Mechanical Properties and Interfacial Characterization of Nextel 312™ Fiber/BN/Blackglas™ Composites

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SUMMARY: Boron nitride (BN)-coated Nextel™ 312 fibers, produced via ammonia nitridation, along with 'as-received' and 'desized' fibers, were composited in a Blackglas™ matrix. The composite mechanical properties, failure properties, and fiber-matrix interfacial chemistry was investigated. BN treated fiber composites show a 90% improvement in flexural strength and substantial increases in shear strength (short beam shear and Iosipescu) over the 'as-received' fiber composite. The composite fabricated with 'desized' underwent spontaneous delamination and therefore mechanical testing was impossible. X-ray photoelectron spectroscopy of the starting materials and of composite fracture surfaces combined with environmental scanning electron microscopy provided data on surface and interfacial chemistry and helped identify the locus of failure for the composites. Examination of the fracture surfaces identified boron and nitrogen on the fiber surface suggesting that the locus of failure for the BN- coated fiber composites occurs at the matrix/BN coating interface.

KEYWORDS: Blackglas, pyrolization, adhesion, boron nitride coating, alumina fiber, fractography, interface characterization

INTRODUCTION

The demand for structural ceramics has lead to an increased interest in the processing and characterization of continuous fiber reinforced ceramic composite systems [1-3]. In particular ceramic composites are being developed as alternatives to monolithic ceramics, because ceramic composites fail in a high strain (>0.5%), damage tolerant manner, as compared to the brittle (<0.1%) failure of monolithic ceramics. For large-scale application of ceramic matrix composites the most critical technical issue is the cost-effective application of stable interface coatings on continuous ceramic fibers. A fiber coating is required for the fabrication of strong, damage tolerant ceramic fiber/ceramic matrix composites. The high strain performance of ceramic composites depends on an interface coating on the fibers which will bebond to produce energy absorbing fracture mechanisms, such as fiber pull-out, crack deflection, and fiber bridging [4]. The interface coating serves as a compliant layer between the fiber and matrix to facilitate load transfer and crack deflection at the matrix-fiber interface

promoting a non-catastrophic fibrous fracture mode of failure. The coating may also serve as a barrier between the matrix and fiber preventing matrix/fiber reactions that could lead to excessive matrix-fiber bonding and the loss of attractive mechanical and fracture properties.

Blackglas™ ceramic is silicon oxycarbide (SiC_xO_y), a highly refractory, silicon-based glass produced from pyrolysis of a cross-linked siloxane polymer [5]. Its processing and performance attributes make it an excellent candidate for composite systems that operate in the 260ºC – 1200ºC regime. Currently, an alumina-silica ceramic fiber containing up to 14 wt. % boria (Nextel 312™) is processed in an ammonia containing atmosphere at elevated temperatures (>1200ºC) to form a boron nitride (BN) coating on the fiber surface. During treatment at elevated temperatures, boria diffuses to the fiber surface and can be reacted with ammonia to form born nitride. This BN coating serves as a compliant layer facilitating crack deflection and producing a non-catastrophic failure mode. Continued development of these ceramic matrix composites requires a more complete understanding of the mechanistic paths involved in composite densification and failure behavior.

The objective of this work is to characterize the mechanical properties and fiber-matrix interfacial relationships of Nextel 312™ fiber/Blackglas™ composites. To accomplish this objective, three different fibers —as-received, desized and boron nitride coated— were composited using a 5 step pyrolization/infiltration process. The flexural and shear strength properties of each of the composites was determined using a 4-pt. flexural test, short beam shear test and Iosipescu shear test. Surface chemistries of the starting materials and fracture surfaces were examined using x-ray photoelectron spectroscopy and energy dispersive spectroscopy. Fractography of composites failed in a flexural mode were investigated using environmental scanning electron microscopy.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials. Fibers of Nextel 312™ (3M Corp.) aluminoborosilicate (64% Al_2O_3, 24% SiO_2, 14%, B_2O_3), with a tensile strength of 1725 MPa (250,000 psi) and a tensile modulus of 138 GPa (20 x 10^6 psi), in a 5-harness satin weave fabric woven using 900 denier tows, were prepared using two approaches. First, the organic sizing was removed by heat treatment forming desized fibers. Secondly, the as-received fibers were heated in a high-temperature ammonia atmosphere to form a boron nitride rich surface layer ~10 nm thick. These fibers, plus the as-received fibers, were composited with a Blackglas™ preceramic silsesquioxane polymer 493 (Allied Signal, density of ~1.09 g/cm^3) using a 5 step pyrolization/infiltration process. After pyrolization the ceramic composition consists of amorphous SiO_xC_y with a density of ~2.2 g/cm^3.

Mechanical Tests. The shear strength of each composite was determined by testing in short beam shear and in-plane Iosipescu, while the flexure properties were evaluated in 4-point bending. A minimum of 8 specimens were tested in each test configuration. The mean and standard deviation were then calculated.

Surface Characterization. Surface chemistry of the starting materials and fracture specimens were determined using a PHI 5600 x-ray photoelectron spectrometer (XPS). Composite fracture surfaces were examined, uncoated, using an ElectroScan 2020 environmental scanning electron microscope (ESEM) and a JEOL JSM-6400V SEM. The JEOL system was equipped with a Noran Vantage system for energy dispersive x-ray spectroscopy (EDS). The system is equipped with a Moxtek window having a lower limit of

detection of beryllium (atomic number of 4) with a Noran Extreme detector with a resolution of 126 eV.

RESULTS AND DISCUSSION

Constituent Materials. Surface morphologies for the as-received, desized and BN-treated fibers are shown by the micrographs in Figures 1a, 1b, and 1c, respectively. The organic sizing on the fiber surface is plainly visible. The underlying fiber microstructure is slightly evident. In contrast, the desized fiber shows a uniform microstructure (though individual grains cannot be discerned) with no indication of coating material. The micrograph shown in Figure 1c shows the presence of a thin BN coating and a slight indication of the fiber microstructure observed through the coating. In addition, the ESEM investigation indicated that the BN treatment uniformly covered the fibers.

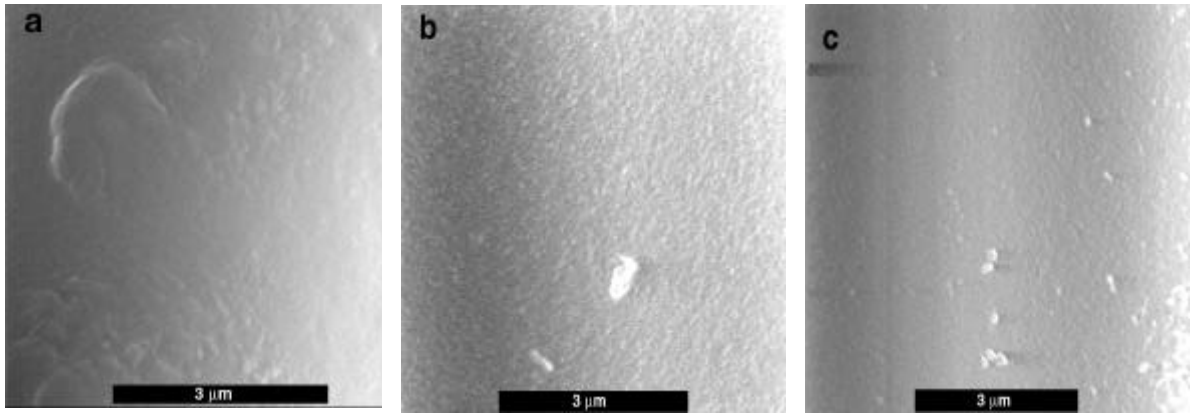

Figure 1: ESEM micrographs of (a) as-received, (b) desized, and (c) BN treated fiber surfaces.

The surface chemistry for each of the fibers is listed in Table 1. The as-received fibers show a large carbon, oxygen, and nitrogen concentration consistent with an organic coating. Minor amounts of boron, aluminum, and silicon are present with trace amounts of chlorine and sulfur. Desizing the as-received fibers removes much of the nitrogen and carbon exposing more oxygen, aluminum, boron and silicon. Thus the surface chemistry of the desized fibers reflects the ideal chemistry of the Nextel™ 312 fibers. The surface composition of BN coated fibers have almost equal amounts of carbon, oxygen, nitrogen, and boron. Smaller amounts of aluminum and silicon are also present. For completeness and comparison, the surface chemistry of the Blackglas™ matrix material was measured and consisted of 17.6% carbon, 38.4 % oxygen, and 44% silicon. Note that no evidence of nitrogen, which is present during the pyrolization process, was found.

Table 1.
Fiber Surface Chemistry (atomic %)

Element	As-received Fibers	BN Coated Fibers	Desized Fibers
Carbon	**63.9**	**22.0**	**27.0**
Oxygen	**21.0**	**21.4**	**45.8**
Nitrogen	**10.7**	**23.4**	**—**
Boron	**1.2**	**21.0**	**5.2**
Aluminum	**1.6**	**8.1**	**18.7**
Silicon	**1.0**	**4.2**	**3.3**
Sulfur	**0.3**	**—**	**—**
Chlorine	**0.3**	**—**	**—**

Mechanical Properties. The mechanical properties of the composites, determined using 4-point flexure, short beam shear, and Iosipescu in-plane shear tests, are summarized in Table 2. Attempts at fabricating composites with desized fibers failed when spontaneous delamination occurred after each pyrolization/infiltration step; therefore, no mechanical property measurements of these composites is reported. The data indicate that the effect of the BN interface on the mechanical properties is dramatic. Increases of ~700% in flexural strength and ~85% in the strain-to-failure were measured for the BN treated composites over the 'as-received' fiber composites. At ultimate strength, both of the composites failed on the tensile stress side. The low values of strength observed for the as-received composites suggest that the Blackglas™ matrix and not fiber/matrix interface debonding is playing the dominant role in determining the ultimate strength.

Table 2.
Mechanical Properties of Blackglas™ Composites

Mechanical Test	As-received	BN-treated
4 pt. Flexure Strength (MPa)	**25.3 ± 3.3**	**178.2 ± 6.8**
Short Beam Shear Stress (MPa)	**5.1 ± 2.9**	**32.0 ± 0.95**
Iosipescu In-Plane Shear Stress (MPa)	**9.2 ± 7.6**	**101.5 ± 12.6**

The action of the Iosipescu fixture is to produce pure shear loading with no bending at the midspan section of the specimen between the notches, while the short-beam shear test provides information concerning interlaminar shear strength. As the data in Table 2 indicates the shear strength of the as-received composites are low. Composites fabricated using BN coated fibers show significant improvement in shear strength.

Table 3.
Surface Chemistry of Fractured Specimens
(atomic %)

Element	As-received Fibers	BN Coated Fibers	Desized Fibers
Carbon	**52.4**	**58.1**	**52.8**
Oxygen	**28.4**	**18.0**	**31.3**
Nitrogen	**0.8**	**8.1**	**—**
Boron	**0.8**	**7.9**	**—**
Aluminum	**3.4**	**0.6**	**—**
Silicon	**14.2**	**7.2**	**16.0**

Fracture Surface Investigation. In an attempt to determine the locus of failure of fractured composites, XPS analysis of fracture surfaces was undertaken. The surface chemistry of the fractured composites is shown in Table 3. Note that the sampled area is approximately 2 mm^2. Thus the XPS data are averaged over a large spatial area and accumulated from both exposed fiber surfaces (including fiber ends) and the matrix surface. This lack of spatial resolution makes definitive identification of the locus of failure difficult. Data for the spontaneously delaminated desized fiber composites indicates the presence of carbon, oxygen and silicon. The lack of an aluminum signal suggests complete coverage of the fibers by matrix material and cohesive failure of the matrix near the fiber surfaces.

The as-received and BN-coated fiber composites show high carbon and oxygen concentrations. In contrast to the desized fiber composites, small amounts of aluminum, nitrogen and boron are seen in the as-received fiber composites. This suggests the possibility of a significant amount of exposed fiber surface. The amount of boron detected in the as-received fiber composites suggests that failure occurred either at the fiber-matrix interface exposing fiber surfaces or within the fiber. The composition of the BN-treated fiber

composite indicates an almost 1:1 correspondence of boron-to-nitrogen ratio. This result suggests that fracture occurred either at the coating-matrix interface; at the fiber-coating interface; or within the coating itself. Furthermore, the small aluminum content suggests that the BN coating remains on the surface of the fiber. Since XPS analysis of 4 pt. flexure specimens is suggestive, but inconclusive in determining if the fiber-matrix locus of failure occurred at the fiber-BN interface or the BN-matrix interface, EDS analysis of the fracture surface was performed.

EDS was used to analyze the BN coated fiber surfaces exposed during the fracture process and the matrix material (fiber channels) exposed during fiber pull-out. Figures 2a and 2b show an EDS spectrum taken from a region of the fracture surface where fiber pull-out occurred. No evidence of boron (0.185 keV) is seen in the spectra, though nitrogen (0.392) is

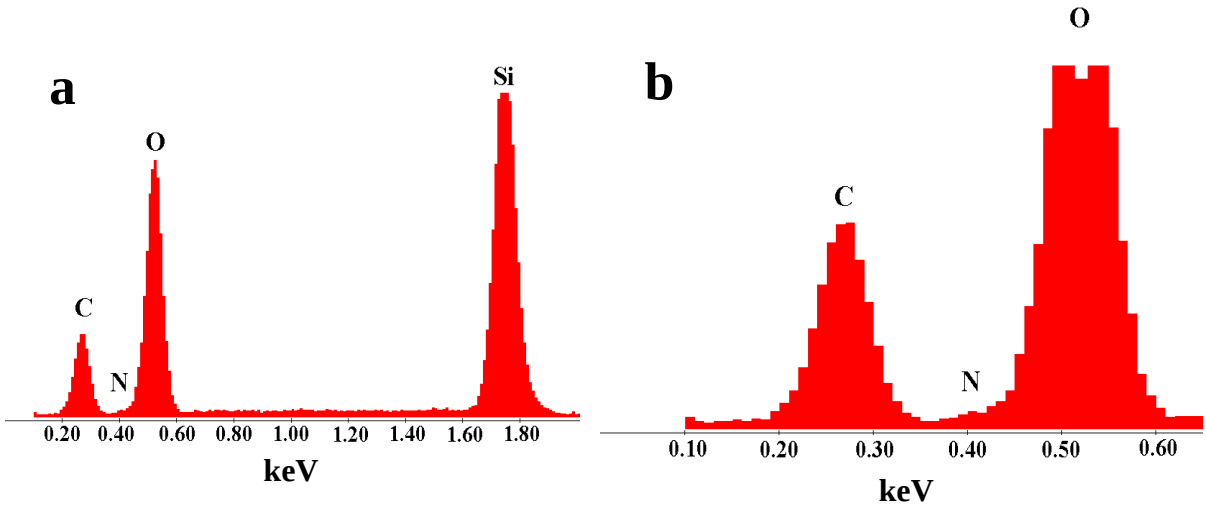

Figure 2: EDS spectra taken from a matrix region exposed during fiber pull-out (a) and an enlargement of the low energy section of (a).

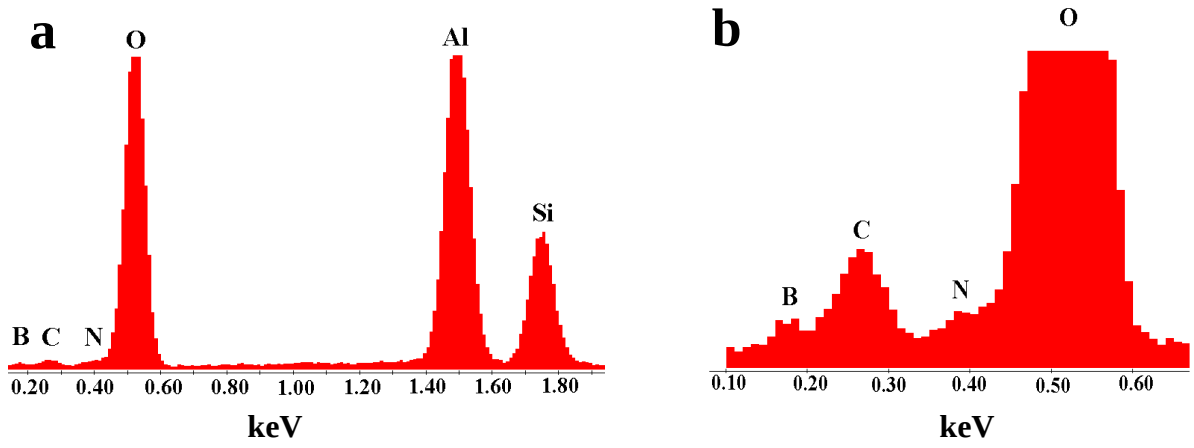

Figure 3: (a) EDS spectra taken from the fiber surface showing the presence of boron and nitrogen and (b) an enlargement of the low energy section of the spectra in (a).

clearly evident. The nitrogen signal could result from nitrogen atoms incorporated into the matrix during composite fabrication (the sampling depth of XPS is much less (2 μm compared to 6 nm) than EDS and thus may not detect surface nitrogen) or could be remnants from the BN coating. To test this, EDS spectrum taken from the fiber surface is shown in Figures 3a and 3b. The EDS spectrum shows boron and nitrogen on the fiber surface. This indicates the

locus of failure occurs primarily at the BN-matrix interface. Failure could also occur in the BN coating; however, the majority of the coating remains on the fiber surface.

During the fabrication of the composites residual stresses arise both in the fiber and matrix. In general these stresses are associated with the difference of thermal expansion coefficients, as well as volume changes that occur upon amorphization of the ceramic matrix. These stresses may limit the composite strength, as demonstrated by the delamination behavior of the desized fiber composites. The fracture properties of ceramic matrix composites are governed by matrix cracking followed by interaction of cracks with the fibers and interfaces. Within the composite, energy-dissipative processes such as fiber-matrix debonding, crack bridging, fiber pull-out, multiple crack formation and crack deflection can be observed [6]. With this in mind, fracture specimens taken from composites which failed in 4-point flex were examined to provide qualitative information on mixed mode failure processes.

The ESEM micrographs in Figure 4a and 4b show the spontaneous interlaminar fracture surfaces of desized fiber composites. Because of the change in density during the conversion of the polymer to the amorphous ceramic, a volume shrinkage occurs during pyrolysis. This, combined with chemical reactions between the fiber and matrix, provide good fiber-matrix adhesion but which also leads to large residual stresses that are unable to relax. These processes cause the observed spontaneous delamination. Figure 4a is a low magnification view showing matrix cracking caused by resin shrinkage. A higher magnification in Figure 4b shows how the crack propagated near the fiber surface. This is consistent with XPS results near the fibers which suggest that the crack propagated through the matrix and is further evidence of the high degree of adhesion between the fiber and matrix.

The micrographs shown in Figure 5a and 5b illustrate of the failure behavior of as-received fiber composites. Figure 5a shows a macroscopically rough surface indicating some crack deflection as it passed through the composite. A higher magnification view shown in Figure 5b indicates a microscopically smooth surface with no evidence of hackles or scallops or fiber pull-out. In particular, there is a smooth transition across the fiber-matrix interface. These observations suggest very good fiber-matrix adhesion and, hence, poor flexural and shear strength since the composite properties are dominated by the mechanical properties of the matrix. This is consistent with the XPS examination of the fracture surface chemistry which indicates that exposed fiber surfaces are observed. These results suggest that the locus of failure alternates between the fiber-matrix interface and cohesive failure of the matrix. The convoluted crack path is a result of the combination of fiber-matrix adhesion and the complicated stress state in a 3-D weave composite. These results also indicate the necessity of having a fiber coating to prevent matrix-fiber reactions from causing large residual stresses.

ESEM micrographs of BN-treated fiber composite fracture specimens are shown in Figures 6a and 6b. The fracture surfaces seen here are significantly different than either the desized or the as-received fiber composites. Figure 6a shows that macroscopically the fracture surfaces are extremely rough with a substantial amount of fiber pull-out. In addition, fiber fracture continues at various planes throughout the composite, resulting in a rough surface of broken fibers and/or bundles. At a higher magnification fiber-matrix separation is observed and rough resin fracture occurs between fibers. In this case, as Figure 6b shows, a significant amount of fiber pull-out results in a cupping surface. The presence of a large amount of matrix debris suggests a large amount of energy dissipation during crack propagation through the composite. These failure surface observations correlate well with the mechanical properties.

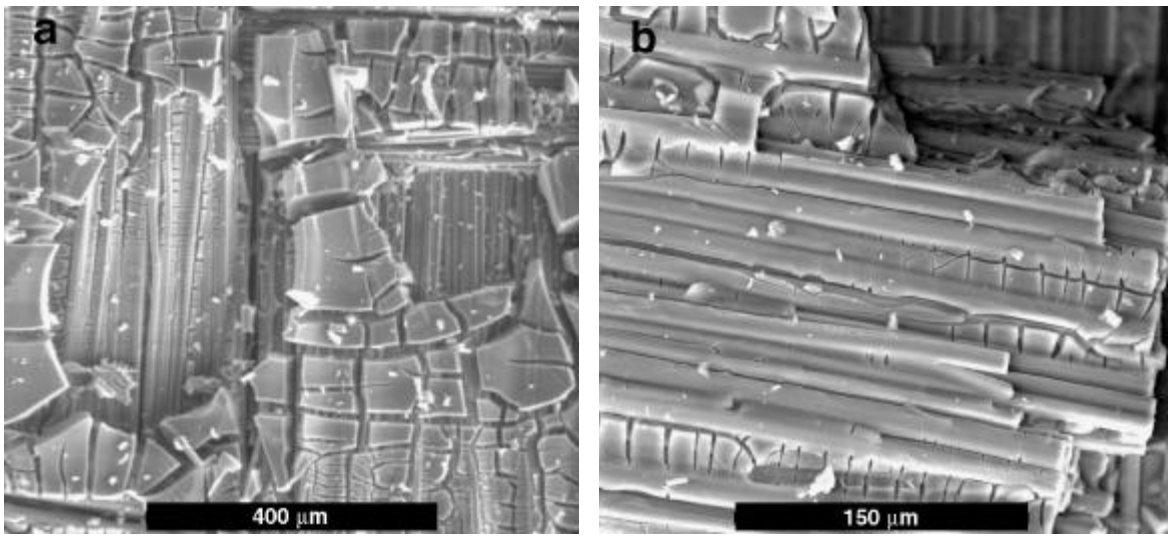

Figure 4: (a) Low magnification ESEM micrograph of a delaminated desized fiber composite and (b) a higher magnification view illustrating matrix material adhering to the fiber.

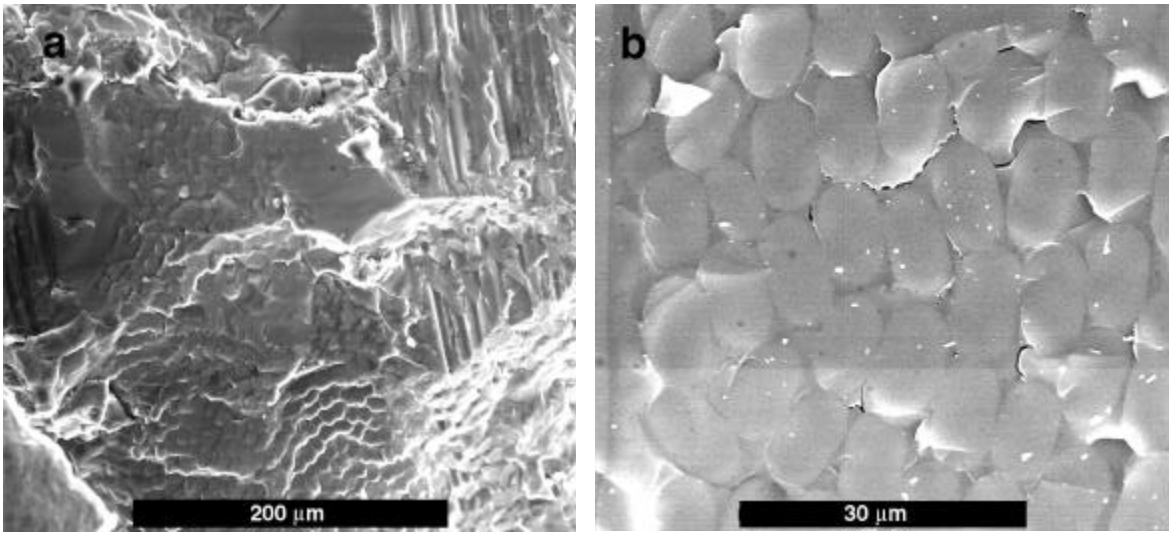

Figure 5: (a) low magnification view of the fracture surface of an as-received fiber composite and (b) a high magnification view of the fracture surface normal to the fiber axis.

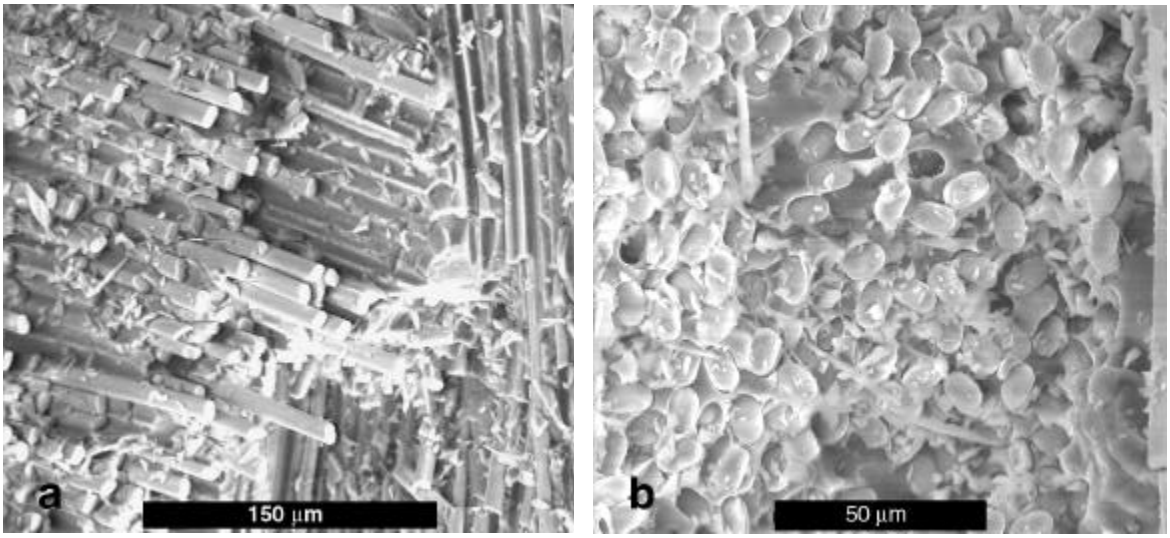

Figure 6: (a) low magnification ESEM micrograph of a boron nitride coated fiber composite and (b) a high magnification micrograph showing cupping behavior of the fibers.

CONCLUSIONS

This work investigates the effect of a boron nitride coating on the mechanical properties of Nextel™ 312/Blackglas™ composite by comparison with composite fabricated with desized and as-received fibers. The presence of the BN interface coatings provides a mechanism for isolation of the reinforcing fibers after fracture which promotes high strength and high strain in these ceramic composites. As a result the composite fracture surface have a very tortuous crack path with extensive fiber pull-out and a cup type of behavior with significant fiber-matrix separation. The high mechanical strengths combined with the damage tolerant failure behavior suggest a fiber-matrix bond strength strong enough to impart strength to the ceramic, but weak enough to provide energy absorption. XPS and EDS analysis suggests that failure occurs at the BN coating-matrix interface. The 'as-received' fiber composite produces low flexural and shear strength indicating that the composite mechanical properties and failure processes are matrix dominated providing little opportunity for energy absorption. Spontaneous delamination of composites fabricated with 'desized' fibers due to the high matrix shrinkage producing high residual stresses points to the need for a properly designed fiber coating material which promotes fiber debonding.

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