is the stress normal to the interface which is generally attributed to thermal residual stresses. Since both the fiber and matrix are alumina within the composite fibers, the residual stresses will be negligible and this law would predict the sliding resistance to be zero.

An alternative law which adds a constant friction term to the Coulombic friction law seems more applicable to the alumina composite fiber:

$$\tau_s = \mu \sigma_r + \tau_o$$  \hspace{1cm} (2.37)

where $\tau_o$ can vary depending on the roughness of the sliding interface.

The model developed by Liange and Hutchinson [131] to calculate $\Gamma_i$ from the push-out tests assumes only Coulombic friction. Since Coulombic friction will not be significant in the alumina composite fibers, $\Gamma_i$ will be estimated as the fracture energy of a slightly sintered alumina which is very low ($\Gamma_m = 3 \text{ J/m}^2$ [158]).

2.2.4 Predictions of Composite Failure: Effective Gauge Length Models

Models for predicting composite failure have been developed which assume global load sharing similar to the ideal bundle model described in section 2.1.6 [116,133,134]. However, there are some important differences between a filament bundle and a composite. First the introduction of a matrix material (even one that is cracked) allows a broken filament to be reloaded. In other words, once a filament breaks it is only ineffective over the length needed to reload the filament. The other important difference is that local trans-
fer of stress from a broken filament to its unbroken neighbors occurs over the ineffective length. Within a dry (matrixless) filament bundle, the stress or load of a broken filament is evenly distributed to the unbroken filaments through the grips (i.e. the load transfer length in this case is the sample length).

The distance required to fully transfer the stress back to the fiber is called the ineffective length, \( l_{in} \) (see figure 2.16). Based on a shear-lag analysis, the ineffective length depends on the fiber stress, \( \sigma_f \), the interface shear resistance, \( \tau_i \), and the fiber radius, \( r_f \) [135]:

\[
l_{in} = \frac{\sigma_f r_f}{2\tau_i}
\]  

(2.38)

If the interface shear resistance is low then the ineffective length is long. As the resistance to shear at the interface increases the ineffective length decreases. In MMCs, if the bonding is strong enough the interface shear resistance may be controlled by the shear strength of the matrix. Nevertheless, as the ineffective length decreases, the stress transfer becomes more localized and the resulting concentration of stress can activate failure via local load sharing. This transition from global to local load sharing will be discussed later.

Effective gauge length models were developed by Rosen [133] and Curtin [116] to describe failure of composites whose matrix does not carry load at failure. Failure occurs from the accumulation of fiber fractures similar to a filament bundle. The basic approach of these models is to divide the composite into a chain of bundles: defining the length of each link as the effective gauge length (see figure 2.16).

The effective gauge length is a function of the ineffective length. The stress distribution in a fractured fiber is shown in figure 2.16. At the fracture point, the stress in the fiber is zero. Over the ineffective length the stress increases approximately parabolically [114]
via stress transfer from the matrix through the interface. As an approximation of this stress distribution, Rosen defined a step function where the stress in the fiber was zero over a length, $\delta$. The remaining fiber was at the full stress, $\sigma_f$. He defined the effective gauge length as $\delta$ and assumed the stress from this ineffective portion of the fracture fiber was redistributed equally among the unbroken fibers of that cell (i.e. global load sharing).

![Diagram of fiber and matrix with stress labels](image)

**Figure 2.16** The ineffective length and its relationship to the effective gauge length used to predict composite strength.

Rosen then predicted the fiber strength in a composite as the bundle strength at a gauge length, $\delta$. Assuming a Weibull fiber strength distribution, the fiber strength in the composite at the point of failure is found by substituting $\delta$ into equation (2.26):

$$\sigma_{f\text{rosen}} = \sigma_o \exp\left(\frac{-1}{m}\left(m\frac{\delta}{L_o}\right)^{-1/m}\right)$$

(2.39)
Curtin [116] also defined the effective gauge length as a function of the ineffective length, but there is an important difference compared to Rosen's definition. Examination of a fractured fiber (figure 2.16) indicates that the fiber is ineffective both above and below the fracture. It is therefore more appropriate to include both sides of the fractured fiber in the approximation of the effective gauge length. Curtin made this modification by defining the effective gauge length as $2l_{in}$, and then assumed the matrix underwent multiple matrix cracking. After the first matrix crack, the fibers reload the matrix for the same reason the fractured fiber in figure 2.16 is reloaded. This allows matrix cracking to occur on multiple planes. The end result is that the matrix only contributes to the strength of this type of CMC via resistance to pullout. Curtin's contribution was to include the effect of pullout and the more appropriate effective gauge length. Thus, Curtin defines the fiber stress in the composite as a combination of the bundle stress at an effective gauge length plus a contribution for fiber pullout $F(\tau)$.

$$\sigma_{\text{curtin}} = \sigma_f (1 - P_f) + F(\tau) P_f$$  \hspace{1cm} (2.40)

The Weibull failure probability, $P_f$, is a function of the effective gauge length.

The contribution of pullout turns out to be approximately $\frac{1}{2} \sigma_f$ and thus equation (2.40) reduces to:

$$\sigma_{\text{curtin}} = \sigma_f \left(1 - \frac{1}{2} P_f \right)$$  \hspace{1cm} (2.41)

Curtin introduces a characteristic strength, $\sigma_{\text{cur}}$ which is a function of the Weibull parameters of the fiber and the effective gauge length.

$$\sigma_{\text{cur}} = \left( \frac{\sigma_0 m \tau \ell_o}{r_f} \right)^{1/(1 + m)}$$  \hspace{1cm} (2.42)
Curtin makes a further approximation of $P_f$ as $\left( \frac{\sigma_f}{\sigma_{cur}} \right)^{1/(m+1)}$. Substituting this approximation for $P_f$ into equation (2.41) and then finding the maximum gives Curtin’s prediction of the fiber strength at composite failure as:

$$
\sigma_{f\text{curtin}} = \sigma_{cur} \left( \frac{2}{m+2} \right)^{1/(m+1)} \left( \frac{m+1}{m+2} \right)
$$

(2.43)

The effective gauge length as defined by Curtin is $2l_{in}$ or $\sigma_f r / \tau_i$. The ratio of the effective gauge length to fiber radius ($2l_{in}/r$) is then $\sigma_f / \tau_i$. Note that the effective gauge length increases as either the fiber stress increases (i.e. as the composite is loaded) or as the interface sliding resistance decreases.

In a typical CMC, the filament radius is about 5 μm. The interface shear resistance is typically controlled by the sliding resistance and is approximately 10 MPa or less [126]. Assuming a fiber strength of 3 GPa, the ratio of the effective gauge length to fiber radius is 300, and the effective gauge length would be on the order of 1.5 mm.

2.2.5 Validity of the Global Load Sharing Assumption

By definition, global load sharing is the uniform distribution of the load once carried by a broken fiber to the remaining unbroken fibers. The redistribution of load may occur over the test gauge length as in a dry bundle or over an effective gauge length as in a composite. Local load sharing, by contrast, is the localized redistribution of load to only neighboring fibers (i.e. a stress intensification). Neighboring fibers in the region of stress intensification have a higher probability of failure than fibers far from the fracture site. The progression of such localized damage would then cause failure earlier than in the global load sharing scenario.
In some respect any unidirectional reinforced composite material tends towards a local load sharing condition. In a dry bundle, a broken fiber is totally ineffective. The load it once carried is redistributed evenly through the grips. Once a matrix is introduced around the fibers, it will localize how the load (or stress) is redistributed. First, along the axis of the fiber, the broken fiber is no longer totally ineffective because the matrix will act to reload the broken fiber via the shear properties at the fiber/matrix interface. The length over which the broken fiber is reloaded is given by equation (2.38). Second, transverse to the fibers, the redistribution of the axial load to the remaining unbroken fibers also occurs via shear through the matrix.

Hedgepeth [136] formulated and solved the local load sharing problem for single and multiple breaks in a plane of filaments (eventually extended to a 3-D array [137]). He assumed the stress or load was redistributed amongst only the nearest neighbors and determined an expression which described the concentration of stress. He assumed the stress in the non-nearest neighbors remained unchanged. Zweben [138] then combined Hedgepeth's work with that of Rosen's to create a model that predicted composite failure with a local load sharing assumption. As a worse case scenario, Zweben first assumed composite failure would occur at the first fiber failure. He then suggested and further explored with Rosen [139] a failure criterion defined as the nucleation of the first multi fiber break (i.e. two adjacent breaks on the same plane). The subsequent modeling [117,118,140,141] has simply varied the local load sharing rules (1. how stress is redistributed to neighboring fibers, and 2. the filament failure criterion) that Zweben used to get more realistic predictions. The disadvantage of much of this work was that there was little connection between the local load sharing rules and the properties of the constituents such as the interface properties which control stress redistribution.
In 1993 He, Evans and Curtin [117] addressed the important issue of a “tough” to brittle transition and related it to fiber and interface properties. He et al. used a finite element approach to model the stress concentrations around a broken fiber. To simplify the problem, they modeled a single broken fiber surrounded by alternating annuli of matrix and fiber material. The numerical calculations of the stress concentrations in the nearest and next nearest neighbor fiber annuli depended on the interface sliding stress, the applied stress, the fiber volume fraction and the Young’s modulus of the fiber and matrix. The criterion for the transition from GLS to LLS was arbitrarily chosen to occur when the failure probability of any next nearest neighbor fiber, $P_{NN}$, equaled that of any nearest neighbor fibers, $P_N$. GLS failure will occur when $P_{NN} > P_N$ while LLS failure will occur when $P_N > P_{NN}$. Their rationale for this criterion was that if $P_{NN} > P_N$ a well defined crack-like defect could not develop. However, this criterion ignores any dependence between the nearest and next nearest neighbor fibers. Therefore the criteria could be extended to include the failure probability of any fibers in a third outer ring, $P_{NNN}$, by stating that GLS failure will occur when $P_{NNN} > P_{NN}$ and $P_{NNN} > P_N$. An important conclusion of their work was that the ratio of the interface shear strength to the fiber stress, $\tau_f/\sigma_f$, needed to be less than 0.1 to assure GLS.

Curtin [118] also explored this issue and raised three important questions: (1) How many fibers must be involved in the load sharing for the global load sharing assumption to be valid? (2) What is the strength of the composite if fewer fibers are involved in load transfer? (3) How is the extent of load sharing related to material parameters such as the fiber strength, moduli and interface shear resistance. Curtin showed that the transition occurs when approximately 100 fibers were involved in the load transfer. He found that there was less than a 10% decrease in strength compared to the global load sharing predictions at this transition. When fewer fibers were involved with the load transfer, the
strength decreased more rapidly. He concluded that the GLS-to-LLS transition occurred when the ratio of the interface shear strength, $\tau$, to Curtin's defined characteristic strength, $\sigma_{cur}$, was approximately 0.02 and that clear degradation occurred at $\tau/\sigma_{cur} \approx 0.03$. Therefore, to promote GLS behavior the fiber strength should be maximized and the sliding resistance or more generally the resistance to shear at the interface should be minimized.

2.3 Consequences for the Alumina Composite Fiber

From the models described in this chapter, the mechanical performance of a metal matrix composite fabricated using the composite fiber approach will be enhanced by maximizing the mechanical properties of the composite fiber: including stiffness, strength, toughness and creep resistance. Stiffness of the alumina composite fiber is directly related to the filament stiffness and filament packing density. Composite fiber strength has a similar relationship to filament strength and filament packing density but is also affected by the precise mechanism of failure. Brittle and weak composites fail from a local load sharing mechanism which results from a “high” shear resistance at the interface. In contrast, a “low” resistance to shear at the fiber/matrix interface will promote failure via global load sharing and subsequently maximize composite strength and toughness. The effects of processing and composite fiber architecture on creep resistance is the subject of a separate ongoing study [162].

The approach taken in this thesis was to create an alumina composite fiber where global load sharing behavior occurs. If global load sharing occurs then it is expected that multiple matrix cracking will be observed and the maximum strength and toughness should result. To accomplish this, the filament strength should be maximized and the interface shear resistance should be low enough to meet Curtin’s criterion for GLS ($\tau/\sigma_{cur} \equiv 0.03$).
CHAPTER 3 Alumina Composite Fibers: Process Development

This chapter will describe the design of a process to manufacture an alumina composite fiber and the investigation of its effects on the strength and toughness of the alumina composite fiber. Optimization of the process to maximize the filament packing density, and thus the stiffening potential was left to future researchers. A slurry approach was chosen to infiltrate alumina particles between the filaments of a Nextel™ 610 (99.5% Al₂O₃) tow. Subsequent, drying, sintering and sizing processes were perfected with the aim of creating an alumina composite fiber with high filament packing, a porous matrix of uniform porosity and a weak fiber/matrix interface. This chapter begins a brief review of the fabrication of the Nextel™ 610 fiber. A description of the process for manufacturing the alumina composite fibers follows and includes a detailed discussion of infiltration, fiber shaping, drying and sintering.
3.1 Fabrication of Nextel™ 610

The Nextel™ 610 fiber used in the work is manufactured via a sol-gel process [17,25]. A flow-chart of the sol-gel process is shown in figure 3.1. The first step produces a concentrated basic aluminum salt which formed a highly viscous sol [17]. This sol is forced through a multi-orifice (420) spinnerette (i.e. spun) to create a bundle of green fibers. As the fiber bundle falls through a humidity controlled tower, the sol is polymerized (gelled) via hydrolisis (i.e. a reaction with H₂O) before being collected on a conveyer belt. The fibers are then calcined or converted to alumina. A final sintering treatment at 1400 °C is used to fully densify the filaments (see figure 3.2). In addition to densification, filaments in contact will sinter together creating filament clusters. It will be shown in Chapters 5 and 6 that this only occurs between 4 and 20% of the as-received filament.

![Flow-chart of the sol-gel process for metal-organic compounds](image)

**Figure 3.1 Schematic of the sol-gel process for metal-organic compounds**

Nextel 610™ fiber tows has approximately 420 filaments. The composition is 99.5% Al₂O₃, and the average filament diameter and grain size are 12 μm and less than 100 nm, respectively [25]. A protective polymer coating (sizing) is often applied to the tow to make handling easier especially during weaving processes.
Figure 3.2 As-received Nextel™ 610 tow fiber with the polymer sizing removed.

3.2 Alumina Composite Fiber Fabrication

The fabrication process can be divided into four different stages: infiltration, fiber shaping, drying and sintering. Slurry viscosity and permeability of the fiber tow are critical parameters for insuring full infiltration. Fiber shaping can be accomplished by pulling the infiltrated tow through a circular die and therefore the diameter of the die is an important parameter. Drying via evaporation of the solvent carrier liquid in the slurry begins after the infiltrated tow leaves the shaping die. Drying shrinkage which results from an increase in the particle packing density as solvent is removed is a critical phenomenon. Sintering, in turn, determines the extent of particle-to-particle, particle-to-filament and filament-to-filament bonding. Processing experiments were designed to investigate the effect of varying the volume percent solids in the slurry, the slurry viscosity, the die diameter and the sintering temperature.

Slurry processing has a long tradition in the processing of conventional ceramics [29]. therefore much work has been done on understanding and optimizing the properties of
slurries. The recipe for the slurry used was taken from Plucknett et al. [31] whose work was directed at understanding the effect of dispersent concentration on the viscosity of a slurry. The recipe was chosen to minimize viscosity in order to insure full infiltration. The procedure was as follows: 65 ml of an azeotropic mixture of trichloroethylene and ethyl alcohol (73/27 [31]) was first placed in a 250 ml mill jar with small cylindrical zirconia grinding media (d = 1 cm) filling 1/3 of the jar. A dispersent (5 ml phosphate ester) was then added to the solvent mixture. The phosphate ester has been identified as both an electrostatic [30] and steric [31] dispersent and the literature is unclear as to the dominant dispersent mechanism. Small diameter (d < 1 μm) alumina powder was heat treated at 150 °C for a minimum of 30 min. to remove moisture. After the heat treatment, the powder was added in 60 g amounts; milling for 15 minutes in between until the target percent solids was obtained. slurries with varying solid fractions were produced to explore their effect on the microstructure of the alumina composite fiber.

The alumina powder used was 99.99% pure. The particle size distribution in terms of weight percent was determined by its supplier (Alfa Aesar) [32] and is shown in figure 3.3. The mean particle diameter and surface area were 0.69 μm and 4.4 m²/g, respectively. Figure 3.4 shows that the characteristic particle shapes are non-spherical but were also not plate-like or fibrous.
Figure 3.3 Alumina powder, particle diameter distribution based on mass percentage

Figure 3.4 A scanning electron micrograph of the alumina powder. The surface area is 4.4 m²/g.
Two processing procedures were developed and evaluated for infiltrating a single tow of Nexel\textsuperscript{TM} 610 with an alumina slurry. A schematic of a horizontal process is shown in figure 3.5. In this process a single alumina fiber tow entered and exited a horizontal glass tube which contained an alumina slurry. The line speed was between 30 and 120 cm/min. and depended on the viscosity of the slurry and the diameter of the exit orifice. Slurry was replaced in the horizontal tubes through a vertical access tube. At the glass tube entrance the slurry infiltrated the loose tow (see figure 3.6a). As the filaments exited the tube, the exit orifice (set at 350 \textmu m unless otherwise noted) acted to pack the filaments together and limit the amount of slurry pulled out of the tube by the filaments (see figure 3.6b). After leaving the exit orifice, the slurry partially dried via solvent evaporation in the ambient air. The composite fiber then entered a burnout furnace (set at 800 °C with a hot zone = 30 cm; total length 60 cm) where final drying occurred and organics were removed. The "green" composite fiber then entered another horizontal glass tube which contained a sizing consisting of a polyvinyl butyral (PVB)/methanol solution (= 5 v% PVB). The methanol was then evaporated in a 100 cm long drying furnace set at 60 °C leaving a polymer sizing on the composite fiber. Finally, the alumina composite fiber was wound onto another spool. This was the processed used in all the subsequent process development experiments.
Figure 3.5 Horizontal Process for fabricating single tow alumina composites. The line speed varied between 30 and 120 cm/min. For sized Nextel fiber, the sizing was removed prior to entering the first horizontal tube. The sizing was a 5 v% polyvinyl butyral (PVB)/methanol solution.
Figure 3.6 Schematics of the entrance and exit of horizontal tube. The diameter of the exit tube was 350 μm unless otherwise noted.
The second process was developed for higher line speeds, 200 cm/min. (see figure 3.7). Higher line speeds are essential for driving down production costs. The line speed was limited by the available winding system not by the design of the process. In this process the infiltration step occurred in a slurry bath which avoided having to continuously feed slurry into the glass tube as in the first process. The tow was then redirected vertically and passed through a glass die with an orifice diameter of 350 µm; similar to the horizontal process. The slurry in this process contained about 3 v% organic polymer (PVB) and 15 v% alumina powder. The organic polymer gave the composite fiber enough “green” strength to be directly wound onto a spool without the resizing step of the horizontal process. Once the fiber left the glass die, it traveled through a drying furnace where the solvents were driven off and the polymer hardened. The alumina composite fiber was then wound onto a spool.
Figure 3.7 High Speed vertical process for fabricating alumina composite fibers.

The slurry composition was 15 v% alumina powder, 3 v% PVB, < 1 v% phosphate ester and 82 v% 50/50 acetone/isopropanol.

A subsequent heat treatment process was developed to remove the organic polymer within the “green” composite fiber and sinter the matrix. The green composites were pulled through a pair of furnaces as shown in figure 3.8. The first furnace was set at 750 °C and was used to burn-out the organic constituents. The second was a sintering furnace set to between 1100 and 1450 °C. The line speed was 30 cm/min and the length of the hot-zone was approximately 30 cm, thus the time at temperature was approximately one minute. This process will be referred to as in-line sintering or ILS.
Figure 3.8  The in-line sintering (ILS) process. The length of the hot zone in the sintering furnace is 30 cm, therefore the effective time at temperature is about 1 min.

In the following sections, the process development experiments are described and discussed in terms of these stages.

3.3 Experiment: varying the percent solids in the slurry

The goal of processing was to create a composite fiber consisting of densely packed filaments in a uniform porous alumina matrix. This microstructure was difficult to produce. In a first series of process development experiments, the percent solids in the slurries were varied from 20% to 49% (the constituents are given in Table 3.1). As the percent solids (i.e. powder fraction) increased from 20 to 49%, the measure viscosity increased from 4 to 90 cP. The resulting microstructures after sintering are shown in figures 3.9 and 3.10. Large voids within the centers of the composite fibers were present. This was espe-
cially true for the low solid slurries where the most drying shrinkage was expected (see figure 3.9). As the percent solids increased, the central void size decreased, and more filaments were surrounded by a porous matrix (see figure 3.10).

Figure 3.9 Microstructure of composite fiber fabricated with 20 and 30 v% alumina powder slurries.
Figure 3.10 Microstructure of composite fiber fabricated with 40 and 49 v% alumina powder slurries.
The fiber volume fraction was determined by dividing the filament area by the measured composite fiber area for each processing condition. The filament (43000 \( \mu m^2 \)) area was calculated by dividing the linear density of the Nextel™ 610 tow (0.167 g/m) by the density of alumina (3.9 g/cm\(^3\)). The filament volume fractions are given for each slurry in Table 3.1.

In order to devise a means to remove these matrix voids, an understanding of their formation is necessary. The voids may form either during infiltration or drying. It will be shown in section 3.4 that the infiltration time is directly related to viscosity. Therefore, the fact that the void volume decreased as the viscosity of the slurry increased strongly suggests that the voids formed during drying. Infiltration of the Nextel™ 610 tow will be shown to have occurred almost immediately upon entering the slurry. The mechanism of the void formation during the drying process is also described and discussed.

Table 3.1: Volume percentage of slurry constituents and fiber volume fraction after processing

<table>
<thead>
<tr>
<th>Solvent(^a)</th>
<th>Alumina Powder</th>
<th>Phosphate Ester</th>
<th>Viscosity (cP)</th>
<th>Fiber Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>20</td>
<td>4</td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td>66</td>
<td>30</td>
<td>4</td>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>56</td>
<td>40</td>
<td>4</td>
<td>43</td>
<td>36</td>
</tr>
<tr>
<td>47</td>
<td>49</td>
<td>4</td>
<td>90</td>
<td>34</td>
</tr>
</tbody>
</table>

\(^a\) Azeotropic mixture 73/27 trichloroethylene and ethanol; total volume used for each slurry was 65 ml.
3.4 Infiltration

The extent of infiltration cannot be directly observed in the process of fabricating these alumina composites. However, models based on Darcy's law for steady-state flow through a porous medium can be used to predict the infiltration time. For example, the impregnation times for resin transfer molding [26] and other polymer matrix composite processes [27] have been determined using models based on Darcy's law. Although infiltration into a tow can occur from all directions, the infiltration time can be estimated using a simple one dimensional analysis.

Darcy's law for flow in one direction relates the fluid penetration velocity, $v_f$, to the permeability, $k$, of the medium, the fluid viscosity, $\eta$, and the pressure drop, $\Delta P$, over some distance, $l$:

$$v_f = \frac{k \Delta P}{\eta \ l}$$

(3.1)

Noting that $v_f = dl/dt$, Integration of Darcy's law gives a relationship between the infiltration distance and time, $t$, which can be rearranged to give:

$$t = \frac{\eta l^2}{2k \Delta P}$$

(3.2)

As the Nextel™ 610 tow enters the slurry (figure 3.6) infiltration must occur from the outside toward the inside in order to displace the atmosphere within the tow. This gives rise to the impregnation profile schematically shown in figure 3.6. In this configuration, infiltration normal to the filament direction will be the limiting impregnation mechanism as opposed to infiltration parallel to the filament direction. Therefore, the impregnation time was estimated by considering the problem of a slurry infiltrating a static single single tow as shown in figure 3.11. The dimensions for $l$ and $d$ are representative of an alumina com-
posite fiber. The height of the slurry seemed a reasonable assumption given the orifice diameter at the entrance is around 2 mm. It was assumed that gas inside the tow was connected to the atmosphere and no separation of the powder and solvent occurred. It was also assumed that bonded filament clusters which block infiltration between filaments were not present. The viscosity of an alumina slurry, the permeability of a fiber bundle and the pressure drop will be estimated and discussed in the following sections.

Figure 3.11 Static infiltration problem. The diameter of the composite fiber was around 300 μm. Therefore full impregnation occurs when \( l \) is equal 150 μm.
3.4.1 Slurry Viscosity

Viscosity, $\eta$, is a measure of a fluid's resistance to shear deformation and is defined as the ratio between shear stress, $\tau$, and the change in fluid velocity parallel to the shear stress ($dv_f$) with respect to the change in distance perpendicular to the shear stress ($dy$) [28]:

$$\eta = \frac{\tau}{dv_f/dy}$$  \hspace{1cm} (3.3)

The viscosity of a slurry mixture depends on the viscosity of the carrier liquid and nature of the interparticle forces [29]. The interparticle forces are affected by the type of surface charges on the particles (repulsive vs. attractive) and the distance between particles (i.e. the packing density or percent solids). For instance when particles are attracted to each other, flocculation occurs and since attractive forces between particles will resist shear deformation, the viscosity increases. To counteract flocculation in the alumina slurries used in this work, phosphate ester was added as a dispersent to reduce the slurry viscosity. Dispersents work either by an electrostatic or steric mechanism [30]. The electrostatic mechanism is a result of a single charge type (+ or -) on the surface of all the particles. These charges create repulsive forces between the particles. The steric mechanism works via adsorbed polymers on the particle surfaces which are strongly anchored to the particles and limit particle/particle distances to 10-20 nm.

Since increasing the volume fraction of powder effectively decreases the distance between particles in a slurry, the viscosity will always increase with increasing powder fraction. For dilute suspensions (< 10 v% solids), the relative viscosity ($\eta_r$) for laminar
flow is linearly related to the volume fraction of powder \( V_{pd} \) via the Einstein equation [29]:

\[
\eta_r = \frac{\eta_s}{\eta_l} = 1 + 2.5V_{pd}
\]  
(3.4)

Where \( \eta_s \) is the viscosity of the slurry and \( \eta_l \) is the viscosity of the liquid carrier.

For slurries with over 10% solids like those used in this work, the Dougherty-Kreiger equation [33] is used:

\[
\eta_r = \left[ 1 - \frac{V_{pd}}{V_{cr}} \right]^{-K_H V_{cr}}
\]  
(3.5)

where \( V_{cr} \) is the critical volume fraction of powder at which flow is limited and \( K_H \) is a factor dependent of the powder shape. \( K_H \) equals 2.5 for spherical particles but increases as the particles become less isometric because rotation of anisometric particles produces a larger effective hydrodynamic volume than an isometric particle of the same volume [29].

To characterize the viscosity and its dependence on the powder fraction, four different slurries were made varying the percent solids (20, 30, 40 and 49 v%). The viscosity (measured with a Brookfield cup/cone viscometer) of the solvent/dispersent mixture, \( \eta_l \), was around 1 cP. The viscosity increased to 4 cP after adding 20 v% powder (i.e \( \eta_r = 4 \)). At 30 v% powder the viscosity doubled to 8 cP (i.e \( \eta_r = 8 \)) and at 40 v%, increase to 43 cP (i.e \( \eta_r = 43 \)). With 49 v% powder the viscosity of the slurry was 90 cP (i.e \( \eta_r = 90 \)). The relative viscosities were plotted versus the volume fraction of powder in figure 3.12. Using the Dougherty-Kreiger model for viscosity the \( V_{cr} \) and \( K_H \) were estimated to be 0.6 and 5.0 respectively. The high \( K_H \) value was anticipated given that the shape of the powder was not spherical.
Figure 3.12 Relative viscosity of alumina slurry versus volume fraction of particles. The line through the data is a best fit of the Dougherty-Kreiger equation ($V_{cr} = 0.6$ and $K_H = 5.0$).

3.4.2 Permeability

The permeability of the fiber bundle will naturally be a function of the packing density. The well-known Kozeny-Carman equation describing permeability of a granular medium as a function of packing density is [34]:

$$k = \frac{p^3}{5(1 - p)^2} \left( \frac{V_p}{S_p} \right)^2$$  \hspace{1cm} (3.6)

Where $p$ is the pore fraction or one minus the packing density. The ratio of the pore volume, $V_p$, to pore surface area, $S_p$, is known as the hydraulic radius [35].

A number of researchers have noted deficiencies in using the Kozeny-Carman relationship to describe permeability through unidirectional fiber mats [36,37]. Specifically,
Kozeny-Carman does not predict the extreme differences between axial versus normal permeability. Assuming a square array of fibers, Gerbart [36] found that the permeability normal to the fiber direction, $k_n$, was:

$$k_n = \frac{16 r_f^2}{9 \pi \sqrt{2}} \left( \frac{V_{f,\text{max}}}{(1-P)} - 1 \right)^{\frac{5}{2}}$$  \(3.7\)

Where $V_{f,\text{max}}$ is the maximum packing density achieved when the fibers touch; equivalent to $\pi/4$ for a square array; $r_f$ is the filament radius. He also determined the permeability parallel to the fiber direction, $k_p$, as a function of pore fraction:

$$k_p = \frac{r_f^2 P^3}{7 (1-P)^2}$$  \(3.8\)

The differences between normal and axial permeability are shown in a plot of the log of the relative permeability, $k/r_f^2$, versus pore fraction (see figure 3.13). In addition the graph also shows the strong dependence of permeability on pore fraction; note the permeability increases 2 orders of magnitude by increasing to pore fraction from 0.5 to 0.9. For the purpose of these calculations the packing density was assumed to be 0.34 ($P=0.66$). This packing density was the measured filament volume fraction for the final process conditions. From equation (3.7), the permeability normal to the fiber direction is approximately $10^{-12}$ m$^2$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 3.13 Relative permeability, $k/r_f^2$, versus pore fraction for both normal, equation (3.7) and parallel, equation (3.8), to the fiber direction.

3.4.3 Pressure Drop

Since, no external pressure was applied to the slurry, the change in pressure over the length, $l$, will only be a function of gravitational and capillary forces. The pressure drop due to gravity is:

$$\Delta P_g = -\rho_s g h \quad (3.9)$$

and will remain constant since the slurry is continually replenished from the top in both the horizontal and vertical processes. Assuming the density of the slurry, $\rho_s$, is 2.4 g/cm$^3$, gravitational acceleration, $g$, is 9.8 m$^2$/s and the height, $h$, of the slurry above the tow is 300 μm, equation (3.9) gives $\Delta P_g = -7$ Pa.
3.4.3.1 Capillary Force

Capillary forces arise because of the pressure gradient across a curved surface [38]. For example, consider a spherical liquid drop surrounded by a vapor phase as shown in figure 3.14. The pressure drop across the solid/vapor interface is defined as the pressure on the concave side, $P_{\text{cave}}$, minus the pressure on the convex side, $P_{\text{ves}}$, or $P_l - P_v$. Laplace [38] determined the pressure drop was the product of the surface tension of the liquid, $\gamma_{lv}$, and the curvature, $\kappa$:

$$\Delta P_c = \kappa \gamma_{lv}$$ (3.10)

In general for any surface, $\kappa$ is locally equal to $1/r_1 + 1/r_2$ where $r_1$ and $r_2$ are the radii of curvatures (see figure 3.15). For a sphere $\kappa$ is $2/r$ where $r$ is the radius. Therefore for a spherical drop, equation (3.10) can be rewritten as

$$\Delta P_c = \frac{2\gamma_{lv}}{r}$$ (3.11)

![Figure 3.14 Two dimensional representation of a liquid drop surrounded by a vapor phase.](image)
Figure 3.15 Schematic of a curved surface element as defined by the radii of curvature, $r_1$ and $r_2$

If liquid is placed in a glass capillary tube and the contact angle is less than $\pi/2$, then radius of curvature of the wetting liquid will be opposite that of a drop of water (i.e. convex). This means that the pressure in the liquid will be lower than the pressure of the vapor. The radius of curvature for the meniscus, $r_m$, can be related to the radius of the tube, $r_c$, and the contact angle, $\theta$, via (see figure 3.16).

$$r_m = \frac{r_c}{\cos \theta}$$ \hspace{1cm} (3.12)

The curvature of the meniscus would be $2/r_m$ and equation (3.10) becomes:

$$\Delta P_c = \frac{2\gamma_{lv}\cos \theta}{r_c}$$ \hspace{1cm} (3.13)
The capillary force acting parallel to the tube then is $\pi r_c^2 \Delta P$ or $2\pi r_c \gamma_{lv} \cos \theta$. The direction of this force is from the low to high pressure side. When $\theta$ is less than $\pi/2$, the liquid is pulled up the tube. As the liquid rises, gravitational forces resist the capillary forces. At equilibrium, the forces are balanced:

$$2\pi r_c^2 \gamma_{lv} \cos \theta = \rho_l g \pi r_c^2 h$$  \hspace{1cm} (3.14)

and rearranging for $h$ gives:

$$h = \frac{2 \gamma_{lv} \cos \theta}{\rho_l g r_c}$$  \hspace{1cm} (3.15)

Figure 3.16 Schematic of a small capillary tube inserted into a wetting liquid. The rise of the liquid is a result of a pressure difference across the curved liquid surface.
For infiltration of a liquid into a porous body, the capillary radius is replaced by the hydraulic radius, $V_P/S_p$, and the capillary pressure becomes [35]:

$$\Delta P_c = \frac{2\gamma_s S_p \cos \theta}{V_p} \quad (3.16)$$

where $\gamma_s$ is the surface energy (tension). The hydraulic radius represents the size of the flow channel or the radius of curvature of the meniscus. The hydraulic radius can be related to density terms and the relative surface area of the solid phase, $S_d (m^2/g)$ [35]

$$\frac{V_p}{S_p} = \frac{1 - \rho_r r}{S_d \rho_s \rho_r} \quad (3.17)$$

Where $\rho_s$ is the density of the solid and $\rho_r$ is the relative density of the fiber mat. For a unidirectional fiber mat with a packing density of 34%, $S_d = 2/\rho_r r_f$ and $V_p/S_p$ is approximately $r_f$.

Estimation of the capillary pressure requires knowledge of the surface tension of the slurry and the contact angle neither of which are known. However, since the slurry/air interface is essentially a solvent/air interface, it can be assumed that the surface tension of the slurry is similar to the surface tension of the solvent ($\gamma_s \approx 0.025 \text{ J/m}^2$). Also since the alumina powder is highly loaded and well dispersed within the solvent (i.e. the solvent readily wets the alumina powder), it was assumed that the contact angle was small and that $\cos \theta$ is on the order of 1. With these assumptions the capillary pressure was calculated to be around 8300 Pa which is much greater than gravitational pressure.

The infiltration time can now be estimated using equation (3.2). For a 49 vol% solids slurry, $\eta$ was 90 cP or 0.09 Pa-s. The length, $l$, over which infiltration occurred was 150 $\mu$m. The permeability of the fibers normal to the filament direction, $k$, was predicted to be $10^{-12} \text{ m}^2$ and the pressure drop, $\Delta P$, was calculated as 8300 Pa (gravitational pressure can
be ignored. With these values, the predicted infiltration time is approximately 0.1 second. Since the total length of the horizontal tube was about 8 cm and the line speed was 30 cm/min., the fiber tow was submerged in the slurry for about 15 seconds. Therefore, full infiltration occurred very close to the entrance of the tube and the observed central voids were not due to lack of infiltration.

In view of these calculations, the final process (described later) used a higher line speed (114 cm./min) and a slurry with a viscosity of 0.3 Pa-s. Although the filaments were submerged for 4 seconds, infiltration still occurred in 0.5 seconds; very close to the tube entrance. In reality, the filaments of the tow are loosely packed as they enter the slurry which creates a distribution of packing densities. This will tend to decrease the capillary pressure but increase permeability. As mentioned previously, the permeability increases two orders of magnitude as the pore fraction increases from 0.5 to 0.9.

3.5 Drying

The above calculations indicate that full infiltration will occur soon after the filament tow enters the slurry. Therefore, the formation of the large center voids observed in figures 3.9 and 3.10 must occur during drying; a result of drying shrinkage. Drying is the extraction or removal of the liquid component of a slip or slurry after casting and consists of three basic stages which are related to the rate liquid is removed [29,35,40-43]. Figure 3.17 is a schematic showing how the drying rate changes with liquid content. At the highest liquid content, the drying rate is constant, and stage I is subsequently referred to as the constant rate period. At a critical liquid content, the drying rate begins to decrease and the first falling rate period begins (stage II). At a second critical liquid content, the slope becomes steeper and drying enters the second falling rate period (stage III). The slope changes are indicative of changes in the drying mechanism.
Depending on the initial percent solids in the slurry, shrinkage must occur as liquid volume is removed. The majority of drying shrinkage occurs during the constant rate period where the solid particles flow more easily. The critical moisture content can also be thought of as a critical particle packing density; a packing structure so dense as to resist the forces of shrinkage. The critical particle packing density for the powder used in this work was estimated from the Dougherty-Kreiger model to be 0.6 (see figure 3.12).

![Diagram showing drying rate during different drying stages of slurry casting compared to drying shrinkage](image)

**Figure 3.17** Drying rate during the different drying stages of slurry casting compared to drying shrinkage [44]

The structure of a powder slurry at various stages of uniform drying is shown in figure 3.18 [29]. During the constant rate period, the drying rate is controlled by evaporation of the liquid at the surface. The liquid surface is the only surface exposed to air. As liquid is removed from the surface, capillary forces pull internal liquid to the surface. This removal and rearrangement of liquid results in the observed shrinkage during the constant
rate period. The critical moisture content or packing density is represented in figure 3.18b where a thin coating of liquid still covers all the powder (i.e. the surface is still entirely liquid/air interface).

At the start of the first falling rate period or funicular state (figure 3.18c), the liquid begins to recede into the porous structure exposing solid/air interface. Drying continues to be controlled by the evaporation of liquid at the surface, but the percentage of liquid surface is decreasing. Capillary forces are still the dominant mechanism for liquid flow to the surface. However, since shrinkage due to particle rearrangement no longer occurs, the removal of liquid volume at the surface must be accommodated by gas pocket formation [40,41]. Eventually as more liquid is removed and replaced by gas, the evaporation front moves inward and liquid becomes isolated around the powder contacts (see figure 3.18d). In the second falling rate period or pendular state, the drying rate is controlled by vapor diffusion from the internal porous structure to the surface.

Figure 3.18 Structure during the stages of slurry drying: a) as-cast structure - constant rate period; b) structure at the end of the constant rate period - shrinkage has ended; c) first falling rate period; d) second falling rate period.
3.5.1 Composite Structure after Drying

In the case of slurry drying, the volume of the slurry changes by the removal of internal fluid to the external drying surface via capillary pressure resulting in the movement of the slurry/air interface toward the center (i.e. shrinkage). Obviously, removal of fluid closest to the surface occurs first or in other words the volume change initiates at the surface and propagates inward. As the particle packing density increases the resistance to shrinkage increases, and when the particles reach a critical packing density, shrinkage ends. The first falling rate period which is still controlled by capillary pressure then begins.

During the drying of the alumina composites, capillary pressure due to the filament-to-filament spacing will keep the slurry/air interface at the surface of the fiber bundle. Now, consider one extreme where the fiber bundle is a rigid structure and resists any shrinkage. The evaporation surface or slurry/air interface would then be stationary. Since the volume change due to evaporation could not be accommodated by an inward motion of the slurry/air interface, the volume change must occur via an increase in the particle packing density near the surface (stage 1). Eventually, the particle packing at the surface will reach a critical value, \( V_{cr} \), and subsequent volume shrinkage of the slurry occurs as the growth of a granular solid layer (stage 2). A schematic of stage 1 and 2 are shown in figure 3.19. Also note that as the particle packing density increases at the surface the capillary forces increase; the capillary forces which were initially controlled by the pore size between fibers become controlled by the pore size between particle. The larger capillary forces in the granular solid layer will drive solvent to the surface for evaporation while the capillary forces within the fiber bundle drive the slurry to the granular solid/slurry interface.
As drying proceeds, the total volume of the rigid structure will not change. This means shrinkage of the slurry must be accommodated by void formation at the center of the bundle. Initially the atmosphere of the void will be a vacuum which will counteract the capillary pressure at the surface. Eventually a crack will likely form in the drying CMC to allow atmospheric pressure to fill the void and eliminate the vacuum back-pressure (see figure 3.9). This is somewhat analogous to the entry suction described by Ceaglske and Hougen [40] for the first falling rate period.

Figure 3.19 Drying of a composite fiber: a) stage 1 - initial increase in packing density near the slurry/air interface prior to reaching a critical packing density, $V_{cr}$ b) stage 2 - development of a granular solid layer; the particle packing with this layer is $V_{cr}$.

As the second extreme assume that the bundle will easily deform as the slurry shrinks. The evaporation of the solvent would continue to occur at the surface of the CMC, and the volume change would be accommodated by the inward motion of this surface. No void
formation would be expected in this case, however, the packing density of the filaments would increase.

In reality, the drying of the composite fiber lay somewhere in between these two extremes though it appears to be closer to the rigid case. It was shown in section 3.3 that as the percent solids decreased, the packing density of the filaments increased from 34% to 47%. This indicated the fiber bundle was somewhat pliable. However, the slurry also collected around the perimeter of the composite fiber leaving a large area of the void which indicated a more rigid bundle. The resistance of the bundle to significant shrinkage is attributed to misalignment and filament cross-over in the bundle. These defects cause filament bending and limit filament rearrangement. It is suggested that processing steps which would increase the filament packing density would also decrease the propensity for the shrinkage voids. A potential processing step might be to apply a radial pressure to the composite fiber during drying.

3.6 Fiber Shaping

It was hypothesized that the drying shrinkage voids could be reduced or eliminated by increasing the volume of slurry removed from the exit orifice or decreasing the filament packing density. Increasing the volume of slurry for a given exit orifice should result in less shrinkage since more powder is removed from the horizontal tube for a constant filament cross section. On the other hand decreasing the filament packing density will increase the bundle pliability and allow more shrinkage at the perimeter of the fiber.

To develop a qualitative understanding of the physics controlling the behavior at the exit orifice, consider an analogous problem of a single fiber moving out of a liquid bath at a velocity, \( v \) (figure 3.20) to create a stable coating of thickness, \( h_c \). Viscous or frictional
forces between the moving fiber and the liquid will pull the liquid out of the bath. In contrast, capillary forces will create a negative pressure within the dynamic meniscus which tends to pull the liquid back. In their review of this problem, de Ryck and Quéré [39] related the coating thickness to the liquid viscosity, \( \eta \), the surface tension, \( \gamma_{lv} \), the fiber velocity, \( v_f \), and radius, \( r_f \):

\[
h_c \propto r_f \left( \frac{\eta v_f}{\gamma_{lv}} \right)^{2/3}
\]

(3.18)

This relationship indicates an increase in viscosity or velocity and a decrease in surface tension will increase the coating thickness which would be analogous to an increase in volume of slurry removed from the glass tube in figure 3.6.

Consider now that the fiber is moving through an orifice whose diameter is only slightly greater than the fiber. The effect of the orifice would be to decrease the length of the dynamic meniscus which would subsequently decrease the coating thickness or analogously the volume of slurry. The coating thickness would increase as the diameter of the orifice increased with equation (3.18) representing the asymptotic behavior at large diameters.
3.7 Experiment: varying slurry viscosity

To increase the amount of slurry being removed from the glass tube, the viscosity of a 49 v% slurry was increased by adding small amounts of polyvinyl butyral (PVB) resin. Referring to equation (3.18), the volume of slurry removed from the glass tube should increase as the viscosity increases. The viscosity of the beginning slurry was 90 cP (recipe in section 3.2). After the addition of 1 g PVB to 150 ml of slurry, the viscosity increased to 130 cP, and after 2 g to 240 cP.

A micrograph of a cross section of a composite fiber fabricated with the 240 cP slurry is shown in figure 3.21. While voids were still present, their shape was more circular.
Figure 3.21 Cross section of an alumina composite fiber fabricated with a slurry that contained 49 v% powder and had a viscosity of 240 cP. Shrinkage voids were still observed.

3.8 Experiment: final processing parameters

In an effort to further increase the volume of slurry entrained in the fiber tow while exiting the horizontal glass tube, the exit orifice diameter and line speed were increased keeping the volume percent solids and the viscosity constant (49 v%, 250-300 cP). Initially only the exit orifice diameter was increased keeping the line speed at 30 cm/min. However at this line speed, slurry began to dry and accumulate around the exit orifice. Occasionally, portions of the dried slurry would detach creating a large bulge in the composite fiber. This resulted from significant drying within the dynamic meniscus. By increasing the line speed to 114 cm/min, the drying process was moved away from the dynamic meniscus, thus avoiding the accumulation of dried slurry around the exit orifice.
The microstructure of the cross sectional area of the composite fiber is shown in figure 3.22. While a few voids within the matrix remained, the vast majority of the filaments are surrounded by the desired porous alumina. Filament separation was also accomplished since few filament clusters were observed. The average cross sectional area of the alumina composite fiber (125000 ± 2000 μm²) was measured from SEM micrographs using MOCHA image analysis software. The cross sectional area of the filament was determined by dividing the linear density of the Nextel™ 610 (0.167 g/m) by the density of alumina (3.9 g/cm³). The area of the filaments were approximately 43000 μm² which translated to a filament volume fraction of 0.34 in the alumina composite fiber.

The final processing parameters were as follows: slurry solids ~ 49 v%, slurry viscosity ~ 250-300 cP (65 ml TCE/ethanol, 5 ml phosphate ester, 270 g Al₂O₃ and 1-2 g PVB), exit orifice ~ 380 μm, line speed ~ 114 cm./min. The subsequent mechanical testing described in chapter 7 was performed on alumina composite fiber fabricated with this process and subsequently in-line sintered.
Figure 3.22 Microstructure of alumina composite fiber fabricated with the final processing parameters: slurry - 49 v% powder, slurry viscosity - 250-300 cP, fiber shaping diameter - 380 µm, line speed - 114 cm/min.
It should be noted that the final composite fiber had a relatively low volume fraction of filaments, 0.34. If a subsequent metal matrix composite were made with 60 vol% of these composite fibers, it would contain only 20 vol% of the filaments. These composite fibers therefore have a very low stiffening potential. However, if the goal is to create a toughened ceramic material (i.e. create a CMC), the low volume fraction of filaments may not be as detrimental.

3.9 Sintering

After drying, the alumina composite was subjected to the in-line sintering process described in section 3.2. Sintering is the process which describes the lowering of the Gibbs free energy of a porous material via elimination of high energy surfaces. To understand the key attributes of this process, consider two neutrally charged spherical particles which are separated and in a state of equilibrium (i.e. there is no driving force for motion or shape change). When these particles come in contact, equilibrium is lost. A magnification of the contact area or neck gives insight into the sudden change to a non-equilibrium state (see figure 3.23). Within the contact area, two surfaces have been converted to a grain boundary with a subsequent lowering of energy equivalent to \(2\gamma_{sv} - \gamma_g\); where \(\gamma_{sv}\) is the surface energy and \(\gamma_g\) is the grain boundary energy (J/m\(^2\)). The curvature of the solid/vapor interface at the neck creates a pressure drop which acts as the driving force for the growth of the contact region similar to the capillary phenomenon discussed in section 3.4.3.1. The deformation processes which react to these forces in solids are diffusional [45]. As the neck grows more surface area is converted to internal interfaces with a subsequent decrease in energy. The new equilibrium state will occur when the surface area is minimized (i.e. when only a single spherical particle remains).
3.9.1 Mechanisms of sintering

Swinkel and Ashby [46] have defined four stages of sintering. Stage 0 corresponds to the initial contact between spheres or wires. Stage 1 corresponds to growth of the contact area or neck via diffusional mechanisms. Stages 2 and 3 correspond to the final densification stage for wires and spheres, respectively. For stage 2 (wires), the pores can be treated as cylinders while for stage 3 (spheres), the pores are isolated (stage 3).

The diffusional mechanisms of sintering are shown in figure 3.23. All mechanisms can contribute to the growth of the neck but only mechanisms with internal sources of atoms (or conversely internal sinks of vacancies) can contribute to densification. Mechanism 1, surface diffusion from a surface source, is often the dominant mechanism of neck growth during stage 1 [46,47]. At higher temperatures and longer times, boundary diffusion from an internal source (mechanism 4) can also be significant in stage 1 [46]. Two other mechanisms that only contribute to neck growth are mechanism 2, lattice diffusion from a surface source and mechanism 3, evaporation-deposition from a surface source. Mechanisms that also contribute to densification are lattice diffusion from a boundary source (mechanism 5) and lattice diffusion from a dislocation source (mechanism 6).
a) Diffusional pathways at particle contact  

b) Neck geometry

Figure 3.23 The mechanisms of diffusional sintering [46]: a = particle radius, x = neck radius and y = shrinkage.

The models describing the effect of each mechanism on the growth rate of the neck were collected and in some cases modified by Swinkel and Ashby [46]. They related the growth rate of the neck, $\dot{x}$, between two spheres to the flow rate ($\dot{V}_i$, m$^3$/s) of each mechanism via:

$$
\dot{x} = \frac{1}{2\pi x \theta \rho} \sum_{i=1}^{6} \dot{V}_i
$$

(3.19)

The linear shrinkage rate, $\dot{y}$, was:

$$
\dot{y} = \frac{1}{\pi x^2} \sum_{i=4}^{6} \dot{V}_i
$$

(3.20)
The equations for each mechanism are given in the appendix.

3.9.2 In-Line Sintering

The in-line sintering (ILS) process as described in section 3.2 is a short heat treatment (= 1 min.) at temperatures range from 1100 to 1450 °C. The extent of particle-to-particle sintering as a function of sintering temperature was first characterized on fracture surfaces of the alumina composite fibers. SEM micrographs of these fracture surfaces for ILS @ 1100 °C and ILS @ 1450 °C are shown in figure 3.24. Arrows in the micrographs point out intact and fractured necks. The structures seem very similar, and it is obvious that even after sintering at 1450 °C, the structure is essentially still granular. The pore structure is open and the particles have retained their shape.

A quantitative measure of the extent of sintering versus heat treatment temperature was accomplished by measuring linear shrinkage and the change in surface area. Matrix pellets were fabricated for these measurements using a procedure described in Chapter 4. The density of the pellets was determined by directly measuring mass and volume. The initial relative density was 62% which compared well with the calculated density of the matrix in the composite fibers. The diameter of the as-cast pellets, \( L_i \), was 4 mm and linear shrinkage was defined as \( \Delta L/L_i \). The change in pellet diameter was measured using calipers. The surface area was measured on a Micromeritics Gemini II 2370 which utilizes the BET gas absorption technique. The surface area measurements on the as-received powder were consistent with that reported by the manufacturer.

Pellets were in-line sintered (ILS) similar to the composite fibers. One difference was that a slow burn-out stage at approximately 600 °C was done prior to the in-line sintering; stresses involved in a fast burn-out caused pellet cracking. 600 °C is well below the temperature required for significant sintering of alumina [45]. The linear shrinkage as a func-
tion of the sintering temperature is plotted in figure 3.25 while the surface area reduction is plotted in figure 3.26. The linear shrinkage corresponded to an increase in relative density from 0.62 to 0.64. The data corresponding to the graphs is given in Table 3.2.

Figure 3.24 Fracture surfaces of the porous matrix after a) ILS @ 1100 °C, b) ILS @ 1450 °C: necks and neck fractures are pointed out with arrows.
Figure 3.25 Shrinkage of porous matrix versus in-line sintering temperature.

Figure 3.26 Reduction of surface area as a function of in-line sintering temperature.
Table 3.2: Data for figures 3.25 and 3.26

<table>
<thead>
<tr>
<th>ILS Temperature (°C)</th>
<th>Diameter (mm)</th>
<th>( \Delta L/L_i )</th>
<th>Surface Area (m²/g)</th>
<th>( \Delta S/S_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>4.00</td>
<td>0.0</td>
<td>4.39</td>
<td>0.0</td>
</tr>
<tr>
<td>1100</td>
<td>3.995</td>
<td>0.00125</td>
<td>4.23</td>
<td>0.036</td>
</tr>
<tr>
<td>1200</td>
<td>3.985</td>
<td>0.00375</td>
<td>4.18</td>
<td>0.048</td>
</tr>
<tr>
<td>1300</td>
<td>3.98</td>
<td>0.005</td>
<td>3.89</td>
<td>0.114</td>
</tr>
<tr>
<td>1400</td>
<td>3.97</td>
<td>0.0075</td>
<td>3.61</td>
<td>0.178</td>
</tr>
<tr>
<td>1450</td>
<td>3.955</td>
<td>0.01125</td>
<td>3.53</td>
<td>0.196</td>
</tr>
</tbody>
</table>

The micrographs in figure 3.24 show that the matrix is still in the initial stage of sintering (stage 1). The porosity is open and particle-to-particle necks are visible. It is during this stage that the two sphere model of sintering is most applicable [45,46]. Exner and Petzow [48] related the linear shrinkage of the two sphere model to the ratio of the neck radius to the particle radius \( (x/a) \) assuming only densification mechanism were active.

\[
\frac{\Delta L}{L_i} = \frac{1}{4} \left( \frac{x}{a} \right)^2
\]  

(3.21)

This relationship tends to underestimate the shrinkage of 2D and 3D powder compacts [45] but seems to be a good approximation when the shrinkage is less than 10% [48].

The reduction in surface area of a loose powder compact can also be related to the neck size using the geometric model [49,50]:

\[
\frac{\Delta S}{S_i} \equiv \left( \frac{x}{a} \right)^2
\]  

(3.22)
In a real powder compact not all the surface area reduction occurs because of neck growth. Some reduction occurs due to powder shape changes (sharp corners become rounded, etc.).

By rearranging equations (3.21) and (3.22), the data in Table 3.2 can be used to predict the normalize neck radius, \( x/a \). The predictions for \( x/a \) are given in Table 3.3. The model relating surface area reduction to \( x/a \) predicts significantly higher neck radii then the model for linear shrinkage which assumes only densification mechanisms. Therefore, non-densifying mechanisms must be contributing to neck growth.

### Table 3.3: Predictions of the normalized neck radius

<table>
<thead>
<tr>
<th>ILS Temperature (°C)</th>
<th>( \Delta L/L_i )</th>
<th>( x/a = 2(\Delta L/L_i)^{1/2} )</th>
<th>( \Delta S/S_o )</th>
<th>( x/a = (\Delta S/S_o)^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1100</td>
<td>0.00125</td>
<td>0.071</td>
<td>0.036</td>
<td>0.19</td>
</tr>
<tr>
<td>1200</td>
<td>0.00375</td>
<td>0.12</td>
<td>0.048</td>
<td>0.22</td>
</tr>
<tr>
<td>1300</td>
<td>0.005</td>
<td>0.14</td>
<td>0.114</td>
<td>0.34</td>
</tr>
<tr>
<td>1400</td>
<td>0.0075</td>
<td>0.17</td>
<td>0.178</td>
<td>0.42</td>
</tr>
<tr>
<td>1450</td>
<td>0.01125</td>
<td>0.21</td>
<td>0.196</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The fact that both densifying and non-densifying mechanisms are active is further highlighted when plotting \( \Delta S/S_i \) versus \( \Delta L/L_i \) (see figure 3.27). Combining equations (3.21) and (3.22) gives a relationship between the reduction in surface area and the linear...
shrinkage assuming that only densifying mechanisms contribute to the surface area reduction:

\[
\frac{\Delta S}{S_i} = 4 \left( \frac{\Delta L}{L_i} \right)
\]  

Equation (3.23) is plotted in figure 3.27 along with the data from Table 3.2 and Hillman and German [51]. If only non-densifying mechanisms were active, the linear shrinkage would remain zero while the surface area decreased (i.e. the curve would follow the y-axis). The current results and those of Hillman and German fall in between the ordinate and equation (3.23) again indicating both densifying and non-densifying mechanisms are contributing to neck growth.

![Figure 3.27 Surface area reduction versus linear shrinkage](image_url)
As an aside, it was somewhat surprising that the current results corresponded so well
the those of Hillman and German. It is well know that the initial relative density and par-
ticle size significantly affect sintering [45]. However, the powder size, powder packing
and heat cycle for the two sets of data were very different. Hillman and German did con-
stant ramp rate experiments to temperatures between 950 and 1600 °C on alumina comp-
pacts with a relative density of 0.32. The mean particle size was 0.06 μm. The current
results were from essentially isothermal heat treatments between 1100 and 1450 °C. The
mean particle size was around 0.7 μm and the relative density was 0.60. The similarities
between the two very different compacts further indicate that the samples are well within
the initial stage of sintering where the physics of the two-sphere model dominate the
behavior. It also indicates that the same mechanisms controlled the sintering process.

The contribution of each mechanism during sintering can be determined by dividing
the neck growth rate for an individual mechanism, \( \dot{x}_i \), by the total growth rate, \( \dot{x} \) (refer to
equation (3.19)) [46].

Using the flow rate equations defined in the appendix, the two dominating mecha-
nisms were determined to be mechanism 1 (non-densifying; surface diffusion from a sur-
face source) and mechanism 4 (densifying; grain boundary diffusion from a boundary
source). The contribution of each source as a function of neck size and temperature is
shown in figure 3.28. Mechanism 1 dominates the neck growth but mechanism 4 becomes
more significant as the temperature increases which corroborates Hillman and German's
conclusions.

The above discussion has considered the effects of sintering on only the porous matrix.
A number of researchers have shown that large solid inclusions will decrease the densifi-
cation rate during sintering of alumina [52,53]. The linear shrinkage in the composite
fibers will therefore be less than the observed shrinkage in the matrix pellet experiments. However, it is uncertain to what extent.

Figure 3.28 Contribution of surface diffusion and grain boundary diffusion versus the non-dimensional neck size

3.10 Summary

Two different processes were developed to fabricate a composite fiber consisting of alumina filaments and a porous alumina binder. The porous binder was introduced into a single Nextel™ 610 tow by a slurry casting process. It was determined that the slurry fully infiltrated the filaments in less than one second. The resistance of the filaments to drying shrinkage was identified as the cause of matrix voids within the composite fiber. These matrix voids were especially prevalent with the lower percent solids slurries. A
process was developed which largely eliminated these matrix voids, but the filament packing density was lowered to 0.34 during process optimization. Filament clusters were minimized so that the sintering phenomenon controlling the properties will be either particle-to-particle or particle-to-filament (Chapter 7). The extent of particle-to-particle sintering was characterized and found to be well within stage 1 sintering. The dominant sintering mechanism was identified as surface diffusion from a surface source. The measured linear shrinkage corresponded to an increase in relative density from 0.62 to 0.64. The results and discussion of filament-to-filament sintering and grain growth are presented in chapters 5 and 6.
CHAPTER 4  Testing Procedures

Test procedures have been developed to measure the mechanical response of the alumina composite fiber and its constituents. These include procedures for measuring the strength distribution of single filaments, saving the single filament fracture surfaces and measuring the stress/strain response of filament bundles and alumina composite fibers. In addition procedures were developed to measure the bend strength of the porous alumina matrix and the properties of a dense alumina/porous alumina interface.

4.1 Tensile Testing Apparatus

Tensile loads of the alumina single filaments, filament bundles and composite fibers were measured on an ATS 1100 series testing machine with a 22.7 kg load cell (10% capacity for the single filament tests; precision ± 0.5 g) and a cross head speed of 2.5 mm/min. The stress was calculated as the load divided by the initial area, and the strain was directly measured in only the filament bundle and composite fiber tests with an OPTRA 3000 laser extensometer. The filament (43000 μm²) area was calculated by dividing the linear density of the Nextel™ 610 tow (0.167 g/m) by the density of alumina (3.9 g/cm³). The cross sectional area of the alumina composite fiber was measured from
micrographs take on a JOEL 840 scanning electron microscope (SEM). The area of the composite fiber varied depending on processing conditions but was 125000 ± 2000 \( \mu \text{m}^2 \) for the fibers fabricated for mechanical testing. A schematic of how strain was measured for the filament bundles and composite fibers is shown in figure 4.1.

![Figure 4.1 Schematic of measurement of strain for the filament bundles and composite fibers. Axial strain was measured directly with an OPTRA 3000 laser extensometer.](image)

4.2 Single Filament Testing

A procedure was developed to measure single filament strength which produced comparable results to 3M [56]. Wilson found their procedure gave better results than ASTM-3379-75 [56]. This new procedure was developed to in order to use standard "rubber" faced grips from ATS. The procedure is as follows. Two pieces of masking tape were
placed on the underside of a glass slide; keeping the edges perpendicular to the glass slide and 25 mm apart. A strip of paper was placed on the tape, connecting them. A single filament was randomly removed from a desized tow and placed over both pieces of tape parallel to the paper strip. Few filaments failed during their removal from the bundle. Another small piece of tape was then placed over the filament. The mounted filament was carefully removed from the glass slide, and the remaining tape folded over such that it also covered the filament (see figure 4.2). The strip of paper was used to easily place the filament into "rubber" face grips. The taped area being placed within the grips and the paper was cut prior to testing.

![Diagram of filament mounting](image)

**Figure 4.2 Schematic for mounting single filaments prior to testing. a) During the mounting procedure, b) Just prior to testing.**

Capturing the single filament fracture surfaces is quite difficult. Typically the filament does not remain in the gauge length because the energy released at failure causes secondary fracture [56]. To dampen the elastic wave propagation of fracture and thus save the fracture surface, the filament was tested while imbedded in petroleum jelly. This was done by applying petroleum jelly to a 30 mm long piece of paper. The mounted single filament was then placed over the coated paper, slightly overlapping the paper onto the
masking tape grip. The petroleum jelly caused the paper to adhere to the masking tape. The mounted filaments were then put into “rubber” face grips avoiding any grip contact with the petroleum jelly-coated paper so that only the filament can carry load. A test was accepted as valid only when failure occurred within the gauge length (approximately 90% of the time). The filaments were then cleaned with ethanol and heat treated in a 25 mm long furnace at ~ 700 °C for 1 minute to burn of any remaining petroleum jelly (see Fig. 4.3).

The fracture initiation site and filament diameter were characterized in a JOEL 840 SEM and a Field Emission Gun Zeiss SEM. The filaments diameters were measured on a portion of the filament mounted lengthwise instead of from the actual fracture surface. It has been reported by Wilson [14] and verified by the author that the filament diameter does not vary measurably over a length of approximately 6 inches. Therefore the diameter measured at some distance from the fracture surface can be considered the actual filament diameter. Also since the magnification on an SEM may be off by 5% or more, a photo of a calibration grid was taken and a correction factor determined. During testing, each filament was numbered to insure the measured diameters were correctly matched with the measure failure loads thus giving an accurate strength measurement.

Some tests were performed without saving the fracture surfaces. In these tests the mounted filaments were directly put into the rubber face grips. Alignment at both 0° and 90° were checked by sight against a reference. The average strength of the as-received filaments corresponded well with 3M results from the same fiber lot [14].
4.3 Bundle Testing

To accurately measure bundle properties, the filaments in the bundle must be aligned and evenly loaded. A number of bundle testing techniques have been develop with varying degrees of success. In one technique desized tows were sandwiched between paper tabs with hot glue. The results were significantly lower than the ideal bundle model predictions [9] which would indicate a non-uniform loading of filaments possibly due to lack of infiltration of the hot glue into the bundle or severe misalignment. In another technique, a lubricant was used to manually align the loose filaments and then held in place with thermo-retractable tubes [142]. The number of initially loaded filament was determined to be 70% of the total which indicates 30% of the filaments were misaligned. He and Clark [143] tested Nextel 610 with the polymer sizing still intact. Their claim was that the infiltration and evaporation of the alcohol/polymer solution acted to self align the filaments via capillary forces. They found that only 10% of the filaments were misaligned and the modulus determined from the bundle stress/filament stress curves was around 360 GPa.

The technique used in this work was similar to that of He and Clark except that the polymer sizing was removed within the gauge length. Prior to testing, the Nextel™ 610 tows were resized in the high rate, vertical process shown in figure 3.7; the alumina slurry was replaced with a PVB/methanol solution. These resized bundles were heat treated in the in-line sintering process and again resized after the sintering furnace before being wound onto the spool. Once the tows had been in-line sintered and resized in an approximate cylindrical shape, they were cut into 13 cm specimens. The specimens were then put into a 25 mm burnout furnace (see figure 4.3); the center of the specimens were in the center of the furnace. It was determined beforehand that the temperature within the furnace
was between 600 to 700 °C. The organics within the furnace burned out leaving a 22 to 25 mm gauge length of only fiber and some residual deposits.

![Burnout furnace for cleaning filament fracture surfaces and for removing organics with the gauge length for bundle testing.](image)

**Figure 4.3** Burnout furnace for cleaning filament fracture surfaces and for removing organics with the gauge length for bundle testing.

The mounting procedures for the filament bundles is as follows (see figure 4.4). Step 1 - A small amount of epoxy was put on the top and bottom of one side of a paper tab with a 50 mm gauge length. The two part epoxy used was made by Devcon. Step 2 - The tow was placed on the epoxy so that the 25 mm gauge length was in the middle of the 50 mm gauge length of the paper tab. The tow should be straight within the tab and the epoxy should completely cover the tow before the second paper tab is placed on top. Graph paper was underneath the paper tab as a reference for aligning the bundle or composite fiber. Step 3 - The second tab was placed onto the first to "sandwich" the tow between the paper tabs. Step 4 - Excess epoxy was then applied over the tow within the gauge length of the paper tabs creating a 25 mm gauge length. The epoxy must mix well with the epoxy between the tabs. This should be done on a flat surface and the epoxy should not stick to the surface. This way after drying, the sample may be removed. The non-stick surface used in this work was polypropalene sheet. Step 5 - Depending on how the surface of the
bundle or single tow CMC reflects the laser, a laser “flag” may be necessary. The tow was “flagged” with another drop of glue. These “flags” are used to increase the reflection of the laser spots. The tow should be lying flush against a surface so that when the glue dries one side will be flat and a portion of the tow is still visible.

![Figure 4.4 Schematic showing the various steps in mounting the bundles and composite fibers. The laser tags were not always necessary.](image)

When saving the fracture surfaces for defect identification, the bundle was infiltrated with petroleum jelly before testing. Also, when a significant number of filaments (= 50) failed near the grips, the test was considered invalid. The gauge length region is shown in figure 4.5. On average the burned out gauge length was 22 mm compared to the 25 mm gauge length of the Optra laser extensometer. Sizing was left on a portion of the filament within the 25 mm gauge length so that the epoxy used for the laser “flags” did not infiltrate the bundle avoiding potential stress concentrations. The error was determined by
comparing the predicted failure strains of an ideal bundle at the two different gauge lengths using equation (2.24) \( (\sigma_o = 3.37 \text{ GPa}, m = 11, L_o = 25 \text{ mm}) \). This error was less than 1\% and can be ignored.

![Region of Burnout](image)

"Flag" for Laser

Laser Spot

**Figure 4.5** Detailed schematic of the gauge length when measuring the stress/strain response of filament bundles.

### 4.4 Composite Fiber Testing

The testing of the alumina composite fibers was similar to the testing of the bundles. Testing was performed with and without a polymer sizing. The polymer sizing helped constrain the filaments during failure and saved important fracture features. The mounting procedures were identical to those of the bundles. The sized samples were used to measure the stiffness of the composite fibers since the sizing modulus is negligible and the surface reflected the laser well enough that a "flag" was not necessary. Composite fiber strength was measured on samples with the sizing removed. Cyclic tests were also performed on desized composite fibers, and a gold coating was applied before testing to increase reflection.
4.5 **Matrix Bend Strength**

As an alternative to measuring the tensile strength of the porous matrix alone the bend strength was measured in 3-point bending. The bend strength will be greater than the tensile strength because the volume of material in tension is less in bending versus a uniaxial tensile test. In the 3-point bending of a cylinder, the maximum tensile stress is actually at a single point [28] compared to a tensile test which has a uniform applied stress over the entire volume. The load was measured on an ATS 1100 with a 22.7 kg load cell; cross head speed = 2.5 mm/min. A schematic of the 3-point bend test is shown in figure 4.6 along with the equation for calculating the maximum tensile stress [28].

\[
\sigma = \frac{8P_l L}{\pi D^3}
\]

\(P_l\) = Fracture Force  
\(D\) = 4 mm  
\(L\) = 12.7 mm

**Figure 4.6 Schematic of the 3-point bend test.** The stress, \(\sigma\), is the maximum stress on the tensile side of the sample directly below the point where the load is applied.

The apparatus used to make the matrix only pellets for bend testing is shown in figure 4.7a. The principle of the system was to force the drying surface to the bottom of the quartz tube by applying a vacuum. All the shrinkage was accommodated by the movement of the top surface down. The pellets were pushed out of the quartz tube and heat treated in the in-line sintering process. Although the mass of the pellets was significantly
larger that the composite fibers, once the pellets entered the hot zone the color of the pellets was within a few second the same as the hot zone. In addition since the surface of a cylinder is heated faster then the interior and the maximum stress in bending is on the surface, the in-line sintering of the pellets was considered to be close to that of the composite fibers. No abnormally large voids were observed after testing. The change in diameter was measure with calipers and the surface area was measured with a Micromeritics Gemini II 2370 surface area analyzer which used the multi-point BET method.

Figure 4.7 a) Apparatus for fabricating matrix only pellets; b) Plug and alumina rod inserted into the casted slurry when fabricating specimens for push-out testing

4.6 Fiber/Matrix Interface Properties

The interface properties in composite materials can be measured either by a pull-out or push-out test. Pullout tests have generally been performed with 140 \( \mu \text{m} \) filaments in vari-
ous matrices [128,166]. Because of the small diameter of the filaments (\(\approx 10 \, \mu m\)), special specimen preparation and test apparatus are required to perform a pullout test with these fibers. The most critical issue being alignment of the filament while applying a tensile load. Pushout testing has therefore been much more prevalent in the literature [128-131]. However, the small diameter of the filaments typically used in ceramic composites also make pushout testing very difficult. To circumvent this problem of scale, Mackin and Zok developed a fiber bundle pushout test [167]. In this technique a small layer of matrix was chemically etched away leaving the filaments protruding. A large diameter (100 \(\mu m\)) push-rod then pushed on multiple filaments and an average response is measured. Since, both the matrix and filaments in the composite fiber are alumina, there was no way to chemically etch one without etching the other. Therefore an alternative pushout technique was developed to measure the debond strength and sliding resistance of a dense alumina/porous alumina interface.

The sample used in this technique consisted of a 0.79 mm alumina rod imbedded in a porous alumina matrix. The samples were fabricated similar to the matrix-only pellets. After pouring slurry into a quartz tube as shown in figure 4.7a, a plug was placed into the tube and an alumina rod inserted into the slurry (see figure 4.7b). The rational for substituting an alumina rod for the alumina filament was that both could be considered flat surfaces compared to the alumina powder. The filament curvature \((1/r_f; \, r_f = 6 \, \mu m)\) is only 5% the average curvature of the powder \((2/r_p; \, r_p = 0.5 \, \mu m)\) while the curvature of the rod \((1/r_r; \, r_r = 395 \, \mu m)\) is about 0.1%. Because curvatures of the filament and rod are similar compared to the powder, the powder packing characteristics at the fiber/matrix interface should be essentially independent of pushrod diameter [159].

The push-out specimens were heat treated in the in-line sintering process with the quartz tube intact. The sample was left in the quartz tube because the alumina rod made
removal difficult. However, the dense quartz tube more significantly affected the temperature profile compared to the matrix pellets sintered for the bend tests. The rod/matrix interface was also in the center of the sample and therefore heated at the lowest rate. Thus, the sintering in these pushout samples was somewhat less than in the matrix pellets and alumina composite fibers. The effect of this on the interpretation of the results will be discussed in Chapter 7.

The debond strength and sliding resistance were determined from load/displacement curves measured on an ATS 1100 (22.7 kg load cell) with a cross head speed of 2.5 mm/min. The debond strength was determined by dividing the peak load by the total interface area. Similarly the sliding resistance was the initial load after the load drop divided by the total interface area. The sample and apparatus are shown in figure 4.8. Since, the average specimen thickness, t, was about 6 mm, the ratio, t/h, was around 4 and the effects of bending could be ignored [132].

![Push-out specimen and apparatus](image-url)

**Figure 4.8** Push-out specimen and apparatus
CHAPTER 5  Single Filament
Mechanical Behavior

Ceramic fibers are defect-sensitive and exhibit a statistical distribution of strengths. This chapter investigates the strengths of single filaments removed from alumina bundles after they had undergone in-line sintering. It will be shown that in-line sintering above 1200 °C resulted in a loss of filament strength. A fractographic analysis indicated that while the filament strengths fitted a Weibull distribution, the flaw population was not of a single type. In all eight different types of defects were identified. The distribution of defects among these types changed as the in-line sintering temperature increased. Grain growth also occurred during the heat treatments and its important role in determining the strength will also be discussed.

5.1 Filament Strengths

“Dry” Nextel™ 610 alumina tows were resized in the shape of the alumina composite fibers and in-line sintered at temperatures ranging from 1100 to 1450 °C. Single filaments were removed from these heat treated bundles and tested in tension using the procedures
described in section 4.2. The filament strengths were calculated from the measured failure loads and filament diameters. The Weibull parameters were determined using the single gauge length technique described in section 2.1.5. Since all the mechanical testing was performed at a gauge length of 25 mm, this technique will give the most accurate results.

At least 45 single filament tests were performed on the as-received, ILS 1300, 1400 and 1450 °C samples. The probability of failure for these samples (using equation (2.21)) is plotted versus stress in figure 5.1. The solid lines represents the Weibull distribution, equation (2.20), with the corresponding Weibull parameters in Table 5.1.

The Weibull modulus was found by plotting $\ln(\ln(1/(1-P_f))$ versus $\ln(\sigma_f)$ which gives $m$ as the slope (see figure 5.2). The reference stress is the stress at $P_f = 0.63$. The Weibull modulus appears to go through a minimum while the reference stress decreased as the aging temperature increased. Fractographic analysis discussed later will show that the initial decrease in Weibull modulus with in-line sintering temperature correlated to greater variations in the average defect strength (see Table 5.3) and that the subsequent increase back to $m = 11$ (or narrowing of the distribution) also correlated with the shift to the dominance of a weld-line defect (a remnant of filament-to-filament sintering).

After heat treating at 1100 and 1200 °C, there was only a slight decrease in reference stress followed by a 0.2 to 0.3 GPa decrease at 1300, 1350 and 1400 °C. At 1450 °C the reference stress decreased almost 1 GPa. Wilson [56] recently reported on the strength distribution of Nextel 610™ using the single gauge length technique described in section 2.1.5. He determined the Weibull modulus of the as-received filaments to be 11.5 and reported that the average strength varied between 3.0 and 3.5 GPa. This compares well to the results of this work for the as-received filaments.
Figure 5.1 Cumulative probability function, $P_f$, for Nextel 610™.

Figure 5.2 Plot of $\ln(\ln(1/(1-P_f)))$ versus $\ln(\sigma_f)$. The Weibull modulus is the slope of these curves. Note the strength distribution is shifting left as the sintering temperature increases.
Table 5.1: The Effect of In-Line Sintering on Nextel 610™: Filament Strength Parameters and Grain Size

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Weibull Reference Stress (GPa)</th>
<th>Weibull Modulus</th>
<th>Average Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>3.37</td>
<td>11.0</td>
<td>65 ± 6</td>
</tr>
<tr>
<td>ILS 1100 °C</td>
<td>3.30</td>
<td>7.1</td>
<td>69 ± 7</td>
</tr>
<tr>
<td>ILS 1200 °C</td>
<td>3.30</td>
<td>7.0</td>
<td>69 ± 8</td>
</tr>
<tr>
<td>ILS 1300 °C</td>
<td>3.09</td>
<td>7.0</td>
<td>75 ± 8</td>
</tr>
<tr>
<td>ILS 1350 °C</td>
<td>3.10</td>
<td>8.1</td>
<td>78 ± 9</td>
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<tr>
<td>ILS 1400 °C</td>
<td>3.00</td>
<td>9.0</td>
<td>91 ± 11</td>
</tr>
<tr>
<td>ILS 1450 °C</td>
<td>2.51</td>
<td>11.0</td>
<td>100 ± 15</td>
</tr>
</tbody>
</table>

5.1.1 Grain Size

The grain size was measured from etched filament surfaces using a line intercept method. The as-received filaments were chemically etched in boiling phosphoric acid for 45 sec. while the in-line sintering heat treatments caused thermal etching. The grain size was observed to increase as the in-line sintering temperature increased (see Table 5.1 and figure 5.3). The initial, average grain size was measured to be 65 nm. After essentially a one minute heat treatment during in-line sintering at 1300, 1400 and 1450 °C, the grain size increased to 75, 91 and 100 nm respectively. The grain size distribution appears to broaden as the grain size increases similar to that reported by Goldsby and Morscher [144].
Figure 5.3 Grain structure of fiber surface after heat treating: a) As-received; b) ILS 1300 °C; c) ILS 1400 °C; d) ILS 1450 °C.

5.1.2 Fractography

The filaments were strong enough to exhibit the classic mirror, mist and hackle surface structures [54], though the boundaries between each region are difficult to distinguish. By following the river lines back to the initiation site, the defects were generally found at the
focal point of the mirror region. In all, eight different types of defects were identified as the cause of crack initiation and catastrophic failure (see figures 5.4 and 5.5).

The defect types were initially classified as either internal or surface. Three types of internal defects are shown in figure 5.4: a single spherical pore, non-spherical pores and an unidentified defect (an area of intergranular fracture or an inclusion). Five different types of surface defects were observed (see figure 5.5). One defect was non-geometric and unidentifiable, but appeared to be associated with a small area of intergranular fracture. The four other defects are geometric in nature. The weld-line defect shown in figure 5.5b was caused by filament-to-filament sintering. Figure 5.5c shows an uneven surface area that was characterized as a blister defect. A surface crack is shown in figure 5.5d, and a surface nodule associated with the crack initiation site is shown in figure 5.5e.
Figure 5.4 Fracture surfaces of single alumina filament tests; internal defects (filament strength, diameter): a) spherical pore (3.75 GPa, 11.1 μm), b) non-spherical pores (3.43 GPa, 11.6 μm), c) unidentified (3.35 GPa, 12.2 μm)
Figure 5.5 Fracture surfaces of single alumina filament tests; surface defects (filament strength, diameter): a) area of intergranular fracture (3.11 GPa, 12.5 μm), b) weld-line (2.25 GPa, 12.0 μm), c) crack (1.76 GPa, 11.9 μm), d) blister (1.91 GPa, 12.0 μm), e) nodule (3.24 GPa, 13.6 μm).
The statistical distribution of the defects is presented in Table 5.2. It can be seen that the flaw population changed with the sintering temperature. In the as-received condition, 50% of the filaments failed from a surface defect and 50% from an internal defect. A small percentage of weld-line defects indicated that filament-to-filament sintering occurred during the initial fiber production. These weld-line defects were approximately 0.3 \( \mu m \) in width and qualitatively defined as shallow; there was little evidence of grain sharing between filaments (see figure 5.6a).

As the in-line sintering temperature increased, the internal defects all but disappeared and the percentage of weld-line defects increased. The internal defects were unlikely to have been removed by the heat treatment; rather other (more severe) surface defects are thought to have been triggered before failure at an internal defect could occur. The increase in the percentage of weld-line defects was an indication of greater filament-to-filament sintering. After ILS@1450 °C, 82% of the filaments failed from a weld-line defect, the defect width had increased to 0.5 \( \mu m \) and the roughness of the weld-line increased - evidence of more grain sharing (see figure 5.6b). Also note that the weld line defect in figure 5.6b is offset from the focal point of the fracture mirror; outlined in white. The outline represents the predicted critical crack size for this filament (discussed further in section 5.2.2). This offset was observed in 90% of the filaments which failed from a weld-line defect after ILS 1450 °C. The reason for this observed offset is unknown.

The average strength of each type of defect as a function of aging temperature was determined when at least three filaments failed from that type. The strengths and standard deviations are reported in Table 5.3. Looking at only the surface unidentified and weld-line defects, the average strength of each defect decreased with increasing temperature but were essentially equivalent after each heat treatment. This suggests that the actual strength limiting mechanism may be the same for these defects. In the as-received fila-
ments, the internal spherical pore was the strongest defect while the internal non-spherical porosity was the weakest. There was more variation in strength of the defects after sintering at 1300 °C which corresponded to the decrease in Weibull modulus.

<table>
<thead>
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<th>Heat Treatment</th>
<th>SU¹</th>
<th>SW²</th>
<th>SC³</th>
<th>SN⁴</th>
<th>SB⁵</th>
<th>IU⁶</th>
<th>IP⁷</th>
<th>IPY⁸</th>
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<tbody>
<tr>
<td>As-Received</td>
<td>24%</td>
<td>17%</td>
<td>-</td>
<td>5%</td>
<td>2%</td>
<td>14%</td>
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</tr>
<tr>
<td>ILS 1300 °C</td>
<td>24%</td>
<td>15%</td>
<td>12%</td>
<td>27%</td>
<td>12%</td>
<td>-</td>
<td>-</td>
<td>10%</td>
</tr>
<tr>
<td>ILS 1400 °C</td>
<td>23%</td>
<td>33%</td>
<td>14%</td>
<td>23%</td>
<td>7%</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
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<table>
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<th>Heat Treatment</th>
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<th>SW²</th>
<th>SC³</th>
<th>SN⁴</th>
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<th>IU⁶</th>
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<td>3.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.3</td>
<td>3.5</td>
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<td></td>
<td>± 0.4</td>
<td>± 0.3</td>
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1 Surface unidentified; ² Surface weld-line; ³ Surface crack; ⁴ Surface nodule; ⁵ Surface blister; ⁶ Internal unidentified; ⁷ Internal spherical pore; ⁸ Internal non-spherical pores;
Figure 5.6 Weld-line defects in a) the as-received condition, $\sigma_f = 2.95$ GPa; b) the ILS 1450 °C condition, $\sigma_f = 2.6$ GPa; the arrows indicate the weld-line defect.
High magnification SEM micrographs in figure 5.7 showed that the cracks initiated along the grain boundaries. A spherical pore defect from an as-received fiber is shown in figure 5.7a. On the left side of the defect, a ring of intergranular failure is observed which then transitioned into a mixed transgranular-intergranular region. Figure 5.7b is a weld-line defect from an ILS 1400 °C fiber. Here a small line of surface grains have failed intergranularly while further propagation mostly occurred transgranularly.

Figure 5.7 Crack initiation from internal defects occurs along the grain boundaries:
I - intergranular fracture; T - transgranular fracture.
Two general trends observed concerning the crack propagation after nucleation were: 1) as the crack propagated away from the defect there is a transition from intergranular to mixed transgranular-intergranular and then back to intergranular fracture; 2) as the sintering temperature increased, the percent of intergranular fracture decreased. The percent of intergranular fracture (PIF) versus position from a surface defect in the as-received condition and in-line sintered at 1400 °C is shown in figure 5.8. The defect area (position 0) consists mostly of intergranular fracture which further reinforces the observation that crack nucleation occurs along grain boundaries. As the crack moved away from the defect, the percent of intergranular fracture initially decreased and then increased. Also note that the percentage of transgranular fracture around the defect increased dramatically after aging.

Fractography of two spherical pore defects further illustrates this last point (see figure 5.9). The first defect is from an as-received fiber where the majority of crack propagation occurs via grain boundaries except for a small region of mixed transgranular-intergranular fracture around the defect. This is compared to a fiber in-line sintered at 1400 °C (figure 5.9b) where a much larger area of transgranular fracture is observed. The increased intergranular fracture with distance from the defect is also evident. Reasons for these observed trends will be discussed in sections 5.2.2 and 5.2.3.
Figure 5.8 Percent intergranular fracture (PIF) versus position from a surface defect. The error bars represent the standard deviation of 3 measurements for the as-received samples and 5, for the ILS @ 1400 °C samples.
Figure 5.9 Spherical pore defects from (a) an as-received and (b) ILS 1400 °C fiber. Note that there is more transgranular fracture around the pore defect after heat treating.
5.2 DISCUSSION

In the majority of the Nextel™ 610 filaments, the crack initiation site was a geometric defect while the initial crack path was along the grain boundaries. As discussed in section 2.1.1, the strength of an alumina filament can be related to the fracture toughness, $K_{IC}$, the critical crack size, $c$, and crack geometry, $\psi$. Rewriting equation (2.12), the filament strength, $\sigma_f$, is:

$$\sigma_f = \frac{K_{IC}}{\psi \sqrt{\pi c}}$$

The following discussion will focus largely on understanding how a critical crack evolves from a natural defect, specifically understanding the relationship between the observed defects and grain size.

5.2.1 Effect of grain size on strength

As discussed in section 2.1.3, grain size has been identified as a critical parameter in controlling the strength of alumina [65-71]. In plots of mean filament strength versus the inverse square root of grain size (see figure 5.10), Orowan and Petch branches have been identified to describe the behavior of ceramics. The Orowan branch results from the critical crack size being directly proportional to grain size. Thus the slope of the Orowan branch is approximately, $K_{IC}/\psi \pi^{1/2}$ and provides a way to deduce $K_{IC}$ if $\psi$ is known. The Petch branches are insensitive to grain size and represent the behavior where extrinsic flaws such as processing or machining defects create the critical crack. The predictions of the Petch branches also use equation (2.12) ($K_{IC} = 2.75 \text{ MPa m}^{1/2}$ [59]) to predict filament strength, but the critical crack size is independent of grain size.
The mean filament strength of Nextel™ 610 measured in this work is plotted in figure 5.10 along with some previous results for Nextel™ 610 from Xu et al. [18] and results for large grain alumina from Chantikul et al. [59]. The large increase in strength of the current Nextel™ 610 compared to Xu et al. resulted from improved processing procedures after 1993 [56].

Figure 5.10 Mean filament strength verses the inverse square root of the grain size compared to Orowan-Petch plots for alumina; assuming semi-circular surface crack ($K_{IC} = 2.75$ MPa m$^{1/2}$ [59] and $\psi = 0.66$ [145,146]).

- Chantikul et al.[59]; ▲ Xu et al.[18]; ● Current results
The current and previous results of the Nextel 610\textsuperscript{TM} alumina fiber are clearly within the Petch branches where the strength is controlled by extrinsic flaws though the data has a non-zero slope. The fractography results support this observation of failure nucleating at extrinsic flaws. However, the decrease in strength with increasing grain size suggests that the defect size depended on the in-line sintering temperature. Of all the defects identified, the defect which became more prominent as the sintering temperature increased was the weld-line. There was evidence that the weld-line defect grew as the sintering temperature increased. The mean width of the weld-line after aging at 1450 °C was 0.5 \( \mu \text{m} \) compared to 0.3 \( \mu \text{m} \) in the as-received filaments. Assuming no subcritical cracking, the width of the weld-line should correspond to the dimension \( 2b \) in the semi-circular crack (figure 5.10). The mean filament strength after aging at 1450 °C was around 2.3 GPa and the critical crack size, \( c \), was calculated as 1 \( \mu \text{m} \) using equation (2.18). Assuming \( b/c=1 \), \( 2b \) would be 2 \( \mu \text{m} \) which is four times the measured weld-line width.

There are two reasons why the predicted critical crack is larger than the average weld-line width. First, subcritical cracking could have occurred until the crack reached the critical crack size as define by \( K_{IC} = 2.75 \text{ MPa m}^{1/2} \) \textsuperscript{[59]}. The possible reasons for this will be discussed in the next section. Second the actual intrinsic fracture toughness in Nextel\textsuperscript{TM} 610 may be lower than 2.75 MPa m\textsuperscript{1/2}. Assuming the weld-line width (0.5 \( \mu \text{m} \)) is equivalent to \( 2b \), the predicted intrinsic toughness would be 1.34 MPa m\textsuperscript{1/2}. This is within the range predicted from surface energies alone (0.9 - 1.5 MPa m\textsuperscript{1/2}; see section 2.1.1). However, Lawn \textsuperscript{[54]} has noted that the measured intrinsic fracture toughness is often greater than that predicted from surface energies alone, although fracture toughness is usually measured in long crack specimens. The following discussion on crack nucleation and subcritical cracking will assume the intrinsic toughness is that reported in the literature.
(2.75 MPa m\(^{1/2}\)) and the issue of predicted versus measured fracture toughness will be addressed again at the end.

5.2.2 Crack nucleation and subcritical crack growth

The understanding of crack nucleation and growth in Nextel\textsuperscript{TM} 610 filaments is as follows. In approximately 70% of the filaments, a sharp crack nucleated from a processing defect along the grain boundaries. In the remaining 30% of filaments, an area of intergranular fracture nucleated on the surface or internally. The crack path then transitioned to a transgranular path. Once the crack reached a critical size, it became unstable, increased velocity and transferred back to an intergranular path.

The likely source of intergranular crack nucleation from surface defects and internal pores are grain boundary grooves. Grain boundary grooves from thermal etching were observed on both external (figure 5.3b - d) and internal (figure 5.11) surfaces. Grooves were also created when separating filaments sintered together (figures 5.5b, 5.6 and 5.7b). The severity of the grooves worsened as the in-line sintering temperature increased. This was especially true for the weld-line defects (figure 5.6) which exhibited significantly more grain sharing (i.e. the weld-line became rougher) at the higher aging temperatures even though the width of the defects changed little (0.3 \(\mu\)m vs. 0.5 \(\mu\)m). As grain boundary grooves become more severe, the stress needed to nucleate a sharp crack will decrease.
Figure 5.11 Grain boundary grooves on the internal surfaces of a spherical pore after in-line sintering at 1400 °C.

Once the sharp crack nucleated, subcritical crack growth could occur. Kurchner and Gruver in a series of papers on alumina [81-84], correlated the transgranular fracture around defects to subcritical crack growth. Similar to the results of this work, they found that in weak samples a large area of transgranular fracture surrounded the critical defect while in higher strengths samples, the area of transgranular fracture was small [82]. Their theoretical calculations of the critical crack sizes were significantly larger than the observed defects, supporting the hypothesis of subcritical crack growth [82-84].

Using a similar fractography approach to determine the presence of subcritical crack growth in Nextel™ 610, the critical crack sizes were calculated for a number of filaments using equation (2.18) and assuming $K_{IC} = 2.75 \text{ MPa m}^{1/2}$ [59]. The crack was assumed to be either semi-circular ($c/b=1$) or semi-elliptical ($c/b=0.25$). A schematic of the crack geometries is shown in figure 5.12. For the semi-elliptical surface crack, the stress intensity factor is not a constant along the crack front [58]. The maximum stress intensity fac-
tor is at the surface and decreases moving inward along the crack front [58]. With this in mind, failure was assumed to occur when the stress intensity factor at the deepest point of the crack is equivalent to the fracture toughness. The geometric factor, $\psi$ has been determined for a generic semi-elliptical surface crack in a long circular cylinder under tension [145,146]: $\psi=0.66$ for $c/b=1$ and $\psi=1.0$ for $c/b=0.25$.

![Diagram of a Nextel™ 610 filament with a semi-elliptical crack](image)

**Figure 5.12 Schematic of surface crack geometries at the surface of a Nextel™ 610 filament.**

The critical crack size with a semi-circular geometry has been overlaid in white for two as-received filaments (figure 5.13). In the high strength filament, a crack initiated at an internal, non-spherical pore near the surface. Since the defect was so close to the surface it was assumed to be a semi-circular surface crack. The calculated critical crack size was $c=0.5 \, \mu m$ and matches quite well the observed defect size. This is evidence that $K_{IC} = 2.75 \, \text{MPa m}^{-1/2}$ is a reasonable assumption. For the lower strength filament, the predicted crack size was $c=0.7 \, \mu m$. In this lower strength filament, the observed defect was a surface nodule. A crack likely initiated in the surface nodule at a low stress subsequently propagating into the filament. Therefore the crack must have grown subcritically to the
critical size. Similar observations of subcritical cracking were seen for other defects in low strength filaments. For example, the critical crack size around the weld-line defect in figure 5.6b was 0.8 \( \mu \text{m} \). It is outlined in white to show how much larger it is compared to the observed defect. A series of filament fractures with the critical crack size outlined are shown in the appendix (section A.2).

When assuming the crack is semi-elliptical where \( c/b=0.25 \), the predicted critical crack depth, \( c \), will be less than the semi-circular. For example, when considering the filament shown in figure 5.13b, the predicted crack depth, \( c \), was 0.3 \( \mu \text{m} \). However, the crack length on the fiber surface, \( 2b \), was 2.4 \( \mu \text{m} \). The areas of both the semi-circular and semi-elliptical cracks for this filament were about 200 times that of the average area of a grain (grain size \( \approx 60 \) nm). It seems unlikely that prior to testing such a large defect would be present around what appears to be a dissimilar material on the filament surface, supporting the hypothesis of subcritical cracking.

The question remains as to the mechanism of the subcritical cracking. As discussed in Chapter 2, subcritical cracking can occur when residual stresses contribute to the stress at the crack tip or when the material exhibits a rising T-curve. One mechanism often associated with subcritical cracking in alumina results from environmental attack at the crack tip [77]. This attack lowers the intrinsic toughness of the material at the crack tip creating the rising T-Curve necessary for subcritical cracking. When environmentally assisted subcritical cracking occurs, strain-rate effects are expected [79,78] (i.e strength is expected to increase with increasing strain-rate). These strain rate effects result from the rate dependence of the environmental attack (see section 2.1.4). Filament strength was measured as a function of strain-rate (room humidity, 40-50%), and the results are plotted in figure 5.14. There was no observed effect of strain rate on strength, thus the environmental mechanism can be excluded as a possibility.
a) $\sigma_f = 3.42$ GPa; $c = 0.5$ $\mu$m

b) $\sigma_f = 2.79$ GPa; $c = 0.7$ $\mu$m

Figure 5.13 Crack initiation sites for two as-received filaments; a) internal non-spherical defect $\sigma_f = 3.43$ GPa b) surface nodule defect $\sigma_f = 2.79$ GPa.
Figure 5.14 Average filament strength versus strain-rate for filaments removed from bundle sintered at 1450 °C.

Subcritical cracking can also occur when in the presence of residual stresses [54,85]. These residual stresses arise from anisotropy of the coefficient of thermal expansion [54] or elastic anisotropy between grains [86]. To better understand the effects of thermal expansion and elastic anisotropy stresses, first consider the stress intensity around the crack tip due to only the applied stress. The stress ahead to the crack-tip can be related to the applied stress intensity factor, $K_I$ (mode I), via [58].

$$\sigma_z = \frac{K_I}{\sqrt{2\pi y}} f(\theta)$$

(5.1)

where $K_I$ is $\psi \sigma_A \sqrt{\pi c}$ (see section 2.1), $y$ is the radial distance from the crack tip and $f(\theta)$ is a function of the angle, $\theta$, from the crack plane: $f(\theta) = \cos(\theta/2)[1+\sin(\theta/2)\sin(3\theta/2)]$, $f(0^0) = 1$. The intersection of $\sigma_z$ and $\sigma_A$ is the boundary of the intensified stress and is rep-
resented in figure 5.15 by the distance, $y^*$, which can be determined by equating $\sigma_z$ and $\sigma_A$ and solving for $y$ in equation (5.1).

![Graph showing the relationship between $\sigma_z$ and $y$, with $\sigma_z = \frac{K_I}{\sqrt{2\pi y}}$ and $y^* = \psi^2 c/2$.

Figure 5.15 The axial stress, $\sigma_z$, along the y-direction due to the applied stress, $\sigma_A$.

Plots of $y^*$ as a function of the crack length, $c$, are shown in figure 5.16 for a semi-elliptical and semi-circular surface crack. The shaded area represents the average grain size of the as-received and in-line sintered Nextel™ 610 filaments. For crack sizes within this shaded area and below, the region of stress enhancement is contained within single grains. For the semi-elliptical crack, this corresponds to crack lengths less than 0.2 $\mu$m. Similarly for the semi-circular crack, the crack length can be as much as 0.5 $\mu$m before the stress intensity encompasses multiple grains. Since these crack lengths are similar to the predicted critical crack size, the initial crack growth must be affected by the stress state within single grains.
Figure 5.16 The stress intensity depth as a function of crack length for a semi-elliptical \((c/b=1.0)\) and a semi-circular \((c/b=0.25)\) surface crack. The shaded area represent the average grain size of the as-received and in-line sintered filaments.

The residual stresses within a 100 nm grain due to thermal expansion and elastic anisotropy will be small. The predicted thermal stress in 100 nm grain size alumina is about 100 MPa [72] and the effect of elastic anisotropy has been shown to be less than the thermal expansion anisotropy [147]. However, there is a very strong dependence of the residual thermal stresses on grain size in the 60 to 100 nm grain size range [72]. Although these stresses are not large, an increase in residual thermal stresses with grain size could help explain the trends of lower strength and greater subcritical cracking with increasing grain size.

Another potential cause of the subcritical cracking is grain bridging which causes rising T-curve behavior in alumina [54,59]. Chantikul et al. [59] predicted rising T-curves
for alumina with grain sizes varying from 2.5 to 80 μm. As the grain size decreased, the region of T-curve behavior decreased. Whereas the 80 μm alumina exhibited a rising T-curve at crack sizes on the order of 10 to 20 times the grain size, the rising T-curve in the 2.5 μm alumina occurred over crack sizes 1 to 3 times the grain size. Since the grain size in the Nextel™ 610 was less than 0.1 μm, the grain bridging affect will likely be small but cannot be entirely discounted.

An alternative explanation may be related to the differences between the predicted and measured intrinsic toughness, $T_o$, of alumina. The predicted $T_o$ is a function of only the energy required to create new surfaces and is between 0.9 and 1.5 MPa√m (section 2.1.1). In contrast, the measured $T_o$ is between 2.5 and 3 MPa√m [54,59,60,64] and was assumed to be 2.75 MPa√m for the calculations of the critical crack size. Since the measurements of $T_o$ were made on samples with relatively long cracks compared to this work, there may be a scaling effect on the intrinsic toughness. The resistance to crack growth over the first few hundred nanometers may only be surface generation (i.e. $T_o = 0.9$ to 1.5 MPa√m). Then as the crack grows, other mechanisms such as heat generation [63] or additional fracture surface area from meandering cracks through grain boundaries or ledges may cause the intrinsic toughness to increase. The effect could create a rising T-curve as the crack grows from microstructural scale defects.

The observed subcritical cracking may result from number of different mechanisms that can not be discounted. The first is from thermal residual stresses between grain which result from anisotropy of the CTE. Second, grain bridging effects may cause a rising T-curve during the initial crack propagation. A rising T-curve may also occur if the intrinsic fracture toughness of very short cracks (50-200 nm) is only a function of surface energies while at larger crack sizes the intrinsic fracture toughness is closer to that reported in the literature.
5.2.3 Catastrophic Crack Growth

Catastrophic or unstable crack growth occurs when the crack extends past the critical crack size as defined by equation (2.18). The crack velocity increases rapidly until it reaches a final terminal velocity [54]. The terminal velocity has been predicted to be approximately 0.4ν_l where ν_l is speed of a longitudinal sound wave [54]. In addition, the region of stress enhancement ahead of the crack-tip as defined by ν^∗ increases. It is during catastrophic crack growth that the mist and hackle surface structures form on the fracture surfaces.

The mist and hackle surface structures are a result of crack branching. Crack branching dissipates excess kinetic energy via the creation of additional fracture surfaces [54]. One possible explanation of how crack branching occurs, first proposed by Yoffe [148], is that the stress field around the crack tip distorts as the velocity of the crack increases. In particular, calculations by Erdogan [149] indicated that as the velocity increases the maximum local tensile stress moved from the plane perpendicular (θ=0°) to as much as 50-70° from perpendicular. In addition as the crack size increases, ν^∗ will encompass more and more grains and subsequently their grain boundaries. The transition from the maximum tensile stress being at θ=0° to θ=50-70° and the addition of more grain boundaries in the stress enhanced region would help explain the transition back to intergranular fracture as the distance from the defect increases (figure 5.8).

Grain size may also have some effect on crack path. Using qualitative observations of the crack path in the as-received and ILS 1400 °C filaments with the same strength, it appeared that more transgranular fracture occurred in the heat treated filaments. Since the filaments strengths were equivalent, the crack velocity as a function of distance from the defect would be approximately equivalent meaning grain size likely has some effect on the crack path.
5.2.4 Fracture Mirror Analysis

The empirical relationship between the fracture mirror boundary and fracture stress was described in section 2.1.2. A generalized relationship can be written as:

\[ \sigma_u r_j^q = A_j \]  \hspace{1cm} (5.2)

where \( \sigma_u \) is the fracture stress, \( r_j \) is the mirror boundary distance, \( A_j \) is the mirror constant and \( q \) is 1/2. Taking the natural logarithm of both sides of equation (5.2) and rearranging gives:

\[ \ln \sigma_u = \ln A_j - q \ln r_j \]  \hspace{1cm} (5.3)

The distances from the flaw to a subjective mirror-mist boundary were measured in filaments with a known fracture stress for the as-received and ILS @ 1300, 1400 and 1450 °C conditions. The measurements were made along the perimeter of the filament. The natural log of the measured fracture stress was plotted versus the natural log of the measured mirror boundary distances and a best fit line was used to determine the mirror constant and to confirm that \( q \) was 1/2 (see section A.3). In the as-received filaments, \( q \) was 0.47 and the mirror constant, 6.4 MPa m\(^{1/2}\). As the in-line sintering temperature increased, \( q \) increased to as much as 0.78, and the mirror constant decreased to 0.14 MPa m\(^{1/2}\). The values of \( q \) and \( A_j \) for the four conditions are given in Table 5.4.

The deviation from \( q=1/2 \) as the in-line sintering temperature increased was likely a result of the subjective nature of the mirror boundary measurements. The mirror-mist-hackle boundaries were difficult to define in these alumina filament and might be confused with the transition from transgranular to intergranular fracture which was discussed in the previous section.
Table 5.4: Values of $q$ and $A_j$ as a function of sintering condition

<table>
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<th>Condition</th>
<th>$q$</th>
<th>$A_j$ (MPa m$^{1/2}$)</th>
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<td>as-received</td>
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<td>6.4</td>
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<tr>
<td>ILS @ 1300 °C</td>
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<td>1.2</td>
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<td>ILS @ 1400 °C</td>
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<td>0.66</td>
</tr>
<tr>
<td>ILS @ 1450 °C</td>
<td>0.78</td>
<td>0.14</td>
</tr>
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</table>

5.3 CONCLUSIONS

The strength of Nextel™ 610 alumina filaments has been found to decrease as the in-line sintering temperature increased. This was correlated with a change in the defect population and grain growth. Internal defects which were observed in the as-received filaments rarely contributed to failure after in-line sintering. Weld-line defects caused by the breaking of filament-to-filament bonds were the prevalent defect as the in-line sintering temperature increased. However, it was observed that the strength of filaments which failed from weld-line and the surface unidentified defects were essentially equivalent at all sintering temperatures. This evidence points to a microstructural feature (grain boundary grooves) playing a critical role in controlling strength.

Crack nucleation was generally found to occur at geometric defects along the grain boundaries. Since the grain boundary grooves deepened with increasing sintering temperature, the stress required to nucleate a sharp crack likely decreased with increasing sintering temperature. Subsequent subcritical cracking was observed via a fractography approach. The cause of the subcritical cracking is believed to be associated with stresses
induced from thermal anisotropy within the alumina or caused by rising T-curve behavior in the short crack regime due to a change in the intrinsic toughness with crack length or less likely grain bridging. Since the measured filament strength did not vary with strain-rate during room temperature testing (humidity, 40-50%), environmentally assisted crack growth [76-78] did not occur.
CHAPTER 6  Filament Bundle
Mechanical Behavior

The stress/strain response of oxide composites is based in part on the mechanical behavior of the filament bundles [116,133]. In this chapter the mechanical properties of the Nextel™ 610 fiber tow are characterized as a function of in-line sintering temperature. These measurements are compared to the ideal bundle response which is based on the single filament measurements. However, the ideal bundle response overpredicts the failure stress and strain of the Nextel™ 610 when significant filament-to-filament sintering occurs. This result was attributed to the fact that the filaments remain bonded until failure. In these bonded filament clusters, individual filaments were found to no longer act independent of neighboring filaments (an assumption in the ideal bundle model). The filament-to-filament weld was also found to create an enhanced stress state around the contact area. Subsequent modeling of these bonded filament clusters indicated that the Weibull parameters determined from the single filament tests could not describe the strength distribution of the bonded filaments.
6.1 Alumina Filament Bundle Behavior

The stress-strain response of dry bundles was measured using the method described in Chapter 4, and the responses after four different sintering temperatures are plotted in figures 6.1 and 6.2. The measured bundle strength is plotted versus in-line sintering temperature in figure 6.3. The predicted response of an “ideal” bundle (see section 2.1.6) whose individual filaments were characterized in Chapter 5 is shown in these figures for comparison and will be discussed later. The testing was performed under constant crosshead displacement conditions. This did not allow the capture of the response during unstable failure, and so the predicted response is only shown to the failure strain.

The difference between the predicted and measured bundle strengths in the as-received state was less then 10%, but increased dramatically after in-line sintering above 1300 °C. The Young’s modulus was unaffected by in-line sintering, and the average modulus measured from all the tests was 355 ± 25 GPa. This was slightly less than the modulus reported for Nextel 610™ single filaments (380 GPa) [14].
Figure 6.1 Stress-Strain measurements and ideal bundle predictions for a) as-received alumina bundles and b) in-line sintered at 1300 °C.
Figure 6.2 Stress-Strain measurements and ideal bundle predictions for a) in-line sintered at 1400 °C and b) in-line sintered at 1450 °C.
Figure 6.3 Bundle strength of Nextel™ 610 versus in-line sintering temperature. The bundles sintered at 800 °C where considered to represent the as-received condition

6.1.1. Fractography

SEM micrographs of individual filament failures within the bundles indicated a similar change in the defect population with increasing in-line sintering temperature compared to the single filament test (see Table 6.1). In the as-received condition over 50% of the failures were due to internal defects, but after in-line sintering at 1450 °C, over 80% of the failures were due to surface weld-line defects. A comparison of Tables 5.2 and 6.1 reveals the defect population sampled in the single filament tests were essentially identical to that observed in the bundle tests for the as-received and ILS @ 1450 °C filaments. However, there were some slight differences in the defect distributions when sintering at 1300 and 1400 °C.

Although the defect populations were similar in the single filament and bundle test, the nature of the weld-line defect changed during testing in the bundle. In Chapter 5, the
weld-line defects from single filament tests were shown to be slightly offset from the focal point of the fracture mirror. In contrast, the weld-line defects from the bundle tests were at the focal point in over 90% of the filaments. This indicates that the stress state around the weld was different in the two tests. There also appeared to be a tendency for the crack to nucleate and grow at an angle to the plane perpendicular to the tensile axis (see figure 6.4).

**Table 6.1: Defect distribution; bundle tests**

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<th>SU¹</th>
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<th>SB⁵</th>
<th>IU⁶</th>
<th>IP⁷</th>
<th>IPY⁸</th>
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<td>4%</td>
<td>4%</td>
<td>7%</td>
<td>-</td>
<td>21%</td>
<td>23%</td>
<td>9%</td>
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<tr>
<td>ILS 1300 °C</td>
<td>25%</td>
<td>25%</td>
<td>2%</td>
<td>6%</td>
<td>6%</td>
<td>17%</td>
<td>15%</td>
<td>4%</td>
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</tr>
</tbody>
</table>

¹ Surface unidentified; ² Surface weld-line; ³ Surface crack; ⁴ Surface nodule; ⁵ Surface blister; ⁶ Internal unidentified; ⁷ Internal spherical pore; ⁸ Internal non-spherical pores;

![Figure 6.4](image) _Example of a fracture surface from a bundle test which failed from crack initiation at the weld-line._

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Filament clusters consisting of two, three and four filaments were also observed (see figure 6.5). If filament failure was independent of neighboring filaments, the probability that a filament would fail within a diameter of its neighbor is equal to the filament diameter (12 μm) divided by the gauge length (2.54 cm): $5 \times 10^{-4}$. Similarly, the probability of a three filament cluster would be $2 \times 10^{-7}$, and for a four filament cluster, $10^{-10}$. Therefore, the observations of the filaments clusters implies that bonded filament are not independent but rather are dependent on neighboring filaments. The welded filaments will transfer load from a broken filament directly to neighboring filaments. Therefore the global load sharing assumption will not be valid for filaments clusters and the cluster will likely fail when the weakest filament within the cluster fails.
Figure 6.5 Failure of filament clusters from ILS 1450 °C. Note the fracture of the filament clusters occur on or near the same plane.
6.1.2. Filament Cluster Characterization

To characterize the extent of clustering, the distribution of clusters was measured from the polished cross section of sintered bundles. The multifilament clusters were counted from SEM micrographs of the cross section of a bundle. The number of single filaments was then determined by subtracting the total number of filaments in clusters from the average number of filaments in a bundle (396). The average cluster distribution from three cross sections at each temperature are shown in Table 6.2. As the in-line sintering temperature increased, the number of filament not in a cluster decreased and the number of large filament clusters increased. It is also interesting to note that even as-received bundles have a few small filament clusters which have also been observed at 3M [14].

Table 6.2: Filament Cluster Distribution

<table>
<thead>
<tr>
<th>In-Line Sinter</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>10</th>
<th>13</th>
<th>14</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Received</td>
<td>383</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300 °C</td>
<td>368</td>
<td>9</td>
<td>2</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400 °C</td>
<td>309</td>
<td>17</td>
<td>7</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>.3</td>
<td>.3</td>
<td>.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1450 °C</td>
<td>254</td>
<td>16</td>
<td>11</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>.3</td>
<td>.3</td>
<td>1</td>
<td>.3</td>
<td></td>
</tr>
</tbody>
</table>
The fractography results indicated over 80% of the filaments failed from weld-line defects after in-line sintering at 1450 °C whereas we would have expected only 35% from the 2-D cluster distribution measurements. This discrepancy indicates the filaments must not be bonded over their entire length. A direct observation of a diminishing filament-to-filament bond is shown in figure 6.6. Both the width and depth of the weld-line defect decrease moving from left to right in the micrograph.

![Image of weld-line defect](image)

Figure 6.6 weld-line defect on a filament removed from a bundle heat treated at 1450 °C. The width and depth of the weld-line defect decrease from left to right indicating the filaments were not bonded over their entire length.

6.2 Ideal Bundle Modeling

The measured stress-strain response for the bundles in-line sintered at or below 1300°C exhibited only slightly less than predicted stiffness and strength (see figures 6.1-6.3). The measurements also captured the predicted non-linear behavior near the ultimate
strength due to individual filament fracture. At 1400 and 1450 °C, the ideal bundle model overpredicted the stress and strain at failure (figure 6.2).

The ideal bundle models assumes that a “large” (> 200 [92]) number of independent, perfectly aligned filaments are uniformly loaded. Global load sharing is also assumed (i.e. when a filament fails, its load is evenly distributed among the remaining unbroken filaments). Also, the filament strengths measured by single filament tests are assumed to be representative of the filament strengths within the bundles. Rewriting equation (2.23), the ideal bundle stress/strain response is:

$$\sigma_b = E_f e^{\exp \left( -\frac{L}{L_o} \left( \frac{E_f}{\sigma_o} \right)^m \right)}$$

where $\sigma_o$, $m$ and $L_o$ are the Weibull parameters determined from the single filament tests.

In the following sections, the assumptions of the ideal bundle model will be scrutinized to discuss the causes of the slight differences between theory and experiment for in-line sintering below 1300 °C and the overprediction of the bundle behavior above 1300 °C. The effect of filament ends within the gauge length, fiber slack and misalignment on the predicted response of bundle in-line sintered below 1300 °C will be discussed. The effect of filament clustering (via filament-to-filament sintering) which occurs mostly after sintering above 1300 °C will also be discussed.

6.3 Non-ideal Bundle Modeling: Filament Ends

Incomplete filaments whose ends are within the gauge length carry no load. This effectively decreases the modulus and potential strength of the bundles. The bundle stress
can be modeled by multiplying the ideal bundle model by one minus the volume fraction of filament ends, $V_{fe}$:

$$
\sigma_b = (1 - V_{fe})E_f \varepsilon \exp\left(-\frac{L}{L_0}\left(\frac{E_f}{\sigma_0}\right)^m\right)
$$

(6.1)

The product of $(1-V_{fe})$ times $E_f$ is the effective bundle modulus. For an effective modulus of 355 GPa, $V_{fe}$ is predicted to be 0.07. Therefore 7% of the filaments would need to be broken within a 25 mm gauge length to explain the differences between the ideal bundle model and the measurements. Given there are approximately 400 filament in a bundle, 7% corresponds to 28 filaments. Since the total length of the filaments within the bundle is 400*25mm, the predicted average breaks per length would be 2.8 breaks/m. According to the manufacturer [14], 2.8 breaks/m is unreasonably high. It is likely to be no more than 0.7 breaks/m. Therefore, the filament ends can not alone explain the slight differences between theory and experiment.

### 6.4 Non-ideal Bundle Modeling: Fiber Slack

Another potential cause for the differences between theory and experiment below 1300 °C is fiber slack. Fiber slack results from variations in filament length over a given bundle gauge length (see figure 3.2). During the straining of a bundle, shorter filaments will be loaded first followed by the longer filaments. This creates a bundle whose filaments have a distribution of strains.
In the early 70's, Phoenix [150] developed a generalized bundle model to consider a bundle with a distribution of strains. The Phoenix approach was to calculate the expected value of the bundle stress:

$$\sigma_b = \sum_{i}^{n} V_i \int_{0}^{\varepsilon_b} E_f \varepsilon (1 - P_f(\varepsilon)) g(\varepsilon) d\varepsilon$$  \hspace{1cm} (6.2)$$

Where \(i\) represent a fiber type; \(n\) is the total number of fiber types; \(\varepsilon_b\) is the bundle strain and \(g(\varepsilon)\) is the probability density function describing the distribution of strains. The integral term is the expected value for the bundle stress of the fiber type, \(i\).

First a fiber slack parameter, \(\Theta\), is defined for each filament, \(j\), of type, \(i\):

$$\Theta = \frac{l_j - l_o}{l_o}$$  \hspace{1cm} (6.3)$$

where \(l_j\) is the total length of an individual filament and \(l_o\) is the initial length of the bundle. By assuming that a filament carries no load when \(\varepsilon_b - \Theta < 0\) and is perfectly aligned when \(\varepsilon_b - \Theta > 0\), equation (6.2) can be rewritten as:

$$\sigma_b = \int_{0}^{\varepsilon_b} E_f (\varepsilon_b - \Theta) \exp (-\frac{L}{L_o} (\frac{E_f (\varepsilon_b - \Theta)}{\sigma_o})^m) g(\Theta) d\Theta$$  \hspace{1cm} (6.4)$$

substituting the Weibull function for the probability of failure.

If the distribution or probability density function of the fiber slack parameters, \(g(\Theta)\), is assumed to be linear as shown in figure 6.7, then the equation for \(g(\Theta)\) is:

$$g(\Theta) = \frac{2}{\Theta_{max}^2} \Theta + \frac{2}{\Theta_{max}}  \hspace{0.5cm} 0 < \Theta < \Theta_{max}$$  \hspace{1cm} (6.5)$$
Figure 6.7 Probability density (distribution) function for the fiber slack parameter

Now for $\varepsilon_b < \Theta_{max}$, the bundle stress can be calculated from equation (6.5) while for $\varepsilon_b > \Theta_{max}$, the expected bundle stress becomes:

$$\sigma_b = \int_0^{\Theta_{max}} E_f (\varepsilon_b - \Theta) \exp \left( \frac{L}{L_o} \left( \frac{E_f (\varepsilon_b - \Theta)}{\sigma_o} \right)^m \right) g(\Theta) d\Theta$$  \hspace{1cm} (6.6)

The stress-strain response of an ideal bundle compared to one with a maximum fiber slack parameter of 0.001 is shown in figure 6.8. The fiber slack model predicted that the initial Young’s modulus is significantly less than the ideal bundle. As more filaments become loaded the stiffness increases until all the filaments are loaded and the stiffness response parallels the ideal bundle. In other words, an initial non-linearity in the modulus is followed by a linear region exhibiting the same stiffness as the filaments. This type of response does not match the measured response which was linear throughout and consistently 90% of the filament modulus. Fiber slack effects can therefore be ignored.
Figure 6.8 Stress-strain response of an ideal bundle compared to one with fiber slack ($\Theta_{max}$); the Weibull parameters used were from the as-received single filaments (see Table 5.1).

6.5 Non-ideal Bundle Modeling: Misalignment

Misalignment is another mechanism that can cause a distribution in filament strains and decrease the modulus and strength. Figure 6.9 is a schematic of a filament aligned at an angle, $\phi_i$, to the axial direction of a bundle of length, $L$, that is displaced, $\Delta L$. If it is assumed that $\phi_i$ does not significantly change as the bundle is strained, then the axial strain in a misaligned filament is:

$$\varepsilon_i = \varepsilon_b \cos^2 \phi_i$$

Again using Phoenix’s model, the bundle stress for a given $\varepsilon_b$ becomes:

$$\sigma_b = \int_{\phi_o}^{\phi_{max}} E_f \varepsilon_b \cos^2 \phi_i \exp \left( \frac{L}{L_o} \left( \frac{E_f \varepsilon_b \cos^2 \phi_i}{\sigma_o} \right)^m \right) g(\phi_i) d\phi_i$$

(6.8)
Figure 6.9 A schematic showing the effect of misalignment on the axial strain of filaments.

Similar to the fiber slack model, the distribution of misalignment angles, $g(\phi_i)$, can be modeled as linear decreasing from zero to a maximum angle, $\phi_{max}$:

$$g(\phi_i) = -\frac{2}{\phi_{max}}\phi_i + \frac{2}{\phi_{max}}$$ \hspace{1cm} 0 < \phi_i < \phi_{max} \hspace{1cm} (6.9)$$

The stress strain response of an as-received Nextel\textsuperscript{TM} 610 bundle with a maximum misalignment of 30° is plotted in figure 6.10 along with the ideal bundle prediction. The predicted modulus for this misalignment distribution is 360 GPa which compares well to the measured bundle modulus. Also, unlike the fiber slack mechanism, misalignment causes a consistent percentage decrease over the entire linear elastic region. However, this distri-
bution of misalignment angles is not realistic. Warren [151] measured the misalignment angles between metal coated Nextel™ 610 filament prior to consolidation and determined that $\phi_{max}$ was no more than $6^\circ$. Using Warren's misalignment distribution, the predicted Young's modulus was 378 GPa. Therefore, misalignment in Nextel™ 610 will only contribute a part of the loss in modulus. It will be shown later that misalignment will affect the ultimate bundle strength when filaments are bonded together.

![Stress-strain response](image)

**Figure 6.10** Stress-strain response of a bundle with filament misalignment ($\phi_{max} = 30^\circ$) compared to the ideal bundle model.

Neither filament ends, fiber slack or misalignment alone can explain the small differences between the ideal bundle model and experiments. The errors must be associated with a combination of all plus possible variations in the cross-sectional area from bundle to bundle. Since the measured response is lower than the predicted response by only 10%, the Nextel™ 610 can be considered essentially ideal prior to significant filament-to-filament sintering.
6.6 Non-ideal Bundle Modeling: Filament Clustering

After in-line sintering at 1400 and 1450 °C where significant filament-to-filament sintering occurred, the ideal bundle model dramatically overpredicted the bundle strength (see figure 6.3). The fractography indicated that bonded filament clusters failed along the same plane meaning that the filaments were no longer independent. Both the generalized Phoenix bundle model and Monte Carlo simulations were used to model the effects of these bonded filament clusters. The assumptions were that a filament cluster failed at the failure stress of the weakest filament within that cluster and the filament strength distribution was described by the measured Weibull parameters from the single filament tests. Therefore the probability of failure for a cluster type \( i \) can be written:

\[
P_{fi} = 1 - \exp\left(-\frac{C_i L}{L_o} \left(\frac{E_r \varepsilon}{\sigma_o}\right)^m\right)
\]  \hspace{1cm} (6.10)

where \( C_i \) is the number of filaments in cluster type \( i \). The term \( C_i \) essentially increases the volume which to detect the weakest link, effectively increasing the probability of failure.

Substituting equation (6.10) into equation (6.2) and calculating the volume fraction of each cluster type from Table 6.2 enables a prediction of the bundle stress/strain response. The response of the cluster model compared to the ideal bundle model and measurements are shown in figures 6.11 and 6.12. The cluster model indicates that the ultimate bundle strength is lowered as clustering increases but does not fully explain the large drop in measured strength after in-line sintering at 1400 and 1450 °C.
Figure 6.11 Comparison of the ideal bundle model and measurements with a non-ideal bundle model of filament clusters using the Phoenix approach. After in-line sintering below 1300 °C, the clusters have little effect on the models.
Figure 6.12 Comparison of the ideal bundle model and measurements with a non-ideal bundle model of filament clusters using the Phoenix approach. After in-line sintering above 1300 °C, the clusters have some effect on the models, but do not fully explain the differences between theory and experiment.
Monte Carlo simulations of bundle tests were also performed to verify the accuracy of the Phoenix approach. The same assumptions were considered: 1) the filaments are perfectly aligned. 2) The strengths of the filaments follow weakest length rules and may be described by the Weibull parameters determined from single filament tests. 3) All the filaments in a cluster fail when the weakest filament fails.

To assign strengths to the 396 filaments in a bundle, a random number between 0 and 1 was generated. This number was taken to be the failure probability, $P_f$. Substituting this $P_f$ into equation (2.20), the strength of that filament was calculated and assigned. This procedure was then repeated for all the filaments. The strength of the clusters were determined by assigning a strength to each filament within the cluster, finding the lowest filament strength and then assigning this lowest strength to all the filaments within the cluster.

With these assumptions and rules for assigning filament strengths, the bundle stress/strain response was simulated using Mathematica™. For each cluster characterization in Table 6.2, two simulations were performed. The results in figure 6.13, show very good agreement between the Phoenix model and the Monte Carlo simulations. However neither model captures the large decreases in strength measured for the in-line sintering at 1400 and 1450 °C.
Figure 6.13 Monte Carlo Simulations compared to cluster modeling using the Phoenix approach. a) as-received, b) in-line sintered at 1300 °C
Figure 6.14 Monte Carlo Simulations compared to cluster modeling using the Phoenix approach. a) in-line sintered 1400 °C, b) in-line sintered at 1450 °C.
As a worst case scenario for predicting the response of the bundles sintered at 1450 °C, it was assumed that 80% of the filaments were in one cluster; 80% corresponds to the percentage of filaments observed to fail from weld-line defects. With a cluster this large, the bundle will essentially fail when the weakest filament fails.

Monte Carlo simulations were performed with the following assumptions: 1) filament strengths were characterized by the single filament tests; 2) the filament cluster fails when the weakest filament fails. The results in figure 6.15 show that this cluster model still overpredicts the measured bundle strength.

![Stress/strain response of bundles in-line sintered at 1450 °C with the monte carlo prediction of the worst case scenario (i.e. bundle fails when the weakest filament fails).](image)

Figure 6.15 Stress/strain response of bundles in-line sintered at 1450 °C with the monte carlo prediction of the worst case scenario (i.e. bundle fails when the weakest filament fails).
6.7 Discussion of Bundle Model Predictions

The evidence of filament clusters failing on essentially the same plane (figure 6.5) clearly indicates that filament failure was dependent on neighboring filaments. The global load sharing assumption being related to the assumption of independence would be invalid for filament clusters. Filament cluster modeling (section 6.3-4), which assumed the filament strengths were characterized by the single filament tests and the filament clusters failed when the weakest filament failed, did not fully explain the differences between theory and experiment. One must conclude then that the strength of filaments removed from filament clusters do not accurately describe the strength of the filaments while they are still bonded together.

An important difference between the single filament and bundle tests concerns the timing of when the filaments are torn from the clusters. In the single filament tests, the filaments were removed before testing so the roughness of the weld-line defects were created before failure. The sintering stresses were also relieved. In contrast, the filaments remained bonded during the bundle testing and the roughness of the weld-line defect was created after testing; either from the shock waves associated with failure or by manually removing the filaments.

The central issue is that when there is significant filament-to-filament sintering, the single filament tests are measuring the strength distribution of defects created by removing the filaments from the bundle. In one sense, the weld-line defects are not actually present in the bundles, and it seems obvious that the strength distribution from the single filament tests would not accurately describe the strength distribution of filaments still bonded together. However, the fact that the strength of the filaments with the artificially
created surface defect is stronger than the filaments when they remain bonded is surprising.

A consideration of the fracture surfaces will give some insight into why there may be differences in filament strength when testing single filaments versus bundles. In the single filament tests, the weld-line defects were shown to be offset from the focal point of the fracture mirror. In contrast, the bonded filaments in bundle tests exhibited different fracture features. First in over 90% of the filaments the weld-line defect was at the focal point of the fracture mirror. Second in approximately 50% of the bundle filaments which failed from a weld-line defect, the initial crack nucleation and subcritical crack growth occurred on a plane at an angle to the perpendicular (figure 6.4). These differences indicated that the stress state around the defect was significantly different in the bonded and unbonded cases.

One potential reason for the different stress state is that the sintering stresses associated with neck were relieved when creating the weld-line defect. The stress state normal to the neck area has been investigated by a number of researchers [152,153]. Zhang and Schneibel [153] showed that tensile stresses on the order of 100 MPa are present at the neck surface; a result of capillary pressure. These stresses decrease moving inward and ultimately change to compression. To the author’s knowledge, the stress state parallel to the axis of sintered fibers has not been determined. However, the fiber is under plain strain condition along this axis, and therefore some induced axial stresses are expected.

In Chapter 5 it was determined that subcritical cracking occurred. Similar to the single filaments, the bundle strength did not vary with strain rate (see figure 6.16) which eliminates environmentally assisted subcritical cracking as a mechanism. One of the suspected causes of the subcritical cracking in the single filaments was the residual stresses between grains which increased the stress intensity factor over and above the applied stress inten-
sity factor (superposition). One factor for why the bonded filaments are weaker than the unbonded filament is that the sintering stress adds to the already present residual stresses which further increases the stress intensity factor. However, these stresses should be very localized around the neck since they are a result of the curved neck surface. Therefore it seem unlikely that they would significantly affect crack growth.

![Graph showing average bundle strength versus strain rate for bundles in-line sintered at 1450 °C.](image)

Figure 6.16 Average bundle strength versus strain rate for bundles in-line sintered at 1450 °C.

Another factor which may cause a lowering of the strength of bonded filaments is induced stress around the weld-line due to its constraint of filament motion. As can be seen from figure 3.2, the filaments will not be perfectly aligned and under a tensile load will move relative to one another. It has also been shown that filaments are not sintered over their entire length and therefore relative movement is possible between bonded filaments. Finite element analysis was used to examine the how the application of tensile,
bending, shear and torsion stresses affect the stress state around the weld-line (figure 6.17). The model geometry was based on a single filament pair with a single weld-line. The results showed that the stress around the weld-line was not enhanced in simple tension, but shear stresses are induced around the weld-line in bending, shear and torsion.

![Diagram showing tension, bending, shear, and torsion](image)

**Figure 6.17** Schematic representation of a welded filament pair and the types of deformation that may occur during tensile testing.

In bending, deformation is assumed to occur only in the y-z plane, therefore, symmetry in the x-direction can be used. The model geometry is shown in figure 6.18. The filament diameter, \( d \), and half the weld-line width were assumed to be 10 \( \mu \text{m} \) and 2.5 \( \mu \text{m} \).
respectively; the length, \( l \), modeled was twice the diameter. The fiber was assumed to be linear elastic with isotropic elastic constants \((E = 380 \text{ GPa}, \nu = 0.25)\). All the nodes on the back face were constrained from displacement in the \( x \) and \( y \)-directions (i.e \( u_x = u_y = 0 \) at \( z = 0 \)). The nodes on the front face were constrained in the \( x \) and \( y \)-directions \((u_x = u_y = 0 \) at \( z = l \)). The \( y-z \) plane of symmetry was constrained in the \( x \)-direction \((u_x = 0)\). The bending was induced by applying a displacement, \( u_y = 0.526 \ \mu \text{m} \), to the nodes at the midpoint \((z = l/2)\) of both the filaments. Significant \( \tau_{yz} \) shear stresses were induced around the weld-line (figure 6.19).

![Diagram of model geometry for bending of sintered filament pairs.](image)

Figure 6.18 Model geometry for bending of sintered filament pairs.
Figure 6.19 Shear stress, $\tau_{yz}$, around the weld-line on the y-z symmetry plane (x=0) of a filament pair in bending: units - GPa

To model shear in a region where the filaments go from a bonded to an unbonded state, a segment of a single fiber ($d = 10 \, \mu m$) was used with a 0.5 $\mu m$ weld-line width; length, $l$, was 20 $\mu m$. The segment height, $h_z$, and diameter, $d_z$, were 1 $\mu m$ and 6 $\mu m$ respectively. The nodes along half the weld-line length were constrained from movement in the x, and y directions ($u_x = u_y = 0$) to represent the bonded area. The remainder of the weld-line was left unconstrained and represents the unbonded state. The nodes on the back face of the filament were constrained from motion in the x, y and z direction. On the nodes of the front face, a displacement of 0.526 $\mu m$ was applied to the -x and z directions to represent both an applied tensile and shear strain. With this model, shear stresses around the constrained to unconstrained boundary were as much as 3.0 GPa (see figure 6.21b) but remain very localized.
Figure 6.20 The finite element model used to determine the effect of relative fiber motion or shear strain in an area where the filaments move from a bonded to undonded state.
Figure 6.21 $\tau_{xy}$ around a weld-line defect loaded in tension and shear: units - GPa.

Torsion was modeled using the full fiber geometry shown in figure 6.17. The nodes on the back-face ($z=0$) were constrained from all displacement and rotation. A displacement in the $z$-direction ($u_z=0.526$) and a moment of $10^4$ N m around the $z$-axis were applied to the nodes on the front-face. The value of the applied moment ($10^4$ N-m) was arbitrary and was chosen only to show that shear stresses were induced around the weld-line. The distribution of $\tau_{xy}$ within a cross section at the midpoint of the filament pair is shown in figure 6.22. Higher shear stresses were induced around the weld-line.
Figure 6.22 Shear stress, $\tau_{xy}$, around a weld-line defect on a cross section plane. Filament pair was loaded in tension and torsion: units - GPa.

The presence of the shear stresses indicates that mixed mode failure may be occurring in the filaments that remain bonded compared to only mode I failure in the filaments removed for single filament tests. The addition of alternative modes of failure besides mode I would help explain the discrepancies between the bundle strength predictions and measurements. In a composite where the filament motion relative to one another is limited by the matrix material, one would expect the shear stresses to be less. This means that strengths of bonded filaments within a composite fiber may be greater than in a “dry” bundle.
6.8 Predictions of the Weibull Parameters for Bonded Filaments

The effect of an enhanced stress around the weld-line will be to alter the strength distribution as measured by the single filament test. Monte Carlo modeling as outlined in section 6.6 was used to get a feel for how the Weibull parameters would change for the fibers in-line sintered at 1450 °C. The Monte Carlo modeling considered the bonded filament dependent on neighboring filaments (i.e. the cluster fails when the weakest filament in the cluster fails). 80% of the filament were considered in a bonded filament cluster as indicated from the defect distributions (Table 6.1). As an upper bound, it was assumed that all bonded filaments were in 2-filament clusters. As a lower bound, the bonded filaments were considered to be in one cluster of 320 filaments (the worst case scenario). The Weibull parameters from Table 5.1 were used for the filaments not in clusters.

The predictions using both models are plotted in figure 6.23 as bundle strength versus reference stress of the clustered filaments. The models were executed with two different Weibull modulii to show that bundle strength will decrease as the Weibull modulus decreases. The shaded areas represent the variation in Weibull modulus. The horizontal line at 0.96 GPa is the measured strength of bundles heat treated at 1450 °C. Since the strength distribution of filament clusters is somewhere in between the upper and lower bounds, the reference stress of the bonded filament is likely to be in the range of 1.5 to 1.8 GPa considering that the Weibull modulus could decrease from $m = 11$. In addition, almost 40 clusters were identified in the two dimensional characterization of the cluster distribution which would indicate that the actual cluster distribution is closer to the assumption of the upper bound.
Figure 6.23 Predictions of bundle strength with varying Weibull parameters using the monte carlo method.

6.9 Conclusions

The strength of the Nextel™ 610 alumina tow decreased as the in-line sintering temperature increased. The bundles essentially behaved ideally when the amount of filament-to-filament sintering was limited to less than 30% (below ILS @ 1400 °C). When greater than 30% of the filaments were in filament clusters (ILS @ 1400 °C and above), the ideal bundle model overpredicted the failure stress and strain. Two complimentary reasons for this discrepancy were identified. First, filaments within bonded clusters are no longer independent of their neighbors and will likely fail when the weakest filament within the cluster fails. Second, bonded filaments will fail at a lower than expected stress when compared to the strength of unbonded filaments.
The lower strength of the bonded filaments was due to a stress intensification around the weld-line which resulted from bending, shear or torsion of the bonded filaments. Specifically shear stresses were induced and thus fracture may occur via mixed mode failure rather than only mode I as in the unbonded filaments. Predictions of the Weibull parameters for bonded filaments sintered at 1450 °C showed the reference stress was in a range of 1.5 to 1.8 GPa which is significantly less than the reference stress determined from the single filament tests (2.51 GPa).
CHAPTER 7 Alumina Composite Fiber Mechanical Behavior

The microstructure of the alumina composite fiber used in the testing of the mechanical behavior was described in section 3.8. The filament packing density was 34% and drying voids in the matrix were minimized. The filament-to-filament contacts were limited to only a few filament clusters as observed in the 2-D cross sections (see figure 3.22). With a limited number of filament clusters, the particle-to-particle and particle-to-filament sintering are the critical sintering events controlling composite failure.

The effect of particle-to-particle sintering was first investigated on matrix only samples via bend testing. The tensile stress/strain response of alumina composite fibers was measured in load to failure and cyclic tests. The properties of the particle-to-filament interface were estimated in pushout tests of large diameter alumina rods. Failure of the composites was dominated by fiber failure. At the lower sintering temperatures, global load sharing (GLS) occurred while at the higher sintering temperatures local load sharing (LLS) mechanisms controlled strength. The role of the particle-to-particle and particle-to-filament sintering in this transition from GLS to LLS behavior will be discussed.

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7.1 Results

7.1.1 Matrix Properties

The matrix strength was determined from 3-point bend tests of the matrix only pellets. Since the matrix is considered to be a defect-sensitive material (similar to the filaments), the strength will be a function of the volume tested. In bending the volume of material in tension is less than uniaxial tension, therefore the bend strength is higher than the tensile strength. With this in mind, the bend strength is plotted versus in-line sintering temperature in figure 7.1.

For a given Young's modulus of the porous matrix, the failure strain can be estimated using Hooke's Law. The Young's modulus of the porous alumina has been modeled and measured as a function of isolated porosity [154,155]. Assuming the porosity is approximately 40%, the modulus is expected to be around 150 GPa. However, the porosity in a slightly sintered powder is not isolated but rather interconnected or open. Green et. al measured the modulus change in a slightly sintered alumina as a function of linear shrinkage. Relating the measured linear shrinkage shown in figure 3.25 to Green's measurements, the Young's modulus was 27 GPa after ILS 1100 °C to 38 GPa after ILS 1450 °C. The failure strain in bending was then calculated from the bend strength results and is plotted versus in-line sintering temperature in figure 7.2. The failure strain was initially around $5 \times 10^{-5}$ and increased to $1.8 \times 10^{-3}$ after sintering at 1450 °C. The average failure strain of the as-received filament bundle was about $7 \times 10^{-3}$ and even after in-line sintering at 1450 °C, the filament bundles failed at a strain of $3 \times 10^{-3}$. Since the failure strain in bending over-estimates the tensile failure strain, the porous matrix is expected to fail (i.e. crack) well before the failure of an alumina composite.
Figure 7.1  Bend strength versus in-line sintering temperature

Figure 7.2  Failure strain in bending versus sintering temperature.
7.1.2 Stress/Strain Response of the composite fibers

The stress/strain measurements of alumina composite fibers after various in-line sintering temperatures are shown in figures 7.3-7.7. These samples were tested without removing the sizing; the sizing created a good reflective surface for the laser extensometer. The initial Young's modulus was measured between 0 and 0.2% strain. The average modulus is around 141 ± 11 GPa but does appear to increase after sintering at 1450 °C (see figure 7.8). A single laser ultrasonic measurement of the modulus was 138 GPa [156]. Assuming a rule of mixtures model, the filaments will contribute $V_f E_f$ or $\sim 0.34 \times 380$ GPa (130 GPa) to the modulus of the composite fiber. Since the observed composite fiber stiffness is greater than the contribution of the filaments alone, the matrix must be contributing to the stiffness.

![Graph](image_url)

Figure 7.3 Stress/strain behavior of the alumina composite fiber after in-line sintering at 1100 °C
Figure 7.4 Stress/strain behavior of the alumina composite fiber after in-line sintering at 1200 °C

Figure 7.5 Stress/strain behavior of the alumina composite fiber after in-line sintering at 1300 °C
Figure 7.6 Stress/strain behavior of the alumina composite fiber after in-line sintering at 1400 °C

Figure 7.7 Stress/strain behavior of the alumina composite fiber after in-line sintering at 1450 °C
Figure 7.8 Average Young's modulus of the alumina composite fiber as a function of in-line sintering temperature. The line is the best fit for the measurements between 1100 and 1400 °C.

7.1.3 Ultimate Tensile Strength and Strain

The strength of the composite fibers with the polymer sizing removed (i.e. desized) were compared to the predicted and measured bundle strengths (figure 7.9). The strength of the "dry" bundles were multiplied by the fiber volume fraction (0.34) to accurately compare them to the composites. The tensile strength of the desized composite fibers decreased with in-line sintering temperature as shown in figure 7.9. The desized samples exhibited ideal bundle strength at the lower heat treatments. However, at around 1400 °C, there is a transition where the composite fiber strength decreased compared to the ideal bundle prediction. At ILS 1450 °C, the strength of the CMC was significantly greater than the Nextel™ 610 dry bundles.
Figure 7.9 Alumina Composite fiber tensile strength versus in-line sintering temperature.

During failure of the ILS 1100 and 1200 °C samples, the matrix disintegrated into a "cloud of dust". With the matrix removed, the filaments dilated during failure similar to the "dry" bundles (figures 7.10a and b). As the sintering temperature increased, the failure became more localized (figures 7.10c and d). At higher sintering temperatures, less matrix left in a "cloud of dust" at failure. There was also less dilatation, especially in the samples in-line sintered at 1450 °C.

The measured effective gauge length was assumed to be twice the pullout length. Since the matrix was pulverized during failure of the desized samples sintered below 1300 °C, pullout did not occur. In these samples the effective gauge length was measured as the length in which all filaments failed. In the desized samples sintered at 1450 °C, the fracture was very localized in two different areas but connected by shear failure in the matrix. The effective gauge length measurement in this case will be an overestimate. The mea-
sured effective gauge lengths are given in Table 7.1 along with the corresponding interface shear resistance calculated from equation (2.38).

![Fractures of sized and desized composite fibers in-line sintered at various temperatures.](image)

**Figure 7.10** Fractures of sized and desized composite fibers in-line sintered at a) 1100, b) 1200 °C, c) 1400 °C and d) 1450 °C.
Table 7.1: Measured effective gauge length (EGL) of composite fibers

<table>
<thead>
<tr>
<th>In-Line Sintering Temperature (°C)</th>
<th>Desized Effective Gauge Length (mm)</th>
<th>Interface Shear Resistancea (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>24 ± 2</td>
<td>0.7</td>
</tr>
<tr>
<td>1200</td>
<td>24.5 ± 0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>1300</td>
<td>21 ± 1.5</td>
<td>0.8</td>
</tr>
<tr>
<td>1400</td>
<td>10 ± 0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>1450</td>
<td>4 ± 5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

a. calculated from equation (2.38) where EGL = 2l_in.

Unlike the strength, the failure strains of the composite fibers followed the failure strains of the measured bundles quite closely and both significantly deviate from the predicted failure strains of the bundle (see figure 7.11). The cross-over of the composite fiber strength and failure strain with respect to the ideal bundle prediction will be correlated to a change in the fracture mechanism (discussed in section 7.2.4).

Figure 7.11 Ultimate strain vs. in-line sintering temperature
7.1.4 Loading/Unloading Stress/Strain Response

The loading/unloading response was measured on a number of samples to further investigate the mechanism of matrix deformation. The polymer sizing was again removed to ensure that it did not affect the deformation of the matrix. Both increasing stress and constant stress cycle tests were performed. The load/unload response for an increasing stress cycle is shown in figure 7.12. The hysteresis and permanent deformation which is usually observed when matrix cracking occurs in CMCs was absent.

\[ E = 150 \text{ GPa} \]

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Max. Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>0.39</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
</tr>
</tbody>
</table>

**Figure 7.12** Load/unload stress/strain response of a composite fiber in-line sintered at 1400 °C; increasing stress cyclic testing.

Cyclic testing at constant stress was also performed. Two composite fibers in-line sintered at 1400 °C were cycled from 0 to 0.58 GPa for 10 and 15 cycles respectively (see figure 7.13). The initial stress/strain response in figure 7.13a was non-linear. There appears to have been some permanent strain after the first cycle (= 0.0004). After this first cycle the curves remain unchanged. In contrast, the initial stress/strain response in figure 7.13b is linear and the observed permanent strain after the first cycle was around 0.0002.
Figure 7.13 The load/unload response of composite fibers in-line sintered at 1400 °C; constant stress cyclic testing. The initial response is marked with an arrow. a) 10 cycles; b) 15 cycles.
7.1.5 Matrix damage during tensile loading

An upper bound of the failure strain of the porous matrix was determined in bend tests to be around 0.0018. Since the composite fiber failure strains were in the range of 0.003 to 0.007, matrix cracks transverse to the loading direction were expected. However, distinct matrix cracking transverse to the loading direction were not observed on the outer surface of the composite fibers tested in tension or after cyclic testing. Distinct through cracks were also not observed within the composite fiber, but localized transverse damage was observed at higher magnification (see figure 7.14). This is an indication that cracking within the matrix has a more diffuse nature compared to a single well-defined crack.

SEM micrographs of the composite fiber surface after cyclic testing also showed no evidence of transverse matrix cracking. Matrix damage was observed as cracks in the axial direction and areas where portions of the matrix had fallen off (see figure 7.15). This type of damage was evidence that an internal pressure was created during loading which caused the material to dilate. From optical microscopy observations, the amount of damage decreased as the sintering temperature increased. This was expected since the failure strain of the matrix increased with sintering temperature and less dilatation was observed during tensile failure.
Figure 7.14 Transverse matrix damage after ILS 1400 °C
Figure 7.15 Micrographs of alumina composite fiber surface in-line sintered at 1300 °C and cycled to 0.55 GPa, 10 times; note the axial cracks within the matrix.
7.1.6 Fiber/Matrix Interface Properties

The fiber/matrix interface properties were measured via push-out testing of a 0.79 mm alumina rod in a porous matrix. The sample and apparatus are shown in figure 4.8 and as discussed in section 4.6, this technique was developed to avoid the specimen preparation and testing difficulties of measuring interface properties with 10 μm filaments. A typical stress-displacement curve is shown in figure 7.16. The average debond strength and sliding resistance (for 3 tests) is plotted versus in-line sintering temperature in figure 7.17. The sliding resistance changed only slightly as the sintering temperature increased while the debond strength changed dramatically. Initially there was little difference in the debond strength and sliding resistance; both were around 0.4 MPa. As the sintering temperature increased the difference between the debond strength and sliding resistance increased. After sintering at 1450 °C, the debond strength increased to over 10 MPa while the sliding resistance remained below 2 MPa.

![Graph](Image)

Figure 7.16 Stress/displacement curve for the alumina rod pushout test; ILS 1300 °C. Interface stress is defined as load divided by total interface area.
Figure 7.17 Average debond strength and sliding resistance versus sintering temperature.

Observations of the alumina rod surfaces after testing gave some insight into the mechanisms which control the interface properties. Photomicrographs of the alumina rod surface after sintering at 1100 and 1450 °C are shown in figure 7.19. On the surface of the ILS 1100 °C sample, powder remained in the grain boundary grooves while the grain surfaces were clean. The grooves created a surface roughness which forced the debond crack to propagate through the sintered powder near the grain boundaries (i.e. through the particle-to-particle contacts). The grain surfaces, however, have only a few powder particles on them indicating the debond interface in this area is between the particle-to-rod contacts. The surface of the alumina rod pushed out of the sample heat treated at 1450 °C was covered with sintered powder with very little of the alumina rod visible. The increase in sintered powder on the alumina rod surface indicated the debond interface translated to a higher percentage of particle-to-particle contacts.
Figure 7.18 Surfaces of alumina rods after being pushed out of porous alumina matrix: a) ILS 1100 °C, b) ILS 1450 °C.
Within the alumina composite fiber, the debond interface appears to be between the particle-to-filament interface. Figure 7.19 shows a filament debonded from the porous matrix after failure. Similarly, fracture surfaces from a composite fiber in-line sintered at 1400 °C (figure 7.20) showed smooth regions in the porous matrix where a fiber had once been. The broken filament in figure 7.20a still has some of the powder particles on its surface, but the majority of the surface is free of powder. At higher magnification, a few grains from the filament appear to have been pulled out. Because these observations were made after failure, it is uncertain if debonding occurred prior to or resulted from failure. This will be discussed further in section 7.2.3 Particle-to-filament debonding brings into question the validity of the alumina rod push-out tests (discussed in section 7.2.2).

![Image of fiber/matrix debond interface]

10 μm

Figure 7.19 Fiber/matrix debond interface between the particle-to-filament contacts.
Figure 7.20 Fiber/matrix interface after ILS 1400 °C. For the most part the debond interface is between the powder/filament contacts. However, some powder remained on the fiber surface and some grains have been pulled out of the fiber surface.
7.2 Discussion

7.2.1 Young’s Modulus

Assuming an isostrain condition, the Young’s modulus of the alumina composite fiber can be predicted from the rule of mixtures [114]:

\[ E_c = V_f E_f + (1 - V_f) E_m \]  \hspace{1cm} (7.1)

The measured filament volume fraction in the composite fiber was 0.34; the fiber modulus, 380 GPa [14]; and the matrix modulus, \( \approx 30 \) GPa [157]. Thus, the predicted modulus would be 149 GPa which compares well with the measured modulus (141 \( \pm 11 \) GPa, section 7.1.2). The variations in the matrix modulus with sintering temperature were ignored because they corresponded to only a 5% change in the predicted matrix modulus.

7.2.2 Validity of pushout tests

Fractographic observations of the debond interface within the composite fibers indicated that debonding and sliding occurred along the particle-to-filament interface. In contrast debonding and sliding in the alumina rod pushout tests occurred progressively more within the porous matrix as the sintering temperature increased. This creates a serious question as to the validity of using the pushout results to describe the interface properties in the alumina composite fibers.

A qualitative argument will be used to justify using the pushout test results to describe the sliding resistance in the alumina composite fibers. The structure at the particle-to-filament interface consists of powder sintered to the filament or rod. The contact area (i.e. neck area) is a function of the sintering temperature and time [45]. One obvious difference between the filament and rod is the diameter. However, since the ratio of the fila-
ment curvature \((1/r_p)\) to the powder curvature \((2/r_p)\) is 0.05, the filament may be considered a flat surface compared to the powder and the diameter difference should not affect the interface properties.

It is also well known within the powder metallurgy community that the powder packing density decreases as a flat interface is approached [159]. This edge effect will result in a lower coordination number (i.e. fewer contacts) for the powder in contact with the filament or rod surface compared to within the porous matrix. The particle-to-filament interface is therefore a more likely debond interface because of the fewer number of contacts. Fractography of the composite fibers supports this conclusion, however, sliding in the alumina rod pushout tests occurred within the matrix. The cause of the shift in the debond and sliding interface was grain boundary grooves which were large enough for the powder to penetrate (see figure 7.18). This created a mechanical lock forcing the debond interface into the matrix. The debond interface within the matrix was significantly rougher than the particle-to-filament interface. It is possible that the mechanical resistance of sliding within the matrix will be greater than that of the smooth particle-to-filament interface, thus the pushout results may actually be an overestimate of the sliding properties.

Another issue concerning the validity of the pushout tests concerns the amount of sintering within the pushout specimens. The mass of the pushout specimens were much larger than the composite fiber so they may not experience the same temperature profiles during in-line sintering. The measurements showed that the sliding resistance was not sensitive to the sintering temperature. Also it was argued above that sliding within the matrix will be greater than at the particle-to-filament interface. Therefore, the sliding resistance within the alumina composite fiber will likely be on the order of 1-2 MPa as measured in the pushout tests. However, the debond strength is more sensitive to sintering temperature. Therefore, the possibility of lower sintering conditions of the pushout speci-
mens compared to the composite fibers combined with the fact that the debond interface was within the matrix instead of at the particle-to-filament interface make the accuracy of the debond strength measurements suspect.

7.2.3 Matrix deformation during tensile loading

As the rule of mixture model suggests, the initial deformation of the matrix is elastic. Since the highly porous matrix has a failure strain significantly less than the composite, the matrix was expected to crack perpendicular to the loading direction at multiple locations prior to failure of the composite. However, distinct matrix cracks which had propagated through the entire composite fiber were not observed. A discussion of possible mechanisms of matrix deformation will begin with calculations of the stress distribution around a single fractured neck. These calculations show that particle packing defects greater than 2 or 3 particle diameters will enhance the stress in the bonds of neighboring particles. Models for predicting fiber/matrix debonding [125] and the matrix cracking stress [127] confirm that matrix cracking should be present. The assumptions of these models will then be used to create a hypothesis as to why matrix cracking was not observed.

In order to better understand how cracks might nucleate and propagate, consider a defect free, two dimensional close-packed array of slightly sintered particles (figure 7.21a). Upon loading in tension, a neck perpendicular to the applied stress will fail creating a straight crack ($c = d/2$, figure 7.21b). Assuming the sample is infinitely large, the geometric factor ($\psi$) is 1.0 and the mode I stress intensity factor ($K_I$) can be determined from equation (2.10). Substituting this relationship for $K_I$ into equation (5.1), gives a relationship for the tensile stress in the z-direction as a function of the distance from the crack tip (y-direction). Assuming that shear failure of the nearest neighbor necks is more diffi-
cult than tensile failure of necks perpendicular to the applied stress, the most likely neck failure will occur at \( y = d/2, \theta = \pi/4 \) and \( y = 3d/2, \theta = 0 \). According to equation (5.1), the ratio of the enhanced stress \( \sigma_z \) to the applied stress \( \sigma_A \) at these two locations is 0.9 and 0.4, respectively. Since this ratio is less than one, the stress on the neighboring necks is not affected by the failure of a single neck.

Defect free particle packing is highly unlikely, and if a packing defect was present which had a total length of \( 3d \) or \( c = 1.5d \), \( \sigma_z / \sigma_A \) would be 1.22 at \( y = d/2, \theta = \pi/4 \). Therefore, neck failure will likely initiate around particle packing defects whose total length is greater than 2 or 3 particle diameters. This analysis indicates the slightly-sintered porous matrix should be defect sensitive similar to other brittle ceramics and models describing crack propagation in ceramic matrix composites with fully dense matrices [125,127] should be valid.

![Figure 7.21](image_url)

**Figure 7.21** Two dimensional, close-packed array of slightly sintered particle; a) prior to loading, b) after failure of a neck perpendicular to the applied stress creating a crack.
He and Hutchinson [125] developed a model for predicting the fiber/matrix debonded. They considered whether a crack approaching a fiber deflected up or down the interface or propagate through the fiber. The criterion for interface debonding is shown graphically in figure 2.9. Since the elastic mismatch for this alumina composite is 0.85 (Poisson's ratio of fiber and matrix are equivalent, 0.23 [55]), the fracture energy ratio \((\Gamma_i/\Gamma_f)\) required to insure debonding is about 1.0. Assuming this crack geometry represents cracking in the alumina composite fiber, the fracture energy ratio was calculated. The fracture energies were calculated from their fracture toughness using equation (2.6). The fracture toughness of the alumina filament was 2.75 MPa \(\sqrt{m}\) [59] and the fracture toughness of the interface was 0.3 MPa \(\sqrt{m}\) [158]\(^1\): \(\Gamma_i = 3 \text{ J/m}^2\), \(\Gamma_f = 19 \text{ J/m}^2\). The fracture energy ratio is 0.16 which is well within the region of debonding.

Since debonding is predicted to occur, the composite stress \(\sigma_{mc}\) where matrix cracking begins can be estimated from equation (2.35). This model assumes that the fiber and matrix are not intimately bonded and permits sliding which gives the minimum theoretical \(\sigma_{mc}\). Given that the sliding resistance is approximately 1 MPa (figure 7.17), \(\sigma_{mc}\) is estimated as 0.18 GPa. Although the models predict that matrix cracking should occur during the tensile loading of an alumina composite fiber, distinct through cracks were not observed. One possible reason for this is that the cracks do not open enough to be observed. However, fractography observations of isolated perpendicular cracks at high magnifications (figure 7.14) imply the cracking was more diffuse than in conventional ceramic composites.

As the above calculations showed, a crack can propagate from particle packing defects of 2 to 3 particle diameters in length. If a tensile stress is applied to a matrix only sample

\(^1\) The fracture toughness of the interface was assumed to be equivalent to the slightly sintered matrix
in load control (i.e. \(dK/dc > 0\)), then the material will fail from the propagation of a single crack from the largest defect. However, in an alumina composite fiber, the deformation of the matrix is controlled by the displacement of the filaments (i.e. \(dK/dc < 0\) within the matrix). Under these conditions the crack propagation will be stable. In addition as a crack grows, the matrix becomes more compliant and will shed load to the filaments effectively decreasing the driving force for crack propagation causing the crack to arrest. This will allow cracks in other areas of the composite fiber to nucleate from packing defects and subsequently propagate and arrest. The strain within the matrix is accommodated by a diffuse distribution of these “microcracks”. The total strain within the matrix may then be determined by integrating the crack opening displacements within all the microcracks.

7.2.4 Predictions of composite strength

The models used to predict composite strength assuming global load sharing (GLS) were described in section 2.2.4. GLS is the even redistribution of stress from a broken filament to the remaining unbroken filament. In these models, an effective gauge length (\(2l_{in}\)) was defined to calculate the fiber contribution of composite strength. Using Rosen’s approach with Curtin’s definition of the effective gauge length, the fiber bundle stress can be rewritten from equation (2.23) as:

\[
\sigma_b = E_f \varepsilon \exp \left( -\frac{2l_{in}}{L_o} \left( \frac{E_f \varepsilon}{\sigma_o} \right) \right) \tag{7.2}
\]

Substituting equation (2.38) for \(l_{in}\) and Hooke’s law for \(\sigma_f\) gives:

\[
\sigma_b = E_f \varepsilon \exp \left( \frac{E_f r/\tau_s L_o}{\sigma_o} \left( \frac{E_f \varepsilon}{\sigma_o} \right) \right) \tag{7.3}
\]
Differentiating $\sigma_b$ with respect to $\varepsilon$ and setting the resulting equation equal to zero gives an expression for the strain at failure:

$$
\varepsilon_{\text{fail}} = \frac{1}{E_f} \left( \frac{\sigma_o^m L_o \tau_s}{2r(1 + m)} \right)^{1/(1 + m)}
$$

(7.4)

Again invoking Hooke's law, the stress in the filaments at failure is:

$$
\sigma_{\text{fail}} = \left( \frac{\sigma_o^m L_o \tau_s}{2r(1 + m)} \right)^{1/(1 + m)}
$$

(7.5)

$\sigma_{\text{fail}}$ is somewhat analogous to Curtin's characteristic strength, $\sigma_{\text{cur}}$ [116]. The effective gauge length at failure may then be determined by substituting equation (7.5) into equation (2.38).

The bundle strength at the defined effective gauge length is found by substituting equation (7.4) into (7.3) to give:

$$
\sigma_b^{\text{max}} = \sigma_o^{m/(1 + m)} \left( \frac{L_o \tau_s}{2r(1 + m)} \right)^{1/(1 + m)} \exp \left( -\frac{1}{2(1 + m)} \right)
$$

(7.6)

and the predicted composite strength is:

$$
\sigma_c^{\text{max}} = V_f \sigma_b^{\text{max}}.
$$

(7.7)

In contrast to GLS, Local load sharing (LLS) is the localized redistribution of stress from a single broken filament. This localized stress redistribution causes sequential failure of neighboring filaments, and in the worst case scenario, the composite fails when the weakest filament fails. Monte carlo modeling similar to that described in section 6.6 was
used to simulate LLS; the assumed failure criteria was the worst case scenario. Also note that the prediction of LLS is not a function of the interface properties.

In both the GLS and LLS predictions, it was assumed that the fiber strength within the composite was measured by the single filament tests presented in Chapter 5. In addition, for the GLS predictions, interface shear resistance ($\tau_i$) was assumed to be either the sliding resistance ($\tau_s$) or the debond strength ($\tau_d$) as measured in the alumina rod pushout test. With these properties for the constituents, the predicted composite strengths for GLS and LLS are plotted in figure 7.22 along with the measured results of the sized and desized composite fibers. The GLS model assuming $\tau_i=\tau_d$ did not predict the composite fiber strength at any condition. However, the GLS model did predict the composite fiber strength below ILS @ 1300 °C when assuming $\tau_i=\tau_s$ indicating that sliding resistance was a good measure of the interface properties. Above 1300 °C there is an obvious transition from GLS to LLS behavior which also corresponded to localized fiber fracture (figures 7.10). It was surprising to discover that the predicted LLS strength was constant with in-line sintering temperature, since the average filament strength decreased with sintering temperature. The reason for this was that the Weibull modulus increased from 7 to 11 as the in-line sintering temperature increased from 1100 to 1450 °C (i.e. the strength distribution narrowed).

The good correlation between the predicted and measured strengths indicates that the measured single filament strengths accurately described the strengths of the filaments within the composite. In effect the particle-to-filament sintering did not degrade the strength of the filaments.
Figure 7.22 Global load sharing (GLS) and local load sharing (LLS) predictions compared to the composite fiber strength measurements as a function of in-line sintering temperature.

The transition from GLS to LLS behavior was reviewed in section 2.2.5 Two criteria have been developed to assure GLS. The first attributed to He et. al [117] is that the ratio $\tau_i/\sigma_{fail}$ must be less than 0.1$^1$ and the second developed by Curtin [118] defined the criterion as $\tau_i/\sigma_{cur} < 0.02^2$. Recognizing that $\sigma_{fail}$ is related to $\sigma_{cur}$ via:

$$\sigma_{fail} = \sigma_{cur} \left(\frac{1}{2(1 + m)}\right)^{1/(1 + m)}$$ (7.8)

Curtin’s criterion can be redefined in terms of $\sigma_{fail}$ as $\tau_i/\sigma_{fail} < 0.025^3$.

---

1. This criteria is for $E_f/E_m = 1$
2. See section 2.2.5 for the definition of $\sigma_{cur}$
3. For $5 < m < 15$, the Weibull modulus term in equation (7.8) is approximately 0.75.
σ_{fail} was calculated for each ILS temperature from the failure strains in figure 7.11 using Hooke’s law (see Table 7.2). The ratio τ_i/σ_{fail} is plotted versus τ_i in figure 7.23 for each in-line sintering temperature along with Curtin’s criterion for the transition from GLS to LLS behavior.

The measured sliding resistance was less than 2 MPa for all the heat treatments. This corresponds to τ_i/σ_{fail} well within the GLS region. Since the composite fibers failed via a LLS mechanism after the highest in-line sintering temperatures, the sliding resistance does not describe the resistance to shear in these samples. As discussed previously, the more appropriate parameter in this case would be the fiber/matrix debond strength or the shear strength of the matrix. The measured debond strength of the samples ILS @ 1400 and 1450 °C was around 15 MPa which is a factor of two below the predicted shear resistance required to cause LLS (30-40 MPa). But more importantly the pushout tests showed a very strong dependence of debond strength with sintering temperature. Given the previous discussion about less sintering occurring in the pushout samples because of heat transfers issues, it is not surprising that debond strengths within the alumina composite fibers are predicted to be in the range of 30-40 MPa.
**Figure 7.23** The ratio of sliding resistance ($\tau_s$) to filament stress at failure ($\sigma_{\text{fail}} = E_f \varepsilon_{\text{fail}}$) as a function of sliding resistance. Curtin's criterion for the transition from GLS to LLS is shown as a reference. The measured sliding resistance was around 1-2 MPa, well within the GLS region.

**Table 7.2: The filament stress at failure**

<table>
<thead>
<tr>
<th>ILS Temperature ($^\circ$C)</th>
<th>$\varepsilon_{\text{fail}}$</th>
<th>$E_f$ (GPa)</th>
<th>$\sigma_{\text{fail}} = E_f \varepsilon_{\text{fail}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0.0066</td>
<td>380</td>
<td>2510</td>
</tr>
<tr>
<td>1200</td>
<td>0.0067</td>
<td>380</td>
<td>2520</td>
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<td>1300</td>
<td>0.0055</td>
<td>380</td>
<td>2100</td>
</tr>
<tr>
<td>1400</td>
<td>0.0048</td>
<td>380</td>
<td>1820</td>
</tr>
<tr>
<td>1450</td>
<td>0.0035</td>
<td>380</td>
<td>1330</td>
</tr>
</tbody>
</table>
The following is a summary of how matrix deformation occurs. The highly porous matrix has a failure strain much less than the composite fiber. Localized matrix cracking perpendicular to the applied load was observed but well-defined through cracks were not present. Tensile deformation in the matrix must therefore be accommodated by isolated or localized cracking. Since the models for predicting fiber/matrix debonding are based on a sharp, well-defined crack geometry, debonding may not necessarily occur. However, the good correlation between the GLS model and composite fiber strength below ILS 1300 °C indicates that debonding and sliding does occur in these samples. The transition from GLS to LLS behavior is believed to be associated with a lack of debonding thus the higher debond strength would control the shear resistance at the fiber/matrix interface. Further work is required to better understand matrix deformation, fiber/matrix debonding and sliding in these alumina fiber composites.

7.3 Conclusions

The increase in stiffness of the porous alumina composites compared to the fiber alone indicated the matrix did contribute to the load carrying capacity of the composite. A decrease in stiffness with increasing strain was observed in some samples which would indicate matrix cracking perpendicular to the applied stress. However, this behavior was not always observed and little or no hysteresis occurred in the load/unload experiments. Macroscopically, no distinct through cracks were observed perpendicular to the applied stress, but localized cracking was observed at higher magnifications. Therefore, matrix deformation occurred via a more diffuse localized cracking rather than by the propagation of a well-defined crack.

The strength of the alumina composite fibers decreased as the in-line sintering temperature increased although failure continued to be dominated by filament failure. The fila-
ament strength determined from single filament testing appeared to describe the strength of the filaments within the composite fiber. Since filament-to-filament bonding was minimized, this indicates that the particle-to-filament contact growth did not degrade filament strength. The failure translated from a GLS mechanism to a LLS mechanism as the in-line sintering temperature increased. Below 1300 °C the composite failed via GLS and above via LLS. The transition from GLS to LLS was predicted using a model developed by Curtin [118]. The model predicted that the interface shear resistance, \( \tau_i \), needed to be above 30 MPa to cause LLS. The measured sliding resistance was less than 2 MPa. However, fiber/matrix debonding may not occur in the alumina composite fiber after significant sintering, and debond strength, \( \tau_d \), may be a more appropriate measure of the interface shear resistance. Therefore though the particle-to-filament sintering did not degrade the filament strength, this mechanism controlled the transition from GLS to LLS behavior. In the samples which failed via a LLS mechanism, the debond strength is suspected to greater than 30 MPa.
CHAPTER 8 Discussion

This discussion will examine whether the alumina composite fiber developed in this research is an appropriate reinforcement for a metal or ceramic matrix. As with any composite system, its appropriateness depends on the performance requirements. For example, should the composite system maximize specific strength or is stiffness more critical? In the following paragraphs, the use of an alumina composite fiber as a reinforcement in a metal or ceramic matrix will be discussed in terms of strength, stiffness, toughness and creep resistance.

The property measured to determine the effect of high temperature heat treatments was the room temperature stress/strain response. However, the alumina composite fiber was designed specifically for high temperature applications. Thus retaining strength at high temperatures is a critical issue. The Nextel™ 610 filament has been shown to retain approximately 85% of its strength at 1000 °C [14]. Since composite strength is directly proportional to the reference strength of the filaments, the alumina composite fiber will also retain much of its strength up to 1000 °C. Similarly, the modulus of alumina will decrease approximately 15% at 1000 °C [55].
Both strength and stiffness of the composite fiber are a function of the filament volume fraction. Because of processing difficulties, the packing density of the filaments was limited to only 34%. As a result, the measured stiffness was 150 GPa and the measured strength was between 600 and 700 MPa. Both of these values would be considered low for a fiber reinforcement. However, the advantage would be high temperature stability and 85% of room temperature properties at 1000 °C. Therefore, the alumina composite fiber would be a candidate for applications which require improved strength and stiffness at high temperatures. For example, the specific strength of Haynes 214\(^1\) at 1000 °C is 100 MPa/8.5 g/cm\(^3\) or 12 MPa-cm\(^3\)/g compared to an alloy reinforced with 35% alumina composite fibers whose specific strength at 1000 °C would be 310 MPa/6.7 g/cm\(^3\) or 46 MPa-cm\(^3\)/g.

The toughness of metal matrix composites is generally much less than that of the matrix alloy alone while in ceramic matrix composites toughness is typically better than the monolithic matrix. In both cases it is desired to maximize toughness. Unlike strength and stiffness, the toughness of the alumina filaments will likely increase with temperature as more deformation processes like diffusional creep and even plastic deformation become active. However, the role of global and local load sharing in relationship to toughness at high temperatures may be very similar to the room temperature response.

Consider then the observed transition from GLS to LLS after in-line sintering at 1300 °C. The transition was a result of greater sintering as the furnace temperature increased. Since sintering is a diffusional process, the mean diffusion distance ($\bar{x} = \sqrt{2Dt}$ [160]) can be used to compare the in-line sintering treatment to isothermal service conditions.

\(^1\) The strength of Haynes 214 at 1000 °C is 100 MPa.
which will likely be below 1000 °C. Rearranging this relationship, temperature can be related to time for a given $\bar{x}$:

$$T = \frac{Q}{R \ln(\bar{x}^2/(2D_o t))}$$  \tag{8.1}

Where $Q$ is the activation energy for surface diffusion (256 KJ/mole [161]); $R$ is the ideal gas constant; $D_o$ is the pre-exponential term (4.8x10^{-5} m^2/s [161]) and $t$ is the time. The mean diffusion distance for the in-line sintering at 1300 and 1450 °C is 4.3 and 8.3 μm respectively. A plot of equation (8.1) for $\bar{x} = 4.3$ and 8.3 μm is shown in figure 8.1.

Since the transition from GLS to LLS was observed to begin after in-line sintering at 1300 °C, the alumina composite fibers should remain “tough” during isothermal service conditions below this boundary. Similarly above the ILS 1450 °C boundary, the LLS failure mechanism will dominate and toughness will decrease. The shaded area then represents the transition from GLS to LLS. A typical temperature cycle used in the consolidation of a nickel matrix composite is 1050 °C for 2 hours; well within the LLS region. Though, bonds due to sintering may break during the consolidation effectively shifting this point toward the GLS region. In addition ignoring any prior processing temperatures, the alumina composite fiber would sustain GLS behavior for 10 hours or less at the target temperatures of 900 to 1000 °C. Maintaining toughness, therefore, is an important concern.
Figure 8.1 Isothermal temperatures and times for the calculated mean diffusion distances at 1300 °C and 1450 °C. The global load sharing (GLS) mechanism will be active in the lower region while local load sharing (LLS) will control failure in the upper region. A typical consolidation cycle for a nickel matrix composite is 1050 °C for 2 hr.

High temperature applications also require limited creep deformation. At the target temperatures for which the alumina composite fiber was developed (900-1100 °C), both the matrix and fiber will creep. However, current results on the creep resistance of the alumina composite fiber are encouraging [162]. For example at 1100 °C, the applied stress on an alumina composite fiber to give a creep rate of 2x10^{-6} s^{-1} is 385 MPa [162] while the stress on a nickel aluminate would be 100 MPa [163]. Hammond et. al [162] also showed that the creep resistance of the alumina composite fiber will increase during service. The reasons for this are currently being investigated.
In summary, the alumina composite fiber would be a good candidate for reinforcing matrices with the goal of improving high temperature properties. It is an especially good candidate for reinforcing certain Ni-based alloys because it will improve the high temperature strength and creep resistance and is stable with respect to both the matrix and oxidizing environments. However, for these advantages to be realized, the transition from GLS to LLS must be extended orders of magnitude greater than the current 10 hours or less at 900 to 1000 °C and the packing density of filaments within the composite fiber should be increased from 0.34 to greater than 0.6.

8.1 Future Work

To increase the stiffening and strengthening potential of the alumina composite fiber, the filament packing density must be increased. A possible solution would be to actively twist the tow during the drying stage of the alumina composite fiber process. The twisting action will force the filaments together toward a close-packed structure [165]. However, as the filament packing density increases, the probability of filament-to-filament contact will also increase. To avoid filament-to-filament contact the twisting should be done during the drying stage where slurry has already been infiltrated into the filament gaps. Filament coating would also provide protection from direct filament-to-filament contacts. A schematic of a modified vertical process for fabricating an alumina composite fiber with a twist is shown in figure 8.2. If the filament packing density was increased to 0.65, the Young’s modulus of the alumina composite fiber would increase from 140 GPa to 250 GPa. In addition the composite fiber strength would increase from about 650 MPa to greater than 1200 MPa assuming the failure load did not change (i.e. $1200 = 0.65\times650/0.34$).
Figure 8.2 Schematic of the vertical composite fiber process with in-situ twisting.

It also appears that the alumina composite fiber in its current form will not be able to withstand more than 10 hours at 900 °C without decreasing toughness. This is a direct result of particle-to-filament sintering which limits debonding. To increase the potential service time of a composite manufactured with an alumina composite fiber, it is suggested a coating be deposited onto each individual filaments prior to infiltration of the alumina slurry. This unfortunately adds another step to the process and will increase cost. In addition, the composition of the slurry must formulated to wet the new filament coating surface. The most important property of the coating is to promote debonding, thus ensuring that the sliding resistance will control the interface shear resistance. Since the sliding resistance (τ_s < 2 MPa) was found to be insensitive to the sintering temperature, the desired global load sharing behavior will occur over much longer service times. As an example a carbon coating could act as a barrier to particle-to-filament contact and elimi-
nate the possibility of strong bonding. Even if oxidation removes this coating during service, a gap is left between the particles and filaments. Particle-to-filament bonding would then occur only by particle rearrangement during service.

This work has also shown that grain boundary grooves caused by thermal etching or breaking of filament-to-filament bonds were the strength limiting flaws. Thermal etching occurs to relieve compressive stresses caused by the curvature of the surface around the grain boundaries. The atoms diffuse via surface diffusion to the flat regions of the grains. The addition of a carbon coating changes the diffusion path to the carbon/fiber interface. Diffusion along the interface will likely be less than surface diffusion meaning the grain boundary grooves will be less severe for a given heat treatment.

To further investigate the effects of grain boundary grooves on the strength of Nextel™ 610, it is suggested that the strength of carbon coated filaments be characterized as a function of in-line sintering. The heat treatment should be done in an inert atmosphere to avoid the burn-off of the coating. The filament strength should then be determined with the coating intact and with the coating removed. Removing the coating will help determine if there is any beneficial aspect of the coating such as restraining the crack opening around the grooves. The defect population must be characterized and compared to the current results. With knowledge of the effects of a carbon coating on the Nextel™ 610 and an alumina composite fiber, the effect of other more complex coatings may be better understood.
CHAPTER 9 Conclusions

An inexpensive alumina composite fiber was developed as a reinforcement in high temperature metals and ceramics for use temperatures between 900 and 1100 °C. Both a horizontal and a vertical process were designed to fabricate an alumina composite fiber by infiltrating the filaments of an alumina Nextel™ 610 tow with a porous alumina binder via slurry casting. During the process development of this alumina composite fiber, it was determined that under typical processing conditions the slurry fully infiltrated the filaments near the entrance. Drying occurred at the slurry/air interface which forced particles to collect around the fiber perimeter to accommodate drying shrinkage. The resistance of the filaments to drying shrinkage left large matrix voids in the center of the composite fibers when low percent solids slurries were used. A process was developed which largely eliminated these matrix voids, but the filament packing density was lowered to 34% during the process optimization. The extent of particle-to-particle sintering was characterized and found to be well within stage 1 sintering. The dominant sintering mechanism was identified as surface diffusion from a surface source.

The effect of subsequent high temperature sintering was investigated using a continuous heat treatment process referred to as in-line sintering. The length of the hot zone and
line speed were such that the "dry" bundles and composite fibers were sintered for approximately one minute at temperatures varying from 1100 to 1450 °C. During these sintering treatments, four important phenomenon were identified which could affect the mechanical properties of the composite fibers: 1) grain growth within the filaments; 2) growth of particle-to-particle contacts; 3) growth of particle-to-filament contacts and 4) growth of filament-to-filament contacts.

The effects of grain growth and filament-to-filament sintering were investigated by characterizing both the single filament and bundle properties of sintered "dry" bundles. It was found that the strength of Nextel™ 610 alumina filaments decreased as the in-line sintering temperature increased. A change in the defect population and grain growth corresponded to the decrease in strength. The equivalent strengths of the weld-line and the surface unidentified defects at all sintering temperatures was evidence of a microstructural feature playing a critical role in controlling strength. Since crack initiation occurred along the grain boundaries, grain boundary grooves were identified as the strength limiting microstructural feature.

Subcritical cracking was observed via a fractography approach. The cause of the subcritical cracking is believed to be associated with stresses induced from thermal anisotropy within the alumina or caused by rising T-curve behavior in the short crack regime due to a change in the intrinsic toughness with crack length.

The strength of the "dry" alumina bundles also decreased as the in-line sintering temperature increased. The bundles essentially behaved ideally when the amount of filament-to-filament sintering was limited (< 30%). When significant filament-to-filament sintering occurred (> 30%), the ideal bundle model overpredicted the failure stress and strain. Two complimentary reasons for this discrepancy were identified. First, filaments within bonded clusters are no longer independent of their neighbors. Second, bonded filaments
failed at a lower than expected stress when compared to the strength of unbonded filaments. The lower strength of bonded filaments was linked to mixed mode failure caused by induced shear stresses around the weld-line which result from relative filament motion due to misalignment (bending and torsion). Since the porous matrix will limit filament motion, the loss of independence which promotes local load sharing will be a more important factor in the composite fiber. Filament-to-filament contacts should, therefore, be avoided in the fabrication of composite materials.

The effects of the particle-to-particle and particle-to-filament contacts were investigated by in-line sintering alumina composite fibers. The highly porous binder did contribute to the stiffness of the composite fiber indicating it does carry some load. However, the slightly sintered alumina binder should crack early and often in order to exhibit the observed strains of 0.003-0.006. Macroscopically, no distinct through cracks were observed perpendicular to the applied stress. However, localized cracking was observed at higher magnifications and it is suspected that this diffuse type of cracking allows the matrix to accommodate the large axial strains. Matrix cracking was observed parallel to the applied stress indicating a tendency of the material to dilate.

Failure of the porous alumina composite fibers were dominated by the filament failure. The filament strength determined from single filament testing appears to describe the strength of the filaments within the composite fiber. Since filament-to-filament bonding was minimized, this indicates that the particle-to-filament contact growth did not degrade filament strength. The failure translated from a global load sharing (GLS) mechanism to a local load sharing (LLS) mechanism as the in-line sintering temperature increased. Below 1300 °C the composite failed via GLS and above via LLS. The predicted interface shear resistance, \( \tau_i \), to cause LLS was above 30 MPa. The measured sliding resistance was less than 2 MPa. However, fiber/matrix debonding may not occur in the alumina composite
fiber, and in that case debond strength, $\tau_d$, would be a more appropriate measure of the
interface properties. Although, the debond strength was measured to be approximately 15
MPa in the samples that exhibited LLS, it is suspected that $\tau_d$ is greater than 30 MPa in
these samples.

Before an alumina composite fiber can realize its full reinforcing potential, the fila-
ment packing density within the composite fiber must be increased to greater than 0.60 so
that both the stiffening and strengthening potential are improved. An increase in filament
packing density may be achieved by twisting the fiber during the fabrication process.
However, improving the filament packing density will encourage filament-to-filament
contact which must be avoided. Therefore, the twisting step should be done after infiltra-
tion so that the slurry will resist filaments coming into contact with one another. Coatings
on the individual filaments might also act as a barrier to filament-to-filament contact.

In addition the time at temperature required to cause a transition from global load shar-
ing to local load sharing must be extended. The current alumina composite fiber cannot
withstand a 2 hour consolidation cycle at 1050 °C without embrittling. Since the transition
from global load sharing to local load sharing was caused by limited debonding, debond-
ing must be promoted; possibly by applying coatings to the filaments. If fiber/matrix deb-
onding can be ensured, the sliding resistance will control the interface shear resistance.
Since thermal residual stress across the interface is zero, the sliding resistance will remain
small (≈ 2 MPa), thus ensuring global load sharing behavior and maximizing mechanical
properties.
References

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Appendices

A.1 Rate equations for two sphere sintering model (Swinkel and Ashby [45])

A.1.1 Non-densifying mechanism

Surface diffusion from a surface source:

\[ \dot{V}_1 = \frac{3 \pi x D_s \delta \gamma_s \Omega (K_3 - K_2)}{d_2 k T} \]  

(2.1)

Lattic diffusion from a surface source:

\[ \dot{V}_2 = \frac{3 \pi x D' \delta \gamma_s \Omega (K_3 - K_m)}{k T} \]  

(2.2)

A.1.2 Densifying mechanisms:

Grain boundary diffusion from a boundary source:

\[ \dot{V}_4 = \frac{16 \pi D_b \delta \gamma_s \Omega}{x k T} \left( 1 - \frac{K_1 x}{2} \right) \]  

(2.3)

Lattice diffusion from a boundary source:

\[ \dot{V}_5 = \frac{32 \pi \rho \theta D_v \gamma_s \Omega}{x k T} \left( 1 - \frac{K_m x}{2} \right) \]  

(2.4)
Lattice diffusion from a dislocation source:

\[ V_6 = \frac{8\pi x^2 \rho ND \gamma_s \Omega}{9kT} \left( -K_m - \frac{3\mu x}{2\gamma_s a} \right) \]  \hspace{1cm} (2.5)

Redistribution mechanism around neck:

\[ V_{sr} = \frac{12\pi D_s \delta_s \gamma_s \Omega (K_1 - K_2)(d_1 + 2d_2)}{kTd_1(d_1 + 3d_2)} \]  \hspace{1cm} (2.6)

Definitions of symbols and values used for alumina

- \( a \) - Particle radius; \( 5.0 \times 10^{-7} \text{m} \)
- \( x \) - neck radius (m)
- \( y \) - one half the interpenetration of two particles (m)
- \( \rho \) - radius of curvature of the neck (m)
- \( K_1, K_2, K_3 \) and \( K_m \) - curvatures (m\(^{-1}\))
- \( d_1, d_2 \) - diffusion distance for surface redistribution and surface diffusion (m)
- \( D_s \delta_s \) - surface diffusion coefficient times effective surface thickness; \( D_s = 4.8 \times 10^{-5} \exp\left(-\frac{577000}{RT}\right) \text{m}^2/\text{s} \) [161]
- \( D_v \) - lattice diffusion coefficient; \( D_v = 13.6 \exp\left(-\frac{256000}{RT}\right) \text{m}^2/\text{s} \) [164]
- \( D_b \delta_b \) - grain-boundary diffusion coefficient times effective grain boundary thickness; \( \text{m}^3/\text{s} \) [164]
- \( \gamma_s \) - surface free energy (J/m\(^2\)); assumed to be 2.0 J/m\(^2\) [62,161]
- \( \Omega \) - atomic volume; assumed to be 2.11 \times 10^{-29} \text{ m}^3 \) [161]
$k$ - Boltzmann's constant ($1.38 \times 10^{-23}$ J/K)

$T$ - absolute temperature (K)

$\mu$ - shear modulus; assumed to be $150 \times 10^9$ N/m$^2$ [55]

$N$ - dislocation density (m$^{-2}$); assumed to be $10^{14}$ [46]

$\theta = \tan^{-1}\left(\frac{a-y}{x+p}\right)$

### A.2 Fractography showing subcritical cracking in the Nextel™ 610 alumina filaments

The critical crack size was predicted using equation (2.18) assuming a semi-circular surface crack in a long cylinder. A schematic of the crack geometry is shown in figure A.1. The results for the predicted critical crack sizes are shown in Table A.1. These predicted critical crack size are drawn onto SEM micrographs of the actual fracture surfaces (see figures A.2-5). The measured diameter of each filament was used as a scale for drawing the critical crack size. The scale markers shown in the figures is only an approximation.

![Figure A.1 Schematic of crack geometry for critical crack size predictions](image)

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Table A.1: Critical crack size assuming a semi-circular surface crack (b/c = 1)

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Strength (GPa)</th>
<th>$\psi^a$</th>
<th>Critical Crack Size $c$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>2.79</td>
<td>0.66</td>
<td>0.7</td>
</tr>
<tr>
<td>As-received</td>
<td>3.0</td>
<td>0.66</td>
<td>0.6</td>
</tr>
<tr>
<td>As-received</td>
<td>3.52</td>
<td>0.66</td>
<td>0.4</td>
</tr>
<tr>
<td>ILS 1300 °C</td>
<td>2.49</td>
<td>0.67</td>
<td>0.9</td>
</tr>
<tr>
<td>ILS 1300 °C</td>
<td>2.87</td>
<td>0.66</td>
<td>0.7</td>
</tr>
<tr>
<td>ILS 1300 °C</td>
<td>3.28</td>
<td>0.66</td>
<td>0.5</td>
</tr>
<tr>
<td>ILS 1400 °C</td>
<td>1.95</td>
<td>0.68</td>
<td>1.4</td>
</tr>
<tr>
<td>ILS 1400 °C</td>
<td>2.64</td>
<td>0.67</td>
<td>0.8</td>
</tr>
<tr>
<td>ILS 1400 °C</td>
<td>3.17</td>
<td>0.66</td>
<td>0.5</td>
</tr>
<tr>
<td>ILS 1450 °C</td>
<td>1.74</td>
<td>0.69</td>
<td>1.7</td>
</tr>
<tr>
<td>ILS 1450 °C</td>
<td>2.26</td>
<td>0.67</td>
<td>1.0</td>
</tr>
<tr>
<td>ILS 1450 °C</td>
<td>2.64</td>
<td>0.67</td>
<td>0.8</td>
</tr>
</tbody>
</table>

a. from references [145,146]
Figure A.2 As-received fracture surfaces
Figure A.3 ILS 1300 °C fracture surfaces
Figure A.4 ILS 1400 °C fracture surfaces
Figure A.5 ILS 1450 °C fracture surfaces
A.3 Fracture Mirror Measurements

Fracture mirror measurements were made by outlining on a transparency the fracture mirror of a filament with known failure stress. The focal point of the fracture mirror was marked and then the distance from the focal point to the mirror boundary, \( r_m \), was measured along the perimeter of the filament. Plots of \( \ln(\sigma_u) \) versus \( \ln(r_m) \) for the as-received and ILS @ 1300, 1400 and 1450 °C conditions are shown in figures A6-A9. The equation representing the linear best fit line gives the values of \( A_j \) and \( q \) from equation (5.3).

![Graph showing a linear relationship between ln(σu) and ln(r_m).](image)

Figure A.6 A plot of \( \ln(\sigma_u) \) versus \( \ln(r_m) \) for as-received filaments.
Figure A.7 A plot of $\ln(\sigma_u)$ versus $\ln(r_m)$ for filaments ILS @ 1300 °C.

Figure A.8 A plot of $\ln(\sigma_u)$ versus $\ln(r_m)$ for filaments ILS @ 1400 °C.
Figure A.9 A plot of $\ln(\sigma_u)$ versus $\ln(r_m)$ for filaments ILS @ 1450 °C.