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DEVELOPMENT OF NONDESTRUCTIVE EVALUATION METHODS AND PREDICTION OF EFFECTS OF FLAWS ON THE FRACTURE BEHAVIOR OF STRUCTURAL CERAMICS*

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ABSTRACT

Characterization of ceramic matrix composites (continuous and whisker-type) by nondestructive evaluation (NDE) methods and an understanding of fracture behavior, together with correlation of fracture and NDE data, may provide insight into the prediction of component performance and the development of process technology. Knowledge of the degradation extent of fiber tows or monofilament degradation after processing, extent of open porosity before densification, and filament/fiber alignments before and after processing are also examples of important variables to be measured. Work in this program has emphasized continuous fiber ceramic matrix composites (CFCCs) that use chemical vapor infiltration (CVI)-infiltrated SiC/SiC materials, primarily those made of Nicalon satin or plain weave with 16 x 16 tows/in. in 2-D layups. All studied samples were provided by Oak Ridge National Laboratory and were made using 100 layers per inch. CVI specimens with 0/30/60, 0/90, and 0/45 were examined by 3-D X-ray microtomography to characterize in-plane fiber orientations. Current information suggests that for Nicalon-type fiber architecture, a ±2-1/2° misalignment may not affect mechanical properties. Thus the near-term goal has been to establish a detection capability for angular orientation. By using 512 x 512 images from 3-D X-ray CT data with pixel sizes of <140 μm and a special 2-D fast-Fourier transform image processing analysis, we have shown that fiber orientations to ±2-1/2° with SiC/SiC CVI type 2-D weave architecture can be measured.

The chemical state of the fiber surface and its potential impact on fiber pullout strength is being examined by multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopic studies. These are being undertaken to investigate the surface chemistry of fibers and the chemistry of the interfacial regions in composites. Initial studies are investigating both the bulk composition of the matrix materials (α, β, amorphous phase, silica, and oxynitride concentration) and the surface chemistry of Si_3N_4 and SiC fibers. The first ^{29}Si NMR experiments focus on enhancing the signal from the surface by selectively reducing the surface relaxation.

Bulk characterization of fiber/matrix interfaces in CFCCs is being studied by a low-frequency (0.5 MHz) acousto-ultrasonic (AU) method that measures time-of-flight (TOF) of P-waves propagating in the composite. The frequency content and the propagation times are different for different AU paths. Higher frequency content and a faster TOF are observed for waves propagating through fibers. The TOF method may detect delaminations in ceramic composites.

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Also evaluated were the effects of processing methods on flaw generation and the resulting strength degradation of Nicalon-fiber-reinforced SiC matrix composites that were obtained from Oak Ridge National Laboratory. The strength distribution of fractured Nicalon fibers in the composites was assessed by measurements of fracture mirror radii, whereas the strength distribution of as-fabricated Nicalon fibers was obtained from bundle tests. Results indicate an approximate 50% reduction in the strength of Nicalon fibers after processing because of flaws generated in the fibers during composite fabrication. A detailed fractographic evaluation of fibers in the composite is currently in progress to investigate the nature of the flaws and possible causes leading to generation of these flaws.

INTRODUCTION

Characterization of advanced ceramic matrix composite materials by nondestructive evaluation (NDE) methods and understanding of their fracture behavior are necessary for process development. The purpose of the work reported for this activity is to develop the NDE methods, examine fracture behavior of composites, and correlate NDE data with fracture behavior. At the present time, NDE work is being conducted on chemical vapor infiltrated (CVI) SiC/SiC continuous fiber composites being produced at Oak Ridge National Laboratory (ORNL). In the case of CVI composites, the specimens are made of Nicalon multi-fiber tows with a cloth architecture of 16 x 16 tows/inch and laid up with 100 cloth layers per inch. Of current interest is the measurement of axial and radial density gradients, as well as measurement of fiber orientation in the layups in the components. To acquire such data, we are working on 3-D micro-focus X-ray computed tomography (XCT)and advanced image processing technology. In addition, of interest is detailed chemistry of the surface on the fibers as well as the fiber/matrix interface after infiltration. In this case, we are developing multinuclear solids nuclear magnetic resonance. For the evaluation of fracture behavior, effort has concentrated on continuous fiber reinforced ceramic matrix composites. High strength of fibers and weak interfaces are requisites for "tough" ceramic composites.[1,2] Strength and toughness of composites are greatly influenced by the strength properties of the reinforcements. These reinforcements are susceptible to thermal degradation and surface defects or damage introduced during composite fabrication, thereby contributing to strength degradation. Therefore, it is important to establish factors that lead to strength degradation during fabrication of the composites. Specifically, in the present study, we have evaluated the effects of processing on flaw generation and resulting strength degradation of Nicalon fibers in a continuous SiC fiber-reinforced SiC matrix composites.

CHARACTERIZATION OF CVI-PRODUCED SiC/SiC CONTINUOUS FIBER COMPOSITES BY X-RAY MICROFOCUS CT

One parameter of interest to continuous fiber ceramic composites with multi-directional lay-ups is the relative angle of the fiber tow between lay-ups. This is important because mechanical properties are impacted by misoriented fiber tows. At present, little theoretical information is available about the impact fiber orientation has on mechanical properties but current information suggests that ±5° will have an impact.

SiC/SiC Continuous fiber specimens

All SiC/SiC specimens produced for this program were made at ORNL by their differential pressure, thermal gradient process [1,2]. The specimens were all made with Nicalon fiber tows of 16 x 16 tow/inch using satin or plain weave in 2D layups. In order to verify the detection sensitivity of XCT data together with subsequent image processing to detect fiber orientation, specimens were made with cloth orientations of 0/30°/60°, 0/90° and 0/45°. The information on 0/30°/60° was presented earlier and presented in an earlier report. This time we studied 0/45°, and 0/90° cloth layups. We examined two specimens as noted in Table 1.

Table 1. SiC/SiC continuous fiber specimens

Specimen Number	Cloth orientation	Specimen dimensions diameter/thickness (μm)
573-2	0/45	40.5/13.05
574-2	0/90	44.5/13.3
261,262	0/30/60	45/12.5

X-ray CT scanner conditions

The details of the 3-D microfocus X-ray CT scanner developed under this program has been described elsewhere.[3] For these two specimens we used 120 KVp accelerating voltage and a 0.16mA filament current with 1 mm of copper filtration. The image intensifier/CCD array camera detector system was corrected for geometric distortion and screen uniformity. The reconstruction matrix was 256 by 256 and the slice or cross-sectional thickness was 700 μm to include three layers of cloth. The pixel size was 197 μm x 197 μm in the reconstructed image. The image reconstruction code

was the volume reconstruction Feldkamp code run in a SUN SPARC 2/GS workstation with a 24-bit/plane graphics driver. We obtained "slices" throughout the complete object. Thus we can reconstruct the entire sample and obtain data from any plane. We are using the shareware program "NIH-Image" for image analysis running in a Macintosh II FX environment. As part of the NIH-Image code, image analysis can be done by application of Fast Fourier Transforms (FFT), specifically, 2-D FFT's. By application of this code, one can study the fiber orientations from the resulting CT images. Data flow for image analysis is shown in Fig. 1.

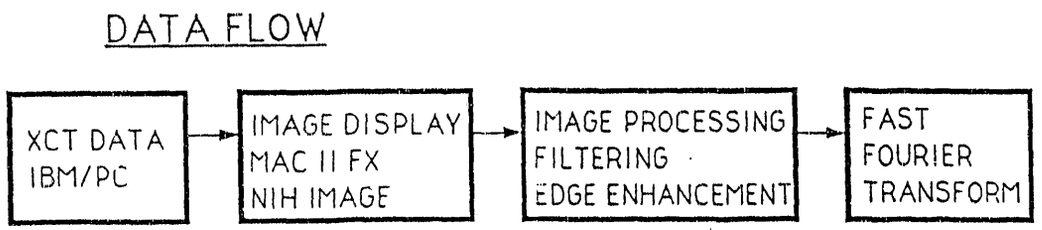


Fig. 1. Schematic diagram of X-ray CT data flow to arrive at FFT for fiber orientation.

By using this process, we established the average fiber oreintation for 4 layers of cloth at three axial locations in each sample. Figure 2 shows a typical resulting FFT image for a 90° specimen. These data are for the mid-section fibers of specimen 574-2 of 0/90°. Since part of the data which also comes from the FFT analysis is spatial frequency, at nominally 6.3 tows/cm (16 tows/in.), assuming equal spacing between tows and gaps, this would equal 1.6 mm/tow-gap pair. Note that since both specimens were made with the same cloth architecture, that is 6.3 tows/cm, the spatial frequency from the FFT image should be constant, and this was confirmed. The data for cloth orientation as determined by FFT analysis for the 0/45 and 0/90 specimens are given below in Table 2.

Table 2. Fiber orientation measurements on CVI SiC/SiC specimens

Specimen Identification	desired angle, degrees	measured angle, degrees
573		
top section	45	45
mid section	45	43
lower section	45	47
574		
top section	90	93
mid section	90	92
lower section	90	90

Fig. 2. Example of FFT image resulting from 4 layers of CVI SiC/SiC. Note the nominal 0, 90°.

CHARACTERIZATION OF CONTINUOUS FIBER COMPOSITES BY NMR

Multi-nuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopic studies are being designed to investigate (a) the composition of bulk ceramic materials; (b) the surface chemistry of these materials; (c) the chemistry of the ceramic interfacial regions; (d) and the chemistry of the whisker and fiber coatings. The ultimately goal of this work is to develop and demonstrate spectroscopic techniques capable of probing the nature of the micro-chemical environments of the ceramic surfaces and the bulk/fiber interfaces, and to correlate results obtained using these techniques with the microstructural and mechanical properties of the composite specimens.

NMR spectroscopic properties of many types of nuclei are generally sensitive to their local chemical environment. These properties often exhibit a strong dependence upon the variety, location and chemical bonding of the surrounding nuclei. ^{29}Si exhibits such sensitivity, and can thus be used as a probe for the bulk, surface and interface characterization in ceramics and ceramic composite materials. For example, using ^{29}Si NMR "Magic-Angle" spinning (MAS), it has been demonstrated that NMR can quantify crystal type in Si_3N_4 (i.e. a, b, and amorphous materials) materials, as well as determine surface coatings such as silica concentration, and oxynitrides concentration. Note that NMR has a distinct and significant advantage over X-ray crystallographic methods in its ability to quantify the amorphous materials. When dealing with materials which are comprised of mixed polytypes, such as SiC, NMR is often capable of quantifying the individual polytypes. Additionally, ^{13}C NMR can be used to characterize and quantify carboniferous coatings on whisker and fibers. These

analysis can all be performed as a function of specimen preparation (i.e. mixing conditions, sintering conditions, and atmospheric constituents).

In this work, ^{29}Si NMR MAS spectra have been obtained for the compositional and morphological analysis of Si_3N_4 (i.e. a, b, and amorphous materials) powders and SiC whisker/ Si_3N_4 matrix powder mixtures, see Fig. 3. Chemical shift differences between the major constituents are clearly discernable. Additionally, these materials exhibit reasonably low but detectable levels of silicon oxynitrides and the silicon oxid s. Studies were also performed to determine the utility of this technique for determining bulk compositional variations using a series of calibrated SiC whisker/ Si_3N_4 matrix mixtures. Spectra obtained from the series of mixtures and the appropriate normalized integrated intensity peak intensities ratios are plotted in Fig. 4a and b respectively.

^{29}Si NMR MAS experiments were also performed as a function of pulse repetition rate. These studies provide an indication of the spin-lattice relaxation rate T_1. Two representative spectra acquired with 15 s and 240 s repetition delay were also obtained. The SiC oxynitrides and the oxides showed a distinctly shorter relaxation time as compared to Si_3N_4. Given that the oxynitride and oxides are generally species on the bulk Si_3N_4, and that NMR in general is a bulk technique, the limited number of nuclei near the surface generally limit NMR's sensitivity for surface analysis. However these experiments indicate that it is possible to maximize the signal obtained from the surface, while minimizing the signal obtained from the bulk constituents. Experiments aimed at increasing the surface sensitivity of this technique will continue

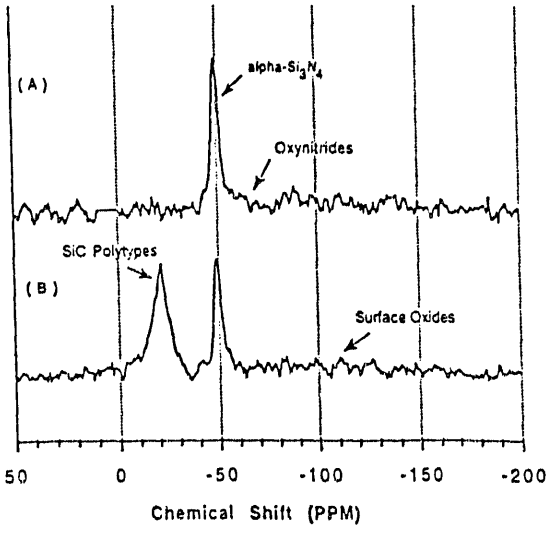
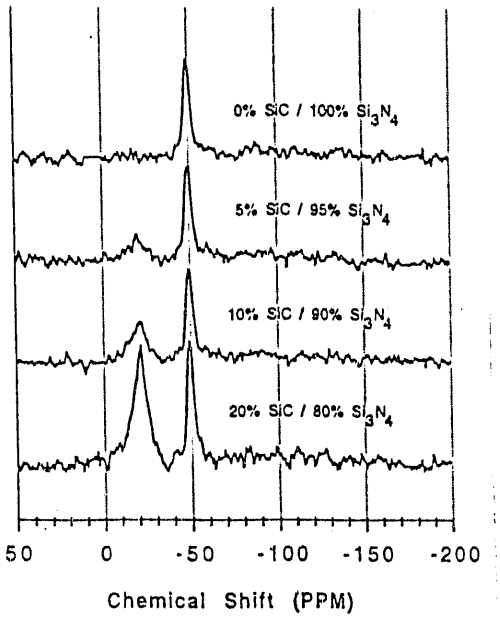
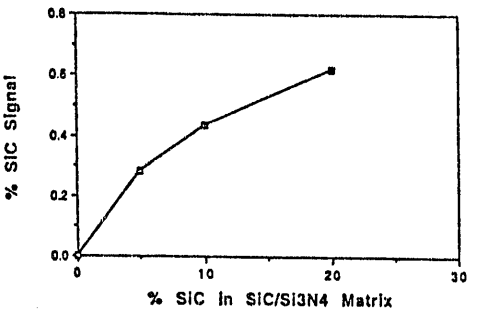


Fig. 3. ^{29}Si NMR MAS spectra of α-Si_3N_4 powder and SiC whisker/ α-Si_3N_4 matrix 20/80 Wt% powder mixture. Spectra were acquired at a magnetic field strength of 7 T, spinning at 5 Khz, using a 70 degree pulse with and a 60 second recycle delay.



(a)



(b)

Fig. 4. (a) ^{29}Si NMR "Magic-Angle" spinning (MAS) spectra of SiC whisker/ α-Si_3N_4 matrix powder mixtures with 0, 5, 10, and 20 Wt% SiC. (b) Plot of normalized peak intensity ratios vs. concentration. Spectra were acquired using identical condition as described in Fig. 3.

CHARACTERIZATION OF CONTINUOUS FIBER Si/SiC COMPOSITES BY ACOUSTO-ULTRASONICS

In order to evaluate the potential of a bulk method to characterize interfacial shear strength of continuous fiber ceramic matrix composites, we developed an acousto-ultrasonic (AU) method for evaluating mechanical properties of fiber reinforced composites. Figure 5 shows the experimental configuration of the AU system. A pair of transducers are used in this method: one acts as a transmitter sending P-waves into the composite and the other receives the AU signals which in most composites separates into two groups of signals differing in their frequency

content. By analyzing the times-of-flight of the AU signals one can clearly determine the fiber orientation. We have also applied the AU method to the evaluation of interfacial strength of fiber reinforced composite materials.

Three composite specimens of SiC matrix with 30 vol.% of Nicalon plain-weave fabric rotated in 0°/± 30° orientation were examined. The fibers in these specimens were coated with carbon of different thickness to vary the interfacial bonding strength of the composites. Figure 6, provided by ORNL, shows the effects of carbon coating thickness on interfacial shear stress. The samples contain carbon coatings of 0.2 μm, 0.3 μm, and 0.4 μm. The AU signals in the composite were produced by transmitting, at normal incidence, ultrasonic pulses with a center frequency of 0.5 MHz and they were detected by another transducer 1.5" away from the transmitter and analyzed in both time and frequency domains. Figure 7 shows the time-domain AU signals detected in the three samples. Frequency analysis shows that an increase in the coating thickness reduces low frequency signals. This observation might indicate the fact that AU signals tend to propagate mainly through the fibers for the thicker coating fiber composites which generally show weaker interfacial strength. Similar results were reported by INEL,[4] which showed that the AU decay rate increases as the interfacial shear stress decreases. However, the present technique can separate the signals propagating through the fibers from those propagating in the matrix. Thus the present AU method can give a better quantitative measure of the interfacial shear stress. The quantitative correlation between the interfacial strength and the AU signal will be further examined. Two physical parameters, wavelength—thickness ratio and sample geometry, will also be examined to determine shape effects and optinum frequency.

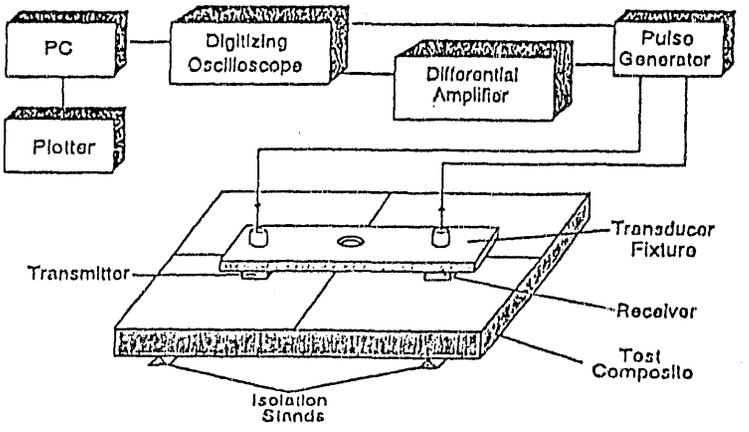


Fig. 5. Experimental configuration of acousto-ultrasonics.

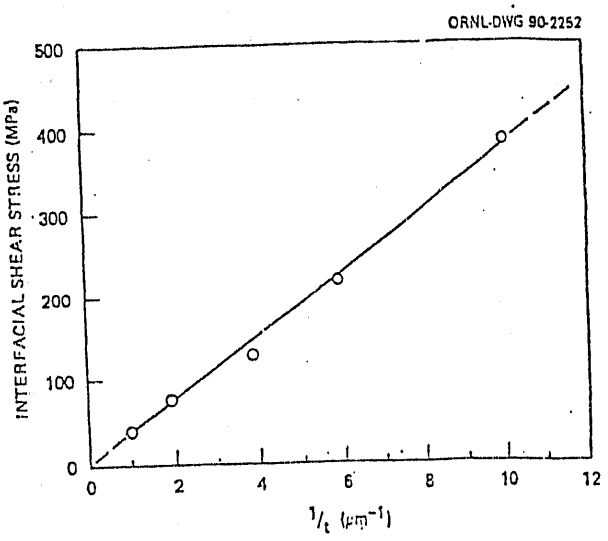


Fig. 6 Effects of Carbon coating thickness on interfacial shear stress. t = carbon coating thickness.

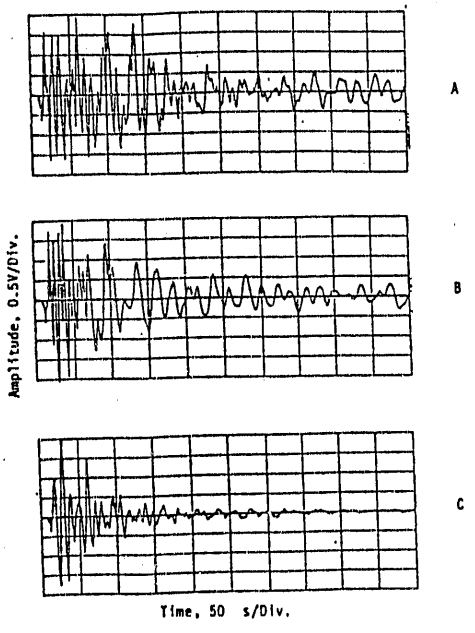


Fig. 7. Time domain acousto-ultrasonic signals detected in SiC matrix composites with Nicalon continuous fiber reinforcement. The fibers contain carbon coatings of thickness (A) 0.2 μm, (B) 0.3 μm, and (C) 0.4 μm.

CHARACTERIZATION OF CONTINUOUS SiC FIBER/SiC MATRIX COMPOSITES BY FRACTURE STUDIES

Composite Specimens for Fracture Studies

To evaluate the effects of processing methods on flaw generation and resulting strength degradation in composites, Nicalon-fiber-reinforced SiC matrix composites fabricated by chemical vapor infiltration (CVI) were obtained from Oak Ridge National Laboratory. These composites were close to 90% dense. Details of specimen fabrication and mechanical properties of the composite are described elsewhere.[1,5]

Strength Evaluation and its Correlation with Critical Flaws

The fiber bundle test[6] was employed to determine the single-fiber strength distribution of as-fabricated Nicalon fibers. Bundle tests were conducted on a

universal testing system on fiber tows with gage lengths ranging from 27 to 100 mm under ambient conditions and at a loading rate of 0.5 mm/min. Strain or displacement in the fiber bundle at a particular load was determined by subtracting the system (grips, connectors, etc.) displacement (using ASTM D 3379–75) from the absolute displacement of the crosshead of the testing machine. Weibull parameters were obtained from the load versus strain plots following the procedure described by Chi et al.[6] Weibull distribution used to describe fiber fracture strengths was as follows:

$$F(\sigma) = 1 - \exp\left[-\frac{L}{L_o}\left(\frac{\sigma}{\sigma_o}\right)^m \right] \qquad (1)$$

where L_o is the fiber gage length at which the Weibull parameters are estimated, L is the standard gage length taken to be 10 mm, $F(\sigma)$ is the cumulative failure probability at an applied stress σ, σ_o is the scale parameter signifying a characteristic strength of the distribution, and m is the Weibull modulus that characterizes the flaw distribution in the material.

Strength distributions from seven tests conducted on fiber bundles with various gage lengths gave an average value for the Weibull modulus and scale parameter as 7.1 and 3.45 GPa, respectively at gage length of 10 mm. These results are in agreement with those of Goda and Fukunaga[7].

The strength of the fibers in composites was evaluated from characteristic features on the fractured fiber surfaces in composites (2.9 x 4.2 x 51.0 mm) tested in a four–point–bend mode at a loading rate of 1.27 mm/min with a loading span of 9.5 mm and a support span of 19.0 mm under ambient conditions. Fractured composites were examined on a scanning electron microscope (SEM) to locate the failure origins and fracture surface morphology of the fibers. Typical surface morphology of a fractured fiber in Nicalon fiber–reinforced SiC composite is shown in Fig. 8. Characteristic features associated with brittle failure, such as mirror (smooth region around the fracture origin) and hackle (region of multiple fracture planes) are clearly observable on the surface of fractured fibers. SEM investigation showed that most of the fibers failed from defects or flaws located at the fiber surface.

The tensile strength was evaluated from the data on characteristic fracture mirror radii through the empirical relationship[8]: $\sigma_f r_m^{1/2} = A_m$. In this equation, σ_f is the tensile strength, r_m represents the mirror radius, and A_m is the mirror constant, which is related to the fracture toughness of the material. In the present study, the value of A_m was taken to be 3.5 $MPam^{1/2}$. The strength data of more than 30 fibers were used to construct Weibull plot from which the Weibull modulus and the corresponding scale parameter were evaluated to be 6.0 and 2.3 GPa, respectively. It

should be noted that for purpose of comparison, this scale parameter was assumed to be the same as that at a fiber gage length of 10 mm. This was done because of the difficulties associated with accurate estimation of individual fiber pullout lengths and relating them to fiber gage lengths. Thus, the Weibull scale parameter estimated for fractured fibers in the composite is an overestimate.

Figure 9 compares the strength distribution of as-fabricated Nicalon fibers with those incorporated in the composite. Generally, the strength of the fibers incorporated in the composite is approximately 50% lower than that of the as-fabricated fibers. It is to be noted that the strength distribution shown in the figure (for fibers in the composite) has a scale parameter of 2.3 which is an overestimated value. If a correction for the fiber gage length is made i.e., the gage length for the fibers in composite is made equal to that used for the testing of as-received fibers, the scale parameter for the fibers in composite will be reduced. This will further decrease the strength value of fibers in composites relative to the strength of as-received fibers. This reduction in fiber strength may have been caused either by the increase in the severity of pre-existing flaws or by the introduction of new flaws during processing. A typical critical surface flaw believed to have been introduced by mechanical and/or thermal damage is shown in Fig. 8.

Strength degradation of Nicalon fibers due to exposure to high temperatures is well documented in the literature.[9] The loss of tensile strength is attributed to microstructural and stoichiometric changes that occur in the fibers at elevated temperatures. To establish the effects of thermal degradation during processing, on the Nicalon fibers used in composites, a quantitative microstructural and phase analysis of the fibers is currently in progress.

Fig. 8. Micrograph of fractured Nicalon fibers in SiC matrix composite showing fracture features and surface defects as the failure origins.

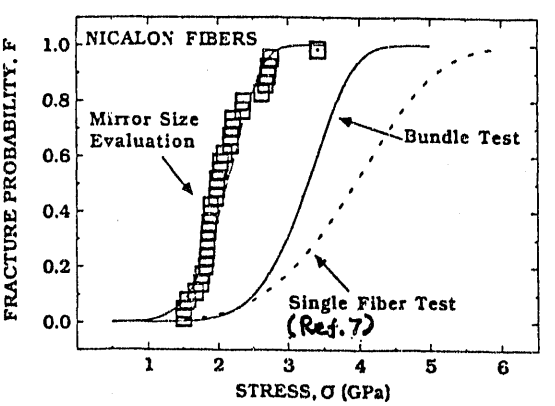


Fig. 9. Weibull strength distribution of Nicalon fibers in as-fabricated state (bundle test) and after processing (mirror size evaluation).

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